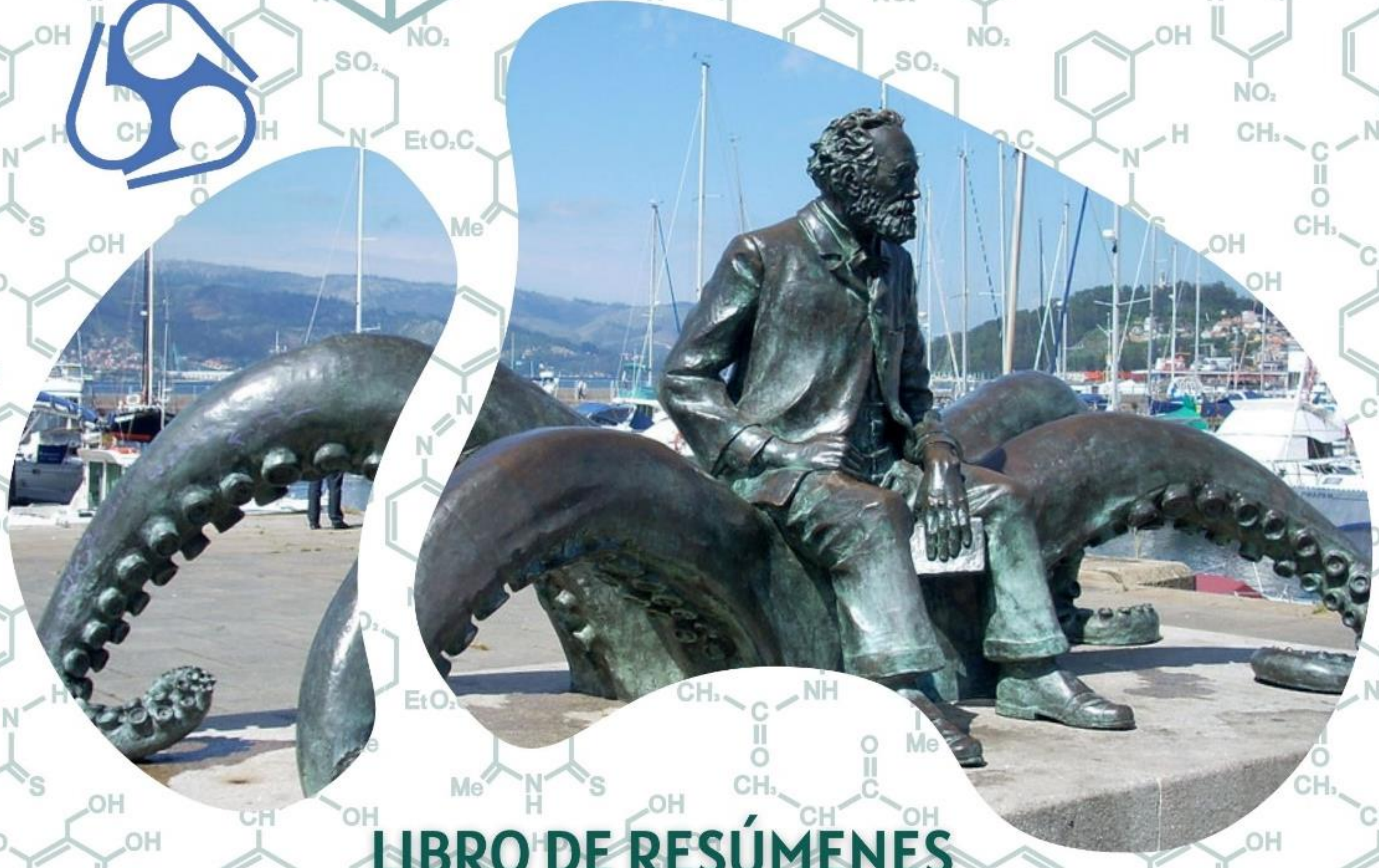
CONGRESO INTERNACIONAL

XXVIII ENCONTRO GALEGO PORTUGUÉS DE QUÍMICA

VIGO - GALICIA - ESPAÑA

13 - 15 de Noviembre 2024



LIBRO DE RESÚMENES

COLEGIO OFICIAL DE QUÍMICOS DE GALICIA

SOCIEDADE PORTUGUESA DE QUÍMICA

ASOCIACIÓN DE QUÍMICOS DE GALICIA

XXVIII ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA.
Noviembre 2024

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PRÓLOGO

XXVIII ENCONTRO GALEGO-PORTUGUÉS DE QUÍMICA

A punto de cumplirse el primer cuarto del presente siglo XXI, la química se ha posicionado como una de las actividades más relevantes para el desarrollo de la actividad humana e industrial. La química es la ciencia central que condiciona el desarrollo de otras ciencias y disciplinas técnicas. La vida humana no sería la que hoy disfrutamos si no hubiera productos químicos como el cloro, que ha permitido potabilizar las aguas haciéndolas aptas para la bebida, tampoco sería lo mismo si no se hubiera creado productos cosméticos para el aseo, ni tampoco sería lo mismo si no se hubiera desarrollado componentes químicos para el uso en equipamiento informático y en la telecomunicación. Recientes acontecimientos relacionados con la conquista espacial, enfocados a la búsqueda de nuevos materiales en otros espacios, presentan un nuevo y prometedor futuro para la química.

Este congreso, los ENCONTROS que nacieron con la intención de intercambiar conocimientos entre jóvenes investigadores a los dos lados del río Miño, ahora se está convirtiendo, manteniendo sus orígenes, en un congreso en donde jóvenes de diferentes nacionalidades presentan sus trabajos de investigación relacionados con el mundo de la química. Los ENCONTROS son congresos generalistas, no relacionados con alguna especialidad química, lo que permite tener una visión de todo lo que se está desarrollando en la investigación química. En resumen, permite tener una idea de los intereses de la sociedad en relación con el mundo de la química.

Este XXVIII ENCONTRO seguimos con la intención que su comisión directiva ha diseñado desde mediados de este cuarto de siglo, de que las personas inscritas al congreso compartan un tiempo y un espacio con personas ya consagradas, y de prestigio, en el mundo de la química con las que intercambiar experiencias y abrir nuevos caminos para avanzar en sus campos de investigación y abrir nuevos caminos para futuras generaciones que quieran hacer de la química su profesión.

Este año, el ENCONTRO se lleva a cabo en la ciudad de Vigo. Esta es la ciudad con más habitantes de Galicia y también la ciudad industrial de esta región de España. En Vigo, muchos proyectos de investigación vieron la luz y se transformaron en plantas de producción que permiten llevar su especialidad química a los consumidores para mejorar su vida o a otras plantas químicas para desarrollar su actividad. Este año, nos juntaremos, en este congreso, con más de 300 personas que están trabajando e investigando en diferentes especialidades de la química que, seguramente, en el futuro dejarán de ser proyectos de investigación para ser realidades, quién sabe si desde esta misma ciudad de Vigo.

La Sociedad Portuguesa de Química y su Delegación Norte, junto con el Colegio Oficial de Químicos de Galicia y la Asociación de Químicos de Galicia, ha vuelto a organizar esta 28ª edición de los ENCONTRO con la esperanza de que sea fructífera para todas las personas inscritas en el Congreso. Este año hemos elegido la sede de la Fundación ABANCA como lugar para celebrar el Congreso. El lugar es un edificio de inicios del siglo XX, ahora adaptado para congresos. El edificio representa la pujanza de esta ciudad que, sin querer olvidar su historia, se adapta para seguir viva y seguir creciendo y teniendo una presencia importante en la ciudad de Vigo. Igual que la química, que avanza sobre una base fuerte gracias a personas que, como vosotros y vosotras, que hoy estáis en este congreso, sentaron los principios para vuestro actual trabajo.

Dr. Manuel Rodríguez Méndez
2 de noviembre de 2024
Colegio Oficial de Químicos de Galicia

Contenido

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LOCALIZACIÓN DEL XXVIII ENCONTRO INTERNACIONAL GALEGO PORTUGUÉS DE QUÍMICA

Vigo: Situado en la provincia de Pontevedra, (Galicia, España). Con una población de 293 652 habitantes (INE 2023), es el municipio más poblado de Galicia y el decimocuarto de España, así como la mayor ciudad del país sin rango de capital provincial. Además, es la zona urbana más densamente poblada de la conurbación formada por el conjunto de localidades que se sitúan a lo largo de 300 km de las Rías Bajas y el centro de un área metropolitana que engloba a otros 13 municipios, los cuales suman 481 782 habitantes censados. Geográficamente está situada en el noroeste de la península ibérica, distando solamente unos 33 km al norte de la frontera con Portugal. El término municipal abarca una extensión de 109,06 km² y su densidad poblacional es de 2686,47 hab/km².

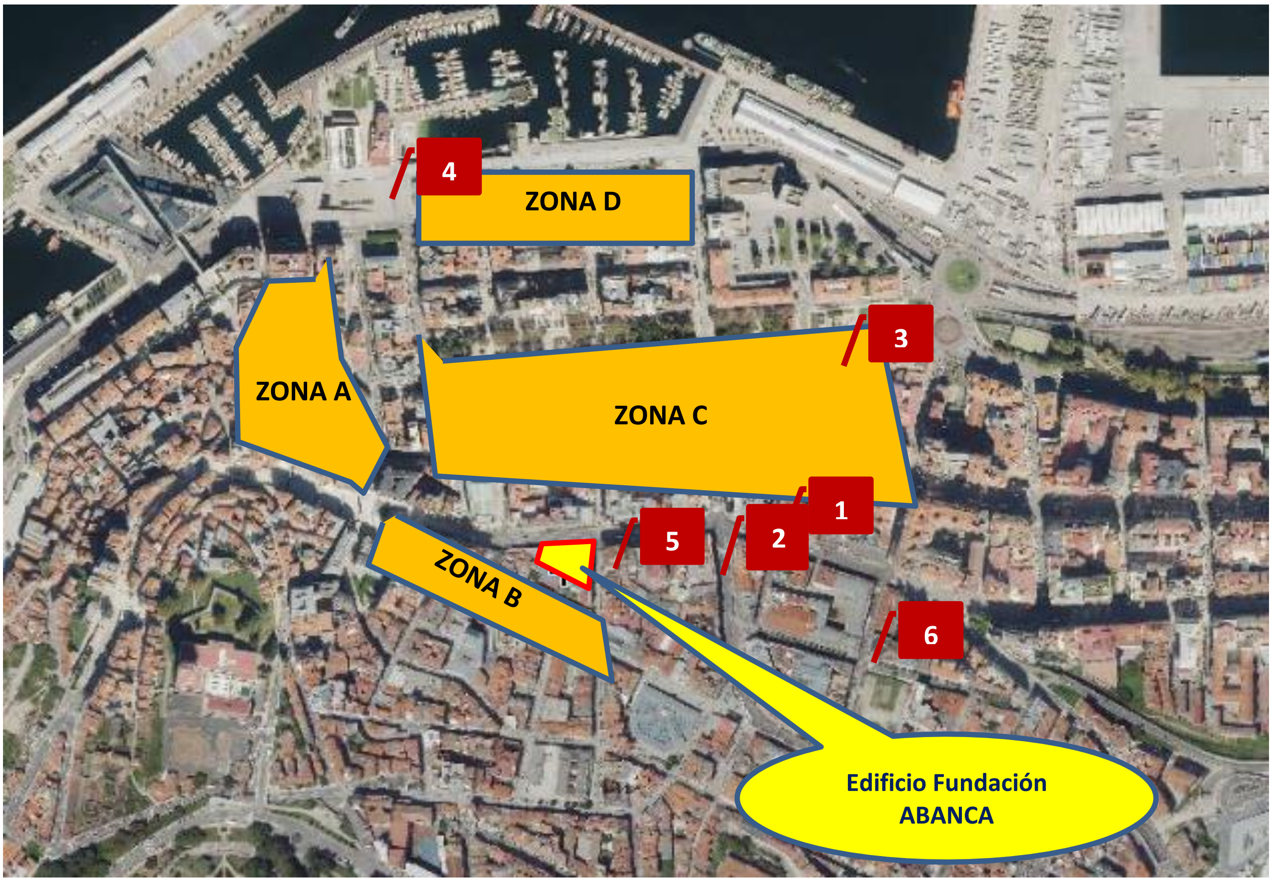
INFORMACIONES VARIAS

El Encontro se celebrará en la sede Afundación Vigo, Rúa Policarpo Sanz, 24-26, 36202 Vigo, Pontevedra, España

SEDE AFUNDACIÓN VIGO

El edificio, sede de la Gerencia de Afundación, fue proyectado en 1879 por el arquitecto Jenaro de la Fuente Domínguez. De estilo eclecticista, luce un virtuoso trabajo de cantería y presenta dos fachadas enlazadas por un chaflán, resaltado con miradores de fundición. En el remate se acentúa la ornamentación con característicos y variados floreros. Tradición y vanguardia se han conjugado en la rehabilitación de este edificio para un nuevo uso multifuncional. Cuenta con más de 13 000 metros cuadrados de superficie distribuidos en cinco plantas.

INFORMACIÓN DE INTERÉS



ZONA A:

Es la zona antigua de Vigo. Puede considerarse el Centro de la ciudad de Vigo. Está situada a unos 350 m. del edificio de la Fundación ABANCA. En esta zona hay restaurantes de todo tipo donde podréis degustar la gastronomía gallega (pescados, carnes y mariscos) a un precio muy accesible. Pudiendo comer, en todos ellos el MENÚ DEL DÍA. En esta zona está la famosa "Piedra", donde podréis degustar las ostras.

ZONA B:

Es la zona comercial de Vigo. Se encuentra en la Calle del Príncipe, es la zona comercial más antigua y conocida de Vigo. Hay tiendas de todo tipo y algunas, pocas, zonas donde poder comer. Está situada en la parte posterior del edificio de la Fundación ABANCA, a unos 80 m. Pudiendo comer, en todos ellos el MENÚ DEL DÍA.

ZONA C:

Es una zona más moderna de Vigo, pero sin perder la esencia de la zona antigua. Es una zona de restaurantes y mesones y también de copas por la noche. Está a una distancia, media, de 200m. del edificio de la Fundación ABANCA. La zona más recomendable está en la Plaza de Compostela y la zona de la Avenida de Rosalía de Castro. Pudiendo comer, en todos ellos el MENÚ DEL DÍA. En la Plaza de Compostela está el edificio de Correos.

ZONA D:

una zona más moderna de Vigo, pero sin perder la esencia de la zona antigua. Es una zona de restaurantes y de copas. En los restaurantes se pueden degustar los platos típicos de la gastronomía gallega. Pudiendo comer, en todos ellos el MENÚ DEL DÍA. Por las noches es una zona, con mucha afluencia de personas. Está a una distancia, media, de 200m. del edificio de la Fundación ABANCA, cerca del muelle.

COMIDAS.

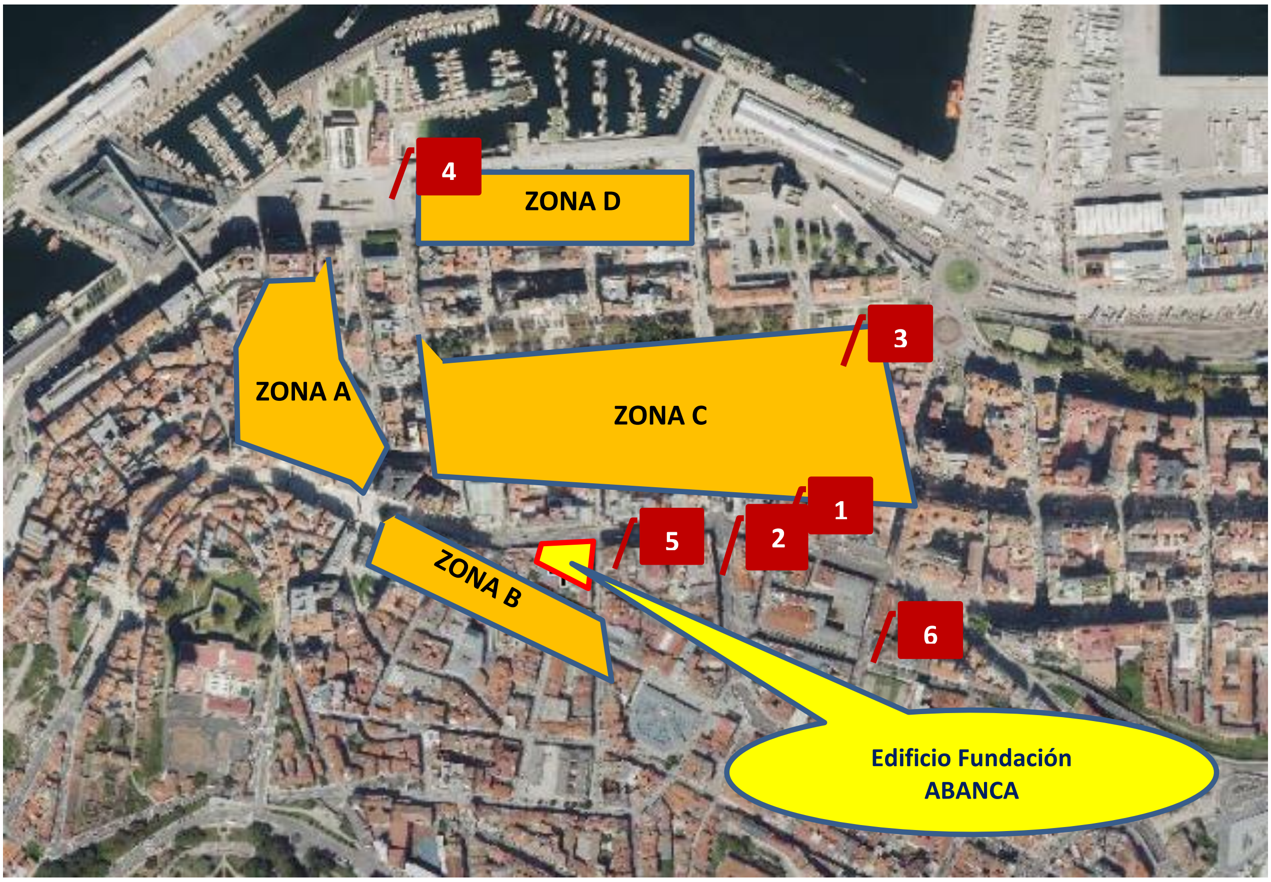
Los días del congreso podéis ir a cualquier zona. En ellas encontrareis restaurantes, mesones, bares en donde podréis degustar el MENÚ DEL DÍA a un precio que puede oscilar entre 12 y 20 euros. Por la noche, para cenar, no hay MENÚ DEL DÍA.

PARKING.

En la zona hay, por lo menos 6 parkings donde, las personas que puedan venir en su vehículo pueden dejarlo durante el tiempo que quieran. Los aparcamientos son:

NÚMERO	LOCALIZACIÓN
1	Hay una entrada a la altura del hotel NH y el aparcamiento llega más allá del edificio de la Fundación ABANCA.
2	Subiendo por la calle Colón, hacia la calle Urzaiz, a la altura de la calle del Príncipe. Antes de llegar a él, hay otro parking
3	Este parking está en a Avenida de Rosalía de Castro, en la Zona C
4	Este parking está en frente a Hotel Bahía. Es un parking moderno donde se deja el vehículo en una plataforma y automáticamente el sistema lo ubica en su lugar de aparcamiento.
5	Este parking no tiene capacidad para muchos vehículos. Está situado en la calle Velázquez Moreno
6	Es un parking debajo de la Plaza de Compostela. Se accede a él desde la Calle Urzáiz.

INFORMATION OF INTEREST



ZONE A:

This is the old part of Vigo. It can be considered the centre of the city of Vigo. It is located about 350 m from the ABANCA Foundation building. In this area there are restaurants of all kinds where you can taste the Galician gastronomy (fish, meat, and seafood) at very affordable prices. In all of them you can eat the MENU OF THE DAY. In this area you can find the famous "Piedra St.", where you can taste oysters.

ZONE B:

This is a renowned Vigo's shopping area. It is located along “Calle del Príncipe”, the oldest and best-known shopping area in Vigo. There are shops of all kinds and a few areas where you can eat. It is located at the back of the ABANCA Foundation building, about 80 metres away. You can eat, in all of them, the MENU OF THE DAY.

ZONE C:

This is a modern area of Vigo, but without losing the essence of the old one. It has restaurants and taverns, as well as a nightlife area. It is at an average distance of 200 m from the ABANCA Foundation building. The most recommendable area is Plaza de Compostela (Compostela Sq.) and the area of Ros7alía de Castro’s Avenue. You can eat in all of them the MENU OF THE DAY. At Plaza de Compostela is the Post Office building.

ZONE D:

A modern area of Vigo, still with the essence of the old part. It is an area plenty of restaurants and bars. In the restaurants you can taste typical dishes of Galician gastronomy. You can eat in all of them the MENU OF THE DAY. At night it is an area with a lot of people. It is at an average distance of 200 m from the ABANCA Foundation building, near the quay.

MEALS.

During the days of the Conference, you can move easily to any area. There you will find restaurants, inns, bars where you can enjoy the MENU OF THE DAY at a price ranging from 12 to 20 euros. Please, notice that for dinner, no MENU OF THE DAY is offered in the different facilities.

PARKING.

In the area there are at least 6 car parks where conferees carrying their own cars can leave them for as long as they need. Please, note that parking at the streets is definitely complicated and most sites require hourly payment. The car parks are:

NUMBER	LOCATION
1	There is an entrance close to the NH hotel and the car park goes beyond the ABANCA Foundation building.
2	Going up Colón Street, towards Urzaiz street, close to Príncipe Street. Before reaching it, there is another car park
3	This car park is on Rosalia de Castro's Avenue, in Zone C.
4	This car park is in front of Hotel Bahía. It is a modern car park where you leave your vehicle on a platform and the system automatically places it in its parking space.
5	This parking does not have capacity for many vehicles. It is in Velázquez Moreno Street.
6	It is a car park below Plaza de Compostela (Compostela Sq.). It is accessed from Urzaiz Street.

INFORMACIÓN SOBRE EL CONGRESO

LA SEDE

El edificio fue proyectado en 1879 por el arquitecto Jenaro de la Fuente Domínguez. Es un edificio de estilo eclecticista, luce un virtuoso trabajo de cantería y presenta dos fachadas enlazadas por un chaflán, resaltado con miradores de fundición. En el remate se acentúa la ornamentación con característicos y variados floreros. Tradición y vanguardia se han conjugado en la rehabilitación de este edificio para un nuevo uso multifuncional.

En la esquina de Velázquez Moreno con Policarpo Sanz, fue promovido entre los años 1898 y 1902 por Manuel Bárcena, figura destacada de finales del siglo XIX, quien, siendo alcalde, fundó la Caja de Ahorros de Vigo y el Monte de Piedad Municipal, el 3 de octubre de 1880.

Antiguamente, el edificio era denominado “Siete Casas”, dado que se estructuraba en siete viviendas por planta, como alquiler para familias acomodadas de la época. El arquitecto Jenaro de la Fuente ideó este edificio de carácter ecléctico y modernista con una fachada espectacular que mezcla vanos y macizos.

El edificio se ha habilitado para la celebración de Congresos.

RECEPCIÓN

La oficina de información y la recepción para retirar la documentación del Encontro, estará localizada en la segunda planta de la Fundación ABANCA. Permanecerá abierta durante todos los días de su celebración.

EQUIPAMIENTO DE PROYECCIONES

Las salas de conferencias están equipadas con ordenador y cañón de proyección. Cada orador deberá transferir el fichero de su presentación al ordenador de la sala que le corresponda, con la antelación suficiente. Siendo aconsejable se realice en la sesión anterior.

PRESENTACIONES ORALES

Las conferencias plenarias tendrán una duración de 45-50 minutos más 10 minutos para preguntas.

La duración de las comunicaciones orales será de 10 minutos más 5 minutos para resolución de dudas. Se solicita a todos los oradores que cumplan el tiempo estipulado, a fin de evitar retrasos en el programa.

Se recomienda que las presentaciones se hagan en formato pdf.

POSTERS

Deberán colocarse el primer día, primera sesión y retirarse el último día antes de las 15:00 h. Se solicita a los autores de los trabajos presentados, estén presentes junto a los mismos durante la sesión de discusión.

SALAS DEL CONGRESO

El congreso tendrá lugar en 4 salas del edificio ABANCA, distribuidas de la siguiente forma.

Planta Segunda

Aquí se encuentra la Recepción del Congreso y la entrada a la Sala A, que es el Auditorio.

Planta tercera

Aquí se encuentra la Sala B.

Planta Cuarta

Aquí se encuentran las salas C y D.

Entresuelo

Zona de pósters y tiene unha zona ajardinada, pero protegida de la climatología donde tendremos el cátering.

CENA DEL ENCONTRO

La cena del ENCONTRO se celebrará el día 14 de noviembre a las 21:30 horas en el Comedor del Hotel NH COLLECTION VIGO, en la calle García Barbón, 17-19, en Vigo, a 400 m. de la sede del Congreso.

El edificio del hotel se le conoce como las casas de Oya. El edificio es un encargo de D. José García Barbón al arquitecto francés Michel Pacewicz, pero ejecutada su construcción por D Manuel Pérez Conde.

El edificio está realizado en cantería de granito gallego, el estilo del inmueble de cinco andares es ecléctico con pisos poco individualizados y poco perceptibles y representó un cambio en la arquitectura de Pacewicz. A diferencia de otras casas pudientes de la época, este edificio posee simpleza ornamental, limpieza y uniformidad en su estilo. Tiene corte francés y base neobarroca de fuerte simetría. La fachada tiene ornamentación, excepto en el tratamiento de las gárgolas de los balcones individualizados y miradores. El bajo es de cantería en las pilastras que soportan los arcos de medio punto. Los miradores de la segunda planta tienen remates neoclásicos y pilastras con capiteles jónicos que aguantan un friso a modo de entablonado. La balconada corrida del primer y último piso refuerzan la horizontalidad del edificio. Sobresalen las cuatro grandes ventanas salientes del segundo piso. La cima de la casa combina pretiles y barandillas de piedra en las que se sitúan unas aberturas rematadas en frontones curvos y partidos rematados con volutas en los laterales inferiores.

La fachada principal es más larga la de García Barbón, la lateral, cara la calle de la República Argentina es pequeña, semejante a la principal, más con una galería en la primera planta de hierro fundido, anteriormente de madera

ENTIDADES COLABORADORAS

Deputación
Pontevedra

PSN
Previsión Sanitaria Nacional

frA
FUNDACIÓN
RAMÓN ARECES

PROGRAMA DEL XXVIII ENCONTRO INTERNACIONAL GALEGO PORTUGUÉS DE QUÍMICA

SALAS		Planta
A	**AUDITORIO**	**2ª**
B	**Sala de Conferencias**	**3ª**
C	Sala A	**4ª**
D	**Sala B**	**4ª**
POSTERS	**SALÓN JARDÍN**	**Entresuelo**

DÍA	HORA	SALAS				
		PLENARIAS SALA A	A	B	C	D
13	**10:00 - 11:30**	**INSCRIPIÓN Y RECEPCIÓN**				
	11:30- 12:00	**SESIÓN DE APERTURA. Aula Magna**				
	12:00-13:00	**CONFERENCIA PLENARIA de APERTURA. Aula Magna**				
	13:00		QS01	AMB01	ALM01	CAT01
	13:15		QS02	AMB02	ALM02	CAT02
	13:30		QS03	AMB03	ALM03	CAT03
	13:45		QS04	AMB04	ALM04	CAT04
	14:00-16:00	**COMIDA**				
	16:00		QS05	AMB05	ALM05	CAT05
	16:15		QS10	AMB06	ALM06	CAT06
	16:30		QS07	AMB07	ALM07	QO01
	16:45		QS08	AMB08	ALM08	QO02
	17:00		QS09	AMB09	ALM09	QO03
	17:15		QS06	AMB10	ALM10	QO04
	17:30-18:00	**COFFE BREAK - POSTERS**				
	18:00-18:45	**CP1**				
	18:45		QS11	AMB11	ALM11	QO05
	19:00		QS12	AMB12	ALM12	QO06
	19:15		QS13	AMB13	ALM13	QO07
	19:30		QS14	AMB14	ALM18	QO08

DÍA	HORA	SALAS				
		PLENARIAS	A	B	C	D
		SALA A				
14	10:00		QS26	AMB15	ALM15	CAT07
	10:15		QS16	AMB16	ALM16	CAT08
	10:30		QS17	AMB17	ALM17	CAT09
	10:45		QS27	AMB18	ALM14	CAT10
	11:00-11:45	CP2				
	11:45-12:15	COFFE BREAK - POSTERS				
	12:15		QS19	AMB19	ALM19	CAT11
	12:30		QS20	AMB20	ALM20	CAT12
	12:45		QS21	AMB21	ALM21	CAT13
	13:00		QS22	AMB22	POL01	CAT14
	13:15		QS23	AMB23	POL02	QT01
	13:30		QS24	AMB24	POL03	QT02
	13:45		QS25	AMB25	POL04	QT03
	14:00-16:00	COMIDA				
	16:00		QS15	AMB26	QF01	QT04
	16:15		QS18	AMB27	QF02	QT05
	16:30		QS28	AMB28	QF03	QT06
	16:45		QS29	AMB29	NN19	BB02
	17:00-17:45	CP3				
	17:45-18:15	COFFE BREAK - POSTERS				
	18:15		QS30	AMB30	NN06	BB03
	18:30		EDU01	AMB31	NN07	BB04
	18:45		EDU02	AMB32	NN03	BB05
	19:00		EDU03	AMB33	NN14	BB06
	19:15		EDU04	AMB34	NN04	BB07
	19:30		QA02	AMB35	NN05	BB08
	21:30	CENA DE GALA				

DÍA	HORA	SALAS				
		PLENARIAS	A	B	C	D
		SALA A				
15	10:00		QA03	AMB36	NN08	BB01
	10:15		QA04	AMB37	NN09	BB09
	10:30		QA05	AMB38	NN10	IND01
	10:45		QA01	AMB39	NN11	IND02
	11:00-11:45	CP4				
	11:45-12:15	COFFE BREAK - POSTERS				
	12:15		QA06	SQ01	NN12	IND03
	12:30		QA07	QI01	NN13	IND04
	13:00		QA08	QI02	NN02	IND05
	13:15		QA09	QI03	NN15	IND06
	13:30		QA10	QI04	NN16	IND07
	13:45		QA11	QI05	NN17	IND08
	14:00-16:00	COMIDA				
	16:00		QA12	QI06	NN18	BB10
	16:15		QA13	QI07	NN20	IND09
	16:30		QA14	QI08	NN21	IND10
	16:45		QA15	QI09	CAT15	IND11
	17:00		IND13	QI10	NN01	IND12
	17:15-17:30	COFFEE BREAK				
	17:30-18:00	CLAUSURA				

RELACIÓN DE CONFERENCIAS PLENARIAS

CONFERENCIA APERTURA:

Prof. Ehud Keinan

Schulich Faculty Of Chemistry Technion – Institute Of Technology. Presidente de la IUPAQ

Humanity faces a bright future, and so Chemistry

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CICECO – Instituto De Materiais De Aveiro Universidade De Aveiro

Marine Polysaccharides: A Sustainable Source for Functional Biomaterials in Biomedical Applications

CP 2 **Prof. M. Arturo López Quintela**

Dpto. Química Física, Imatus Universidade Santiago De Compostela

Wet-chemical synthesis and exceptional catalytic properties of metal clusters of small atomicity without protecting ligands

CP 3 **Prof. Doctor Javier García Martínez**

Laboratorio de Nanotecnología Molecular, Dpto. Química Inorgánica, Universidad de Alicante

Catalyzing the Green Revolution: Unlocking Previously Inaccessible Chemical Processes

CP 4 **Prof. Salette Reis**

LAQV/REQUIMTE, Dpto. De Ciências Químicas. Facultad De Farmácia Universidade De Porto

Exploiting the role of lipids for innovative therapies and delivery strategies

RELACIÓN DE COMUNICACIONES

CONFERENCIAS PLENARIAS

CONFERENCIA DE APERTURA

Prof. Ehud Keinan

Humanity faces a bright future, and so Chemistry

CP 1 **Dr. Cláudia Nunes**

Marine Polysaccharides: A Sustainable Source for Functional Biomaterials in Biomedical Applications

CP 2 **Prof. M. Arturo López Quintela**

Wet-chemical synthesis and exceptional catalytic properties of metal clusters of small atomicity without protecting ligands

CP 3 **Prof. Doctor Javier García Martínez**

Catalyzing the Green Revolution: Unlocking Previously Inaccessible Chemical Processes

CP 4 **Prof. Salette Reis**

Exploiting the role of lipids for innovative therapies and delivery strategies

COMUNICACIONES

Química Alimentaria

Oral

ALM01 Recuperación de antocianinas y otros polifenoles del bagazo de uva tinta mediante extracciones hidrotérmicas en cascada

ALM02 Fermented fruit juices: exploring the benefits of the ancient technique for today's juice production

ALM03 A milky way towards novel antioxidant nutraceuticals

ALM04 Estudo do impacto da interacción molecular dos polifenois do millo corvo e fariñas de trigo autóctonas galegas na bioaccesibilidade do glute

ALM05 Avaliação da Atividade Antioxidante de Extratos de Borra de Café: Comparação de Métodos de Extração para Aplicação Cosmética

ALM06 Is the Natural Fermentation of Olive Pomace Feasible for Food Purposes? A Detailed Chemical and Microbiological Characterization

ALM07 Chemical characterization of Lycium barbarum L. and Lycium chinense Mill. berries and development of high-value goji sorbets

ALM08 Impacto do intercropping e do sistema de irrigação nos parâmetros físico-químicos e nutricionais de Prunus dulcis no nordeste de Portugal

ALM09 Caracterização Bioquímica de Excedentes da Produção de Brassica spp.

ALM10 Rhus spp.: Estudo da caracterização nutricional, química e bioativa

ALM11 Extrato otimizado de Tradescantia zebrina L.: um corante alimentar alternativo e os seus efeitos na dieta de Drosophilas melanogaster

ALM12 Impacto do extrato corante de Clitoria ternatea L. na progressão da doença de Parkinson

ALM13 Application of an oral cell-based assay to study the astringency of Clitoria ternatea L. tea

ALM14 Cyclodextrin-assisted extraction of phlorotannins from Fucus vesiculosus

ALM15 Molecular insights into the modulation of black tea polyphenol interactions with oral components by orange peel pectic polysaccharides

ALM16 Characterization and Valorization of Pinus pinea Nut Shell Extracts for Sustainable Crop Production

ALM17 Valorização de Resíduos de Cogumelos Comestíveis na Produção de massa penne: Fermentação e Melhoria Nutricional

ALM18 Nutritional and Antioxidant Potential of Dried Coffee Pulp from Azores: A Sustainable Approach to Valorising Coffee By-Products

ALM19 Promoção de estratégias sustentáveis no setor agroalimentar: valorização de subprodutos vegetais

ALM20 Biofortificación de microvegetales de guisante mediante priming de semillas con selenio

ALM21 Otimização da extração assistida por ultrassons de compostos hypocholesterolémicos a partir de residuos de cogumelos comerciais

Poster

ALM22 Vertical farming of micro- and baby greens: Influence on organic acid, free sugar, betalain, and phenolic compound contents

ALM23 Comprehensive Analysis of Emerging and Persistent Contaminants in Widely Consumed Fish Species from the Portuguese Coast

ALM24 Aromatic changes in Albariño wine processed by High Pressure Processing (HPP)

ALM25 Comprehensive Profiling of Phenolic Compounds in Olive Pomace using HPLC-DAD-MS-ESI+

ALM26 Evaluation of Bacillus cereus growth in different nutritional food matrices containing a biosurfactant extract from corn steep liquor produced at pilot scale

ALM27 Amêndoas consorciadas com outras culturas cultivadas em Selca (Croácia): estudo das propriedades nutricionais e bioatividades

ALM28 Unveiling the Geographical Influence on Honey's Physicochemical Profile: A Case Study from Montesinho Natural Park

ALM29 Valorização de compostos bioativos em excedentes da produção de Lactuca sativa L.

ALM30 Development of hydroelectrolytic beverages using subcritical water extract from kiwano (Cucumis Metuliferus) peel

ALM31 Estudo da aplicação do extrato de curcuma como ingrediente corante natural em queijadas de laranja

ALM32 Optimization of fish by-products hydrolysis process using bromelain: a comparative study with alcalase

ALM33 Mineral composition of Azorean coffee pulp

ALM34 Advancing Clean-Label Meat Products: Enhancing Texture and Color with Plant-Based Bioactive Ingredients

ALM35 Metal-adsorbed polysaccharides: synthesis and structural characterization

ALM36 Economia circular na indústria alimentar: aproveitamento e valorização do subproduto de carambola

ALM37 Color stability of a natural cyanidin-3,5-diglucoside and its derivative methylpyranocyanidin as potential food additives

ALM38 Mejoramiento de la calidad nutricional y de la tolerancia al estrés de microvegetales mediante el uso de bioestimulantes naturales

ALM39 Obtenção de estatinas e ergosterol de bio-resíduos de Agaricus bisporus: extração convencional vs emergente

ALM40 Opuntia ficus-indica (L.) Miller cladodes: a mineral-focused strategy for sustainable flour production

ALM41 A comprehensive analysis of the protein fraction within the cladodes of Opuntia ficus-indica (L.) Miller

ALM42 Biofortification of Swiss chard microgreens with selenium under indoor vertical farming

Química Ambiental y Sostenible

Oral

AMB01 Estudio en el aula de un Plan de Sostenibilidad Ambiental

AMB02 Exploring living and non-living macroalgae based biosorbents in interaction with complex multi-element mixtures

AMB03 Adsorption of nitrophenolic compounds on porous photopolymer-derived carbons

AMB04 Optimizing MnFe2O4 Nanoparticles for Efficient Rare Earth Element Recovery from Contaminated Waters: A Response Surface Methodology Approach

AMB05 Application of magnetic Nanoparticles for the removal of Microplastics from aquatic systems

AMB06 Advanced Functional Materials for Water Pollutants Adsorption

AMB07 Estudio del Análisis de Ciclo de Vida

AMB08 Green processes to valorize Paulownia wood based on deep eutectic solvent (DES)

AMB09 Macroalgae for a circular economy: Recovering critical elements from acid mine drainage

AMB10 Selective Copper Removal from Multi-Element Solutions with Thiourea Formaldehyde-Graphene Oxide Composite

AMB11 Cork Boiling Wastewater: a promising sustainable water source for cosmetic application

AMB12 Synthesis and evaluation of a pine cone-derived adsorbent for remediation of recalcitrant pollutants in water

AMB13 Remoção de fluoxetina de efluentes aquosos usando adsorventes à base de casca de noz

AMB14 A Sustainable Approach to Cellulose Extraction from Wood Waste

AMB15 Defect engineering of UiO-66 using a mixed-ligand strategy via microwave-assisted synthesis to enhance CO2 capture and conversion potential

AMB16 Uso de Óleos Essenciais como Conservantes Naturais em Cosméticos: Desafios e Eficácia no Controlo Microbiano

AMB17 Estrogen Removal through Adsorption by Carbon Materials Prepared from Biomass Wastes: A Review

AMB18 Recyclable 3D Spongin Scaffold for Enhanced Recovery of Rare Earth Elements from Aqueous Waste Streams

AMB19 Remoção de cloridrato de sertralina com carvão ativado produzido a partir de casca de noz ativada com $ZnCl_2$

AMB20	Purificação a seco do biodiesel etanólico através de adsorção utilizando materiais à base de casca de amêndoa
AMB21	Remoção de Metformina de Matrizes Aquosas por meio de Adsorventes à base de Cortiça
AMB22	Neodymium extraction and recycling from magnet leachates using magnetic nanoparticles
AMB23	Development of an extraction method for the multiresidue analysis of 40+ pharmaceuticals in biota (mussels and red mullets) using QuEChERS-LC-MS/MS
AMB24	Polystyrene recycling with green solvents using a dissolution-precipitation method
AMB25	Affectation of Galician beaches by microplastic pellets after the spillage from the Toconao ship
AMB26	Recovery of all the raw materials from the waste light-emitting diodes
AMB27	Extração Eficiente de Compostos Fenólicos: Aplicação de Métodos Assistidos por Calor e Ultrassons em Partes Aéreas de Crithmum maritimum L. e Scolymus hispanicus L.
AMB28	Optimized Ultrasound-Assisted Extraction of Bioactive Compounds from Raspberry and Blueberry Pruning Residues for Sustainable Cosmetic Applications
AMB29	Integrated Circuits: proposal of a closed recycling method for the recovery of gold
AMB30	Optical Setups for Monitoring Nitrates, Carbon Dioxide and Turbidity in Macroalgae Production Tanks
AMB31	Breakthrough Curve of Activated Carbon and Geopolymer for the Adsorption of Sulfamethoxazole, Acetaminophen, and Gallic Acid
AMB32	Synthesis and Characterization of Activated Carbon, Geopolymers and Carbon Nanotubes from Waste-Derived Sources
AMB33	Microplásticos en Sistemas Estuarinos: Interacciones con Mejillones e Implicaciones Ambientales
AMB34	Exploring Lignin Valorization as a Sustainable Modulating Agent: Impact on the Physicochemical Properties of Port Wine
AMB35	Production and characterization of different green adsorbents for the removal of free glycerine in the biodiesel purification process
AMB36	Development of a multi-phosphor system from Chlorella pyrenoidosa for luminescent solar concentrators
AMB37	Valorización de Salmo trutta: Caracterización nutricional, fitoquímica y antioxidante para el desarrollo de productos sostenibles
AMB38	Materiales carbonosos a partir de materiales lignocelulósicos para baterías ion litio
AMB39	Synthesis of choline-amino acid ionic liquids and application to the extraction of biomolecules and pharmaceuticals

Poster

AMB40	Impact of Damming on Fluvial Nutrients and Trace Element Fluxes to the Ria of Ares-Betanzos (NW Iberian Peninsula)
AMB41	La madera de Robinia pseudoacacia como fuente de compuestos de valor añadido: empleo de microondas como método de extracción sostenible
AMB42	Versatilidad del Fe-MOF en diversos procesos de oxidación avanzada para la descontaminación y desinfección de aguas

AMB43	Sustainable Synthesis of Gold Nanoparticles from Osmundea pinnatifida: A Green Approach for Antioxidant and Antitumoral Applications
AMB44	Dual Photocatalytic and Antibacterial Performance of Green-Synthesized Ag-TiO_2 Nanocomposites for Water Treatment
AMB45	O futuro sostible dos cosméticos con lúpulo
AMB46	Assessing the Ecotoxicity Effects of Magnetic Nanoparticles applied for Microplastic Removal
AMB47	Water supply physico-chemical parameters in a Guinea-Bissau population district measured through the Water Quality Index (WQI)
AMB48	Sustainable food packaging solutions: Bioactive bacterial nanocellulose films loaded with Paulownia wood extract
AMB49	Valorization of Himanthalia elongata seaweed for the recovery of bioactive compounds by green processes
AMB50	Estructuras metal-orgánicas de Fe-Cu como catalizadores para la degradación de pesticidas mediante procesos de oxidación avanzada
AMB51	Evaluation and optimization of a multielectrode system for the treatment of effluents with high organic matter content
AMB52	Sustainable Synthesis of High Purity Biosilica from Rice Husk: Overcoming the Limitations of Mineral Acid Leaching
AMB53	Removal of Zn(II), Cu(II) and Pb(II) from rainwater: white bean peel sorbent
AMB54	STUDY OF THE ADSORPTION CAPACITY OF ACTIVATED CARBON DERIVED FROM KRAFT LIGNIN TOWARDS SULFAMETHOXAZOLE
AMB55	Fixed-bed column adsorption studies for the removal of antibiotics from water using regenerable biochar obtained from brewery wastes
AMB56	Enhancing nanocelluloses modified with succinic anhydride for efficient removal of heavy metals in aqueous medium
AMB57	Evaluating the Cytotoxicity and Environmental Impact of Nanoparticles: Insights from Microtox® Bioassays
AMB58	*Sustainable extraction techniques for bioactive compounds from marine biomass*
AMB59	Multiresidue analysis of 7 therapeutic classes of pharmaceuticals in sediments by US-SPE-LC-MS/MS
AMB60	Valorization of cork industry residues and its application for wastewater treatment
AMB61	Study of the adsorption of triazinic herbicides on microplastics
AMB62	Adsorption behavior and mechanisms of terbutryn in polyethylene microplastics in marine environment
AMB63	Potencial bioactivo de extractos ricos en compuestos fenólicos de Arnica montana L. obtenidos mediante métodos verdes optimizados
AMB64	Identificación de microplásticos mediante técnicas de aprendizaje automático multimodelo
AMB65	Evaluación de tres técnicas de flotación para la separación eficiente de microplásticos en sedimentos
AMB66	Metal(oid)s oral and inhalation bioavailability estimation in recycled tire rubber and related materials
AMB67	Oxidative stress associated with recycled tire samples and related materials through an in-vitro assay

AMB68	A first inventory of plastic litter at the coastline of Bay of Asunción and associated total metal contents
AMB69	Evaluation of Carbon and Nitrogen content of residual biomass from corn steep liquor after biosurfactant and gramicidin extraction for nutritional fermentation media
AMB70	Preliminary stability of cell-bound biosurfactant extract produced in corn steep liquor
AMB71	Mechanical performance of fly ash-based geopolymer concrete as a sustainable alternative to ordinary Portland cement Sustaineble Chemistry
AMB72	Novel Biodegradable Depigmenting Agents: Safe and Sustainable by Design to Address Environmental Concerns in Cosmetic Formulations
AMB73	Energy and Sustainability: Shaping Our Energy Future
AMB74	Detection and quantification of carbamazepine in water matrices using a simple MIP-based electrochemical sensor
AMB75	A Sustainable Strategy in Peptide Synthesis for the Preparation of cis-4-Hydroxy-L-Prolyl Amides
AMB76	Protic Organic Salts as additives in Vanadium Redox Flow Batteries
AMB77	The Impact of Grid-Connected Battery Storage Systems on Electrical Grid Variables
AMB78	Quality of biofertilizer produced in home composting
AMB79	Rugulopteryx okamurae's Surprising Potential for Metal Nanoparticles Synthesis
AMB80	Ulvan-Functionalized Gold Nanoparticles: Advancing Green Nanotechnology from Algae
AMB81	INNOAQUA: Innovative Approaches for an Integrated use of Algae in Sustainable Aquaculture Practices and High-Value Food Applications
AMB82	Advancing Sustainability with Lithium-Ion Batteries: Economic and Environmental Impacts in Residential Energy Systems
AMB83	Perspectivas Futuras y Desafíos en la Transformación Energética Globa
AMB84	The Impact of Battery Size and Depth of Discharge in Battery´s Sustainable Use and Carbon Emission: Energy Management According to Spanish Electricity Tariff

Bioquímica y Biotecnología

Oral

BB01	Biosensing platforms for exosome detection in liquid biopsies. Applications in cancer diagnostics
BB02	Características de la superficie celular asociadas a la virulencia de mutantes de Mycobacterium tuberculosis defectivos en los transportadores de membrana CtpF y MmpL7
BB03	ChemSensing – A biosensor to detect human sensitizers
BB04	Application of adjuvant factors in differentiated intestinal epithelial cell systems: assessment of gluten-induced perturbation in cells' homeostatic and inflammatory states
BB05	Severity scale of post-COVID condition using advanced spectroscopy
BB06	Evaluation of the Cytotoxicity Profile of Prebiotic Biosurfactants Produced by Lactic Acid Bacteria for Dermal Applications

BB07	Extraction of hydrophilic cell bound surface active compounds from biomass contained in olive residual sludge
BB08	Engineered Defensosomes: Quantifying and improving the cytoprotective efficiency of extracellular vesicles (EVs) against Staphylococcus aureus Alpha Hemolysin (Hlα)
BB09	Development of a nanoplatform for a vaccine against toxoplasmosis
BB10	Integrated glucose oxidase biocatalyst and Fenton-based system for cancer therapy

Poster

BB11	Herramientas moleculares para la detección de Mycobacterium bovis, genes de resistencia antibiótica y la microbiota de leche y queso de bovinos de la región de Sumapaz, Colombia
BB12	Efecto de Análogos de Brasinoesteroides (BRs) del tipo 24-norcolanos para la inducción de callo de Aristotelia chilensis (Mol.) Stuntz y ultraestructura del callo productor de antocianinas.
BB13	Extracción de xilano β-1,3 a partir de algas marinas
BB14	Antimicrobial Activity Evaluation of the Biosurfactant Extract Obtained by Membrane Technology Against Different Pathogenic Bacterial Strains
BB15	Improving Hybrid Carrageenan Gel Properties and Extraction Efficiency from Mastocarpus stellatus and Chondrus crispus with Subcritical Water
BB16	Tratamento hidrotérmico da macroalga invasora Sargassum muticum para a produción de oligosacáridos, bioetanol e ácido succínico
BB17	Antimicrobial Susceptibility Pattern of Fecal Bacteria isolates from Wastewater: Impact of WWTP Effluents Biochemistry and Biotechnology
BB18	Isolamento e estabelecimento de condições de crescimento do fungo Terana caerulea para potencial produção de pigmentos
BB19	Aislamiento e inoculación de especies de Trametes versicolor del Parque Natural de Montesinho
BB20	In Vitro Cell Models for Assessing Ingestion Exposure in Firefighters: New Insights into Occupational Risk
BB21	Impact of Subcritical Water Extraction on the polysaccharide characteristics of hybrid carrageenans from Mastocarpus stellatus and Chondrus crispus
BB22	Study of the Cosmeceutical Properties of the Plant Anacyclus monanthos subsp. cyrtolepidioides

Catalisis y Fotocatálisis

Oral

CAT01	Iron-based metal organic framework as a suitable catalyst in photo-PMS activation for venlafaxine degradation
CAT02	β -Ketoenamine linked Covalent Organic Frameworks as photocatalyst for direct sulfonilation of anilines
CAT03	Modificaciones y optimización del nitruro de carbono grafítico y sus técnicas de inmovilización para la eliminación de contaminantes coloreados en agua
CAT04	High-performance Fe-modified black tea biochar as electrocatalyst for water splitting applications
CAT05	Implementation of novel Zn-MIL53(Fe) catalyst in Advanced Oxidation Processes to degrade pharmaceuticals in wastewater

CAT06 Empleo de materiales organometalo-silíceos de iridio (III) en procesos fotocatalíticos de transferencia electrónica

CAT07 Molybdenum oxide hybrid catalysts with bipyridine ligands as heterogeneous and RISS catalysts in olefin epoxidation

CAT08 Síntesis de organometalo-titanias híbridas y su aplicación en la fotodegradación de colorantes con luz visible

CAT09 Electrospun Fe-MOF nanofiber membranes: Synthesis and catalytic application in the Electro-Fenton process

CAT10 COMUNICACIÓN DADA DE BAJA

CAT11 Hybrid nanomaterials based on semiconductor–metal sulfides/oxides; synergetic promotion of photocatalytic activity

CAT12 Heteropoly acids @PVA membranes for glycerol acetalization

CAT13 Effective Porous Metal-organic Frameworks catalysts for ring-opening reaction

CAT14 Microwave-assisted ethyl levulinate production using as catalyst rice husk biobased materials

CAT15 Evaluating the Impact of Thermal Treatment pn the Catalytic Efficiency of Carbon Nanotubes as Catalytic Support in Fischer-Tropsch Synthesis

Poster

CAT16 Surface response methodology to optimise orange peel biochar synthesis for water splitting applications

CAT17 Nitruros de carbono grafíticos modificados como fotocatalizadores verdes para la eliminación de contaminantes emergentes

CAT18 COMUNICACIÓN DADA DE BAJA

CAT19 Synthesis of Zn and Fe nanocomposites obtained by pyrolysis of ternary deep eutectic solvents for catalytic water treatment applications

CAT20 Copper effect in catalytic performance of transition metal-doped ferrites involved in the synthesis of tacrine derivatives

CAT21 Nitrogen catalytic sites on carbon surface able to promote the Friedländer reaction: DFT calculations

CAT22 Stable and cost-effective catalysts for the degradation of dyes in water

CAT23 Removal of a micropollutant model using novel three-electrode cells with advanced oxidation treatments

CAT24 *Eco-Friendly Catalysts Derived from Biowaste for Efficient Hydrogen Production*

CAT25 g-C3N4-TiO2-SiO2 nanocomposites for producing multifunctional buildings with hydrophobic, self-cleaning and depolluting properties

CAT26 Immobilised Cs3Bi2Br9 Perovskites for Photocatalytic Imines Synthesis

Enseñanza de la Química

Oral

EDU01 "El uso de los gráficos en la enseñanza de la química"

EDU02 Reacciones microquímicas: Un interesante recurso para el ahorro de reactivos y residuos.

EDU03 El color que te puede salvar la vida: una aproximación experimental a la química de fármacos en el aula de Educación Secundaria Obligatoria, Bachillerato y Formación Profesional

EDU04 De las chicas del Radio al enemigo invisible: aprendizaje experimental de la radiactividad en el aula de ciencias experimentales

Poster

EDU05 Cinética de las reacciones químicas

EDU06 Práctica virtual de Laboratorio de Química: Determinación del calor específico del plomo

EDU07 Caso Práctico: uso de herramientas Jupyter Notebooks para la resolución de problemas de gases reales

EDU08 Caso Práctico: uso de herramientas Jupyter Notebooks para la resolución de problemas de cinética

Química Industrial e Ingeniería Química

Oral

IND01 Produción de ácido biosuccínico mediante estratexias fermentativas a partir de peles de pataca: optimización do proceso

IND02 Synthesis of novel Carboxymethyl Cellulose-Coated Metal-Organic Framework and its use in heterogeneous Electro-Fenton

IND03 Extraction of Hydroxyapatite at Moderate Temperature Using Ionic Liquids

IND04 Rheological measurement of corn starch gel hydrolysis rate at different α-amylase concentrations

IND05 PEG/Sodium Citrate Aqueous Two-Phase Systems: Phase Diagrams

IND06 Fish Protein recovery using Aqueous Two-Phase Extraction

IND07 Optimisation of pectin extraction from inner lime peel using succinic acid aqueous solutions

IND08 A comparative study of leather dyeing with different colourants: synthetic versus natural mordant

IND09 Leather natural dyeing with Mulberry (Morus alba) leaf extract: a comparative study with different natural mordants

IND10 Enhanced Gelatine Extraction from Tuna Skin Using a Non-Dissolution Ionic Liquid Pretreatment

IND11 Enhancing Grid Stability and Sustainability Through Battery Storage Systems Integration with Renewable Energy Sources

IND12 Engineering of Chemically Resilient FTO Current Collectors for Stable and Efficient Upscaled Photovoltaics and Photoelectrochemical Devices for Water Splitting

IND13 Phosphomolybdic acid as a high-capacity electrolyte in aqueous redox flow cell

Poster

IND14 Autothermal pyrolysis of a photopolymer demonstrated by TGA-DSC and simulated by ASPEN Plus software

IND15 Analysis of gorse flower extracts obtained by ultrasound assisted technology: determination of phenolic compounds and antioxidant activities

IND16 A biorefinery approach for the manufacture and characterization of oligosaccharides and antioxidants from gorse

IND17 Obtención de 5-HMF a partir de bagazo de mazá usando disolventes verdes asistidos con microondas

IND18 Physical Properties of Cholinium L-Lysinate and its Mixtures with Different Solvents

IND19 Neutralization of Bauxite Waste (Red Mud) through CO2 Absorption

IND20 Evaluation of the effectiveness of impregnated activated carbon in monoethanolamine or diethanolamine for CO2 capture

IND21 Strategies for the integral valorisation of wine industry waste through sustainable processes

IND22 MICROWAVE PYROLYSIS OF KRAFT LIGNIN FOR SUSTAINAGLE ACTIVATED CARBON PRODUCTION

IND23 Impact of organic acids during pilot-scale dialysis for biosurfactant recovery

IND24 Metals dynamics in pilot-scale dialysis for biosurfactant recovery

IND25 Microwave hydrodiffusion and gravity as pretreatment to enhance phenolic compounds and polysaccharides extraction from terrestrial and marine biomass

IND26 Extraction of pectin from inner orange peel with aqueous solutions of different biobased organic acids

IND27 Sequential extraction of biosurfactants from corn steep water combining liquid-liquid extraction and dialysis process: A comparative study

IND28 Renewable Energy Sources: Battery Storage Systems for a Sustainable Future

IND29 Synthesis and purification of ethyl lactate (EL) using a sustainable process

IND30 Simulated Moving Bed Reactor for 1,1-Diethoxybutane Synthesis

IND31 Industrial By-Products for Biogas Production

Nanoquímica y Nanotecnología

Oral

NN01 Preparation, characterization and stability evaluation of self-assembled anthocyanins-loaded zein/polysaccharide nanoparticles

NN02 Interplay Between Spin-Spin Interactions and Molecular Conductance in Boron-Doped GNRs

NN03 Emprego de carbon dots como material sensor fluorescente para a detección de nanopartículas de titanio en auga

NN04 Sol-Gel Coordination Chemistry for sustainable applications

NN05 MoS2-Fe3O4 nanomaterials for effective water treatment: A study on acetamiprid removal

NN06 Energy monitoring by color change in electrochromic textile supercapacitors using PEDOT:PSS and nitrogen-doped porous carbon from glucose

NN07 Magnetic CNT@MnFe2O4-based Thermally-Chargeable Textile Supercapacitor with Glow-in-the-Dark Properties

NN08 Quantum-dot mediated fluorescence detection of miRNAs

NN09 Quantum Dot-Based Nanosensors for Early Detection of Cancer Biomarkers via TR-FRET Technology

NN10 Análise de glóbulos vermellos expostos a AgNPs mediante single-cell ICP-MS

NN11	Breaking bAD: using chemistry, biophysics and biotechnology to unburden Atopic Dermatitis
NN12	Biodispoñibilidade de nanopartículas de Ag e TiO2 en organismos mariños
NN13	Cationic polyurea (PURE) dendrimers an Escape from antimicrobial resistance
NN14	Development of Gold NanoProbes for detection of DNA mutations
NN15	Science Inspired by Nature: Milk-Based Delivery Systems
NN16	Engineered Liposomes as an efficient strategy for enhancing the treatment of Mycobacterial infections
NN17	Nanocellulose for Applications in Strategic Sectors: Production, Modification, and Application
NN18	Lipid Nanoparticles in Action: Powering Hyaluronic Acid Production in Skin Cells
NN19	Engineering Efficient Energy Transfer in DNA Hybrid Systems
NN20	Rosamine-Loaded Metal-Organic Framework: A Bright Sensor for Cu(II) Detection
NN21	Formulation of Ethosomal Suspensions Loaded with Rubus idaeus Leaf Extract for Cosmetic Application

Poster

NN22	Digital Image Colorimetry Smartphone Determination of ZnO NPs
NN23	Detection of CuO NPs in ethanol-water solution using a fluorescent probe
NN24	Does quercetin protect intestinal cells from silver nanoparticle-induced pro-inflammatory effects?
NN25	Synthesis and characterization of ZnO nanostructures using olive leaf extract for prospective application in food packaging
NN26	Engineered bioactive casein micelles for hypertension treatment
NN27	Sustainable nanomaterials from biomass: potential for scale-up and commercialization in the near future

Química de Polímeros

Oral

POL01	Proyecto REGATEX: Escalado de un proceso de reciclaje químico de residuos textiles
POL02	Isocyanate-terminated prepolymer synthesis targeting cork composites for the footwear cluster
POL03	Water-based Polyurethane-urea dispersions as adhesives for the footwear industry: Developing high biobased content solutions
POL04	NIPUs a partir de lignina kraft de ENCE

Poster

POL05	Viscosidad intrínseca y peso molecular viscosimétrico medio de diferentes quitosanos
POL06	Empleo de sarmientos procedentes de la poda de vid para la fabricación de pasta de papel y cartón, VINEBOX
POL07	Gelatine-alginate hydrogels: evaluation of swelling and 3D-printability targeting wound healing applications
POL08	Lignina kraft de ENCE para la fabricación de espumas de poliuretano y poliuretanos termoplásticos

POL09	Recent advances in biodegradable polymers for fishing gear manufacturing

Química Analítica

Oral

QA01	Portable electrochemical biosensing device for point-of-care diagnostics. Applications in communicable diseases
QA02	Screening y determinación de plaguicidas en aguas superficiales y subterráneas mediante cromatografía líquida acoplada a espectrometría de masas con analizador de tiempo de vuelo
QA03	Identificación de sustancias orgánicas peligrosas en residuos de aparatos eléctricos y electrónicos
QA04	Simultaneous detection of human neutrophil elastase and Cathepsin G on a single substrate using a fluorometric quantum dots probe and chemometric models
QA05	Nanosensores Ópticos para la Detección de Iones y Compuestos Volátiles en Muestras Ambientales y Alimentarias
QA06	Innovative strategies for trapping metals and metalloids using noble-metal nanoparticles immobilized onto cellulose substrates
QA07	DESIGN OF PAPER-BASED ANALYTICAL DEVICES FOR CHEMICAL AND BIOCHEMICAL ASSAYS OF BIOMARKERS IN BIOLOGICAL FLUIDS OF NON-INVASIVE COLLECTION
QA08	Análise elemental e isotópica de alta precisión de metais para o estudo da metalómica de peixes infectados por parasitos
QA09	Cytochrome P450 Testosterone Biosensor using Modified Carbon Screen-Printed Electrodes
QA10	Flow-based method for total protein content monitoring in by-products hydrolysates
QA11	Utilização de diferentes dados de segunda-ordem para a determinação de tiamina explorando a reversão de um processo FRET entre Pontos Quânticos de Carbono e Nanopartículas de Prata
QA12	Innovative extraction procedure based on deep eutectic solvent and cellulose membrane for the determination of synthetic musks in surface waters
QA13	Binding studies of synthetic cannabinoids to human serum albumin by high-performance affinity chromatography
QA14	Ensuring food safety: Electrochemical genosensors for the authentication of plant honey origin
QA15	N-hydroxyamides’ pKa determination by NMR spectroscopy

Poster

QA16	Isothiazolinones: Chemical and ecotoxicological screening
QA17	End-of-life plastics from vineyards. A hot spot of pesticides in the terrestrial environment
QA18	Estudio de la distribución de fungicidas orgánicos en el sistema uva-suelo-vino
QA19	La huella del empleo de plaguicidas en el polietileno de uso agrícola
QA20	Identificación y cuantificación de saponinas en muestras silvestres de Quillaja saponaria Mol. mediante HPLC-PDA
QA21	Optimización de condiciones de separación por HPLC mediante inteligencia artifial

QA22	Aplicación de un Diseño Central Compuesto para la optimización de separaciones mediante HPLC
QA23	Curcumin-containing paper based analytical devices for boron determination in environmental waters
QA24	Photochemical synthesis of carbon dots: Applications in analytical chemistry
QA25	A paper-based analytical device for the simultaneous scanometric determination of nitrite and sulfide in environmental waters
QA26	Rapid and eco-friendly chromatographic method for the determination of polyphenolic compounds in leaf water extracts
QA27	SMART SAMPLING PROCEDURE FOR METAL IONS ASSESSMENT IN DYNAMIC WATER SYSTEMS
QA28	Separación de proteínas mediante electroforese offgel en mostras de algas expostas a nanopartículas de prata
QA29	Determinación de elementos críticos tecnolóxicos en cunchas de moluscos mediante Espectrometría de Masas con Plasma de Acoplamento Indutivo
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Oral

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QO04 A new porphyrin–rosamine conjugate as a potent singlet oxygen generator

QO05 Factorial design for optimization of tetra-substituted meso-aryl porphyrin synthesis through flow chemistry

QO06 Acidochromic free-standing multilayered chitosan-pyranoflavylium/alginate membranes towards food smart packaging applications

QO07 Preparation of A2B2-type porphyrins through C–N bond formation as useful components in perovskite solar cells

QO08 Click on Click: Unlocking the Potential of Click Chemistry in Drug Delivery and Small Molecule Synthesis

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QS31	Novel avenues into adipogenesis inhibition: optimization and validation of an in vitro methodology to study the role of flavonoids in 3T3-L1 adipocyte cell line differentiation
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QS36	Pyrimido[5,4-d]pyrimidines as efficient and specific anticancer agents in the osteosarcoma 143B cell line
QS37	Produção de Pontos de Carbono Fluorescentes com Potencial Antioxidante a partir dos Ouriços da Castanha
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QS46	Development of Chondroitin Sulfate-loaded Chitosan/Hydroxyapatite Scaffolds Targeting Bone Regeneration
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QS51	Composición de ácidos grasos y potencial antioxidante del aceite de andiroba
QS52	Avaliação de biomarcadores de dano renal em bombeiros com participação ativa num fogo controlado urbano

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QT02	Líquidos porosos y el comportamiento absortivo selectivo de CO_2 y SO_2 mediante Dinámica Molecular.
QT03	Unraveling the cellular battle: Antimicrobial peptides and membranes disrupted by COVID-19 using Molecular Dynamics
QT04	Exploring the Membrane Binding Interactions and Reaction Pathways of Snake Venom Phospholipase A2 Toxin: A Computational Study
QT05	Ensemble-weighted prediction of phtotophysical properties of BODIPY derivatives
QT06	Molecular basis of a photoswitchable histone deacetylase inhibitor: N-(2-Aminophenyl)-3-(4-((methoxyphenyl)diazenyl)phenyl)propanamide.

Poster

QT07	A machine learning-based approach to understand dynamic topological changes of the charge density
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Seguridad Química

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Poster

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SQ03	ControlQ_LABCOMB: EVALUACIÓN DE LA EXPOSICIÓN AL RUIDO

CONFERENCIAS PLENARIAS

APERTURA

Humanity faces a bright future, and so Chemistry

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Humanity faces six global challenges:

1. Climate change and air quality
2. Sustainable energy
3. Dwindling raw materials
4. Water scarcity and safety
5. Food for everybody
6. Health problems

These problems are complex because they cannot be solved by known technologies, but future technologies will solve them. Because all six problems are primarily chemical issues, it is our responsibility and opportunity, as chemists, to meet these challenges. Everything is chemistry, and all sciences are chemistry because they all deal with matter, and all matter is made of atoms and molecules.

Humanity faces a bright future due to four reasons:

1. Knowledge explosion
2. Unpredictability of science
3. Evolution of network society
4. Human spirit and creativity

We live in artificial environments, eat genetically engineered food, wear synthetic and genetically modified fibers, and travel by fabricated devices. Since we live on products of human imagination and creativity, and since imagination and creativity have no limits, the effective area of planet Earth has no limits.

Therefore, the best ways to meet global challenges are:

1. Invest in education at all levels – encourage curiosity.
2. Invest in basic, high-risk, exploratory science.
3. Bolster human liberty, dignity, and democracy.
4. Encourage economic growth because only rich countries can afford good education, health, scientific innovation, and adaptation.

Marine Polysaccharides: A Sustainable Source for Functional Biomaterials in Biomedical Applications

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Polysaccharides derived from marine environments represent an emerging class of renewable and functional molecules. Sulfated polysaccharides, unique to these ecosystems, hold significant potential for valorization due to their distinctive physical and biological properties. Structurally and functionally analogous to mammalian glycosaminoglycans, these compounds have garnered increasing interest for various biomedical applications. Beyond their roles as natural drugs—such as anticoagulants and anticancer agents—they are being explored for tissue engineering, biomolecule immobilization, and drug delivery, enhancing the bioactivity of materials. However, to ensure their sustainable use, it is crucial to establish a clear relationship between the structure of these polysaccharides and their biological activity.

In the biomedical field, the demand for new biocompatible and biodegradable materials is rapidly increasing. Biopolymers, particularly polysaccharides, have garnered significant attention due to their biocompatibility, biodegradability, and abundance, as well as their functional groups that enable modification. This approach facilitates the design of composites that harness the strengths of various materials, resulting in enhanced mechanical performance and stability while preserving (bio)compatibility. Moreover, new functionalities can be integrated into these biomaterials, including antimicrobial properties, electrical conductivity, magnetic characteristics, and piezoelectricity, expanding their potential applications. As a result, these innovative materials address the growing need for durable and sustainable solutions, aligning with the global trend toward biobased and environmentally friendly alternatives.

The focus of this work is the structural analysis of polysaccharides derived from various marine resources, specifically seaweeds and microalgae, and their relationship to biological activities. This approach reveals significant potential for harnessing the marine environment as a source of polysaccharides, paving the way for the development of functional and sustainable biomaterials tailored for specific biomedical applications.

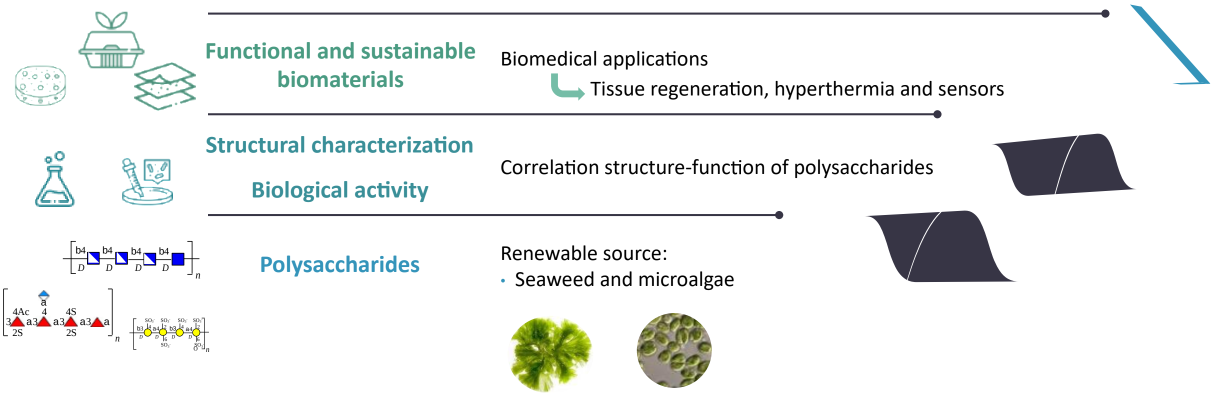

Fig.1. Schematic representation of polysaccharide analysis from marine resources and their application in biomedical field.

Acknowledgments
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Wet-chemical synthesis and exceptional catalytic properties of metal clusters of small atomicity without protecting ligands

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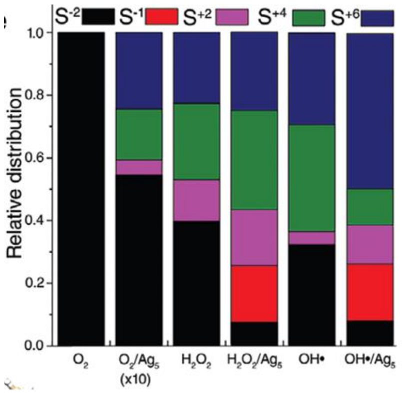
Metal nanoclusters exhibit distinct properties compared to both nanoparticles and bulk materials due to the quantum confinement of free electrons [1]. These nanoclusters behave like super-atoms or molecules, where atoms are bound by strong covalent bonds [2]. Over the past two decades, we have developed ligand-free, kinetically controlled wet-synthesis methods to produce monodisperse nanoclusters (primarily of Au, Ag, and Cu) with small atomicity (<20 atoms) at pilot-scale production levels (>1 g/day) [3]. In this presentation, we will discuss the fundamentals of this technique and explore the catalytic activities of nanoclusters in both solution and when supported on various substrates. Notably, gold pentamers (Au_5 clusters) have shown high efficiency in catalyzing the aerobic oxidation of thiophenol to disulphide [4]. More recently, we have demonstrated the remarkable catalytic performance of silver pentamers (Ag_5 clusters) in the irreversible aerobic oxidation of thiols, with size-dependent activity peaking at around five atoms [5]. We also observed increased catalytic activity across the series $O_2 < H_2O_2 <$ OH radicals, which has been applied in novel approaches to cancer therapy [6]. Additionally, Ag_5 and Cu_5 clusters supported on different metal oxides exhibit significant selectivity and versatility, enhancing industrially relevant reactions like clean hydrogen production and CO_2 valorization [7]. Finally, we will briefly comment on the use of Cu_5 clusters for the activation of 2D polymerization on insulating surfaces reducing the polymerization temperatures by ≈ 100ºC [8].



Population of S-oxidized species for thioredoxin (Trx) with different oxidating species, obtained from S K-XANES for [Ag5]/[Trx] = 1:5000, after 10 min of reaction.

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Catalyzing the Green Revolution:
Unlocking Previously Inaccessible Chemical Processes

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The development of intracrystalline mesoporosity within zeolites has been a long-standing goal in catalysis as it greatly contributes to alleviating the diffusion limitations of these widely used microporous materials. During my presentation, I will discuss the main techniques that have been developed during the last years to produce zeolites with controlled mesoarchitectures comparing the different methods, their advantages and limitations. Among the different techniques used to characterize the composition, porosity and structure of these materials, I will present unprecedented insights on the formation of intracrystalline mesoporosity in zeolites obtained by *in situ* synchrotron X-ray diffraction, Atomic Force Microscopy (AFM), and Liquid Cell Transmission Electron Microscopy (Liq-TEM). By combining experimental results and theoretical calculations, the presence of intracrystalline mesoporosity was recently confirmed. Moreover, through the direct observation of individual zeolite crystals by in situ AFM and Liq-TEM, we have been able to provide the first time-resolved visualization of the formation of mesoporosity in zeolites.

During the presentation, I will describe a new strategy for the synthesis of superior hierarchical catalysts, which lack long-range order but at local scale contain zeolite building units. [1,2] In fact, they are made out of fragments of one or even various zeolite structures and display improved accessibility, strong acidity, and excellent stability. Because of these features, they effectively catalyze reactions involving very bulky molecules, which currently are produced using highly corrosive homogenous catalysts (Fig. 1). To achieve this goal, we built on a well-known technique, namely the interconversion of zeolites, which we interrupted at different times to yield the desired amounts of building units of the zeolites involved. The addition of quaternary ammonium surfactants during their preparation allows the development of well-defined mesoporosity and large surface areas. Using this simple procedure, we were able to produce families of materials with controlled amounts of different zeolitic building units and, consequently, optimize their catalytic performance for various reactions including Friedel-Crafts alkylations and Claisen-Schmidt condensations, and the cracking of 1,3,5-triisopropylbenzene.

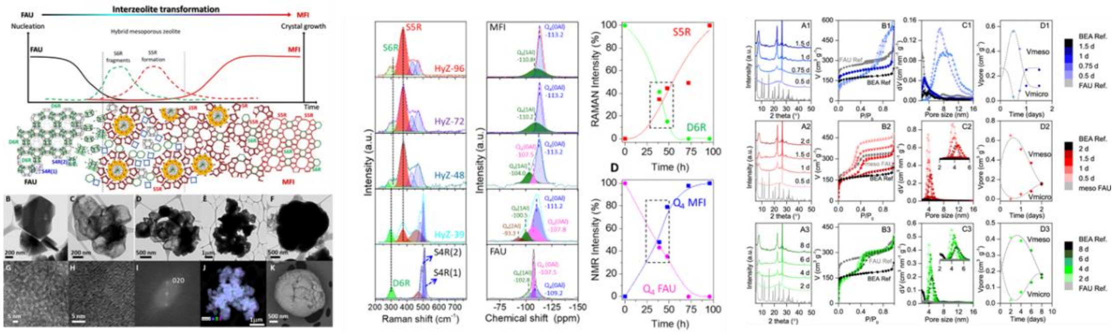

Figure 1. Textural, structural, and morphological characterization of some intermediates of the interconversion of zeolite FAU into MFI and BEA structures.

An important advantage of this strategy is that the physicochemical properties and, therefore the catalytic performance, of the hierarchical catalysts can be finely tuned by simply stopping the interzeolite transformation at different times. This creates countless opportunities for the development of hierarchical catalysts [3] with optimized properties and superior catalytic performance for those reactions in which zeolites present significant diffusion limitations (Fig. 1). This paves the way for the fabrication of hybrid hierarchical catalysts with optimized properties for those processes in which the combined use of different zeolites yields improved performance.

The presence of this mesoporosity was further evidenced through *ex situ* gas adsorption, which also confirmed the preservation of most of the microporosity of the zeolites. All these new insights, obtained by combining a number of time-resolved techniques, are an example of the enormous potential of current *in situ* characterization methods for the rational design of hierarchical zeolites with superior properties and optimal catalytic performance as it has been proved at lab, pilot plant, and industrial scale.

In several operations in a number of refineries, a steady increase in LPG olifinicity was observed when replacing the incumbent FCC catalyst with another containing our mesostructured Y zeolite. Commercial data confirmed what we observed in equilibrium catalysts, i.e. a gradual increase in the LPG olefinicity, as the concentration of the FCC catalyst containing mesostructured Y zeolite in the circulating inventory steadily increased. Furthermore, a very valuable increase in gasoline octane is typically observed due to a higher concentration of olefins in the lighter gasoline fraction.

The commercialization of hierarchical zeolites, first through the MIT spin-off Rive Technology and now by Shell and GRACE, as superior refining catalysts is an example of academic entrepreneurship, which is expected to foster the development of new hierarchical zeolites and their use in both existing processes and new opportunities. Finally, I cover other applications of hierarchical zeolites in catalysis, including biomass valorization and fine chemistry, ending with a personal view of the new directions, and opportunities in this field.

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Exploiting the role of lipids for innovative therapies and delivery strategies

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Lipids, as fundamental components of biological membranes, play a pivotal role in the interaction with various drugs, influencing their efficacy, toxicity, and mechanisms of action. Their amphiphilic nature allows them to engage in complex interactions with drug molecules, which can either facilitate or impede drug delivery depending on the physicochemical properties of both the lipid and the drug. This interplay often impacts drug bioavailability and toxicity profiles, making lipids a key focus in the development of more targeted and safer therapeutic strategies.

On another hand, one of the most promising features of lipids is their inherent capacity to self-assemble into diverse nanostructures such as liposomes, micelles, and lipid nanoparticles. These structures can be modulated into drug delivery systems that enhance drug solubility, stability, and controlled release. Lipid-based carriers offer the advantage of biocompatibility and reduced toxicity, making them suitable for delivering both hydrophilic and hydrophobic drugs. Moreover, their structural versatility allows for surface modifications, enabling targeted delivery to specific tissues or cells, thus improving therapeutic outcomes and reducing side effects.

Furthermore, lipid mimetic models are valuable tools in understanding drug-lipid interactions at a mechanistic level. These models, such as artificial membranes and lipid bilayers, allow for the systematic study of how drugs interact with lipid environments, providing insights into drug partitioning, permeability, and potential membrane disruption.

Lipids are not only passive components in drug formulation but are active players that can be exploited to refine drug delivery strategies. Their self-assembly capabilities and use in lipid mimetic models offer prospects for creating more effective and safer therapeutic approaches, while providing deeper insights into drug-lipid interactions and their influence on drug action. Thus, this communication will explore these 3 branches of lipid research, proving case studies, that we have developed, that focus each one of these perspectives.

Acknowledgements

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COMUNICACIONES ORALES

QUÍMICA ALIMENTARIA

Recuperación de antocianinas y otros polifenoles del bagazo de uva tinta mediante extracciones hidrotérmicas en cascada

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La viticultura es una actividad de gran importancia en Europa, con extensiones de cultivo superiores a 3 millones de ha [1]. Esta práctica genera millones de toneladas de residuos, destacando el bagazo de uva (formado por tallos, semillas y piel), cuya acumulación provoca severos problemas medioambientales [2]. Sin embargo, actualmente se considera un subproducto interesante por su riqueza en polifenoles bioactivos, cuyos beneficios sobre la salud humana han sido probados en numerosos estudios [3].

Para un adecuado aprovechamiento es necesario aplicar un proceso de extracción respetuoso con el medio ambiente y que proporcione extractos de elevada calidad. Así, la extracción asistida por microondas (MAE) es una tecnología verde y energéticamente más eficiente que los métodos convencionales, permitiendo un calentamiento más uniforme y con tiempos de residencia más cortos, reduciendo la degradación de los polifenoles [4]. No obstante, el alto contenido en antocianinas del bagazo y su alta termo-sensibilidad, requieren de procesos menos agresivos.

El principal objetivo de este trabajo fue la evaluación de dos tratamientos hidrotérmicos secuenciales (convencional y MAE) para la extracción de antocianinas y otros polifenoles con actividad antioxidante del bagazo de uva tinta. Los extractos obtenidos fueron caracterizados mediante la determinación de fenoles totales (TPC), flavonoides totales (TFC) y antocianinas monoméricas totales (TMAC). Asimismo, se evaluó su actividad antioxidante por los métodos DPPH, ABTS, FRAP, CUPRAC y TAA. Los resultados obtenidos revelaron la idoneidad del acoplamiento de ambos tratamientos para la recuperación de compuestos de naturaleza fenólica del bagazo de uva tinta.

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Fermented fruit juices: exploring the benefits of the ancient technique for today's juice production

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The evolving consumer focus on the health-promoting properties of food matrices has significantly boosted the functional food and beverage market, driving the industry to innovate and diversify its offerings. While prebiotics and probiotics currently dominate the market, postbiotics are gaining increasing attention for their potential health benefits [1]. Fermentation, a well-known ancient preservation technique, offers numerous advantages, including enhanced bioaccessibility, biotransformation, reduced sugar content, and the production of postbiotics. These factors contribute to the health benefits associated with fermented fruit juices. Notable examples of postbiotics include short-chain fatty acids (SCFAs), extracellular polysaccharides, cell lysates, and vitamins [1], [2].

In this work (Fig.1), orange and red grape were subjected to an alcoholic fermentation process using a yeast strain to investigate the influence of this metabolic process on enhancing the nutritional and bioactive properties of the fruit juices. The evaluation was performed in terms of: (i) phenolic profiling using High Performance Liquid Chromatography (HPLC) coupled with diode array detection (DAD) and mass spectrometry (MS); (ii) water- and fat-soluble vitamin content analyzed by HPLC-DAD; (iii) SCFAs and organic acids content determined via a derivatization method with 3-nitrophenylhydrazine; (iv) beta-glucans content quantified using a spectrophotometric commercial kit; (v) antioxidant activity assessed through colorimetric methods; and (vi) sugar levels measured by HPLC-MS method.

The main results highlighted significant changes in the phenolic profiles of the primary classes of (poly)phenols studied across both matrices. Fermentation resulted in reduced sugar levels in the juices. Additionally, a distinct vitamin profile was observed following fermentation. In the evaluation of SCFAs and organic acids, the most outstanding findings included increased levels of succinic and pyruvic acids. The insights from this study support the use of fermentation metabolism as an innovative technology in juice production, enhancing the nutritional profile of juices and aligning with evolving consumer preferences for functional and health-promoting products.

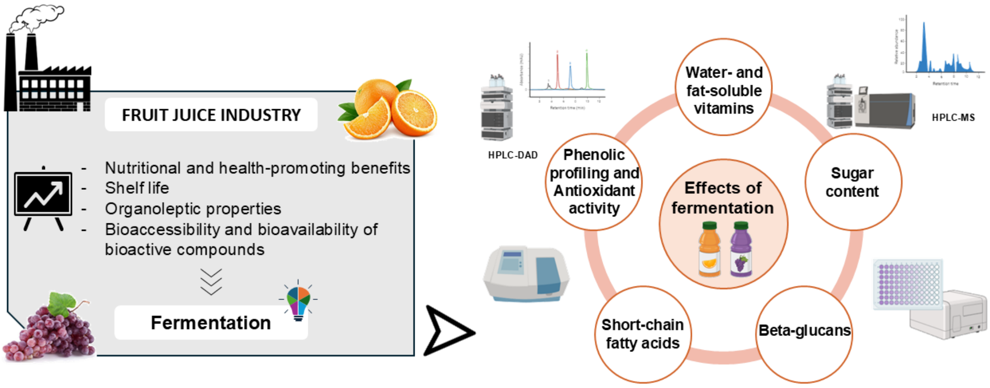

Fig.1. Graphical abstract of the proposed theme.

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A milky way towards novel antioxidant nutraceuticals

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The recent years have witnessed an increased search for healthier and more nutritious food products but also a rise in consumer concern and awareness regarding the origin and sustainability of those same products. With both these issues in mind, this project focused on producing nanocarriers (NC) from milk-derived components, thus bringing added value to this product but also reducing overall waste. These novel NC were designed to encapsulate bioactive agents, thus improving their stability and bioavailability, and be applied in nutraceuticals. Nutraceuticals are foods that possess functional benefits beyond their nutritional value, such as antihypertensive, antioxidant or antimicrobial effects.

In this work, milk fat-derived NC were produced using organic solvent-free methods [1] already used in food technology and loaded with vitamin E, a powerful natural antioxidant, envisioning the development of antioxidative supplements for the food industry. The NC presented two distinct populations, with diameters around 200 and 600 nm respectively, which are optimal dimensions for oral administration and intestinal absorption of lipid-based particles [2]. The NC also possessed a zeta potential value of -20 mV, translating to a good colloidal stability. Moreover, the developed NC were able to maintain these properties for at least 10 months of storage at room temperature, indicating a long shelf-life. They were additionally found to be resistant to gastrointestinal conditions, using biomimetic media, thus enabling the protection of more delicate molecules across the digestive tract. Their *in vitro* biocompatibility was also assessed, registering non-cytotoxic and non-hemolytic results with concentrations of at least 2.5 mg/mL of NC. Lastly, the antioxidant capacity of vitamin E-load NC was determined using the ABTS radical scavenging and oxygen radical absorbance capacity (ORAC) assays in which they were found to exhibit considerable antioxidant activity (Table 1). Moreover, the NC themselves also presented some antioxidant activity (Table 1), indicating their potential to be used as antioxidants and enabling the development of food additives with multiple functional properties.

To summarize, the developed milk fat-derived NC are exceptional candidates for the oral delivery of bioactive compounds, presenting antioxidant effects on their own, highlighting their enormous potential for nutraceutical development. Furthermore, the selected NC building blocks bring an added value to dairy fat-based products and promote a circular economy approach.

Table 1. Trolox equivalent (TxEq) concentrations of vitamin E loaded (NC_E) and unloaded nanocarriers (NC), for both the ABTS and ORAC assays

Formulation	ABTS assay TxEQ (μmol/μg)	ORAC assay TxEQ (μmol/μg)
NC	0.11	0.17
NC_E	0.20	0.50

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Estudo do impacto da interacción molecular dos polifenois do millo corvo e fariñas de trigo autóctonas galegas na bioaccesibilidade do glute

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A doenza celíaca é unha enteropatía crónica mediada polo sistema inmunitario, que se desenvolve tras a inxestión de glute en persoas con predisposición xenética [1]. O glute é un grupo de proteínas (gliadinas e gluteninas) presentes en cereais como o trigo, a cebada, o centeno e a avea. Pese a que a prevalencia nesta doenza está en aumento, até ao momento, o único tratamento eficaz é levar unha dieta libre de glute [2,3]. Neste sentido é prioritario buscar alternativas de prevención e control da doenza ao tempo que se mellore a calidade de vida dos afectados.

Neste contexto, os polifenois xorden como unha forte ferramenta pela súa probada capacidade antioxidante, antiinflamatoria e pola capacidade para unirse molecularmente coas proteínas do glute [4]. As proteínas do glute e os polifenois son dous grupos de biomoléculas de diversa natureza e elevada variabilidade de estruturas químicas. Así tornase crucial a caracterización das matrices alimentarias en estudo avaliando a relación estrutura-actividade e efecto matriz como base para establecer estratexias nutricionais sólidas. Deste xeito, neste traballo avaliouse a capacidade dos polifenois de millo corvo de interaccionar molecularmente coas gliadinas de tres variedades de trigo autóctonas galegas (caaveiro, grandal e callobre), ambos cereais comunmente cultivados en Galicia e empregados para a elaboración de pan e produtos de panadaría, e posteriormente se avaliou o impacto desta interacción molecular na bioaccesibilidade dos péptidos immunoxénicos formados durante o proceso de dixestión de pan.

Para atinxir obxectivos, obtivéronse extractos proteicos das fariñas de trigo e de polifenois de millo corvo. Caracterizáronse os perfís proteómicos e de compostos bioactivos (polifenois) nos ditos extractos empregando espectrometría de masas. Realizáronse estudos de interacción molecular *in vitro* para destacar a reactividade/selectividade dos compostos extraídos. Finalmente, co gaio de avaliar o efecto dos polifenois do millo corvo na liberación dos péptidos immunoxénicos do trigo, deseñouse unha formulación de pan de trigo enriquecido con fariña de millo corvo. Este foi dixerido mediante unha simulación humana *in vitro* e os péptidos resultantes foron analizados por LC-MS/MS.

Os resultados deste traballo mostraron que o millo corvo é un cereal con elevado contido en antocianinas, principalmente derivados de cianidina. Igualmente salientáronse diferenzas significativas na composición de proteinas do glute das tres variedades de trigo testadas que afectou á reactividade dos polifenois. Ademais, comprobouse que como resultado desta interacción se reduciu significativamente a produción de péptidos inmunoxénicos durante a simulación *in vitro* da dixestión humana.

Este traballo establece as bases para unha nova liña de estudo que axude a comprender como os polifenois poden interferir na imunoxenicidade dos alimentos que conteñen glute axudando a crear unha rede de datos útil no deseño de novos alimentos saudables, sostibles, resilientes e inclusivos.

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Avaliação da Atividade Antioxidante de Extratos de Borra de Café: Comparação de Métodos de Extração para Aplicação Cosmética

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O café é uma das bebidas mais consumidas no mundo e apresenta uma cadeia produtiva complexa, a qual resulta na geração de subprodutos, de entre os quais se destaca a borra de café. Apesar de ser frequentemente descartada como resíduo, a borra de café é rica em compostos antioxidantes, que possuem elevado potencial bioativo. Esses compostos desempenham um papel essencial na neutralização de radicais livres, os quais estão relacionados ao envelhecimento celular e a génese de doenças crónicas [1]. A incorporação desses antioxidantes em produtos cosméticos pode conferir benefícios tanto para a saúde quanto para a estética. O presente estudo teve como objetivo investigar a atividade antioxidante de extratos de borra de café utilizando diferentes métodos de extração, a fim de identificar o mais eficiênte e aplicá-lo em formulações cosméticas. A borra de café utilizada, proveniente de grãos 100% arábica, foi obtida num café localizado em Bragança, Portugal. Para a análise da atividade antioxidante, foram empregues os métodos de sequestro de radicais livres 2,2-Difenil-1-Picrilhidrazilo (DPPH) [2] e o ensaio de poder redutor [3]. Os valores de EC_{50} (concentração necessária para reduzir 50%) foram calculados para cada amostra e estão expostos na **Tabela 1**. O extrato obtido pelo método de ultrassom apresentou os menores valores de EC_{50}, indicando maior eficiência. Esse desempenho superior pode ser atribuído ao fenómeno de cavitação ultrassónica, que promove a ruptura das células vegetais, libertando uma maior quantidade de compostos bioativos. Em acréscimo, o ultrassom é um método de extração que não utiliza altas temperaturas, o que o torna mais eficaz na preservação de compostos com elevada atividade antioxidante.

Tabela 1**.** Valores de EC_{50} de DPPH e poder redutor de diferentes extratos

Método de Extração	**Poder Redutor** **EC_{50} mg/mL**	**DPPH** **EC_{50} mg/mL**
Ultrassom	0,22±0,004	0,0060 ± 0,0008
Maceração	0,30± 0,06	0,0075 ± 0,0005
Decocção	0,27± 0,08	0,0092 ± 0,0019
Infusão	0,34±0,08	0,0211 ± 0.0024
p-value[a]	>0,05	<0,001

[a] Valores foram expressos como média ± D.P. (n=3). O valor do p calculado a partir da análise ANOVA.

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Is the Natural Fermentation of Olive Pomace Feasible for Food Purposes? A Detailed Chemical and Microbiological Characterization

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Natural food fermentation, driven by the microbiota in raw materials, introduces complex flavours and aromas while offering potential for waste/by-products valorisation. An example is olive pomace (OP), the solid residue generated after olive oil extraction, which poses significant environmental challenges due to its phytotoxicity. As the olive oil sector expands, sustainable methods for the valorisation of OP are crucial to mitigate waste management challenges. This study explores the feasibility of OP natural fermentation at room temperature over 32 days (T0-T32), through detailed chemical and microbiological analyses.

Moisture and ash contents remained stable along fermentation, while protein levels rose gradually. Total fat increased from 12.1% (T0) to 14.6% (T32), as well as total fibre (from 54.9% to 57.9%, respectively). The major amino acids (glutamic acid, leucine, and aspartic acid) peaked at T16 (7.6, 6.9, and 6.2 g/100 g, respectively). Oleic acid, the dominant fatty acid, slightly decreased from 74.2% (T0) to 72.8% (T16), before stabilizing at 74.1% (T32). α-Tocopherol, the major vitamin E isoform, was initially present at 10.2 mg/100 g (T0), slightly decreasing during fermentation, before rising again at T32 (9.2 mg/100 g). Total phenolics remained relatively stable, with a slight increase at T32, whereas hydroxytyrosol and tyrosol contents increased substantially throughout fermentation (4.9 and 1.5 mg/g, respectively, T32). The ferric reducing antioxidant power (554 µmol ferrous sulphate equivalents/g) and the 2,2-diphenyl-1-picrylhydrazyl radical scavenging activity (52 mg Trolox equivalents/g) also peaked at T32, indicating enhanced antioxidant properties by the end of fermentation. Initially, the volatile compounds were mainly aldehydes and siloxanes, contributing with fresh, green, and floral scents. By T4, alcohols and esters appeared, indicating fermentation with more complex fruity and floral aromas. At T8, new esters emerged, reflecting a more mature and waxy profile. By T16, ethanol appeared, and the aroma evolved with richer fatty and fruity notes. By T32, protein breakdown introduced ammonia, adding pungency, and resulting in a complex profile dominated by fatty, fruity, and nitrogenous compounds, indicating advanced fermentation. During the initial phase of the microbial growth curve, total microbial count (TMC) rapidly increased to 1.4×10^7 colony forming units (CFU)/mL by T2, indicating active microbial proliferation. A secondary growth peak was observed at T16 (9.0×10^6 CFU/mL). By T32, TMC dropped sharply, approaching zero, likely due to nutrient depletion or the build-up of inhibitory products in the culture medium.

The overall results indicate that OP natural fermentation at room temperature is feasible, resulting in significant changes over the 32-day period. The nutritional profile was enhanced by increasing protein, fat, and fibre contents as well as antioxidant properties. Volatile compound analysis reflected the different stages of fermentation. Overall, the findings suggest that fermentation could be a sustainable method for valorising OP, transforming it into an added-value food product with improved nutritional attributes.

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Chemical characterization of *Lycium barbarum* L. and *Lycium chinense* Mill. berries and development of high-value goji sorbets

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Lycium barbarum L. (LB) and *Lycium chinense* Mill. (LC), commonly known as goji, have attracted significant interest from the scientific community due to its excellent nutritional and medicinal value. These berries are valued for their polysaccharides, phenolic compounds, carotenoids, vitamins, and minerals, which are associated with diverse biological benefits, including antioxidant, immunomodulatory, hypoglycemic, anti-aging, and cardioprotective properties. The cultivation of goji is expanding in Europe, with Portuguese producers prioritizing organic cultivation and fresh fruit commercialization to differentiate their products from China's dried fruit market [1,2]. Notably, compared to LB berries, LC berries are small and have a bitter/astringent taste, making them unpalatable for direct consumption. So, more research is needed to explore LC berries composition and potential in food products [3].

Sorbets are frozen desserts made primarily of water, sugar, and fruit syrup, featuring a matrix of ice crystals within a concentrated liquid phase, with at least 25% fruit content. They are very popular in warm climates and offer health benefits from fruits and processing methods, appealing to health-conscious consumers, including vegetarians and vegans. Furthermore, they provide a platform for utilizing imperfect fruits and offer simplified production processes, which makes this matrix a good choice to develop with goji berries [4].

This study aims to characterize frozen LB and LC berries in terms of total phenolic content, phenolic profile, carotenoid content, and antioxidant activity, and to explore their use in the preparation of sorbets using a mixture of the two species at three specific ratios. Characteristics such as colour, viscosity, °Brix, pH, melting rate, melting behaviour, and the amount of air incorporated during freezing (overrun) were analysed for goji-based syrups (with same specific ratios using in sorbets) and sorbets. Chemical characterization of these berries after formulation of sorbets was also evaluated. Finally, a sensory analysis of these sorbets was conducted to assess consumer acceptance.

The chemical analysis of both berries revealed the presence of phenolic compounds (1.2-1.4 mg GAE/g of frozen berries) and carotenoids (26.6-34.7 mg of carotenoids/g of FW), underscoring their antioxidant potential. Among distinct sorbet formulations, there were no significant changes between syrups. Sorbets with equal amounts of LC/LB berries had a lower melting rate and, consequently, retained their shape better, which is associated with a lower overrun. While phenolic compounds were largely preserved during preparation, the carotenoid content in the sorbets were significantly less compared to fresh berries. Sensory analysis showed that all sorbet formulations were well accepted. These results underscore the potential for using frozen goji berries as ingredient to create innovative sorbets.

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Impacto do *intercropping* e do sistema de irrigação nos parâmetros físico-químicos e nutricionais de *Prunus dulcis* no nordeste de Portugal

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Uma das principais prioridades da agricultura é assegurar a produção de alimentos seguros e nutritivos, atendendo às necessidades alimentares da população e promovendo sistemas produtivos mais sustentáveis, que maximizem a eficiência do uso dos recursos disponíveis [1]. Nesse contexto, a diversificação das culturas em amendoais tem como objetivo melhorar a saúde do ecossistema, prevenindo a erosão através de práticas sustentáveis, além de mitigar os impactos das mudanças climáticas e melhorar a fertilidade do solo [2,3]. Assim, este estudo teve como objetivo avaliar as propriedades físico-químicas e nutricionais das amêndoas de forma a verificar o impacto gerado pela interação entre as culturas em diferentes condições ambientais de cultivo (solo seco e irrigado) ao longo de 2 anos de produção. Para a análise física das amêndoas, recorreu-se a um colorímetro para a avaliação da cor e, de um texturómetro *TA.XT plus* para avaliar a textura. A composição nutricional foi determinada através das Metodologias Oficiais da Análise (AOAC), incluindo teores em proteínas, gorduras, cinzas, hidratos de carbono e humidade. Os ácidos gordos foram determinados por cromatografia gasosa acoplada a um detetor por ionização de chama (CG-FID), e os açúcares por HPLC acoplado com um detetor de índice de refração (HPLC-RI). Em relação aos parâmetros físicos verificou-se que, no primeiro ano de colheita as diferentes amostras de amêndoas não apresentaram diferenças significativas na cor e textura. No entanto, no segundo ano, as amêndoas não irrigadas apresentaram uma coloração mais escura em comparação com as demais. Além disso, também foram observadas diferenças nos parâmetros de dureza e gomosidade. Os resultados demonstraram que as amêndoas obtidas no primeiro ano sob sistema de sequeiro apresentaram maiores teores de proteína, sendo que as amendoeiras consorciadas com trevo e grão-de-bico apresentaram diferenças significativas entre si, nomeadamente 18 ± 1 e 15,8 ± 0,3g/ 100g pf, respetivamente. Em relação ao teor de gorduras, o sistema de regadio apresentou uma quantidade maior, tanto no primeiro quanto no segundo ano de consorciação. A sacarose foi o único açúcar detectado nas amostras, apresentando concentrações mais elevadas nas amêndoas irrigadas em ambos os anos. Em relação aos ácidos graxos, foi detectada uma maior quantidade de ácidos graxos monoinsaturados, entre eles o ácido oleico e o ácido palmitoleico, em ambos os anos. Em suma, este estudo demonstra que os sistemas de culturas intercalares oferecem vantagens não só para a sustentabilidade ambiental, melhorando as práticas de produção, mas também para preservar a qualidade das amêndoas em condições de estresse hídrico.

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Caracterização Bioquímica de Excedentes da Produção de *Brassica* spp.

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A crescente industrialização agrícola que se tem verificado nas últimas décadas tem causado um aumento significativo de excedentes, desperdícios e perdas agroalimentares. Estas perdas verificam-se ao longo do processo produtivo e de distribuição, comprometendo a sustentabilidade [2]. Os brócolos e a couve-flor estão entre os vegetais mais consumidos e produzidos no mundo devido à sua riqueza em nutrientes e fitoquímicos, mas grande parte da produção é desperdiçada por práticas inadequadas e devido às exigências dos padrões de qualidade (ex: dimensão, forma, cor, aparência) [1;3]. Este estudo tem como objetivo avaliar as propriedades bioquímicas dos excedentes gerados durante a produção e/ou distribuição de brócolos e couve-flor. As amostras de brócolos (*Brassica oleracea* var. *italica*) e couve-flor (*B. oleracea* var. *botrytis*, *B. oleracea* var. *botrytis* 'romanesco', *B. oleracea* var. *botrytis* 'laranja' e *B. oleracea* var. *botrytis* 'roxa') foram cedidas por um armazenista local, em Bragança, Portugal. Foram liofilizadas e submetidas a processos de extração por decocção e maceração com etanol/água (80:20, *v/v*). Foram ainda analisadas em termos de composição química, incluindo tocoferóis (HPLC-FL), ácidos orgânicos (UFLC-PDA) e minerais (espectrofotometria de absorção atómica). A atividade antioxidante foi determinada através de ensaios DPPH (efeito de captação de radicais livres), poder redutor e TBARS (inibição da peroxidação lipídica), e a atividade antibacteriana foi testada utilizando estirpes bacterianas de origem alimentar. A couve-flor roxa apresentou teores elevados de tocoferóis totais (2,38 mg/100g de massa seca, ms); enquanto a variedade laranja apresentou teores elevados em ácidos orgânicos totais (21,0 g/100g ms). Relativamente aos minerais, todas as amostras apresentaram teores elevados de potássio (14,9-26,8 g/kg). Ambos os extratos de couve-flor roxa apresentaram melhor atividade antioxidante comparativamente com as restantes amostras estudadas. Os extratos hidroetanólicos de couve-flor branca, laranja e roxa demonstraram melhor atividade, com valores de concentração mínima inibitória (CMI) de 0,007 mg/mL, contra a estirpe bacteriana *Yersinia enterocolitica*. Por outro lado, o extrato hidroetanólico das amostras de brócolos apresentaram melhor atividade contra a bactéria *Bacillus cereus*, com valores de 0,6 mg/mL. Em geral, os resultados indicam que estes vegetais representam uma fonte promissora de compostos bioativos, evidenciando o seu potencial e reforçando a importância da valorização destes excedentes agroalimentares, que podem ter diferentes aplicações na área alimentar, humana e animal. Desta forma, estes excedentes seriam destinados a aterros sanitários apenas em última instância, o que contribuiria para a sustentabilidade e economia circular.

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Rhus spp.: Estudo da caracterização nutricional, química e bioativa

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Rhus spp., comumente conhecido como sumagre, é um arbusto que pertence à família Anacardiaceae. É amplamente utilizado como tempero em várias cozinhas tradicionais, especialmente no médio oriente [1, 2]. É rico numa variedade de fitoquímicos, como flavonoides, taninos, entre outras moléculas bioativas que contribuem para os seus inúmeros benefícios para a saúde [3]. Este estudo teve como objetivo a caracterização proximal e química do fruto, bem como a avaliação bioativa dos extratos hidroetanólicos dos frutos, folhas e caules do arbusto colhido na região de Foz Côa, Portugal. Procedimentos AOAC, cromatografia, espectrofotométricos, e ensaios *in vitro* foram utilizados para determinar a composição proximal (lípidos, cinzas, proteínas, fibras, hidratos de carbono e valor energético), química (carotenoides, tocoferóis e ácidos gordos) dos frutos. Os compostos fenólicos e as propriedades bioativas dos extratos hidroetanólicos dos frutos, folhas e caules foram também avaliados (a atividade antioxidante mediante os ensaios de DPPH, poder redutor e TBARS; e a atividade antimicrobiana avaliada contra cinco bactérias Gram-negativo, três Gram-positivo, e dois fungos de origem alimentar. Os resultados indicam que o fruto apresenta 12,64 g/100g de massa seca (ms) de lípidos, 3,59 g/100g ms de proteínas, 2,8 mg/100g ms de cinzas, 49 g/100g ms de fibras, 35 g/100g ms de outros hidratos de carbono e apresentou um valor energético de 365 kcal/100g ms. Relativamente à caracterização química, o fruto apresenta 17,9 mg/100g ms de β-caroteno, 7,4 mg/100 ms de tocoferóis totais, 28% de ácidos gordos saturados, 38% de ácidos gordos monoinsaturados e 35% de ácidos gordos polinsaturados. Os extratos hidroetanólicos dos frutos, folhas e caules apresentam 23,6, 22,7 e 19,3 mg/g de extrato de compostos fenólicos totais, respetivamente. O extrato hidroetanólico das folhas destacou-se com maior potencial antioxidante em todos os ensaios *in vitro*: no ensaio de DPPH, apresentou melhor atividade comparativamente com o fruto e o caule (valores EC_{50} de 1,63, 6,04 e 4,80 µg/mL, respetivamente). No ensaio de poder redutor, a folha também se destacou com valor EC_{50} de 5,47 µg/mL, seguida do fruto com 5,78 µg/mL e do caule com 14,2 µg/mL. No ensaio de TBARS a folha destacou-se novamente com valores EC_{50} de 2,02 µg/mL, seguida do fruto com 4,3 µg/mL e do caule com 8,61 µg/mL. Quanto à atividade antimicrobiana as folhas apresentaram concentrações mínimas inibitórias (CMI) de 0,3 mg/mL contra a *Escherichia coli*, *Bacillus cereus*, *Listeria monocytogenes* e *Staphylococcus aureus*, CMI de 0,15 contra a *Salmonella enterica* e 0,6 contra a *Yersinia enterocolitica*. O caule apresentou CMI de 0,6 e 0,3 contra as estirpes *Enterobacter cloacae* e *E. coli*, e o fruto de 0,6 contra a *E. coli*. Na avaliação antifúngica, o fruto apresentou CMI de 5 mg/mL contra a estirpe *Aspergillus fumigatus*. De mencionar que foi avaliada e não se verificou toxicidade nos extratos hidroetanólicos avaliados. A caracterização das diferentes partes do sumagre expande o conhecimento científico sobre este arbusto e abre portas para o seu uso sustentável e inovador na indústria alimentar, agregando valor económico e promovendo novos produtos funcionais e saudáveis.

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Extrato otimizado de *Tradescantia zebrina* L.: um corante alimentar alternativo e os seus efeitos na dieta de *Drosophilas melanogaster*

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Os aditivos alimentares, especialmente os corantes artificiais, têm sido associados a diversas condições patológicas, como alergias alimentares, distúrbios gastrointestinais e alterações comportamentais e de desenvolvimento [1]. Neste contexto, o presente estudo teve como objetivo investigar o efeito *in vivo* do extrato otimizado de antocianinas obtido das folhas de *Tradescantia zebrina* L. como uma alternativa natural aos corantes alimentares, utilizando o modelo de *Drosophila melanogaster*. Inicialmente, a extração por maceração das folhas de *T. zebrina* foi otimizada utilizando o delineamento experimental Box-Behnken com 17 pontos, mantendo constantes o pH e a relação sólido-líquido (S/L). As variáveis independentes incluíram o tempo de extração (5 a 120 minutos), a concentração de etanol (0% a 100%, *v/v*) e a temperatura (20 a 100 °C). A quantidade total de antocianinas (mg de antocianinas/ g de extrato) foi determinada como variável de resposta por cromatografia líquida de alta eficiência (HPLC, Dionex Ultimate 3000, Thermo Scientific). Em seguida, o extrato de ETZ foi preparado nas condições otimizadas e incorporado na dieta de *D. melanogaster* com até três dias de idade e distribuídas em cinco grupos: (1) Dieta Padrão (DP) controlo; (2) DP com 0,2 mg/mL de ETZ; (3) DP com 0,6 mg/mL de ETZ; (4) DP com 2 mg/mL de ETZ; e (5) DP com 6 mg/mL de ETZ, sendo expostas à dieta por 10 dias. Durante o período de exposição, a mortalidade de cada grupo foi registada, seguida de avaliações comportamentais dos sobreviventes (testes de geotaxia negativa e campo aberto). Os resultados indicam que a sobrevivência das moscas expostas à dieta suplementada com ETZ foi significativamente maior nas concentrações de 0,2 e 0,6 µM, em comparação ao grupo controlo. Nas avaliações comportamentais, observou-se que, no teste de geotaxia negativa, as moscas expostas à concentração de 0,6 µM apresentaram uma redução significativa no tempo de escalada em relação ao grupo controlo. No entanto, no teste de campo aberto, não foram detetadas diferenças significativas no número de cruzamentos entre as diferentes concentrações de ETZ avaliadas. Embora não tenham sido observadas melhorias significativas na atividade motora, os resultados indicam que o extrato ETZ não causa danos comportamentais às moscas, demonstrando a sua segurança em relação ao comportamento locomotor. Estes resultados sugerem o potencial da utilização do extrato, no entanto uma investigação mais profunda será necessária para explorar outras propriedades biológicas e possíveis mecanismos de ação.

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Impacto do extrato corante de *Clitoria ternatea* L. na progressão da doença de Parkinson

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As antocianinas são amplamente utilizadas na indústria alimentar devido às suas cores intensas, oferecendo benefícios à saúde, nomeadamente como protetor cardiovascular e neuroproteção [1]. No entanto, a instabilidade desses compostos representa um desafio para sua aplicação em larga escala [2]. As flores de *C. ternatea* apresentam antocianinas poliaciladas de cor azul intensa, que têm atraído a atenção do meio científico [3]. Neste sentido, o presente estudo pretendeu investigar os efeitos do extrato otimizado de antocianinas (CTE), proveniente das pétalas azuis de *C. ternatea*, nas alterações comportamentais induzidas em *D. melanogaster* num modelo semelhante à doença de Parkinson. Para isso, foi realizada uma otimização da extração por maceração, utilizando o delineamento experimental Box-Behnken, onde o pH e a razão sólido-líquido foram mantidos constantes, enquanto as variáveis independentes incluíram o tempo de extração, a concentração de etanol e a temperatura. A quantidade total de antocianinas foi quantificada por cromatografia líquida de alta eficiência (HPLC, Dionex Ultimate 3000, Thermo Scientific). Com base nas condições ideais determinadas pela Metodologia de Superfície de Resposta, o CTE foi incorporado na dieta de *D. melanogaster* (até três dias de idade) durante 10 dias, distribuídos em cinco grupos: dieta padrão controlo (DPC); DPC com 0,5 mg/mL de CTE; DPC com 1,5 mg/mL de CTE; DPC com 5 mg/mL de CTE; e DPC com 15 mg/mL de CTE, visando encontrar a concentração ideal para aplicação ao modelo semelhante à doença de Parkinson. Após estudos comportamentais, incluindo geotaxia, campo aberto e análises de sobrevivência em todos os grupos, a concentração de 15 mg/mL de extrato CTE foi identificada como ideal para aplicação no modelo de Parkinson. Assim, o extrato de CTE na concentração de 15 mg/mL foi testado novamente por 10 dias. Contudo, a partir do terceiro dia de dieta, o herbicida paraquat foi administrado. Deste modo, novos grupos de tratamento foram monitorados: grupo controle DPC, grupo com extrato DPC e CTE 15 mg/mL, grupo DPC exposto somente ao paraquat e grupo DPC, paraquat e CTE 15 mg/mL. Durante a exposição ao modelo da doença, a mortalidade de cada grupo foi registrada, seguida por avaliações comportamentais dos sobreviventes, com testes de geotaxia negativa e campo aberto. Os resultados demostram que a adição de CTE 15 mg/mL na dieta reduziu parcialmente a mortalidade das moscas ao longo dos dias de tratamento, uma vez que os grupos com CTE 15 mg/mL apresentaram maior mortalidade em relação ao controle. Nos estudos comportamentais, observou-se que a administração do CTE 15 mg/mL reduziu o tempo de escalada das moscas em comparação aos grupos com administração do herbicida. No teste de campo aberto, não foram observadas diferenças significativas entre os tratamentos quanto ao número de cruzamentos. Assim, este estudo apresenta informações importantes sobre o impacto da administração do extrato CTE 15 mg/mL na sobrevivência e no comportamento locomotor das moscas.

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Application of an oral cell-based assay to study the astringency of *Clitoria ternatea* L. tea

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Astringency is perceived as a tactile and diffuse sensation characterized by roughness, puckering and tightening in the mouth [1].It is an essential aspect of the sensory experience in various products rich in polyphenols, such as red wine and tea. In this type of products, astringency is desirable in moderate levels. However, in other products such as fruits and vegetables, excessive astringency can lead to consumer rejection [3].

Polyphenols, abundant in plant-based foods, are well-known for their health benefits products and are divided into three major families: non-flavonoids, flavonoids, and tannins [6]. Anthocyanins are among the subgroup of the flavonoids family were they contribute not only to the color changes seen in response to pH variations[5], but also to the perception of astringency.

Clitoria ternatea L., or butterfly pea flower, is recognized for its vivid blue color, which changes to light pink in mildly acidic solutions while remaining blue in neutral or basic environments [4]. Native to Southeast Asia, this plant is rich in ternatins, a type of (poly)acylated anthocyanins [7]. Traditionally, tea made from the butterfly pea flower has been consumed for its medicinal properties [7]. Known for its herbal flavor, often compared to black tea and coffee [2], the tea can also induce astringency, which is commonly reduced with the addition of lemon and honey [2].

Although sensory analysis has explored anthocyanins' role in astringency, there remains a gap in understanding the molecular mechanisms behind astringency perception within this polyphenol group. To address this, the study examined how compounds from butterfly pea tea interact with different oral components at neutral and acidic pH levels. Using a cell-based model that includes main oral constituents involved in astringency perception—human saliva, the mucosal pellicle, and an oral cell line (HSC-3). The results showed stronger interactions with oral cells, while the presence of salivary proteins reduced these interactions. Additionally, polyphenols with higher levels of ρ-coumaroyl residues exhibited stronger binding to the oral models, whereas those with more rhamnose residues demonstrated weaker interactions. This effect was most noticeable in acidic conditions, suggesting that an acidic environment enhances these compounds' binding ability without affecting their interaction with oral constituents.

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Cyclodextrin-assisted extraction of phlorotannins from *Fucus vesiculosus*

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Phlorotannins are phenolic compounds exclusive from brown macroalgae that have raised much interest due to their versatile bioactive properties. However, considering diet as the main entry route of these compounds into our organism, it is necessary to take in account the degree of biotransformation they may undergo while crossing the gastrointestinal tract. Indeed, similar to what happens with land plant phenolics, gastrointestinal digestion has been shown to affect phlorotannins' stability [1]. In this context, cyclodextrin-assisted extraction can offer an effective strategy for protecting these compounds from the moment they are extracted until the moment they are exposed to the harsh conditions of the digestive system, providing a controlled release in more advanced stages of the GI tract.

In this work, several concentrations of γ- and β-cyclodextrins were used during the aqueous-microwave extraction of phlorotannins from *Fucus vesiculosus,* and the resulting extracts were submitted to a simulated gastrointestinal digestion protocol. Overall, increasing cyclodextrin concentrations during the extraction resulted in higher extraction yields, and slight alterations in the total phlorotannin content. Likewise, higher concentrations of cyclodextrin resulted in reduced loss of total phlorotannins along the different gastrointestinal digestion stages, with β-cyclodextrin showing the highest protective potential. In fact, this cyclodextrin was able to prevent close to 100% of the total phlorotannin content loss in both oral and gastric phases, and approximately 35% of their loss in the intestinal phase. This suggests an increase of the compounds' resistance and residence time in the intestinal lumen, likely resulting from the sustained-release properties of cyclodextrins.

Finally, the addition of β-cyclodextrin was tested at a post-extraction stage to estimate its impact on phlorotannins stability along the gastrointestinal tract. Interestingly, although post-extraction encapsulation reduced the total phlorotannin content loss compared with the non-encapsulated extract, it was less efficient than the extract encapsulated during the extraction, indicating that stronger guest-to-host interactions are formed between phlorotannins and cyclodextrins during the extraction, possibly due to the increased enthalpy generated from the microwave heating.

Overall, this study demonstrates that β-CD assisted extraction could be a viable approach to ensure a better stability of phlorotannins through the gastrointestinal tract, ensuring they reach the intestinal lumen where they will be released and available for absorption.

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Molecular insights into the modulation of black tea polyphenol interactions with oral components by orange peel pectic polysaccharides

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Food innovation requires the development of healthy, tasty and sustainable diets, focusing on minimally processed, nutrient-rich foods with appealing sensory qualities and beneficial compounds like polyphenols and fibers. However, some polyphenol-rich products often face negative consumer reactions due to unpleasant taste properties, particularly astringency. Astringency is a complex sensory attribute characterized by sensations of dryness, roughness, and puckering perceived in the mouth[1]. While balanced astringency can enhance food quality, excessive levels lead to consumer rejection. Beyond the well-known interactions of polyphenols with salivary proteins, recent research shows that other oral components, including oral cells and the mucosal pellicle, also contribute to astringency perception. Recent studies suggest that polysaccharides could modulate astringency by disrupting polyphenol-salivary protein interactions, offering promising potential to improve sensory experiences and consumer acceptance of healthy diets [2]. Additionally, vegetables and fruits, which generate a large amount of waste during processing (e.g., peels and seeds) could be a valuable source of bioactive compounds, such as pectic polysaccharides, that can reduce polyphenol-oral component interactions[3].

Thus, this study aimed to explore the effect of various pectic polysaccharide fractions from orange peels on disrupting interactions between black tea polyphenols and several oral components (salivary proteins, tongue epithelial cells and mucosal pellicle), simulating the typical food intake conditions. Using an advanced and representative quaternary cell-based model of the oral cavity, interactions between black tea extract (BTE) polyphenols and oral components, including oral epithelial cells (HSC-3 cell line), mucosal pellicle and human saliva, were studied. The effect of several polysaccharide fractions obtained from orange peels (e.g., high methyl esterified pectins (HMEP), medium methyl esterified pectins (MMEP), low-molecular weight pectates (LMWP), high-molecular weight pectates (HMWP) was evaluated using this model. These polysaccharides were obtained by sequential extraction with several solutions, each exhibiting distinct sugar compositions.

This work showed evidence that orange peel pectic polysaccharides were able to decrease the interaction between black tea polyphenols and different oral components, mainly in the complete oral model (HSC-3-mucin-salivary proteins). The results showed that the polysaccharide´s effect can be explained by the structural features of the compounds involved. MMEP and LMWP were among the most effective in reducing the interactions of catechins and catechins dimers, including theasinensins and theaflavins. The low molecular weight, the highest uronic acid content and the presence of free hydroxyl groups could explain the high reduction ability. In general, polysaccharides had the greatest effect on reducing interactions between BTE and glycosylated proline-rich proteins, acidic proline-rich proteins, statherin and P-B peptide. Finally, from a circular economy perspective, the reuse of these fruit peels could enhance waste management practices within the food industry.

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Characterization and Valorization of *Pinus pinea* Nut Shell Extracts for Sustainable Crop Production

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The umbrella pine (*Pinus pinea* L.), native from the Mediterranean basin, is abundant in southwestern Europe. In Portugal, its forest area increased by 61% between 1995 and 2015, now covering 193,000 ha [1]. The primary economic product, pine nuts, are highly valued internationally, however, nut processing generates large quantities of underutilized by-products, particularly shells, which account for over 77% of the nut's weight. In Portugal, around 2800 tons of pine nut shells are generated each year, mostly used for biomass, yet they are still insufficiently studied and largely unexploited for higher-value applications. A promising path concerning the valorization of this by-product relates to its use in agriculture/crop production systems. The recent EU efforts to reduce the impact associated with the use of synthetic agrochemicals and the incentives towards a transition to a climate neutral economy increased the demand for greener and innovative products in this sector [2]. In line with this, this work aimed to evaluate the potential of *P. pinea* nut shells to be used in agriculture as an alternative to synthetic agrochemicals, particularly as i) biostimulant and ii) herbicide.

To obtain isolated fractions rich in metabolites of interest, pine nut shells were submitted to sequential extractions, first with dichloromethane (E1) and next with ethanol:water (80:20, v:v) (E2) and the resulting extracts were characterized by GC-MS and HPLC-DAD-ESI-MSn, respectively.

The E1 extract was found to be rich in fatty acids such as oleic, linoleic and palmitic acid, and was applied to seeds of purslane, ribwort plantain, and clover in varying concentrations (0 to 10 mg/mL), to assess its herbicidal potential. Germination and growth parameters were recorded. The E2 extract, found to be rich in flavonoid compounds namely chrysine derivatives and crisoeriol, was then evaluated for its biostimulant activity on tomato and wheat germination and seedling development (0 to 1 mg/mL).

At higher concentrations, the E1 extract significantly impacted purslane growth, reducing its length and biomass by 28% and 20%, respectively. In ribwort plantain, E1 primarily affected seedling biomass, with notable reductions in length observed only at the highest concentration. Regarding germination rate, the E1 extract completely inhibited purslane germination and reduced ribwort plantain germination by 70%, while clover germination was unaffected. Regarding the E2 extract, it enhanced root and shoot growth, as well as biomass in tomato and wheat seedlings, even at the lowest concentration, although it did not influence germination rates. These findings provide valuable insights into the valorization of this underutilized by-product, aligning with the EU's goals for greener agricultural practices, and supporting the further exploration of pine nut shells in high-value applications.

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Valorização de Resíduos de Cogumelos Comestíveis na Produção de massa *penne*: Fermentação e Melhoria Nutricional

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Os cogumelos são ricos em proteínas, hidratos de carbono, vitaminas e minerais, com baixo teor de gordura, oferecendo vários benefícios funcionais. A fermentação láctica, além de prolongar a vida útil desta matriz sem conservantes, melhora as características sensoriais e pode aumentar a funcionalidade do alimento pela formação ou extração de compostos bioativos [1-3]. Resíduos de *Agaricus brunnescens* foram colocados em fermentação durante 7 dias a 20ºC, usando a *Lactobacillus plantarum,* após o qual foram desidratados durante 24 horas a 40ºC (cogumelos fermentados, F). Os não fermentados (NF) foram secos durante 72 horas (a 40ºC). Para a incorporação das farinhas de F e NF na massa *penne*, foram utilizados três níveis de substituição da sêmola de trigo (ST), 1%, 5% e 10 %. Amostra controlo (100% ST). Parâmetros de a cor, teor de humidade, pH, viscosidade e capacidade de retenção de água (CRA), retrogradação, tamanho das partículas, tempo de cozedura ótimo, perda de sólidos, poder de intumescimento e textura foram estudados namassa crua e cozinhada. O aumento na % de farinha de cogumelo (F e NF) resultou num escurecimento mais acentuado da massa, especialmente nas formulações com maior teor de farinha. As massas contendo farinha F apresentaram valores de pH significativamente mais baixos. Verificou-se também que as massas enriquecidas com as farinhas de cogumelo (F e NF) exibiram maior capacidade de retenção de água. No entanto, o tempo de cozedura e a firmeza das amostras diminuíram proporcionalmente com o aumento da quantidade de farinha, especialmente nas amostras contendo farinha de cogumelo F. Este fenómeno foi atribuído à diluição do amido, corroborado pelas análises de viscosidade e poder de intumescimento das misturas de sêmola e farinha de cogumelo. A perda de sólidos durante a cozedura aumentou com a adição de farinha de cogumelo, particularmente nas formulações com 10% de farinha de cogumelo F, embora não tenham sido observadas diferenças significativas no poder de intumescimento entre as amostras. As propriedades físico-químicas das farinhas enriquecidas com cogumelos demonstram grande potencial, havendo uma notória melhoria de algumas propriedades reológicas importantes para o desenvolvimento de novos produtos alimentares mais saudáveis e sustentáveis.

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Nutritional and Antioxidant Potential of Dried Coffee Pulp from Azores: A Sustainable Approach to Valorising Coffee By-Products

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In coffee production, a large portion of by-products is discarded and left unutilized. Adding value to these by-products is essential to minimize waste and create additional income streams. Coffee pulp, produced during the first stage of wet coffee processing, can become an environmental hazard when improperly disposed of in large quantities due to its phytotoxicity and high organic load [1].

Having in view the use of this by-product for food purposes this study aimed to analyse centesimal composition (by AOAC methods) [2], sugar content (by HPLC-ELSD) [3], vitamin E (by HPLC) [4] and antioxidant activity (by spectrophotometric methods) [5] of dried coffee pulp provided by Quinta do Avô João, a coffee producer from S. Miguel, Azores, Portugal.

A relatively high percentage of total mineral content (~10.6%) and protein (~10.1%) suggests that coffee pulp is rich in essential minerals and a potential source of protein. A very high fiber content (~52%) is one of the highest valuable aspects of coffee pulp, most of which is insoluble dietary fiber (~44.4%) with an important role in promoting digestive health.

With low values to total sugar content (~5%) and total fat (~1.6%) turn the use of coffee pulp an attractive ingredient for healthy food applications.

The results obtained for antioxidant activity, DPPH•- Scavenging Activity (~21.49 mg TE/g dw) and Ferric Reducing Antioxidant Power (~487.47 µmol FSE/g dw) indicates that coffee pulp is reach in bioactive compounds as phenolic compounds (~45.9 mg CAE/g dw) and flavonoids (~21.7 mg CE/g dw) and others antioxidants, such as vitamin E (~75.7 mg/100 g).

In summary, the results indicate that coffee pulp reveals a significant nutritional and antioxidant potential. Phenolic and flavonoid content, along with high vitamin E levels, give it strong antioxidant properties that can be leveraged in various industries, from food and nutraceuticals to cosmetics. Additionally, the high fiber and moderate protein content make it a versatile ingredient for functional food products and sustainable agricultural practices. By transforming coffee pulp from waste into valuable products, it holds great promise for both economic and environmental sustainability.

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Promoção de estratégias sustentáveis no setor agroalimentar: valorização de subprodutos vegetais

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Para impulsionar bioeconomias sustentáveis, é crucial integrar materiais vegetais desperdiçados como recursos valiosos. Explorar suas aplicações e adotar princípios de economia circular são ações essenciais para maximizar sua contribuição as ações de desenvolvimento sustentável [1]. Neste sentido, o objetivo deste estudo centrou-se na caracterização fenólica e bioativa do extrato hidroetanólico de três subprodutos vegetais amplamente produzidos: casca de cebola (*Allium cepa* L.), couve (*Brassica oleracea* L.) e courgette (*Cucurbita pepo* L.), assim como na caracterização nutricional do respetivo resíduo resultante do processo de extração. O perfil individual de compostos fenólicos do extrato foi determinado por LC-DAD-ESI-MSn e a caracterização da bioatividade por meio de testes *in vitro* de atividade antioxidante (TBARS e DPPH), atividade antidiabética (inibição da α-glicosidase e α-amilase) e atividade antimicrobiana (antibacteriana e antifungica). O valor nutricional do resíduo proveniente do processo de extração foi caracterizado em termos de cinzas, gorduras, fibras dietéticas totais, solúveis e insolúveis, e proteína bruta e total através de métodos oficiais de análise AOAC, bem como a identificação do perfil de aminoácidos a partir de métodos cromatográficos. O extrato hidroetanólico da mistura dos subprodutos vegetais evidenciou um perfil individual de compostos fenólicos rico em quercetina glicosilada ($[M\text{-}H^-]$ em *m/z* 625) e uma capacidade bioativa promissora, evidenciada por uma atividade antioxidante com valores de EC_{50} de 165 ± 2 µg/mL no ensaio de DPPH e de 309 ± 14 µg/mL no ensaio de TBARS. Na atividade antidiabética, observou-se uma inibição significativa da α-glicosidase, com IC_{50} de 381 ± 28 µg/mL. Em relação à atividade antibacteriana, o extrato mostrou valores de concentração mínima inibitória e concentração mínima bactericida similares ao controlo E221 (sulfito de sódio). No que concerne ao resíduo da extração, o conteúdo de fibras totais e proteínas foram as macromoléculas maioritárias identificadas, com 53,6 ± 2%, sendo composto principalmente por fibras insolúveis, e 18,49 ± 1,01% para proteína real e 18,7 ± 0,7 para proteína bruta. Adicionalmente, o resíduo apresentou um conteúdo de aminoácidos essenciais bastante promissor, com 65,88 ± 3,27 mg/g de peso seco. Estes resultados permitiram identificar possíveis vias de valorização para estes subprodutos vegetais, onde o extrato e o respetivo resíduo de extração podem ser reintroduzidos na indústria alimentar como ingredientes com propriedades nutricionais e bioativas, contribuindo para o Plano de Ação da Economia Circular proposto pela União Europeia, focando-se nas estratégias de "Resíduo Zero". Para além disso, avaliar os efeitos combinados desses subprodutos suprime os desafios da sua separação durante o processo de descarte de resíduos na indústria de processamento de alimentos e, desta forma, viabilizar um possível crescimento económico por parte do setor.

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Biofortificación de microvegetales de guisante mediante *priming* de semillas con selenio

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El selenio (Se) es un micronutriente esencial para la salud humana, que desempeña un papel crucial como componente de diversas enzimas y proteínas implicadas en la defensa antioxidante y la regulación inmunitaria. En pequeñas cantidades, el Se puede mejorar el rendimiento y la calidad de las plantas y modular los genes que responden al estrés [1-3]. Sin embargo, los alimentos vegetales cultivados en suelos deficientes en Se contienen inevitablemente bajos niveles de este micronutriente. Este estudio pretende abordar este problema al biofortificar microvegetales de guisante (*Pisum sativum* L.) mediante el tratamiento de las semillas con Se. El *priming* de semillas es un método rentable y ecológico para biofortificar plantas comestibles, promoviendo una germinación uniforme y una rápida emergencia, lo que conduce a una mejora de los rendimientos en ambientes estresados.

En este experimento, las semillas se sometieron a tratamientos de *nutri-priming* utilizando soluciones de 25-100 µM de Se durante 6 y 12 h, con selenato de sodio como fuente de Se debido a su mayor translocación a las partes aéreas en comparación con el selenito de sodio. Las semillas con *hidro-priming* y las que no recibieron *priming* sirvieron de control. Tras el tratamiento, un lote de semillas se sometió a pruebas de fuga de electrolitos, mientras que otro se cultivó en un invernadero para producir microvegetales de guisante. La tasa de emergencia y los parámetros morfológicos se controlaron diariamente. Tras la cosecha, se midieron la biomasa y la longitud de las raíces de los microvegetales, y se analizó el contenido de Se y otros minerales en las raíces y las partes aéreas mediante espectrometría de absorción atómica. Además, se cuantificaron los niveles de clorofila, azúcares solubles, ácidos orgánicos, fenoles totales y actividad antioxidante en las partes aéreas mediante técnicas colorimétricas y de cromatografía líquida y ensayos *in vitro* [4].

El tratamiento de las semillas influyó en la emergencia y el crecimiento de los microvegetales de guisante. El tratamiento de *priming* de 6 h fue más prometedor que el de 12 h en términos de rendimiento agronómico y acumulación de biomasa por planta. Sin embargo, el control sin *priming* mostró la mayor tasa de emergencia. A pesar de ello, el *priming* con Se aumentó significativamente las concentraciones de este micronutriente en las partes aéreas de los microvegetales, confirmando la eficacia de esta estrategia de biofortificación. Estos resultados subrayan la importancia de equilibrar la producción de biomasa con la acumulación de Se para optimizar los protocolos de producción, contribuyendo en última instancia al desarrollo de alimentos enriquecidos con Se.

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Otimização da extração assistida por ultrassons de compostos hypocholesterolémicos a partir de residuos de cogumelos comerciais

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Ricos em compostos bioativos, os cogumelos são uma fonte natural de moléculas com uma vasta gama de benefícios para a saúde. Nomeadamente, o ergosterol tem a capacidade de reduzir a absorção de colesterol ao competir com o colesterol exógeno devido à sua similaridade estrutural. Além disso, estudos recentes identificaram estatinas em certas espécies de cogumelos. Esses compostos, como a pravastatina e a lovastatina, inibem a enzima principal na síntese de colesterol no fígado [1]. Esta dupla ação de redução da absorção e inibição da produção endógena de colesterol pode acrescentar um valor significativo no potencial dos cogumelos na saúde cardiovascular. Além disso, o mercado de produção de cogumelos continua a crescer levantando uma grande questão de sustentabilidade, uma vez que até 20% da sua produção é descartada por não cumprir os parâmetros de comercialização, surgindo uma necessidade urgente de inovação na utilização de subprodutos da indústria de cogumelos comestíveis [2].

O projeto Mush4Chol pretende apresentar uma solução inovadora e promissora que consiste na exploração exaustiva de bio-resíduos de cogumelos para obter extratos ricos em compostos hipocolesterolémicos para obter uma formulação que iniba tanta a síntese quanto a absorção do colesterol para diversos fins económicos. Este trabalho teve como objetivo a otimização da extração assistida por ultrassons de ergosterol e estatinas, a partir de residuos de duas variedades de *Agaricus bisporus*, utilizando três variáveis independentes: tempo (t, minutos), solvente (S, % de metanol/etanol) e potência (P, W), utilizando um desenho composto central circunscrito com cinco níveis, aplicando a metodologia de superfícies de resposta (RSM), que resultou em 25 pontos de extração. O rendimento de extração e a concentração de ergosterol e estatinas foram as respostas obtidas, tendo os compostos-alvo sido identificados e quantificados por HPLC-UV. Os pontos ótimos que maximizam o rendimentos nos compostos-alvo foram determinados e embora se trate da mesma espécie, as condições para otimizar a extração dos compostos hipocolesterolémicos-alvo nas duas variedades de cogumelo diferiram. Ainda assim, quer o ergosterol quer a pravastatina foram identificadas nos 25 extratos obtidos.

Para representar uma abordagem de zero desperdício, os resíduos de extração restantes serão reciclados como substrato rico em nutrientes para cogumelos, promovendo uma economia circular, um dos objetivos do projeto Mush4Chol, no qual este trabalho se insere.

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QUÍMICA AMBIENTAL Y SOSTENIBLE

Estudio en el aula de un Plan de Sostenibilidad Ambiental

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En el contexto europeo, los países que lo integran tienen el propósito de cumplir con la Agenda 2030 y con los objetivos de desarrollo sostenible (ODS) y en los últimos años se ha producido un aumento muy significativo de la demanda de información sobre los impactos ambientales y las acciones de mejora hacia la sostenibilidad de las empresas e instituciones. Para establecer el nivel general de sostenibilidad ambiental que presentan organismos, empresas e instituciones, se pueden utilizar diversas herramientas, una de ellas es el plan de sostenibidad ambiental.

En la actualidad, un Plan de Sostenibilidad Ambiental (PSA) [1] es un estudio que se desarrolla con el fin de establecer objetivos medibles y realistas que vayan superando los diversos impactos ambientales derivados [2] y que esté acorde con los (ODS).

Para la realización de un PSA, es necesario hacer una evaluación de impacto ambiental y social, de las operaciones y procesos de la empresa; se ha de integrar las tecnologías sostenibles, realizar una gestión eficiente de recursos, posteriormente identificar los objetivos y metas y finalmente establecer un sistema de evaluación continua para realizar medidas del progreso hacia los objetivos establecidos.

En este trabajo nuestro propósito es incorporar el tópico de PSA, mediante una actividad teórico-práctica en la formación de estudiantes universitarios en grados de ciencias y de ingeniería. Se trata de ir adecuando el contenido, metodología y actividades a las exigencias formativas y competenciales de sus estudios. En dicha propuesta se trabajará con la metodología de trabajo en equipo en el que cada estudiante se implique activamente en su aprendizaje y se prepararán para ello una colección de "fichas didácticas" [3].

Este estudio se orientará en dos vertientes de interés, la empresarial y la institucional. Como actividad previa, el/la docente aportará información sobre lo que es un PSA y la importancia de realizarlo, junto con diversos recursos web de apoyo, que ellos podrán ir completando justificadamente. Se les aportará ejemplos de PSA de empresas que proponen, por ejemplo, energías renovables en sustitución de otros tipos de energía anteriormente utilizadas. De similar manera se les mostrará ejemplos de PSA de universidades que proponen mejoras, por ejemplo, en los laboratorios de química o en la recogida de residuos.

Cada equipo de trabajo presentará un informe en el que se muestre el grado de comprensión de conocimientos en general y de aspectos teóricos y prácticos en este tópico. Como actividad práctica, cada grupo presentará un plan de sostenibilidad ambiental con datos de una comunidad autónoma o de una universidad, en el que debe incluirse una propuesta justificada de mejoras en términos de sostenibilidad ambiental y en relación con los ODS.

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Exploring living and non-living macroalgae based biosorbents in interaction with complex multi-element mixtures

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Macroalgae based sorbents have been explored as a more sustainable alternative technology for the removal and recovery of Critical Raw Materials (CRMs) [1], where Rare Earth Elements (REEs) are included. The scale-up of this technology implies different stages, such as the growth and cultivation of macroalgae. Moreover, their application at the industrial level requires further knowledge of the sorption process under relevant industrial-related conditions, such as the presence of competing ions and the presence of nutrients. There is also a need to apply certified methods such as Life Cycle Analysis (LCA) [2] to measure the environmental burden that this technology would represent.

Therefore, the present study focused, first, on a mixture that intended to mimic effluents or contaminated waste streams from industries producing, for example, fluorescent lamps or from mining activities. A comparison between the efficiency of the simultaneous uptake of Y, La, Nd, Eu, Gd and Dy (REEs) from an equimolar mixture also containing the classical contaminants Hg, Cd, Pb and As by *Ulva lactuca* and *Gracilaria gracilis* applied as living and non-living biomass was evaluated. Batch sorption experiments were run for 72 h, at previously optimized values of salinity (10) and pH (7.8 – 8.0) by contacting 5 g of living macroalgae, or the corresponding dried mass, with natural seawater spiked with the contaminants under study, at 800 rpm.

As and Cd were always less removed from the solution, while the REEs, Hg and Pb were removed, generally over 80 % for living biomass. After, to the same mixture of contaminants, living *Gracilaria gracilis* was selected to be exposed for 48 h, in a experimental design obtained by Box-Behnken Design (BBD) of 3 factors, where the initial concentration of the contaminants (1, 3 and 5 µmol/L), mass of the sorbent (2, 8 and 14 g/L), and concentration of nutrients (0 µg/L P /0 µg/L N; 100 µg/L P/ 500 µg/L N; 200 µg/L P /1000 µg/L) were evaluated for their impact on the biosorption process. Removal profiles of the elements plus response surface methodology analysis, revealed that the sorption of these contaminants was not significantly affected by the presence of nutrients.

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Adsorption of nitrophenolic compounds on porous photopolymer-derived carbons

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Porous carbon materials have been extensively used in various fields, due to their porous structure and high specific surface areas that lead to high efficiencies in the adsorption of compounds, such as the removal of emerging pollutants [1]. Carbons can be prepared by carbonization of polymers to obtain inorganic-free carbon with fine-tune properties defined by the manufacture of the polymer [2,3]. In this study, a DLP 3D printer was used to synthesize the carbon-derived photopolymer (developed by EtzoldLab) to use in the adsorption of 2-nitrophenol and 4-nitrophenol (2-NP and 4-NP, respectively), as model pollutants. The monolith-structured polymer (PPP) was subjected to a thermal treatment that involved two stages: 1) pre-oxidation (air, 300ºC, 6 h, 10ºC/min), and 2) pyrolysis (N_2, 850ºC, 80 min, 4ºC/min), to obtain the carbon material (CPPP). To improve its textural properties, a physical activation with steam was performed in the final stage, obtaining the activated carbon (A-CPPP). Subsequently, sorption isotherms and kinetic analyses have been carried out in an orbital shaker (25ºC, 120 rpm, 72 h) using stock solutions of 2-NP and 4-NP (20-200 mg/L), employing both powdered carbon materials. The characterization and yields of the materials are shown in Table 1. Starting from a low porosity polymer, carbons with a high specific surface area have been successfully synthesized, and further enhanced through steam activation. The kinetic profiles of 2-NP and 4-NP have revealed that the adsorption rate increases when A-CPPP is used as adsorbent, reaching the equilibrium capacity at 6 h. Similarly, A-CPPP material provides much higher adsorption capacities for the same initial concentration of 2-NP and 4-NP (Fig.1), probably due to its higher porosity. On the other hand, the adsorbate has higher affinity for 2-NP, a compound with lower solubility in aqueous media, probably due to hydrophobic interactions between the apolar surface of the carbon and 2-NP. Different models were used for fitting the sorption isotherm and kinetics. Alternatively, experiments performed with a mixture of 2-NP and 4-NP revealed a decrease in the adsorption capacity for each NP compared to the single solute system, exhibiting adsorbent saturation at high concentrations. In addition, the reuse of activated carbon was tested. The regeneration efficiency of 4-NP by using ethanol was 80% after the first regeneration cycle.

Table 1. Characterization of carbon materials and yield obtained during their preparation.

Material	SSA_{BET} (m^2/g)	C (wt.%)	H (wt.%)	O (wt.%)	[a]Remaining (wt.%)	Yield (wt.%)
PPP	94	70.8 ± 0.8	6.80 ± 0.09	19.4 ± 0.1	3.00	-
CPPP	512	95.6 ± 2.1	0.49 ± 0.08	1.86 ± 0.03	2.05	21.9
A-CPPP	886	95.7 ± 1.3	0.53 ± 0.01	0.97 ± 0.07	2.80	8.8

[a] 100 (wt.%) – C (wt.%) – H (wt.%) – N (wt.%) – S (wt.%) – O (wt.%)

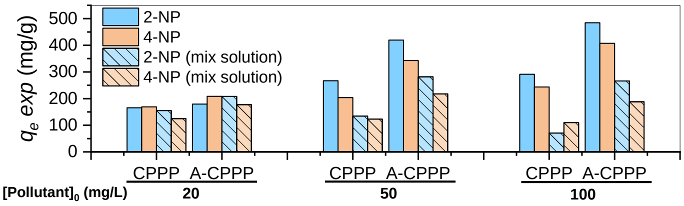

Fig.1. Adsorption capacities of CPPP and A-CPPP at initial 20, 50 and 100 mg/L of 2-NP and 4-NP.

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Optimizing $MnFe_2O_4$ Nanoparticles for Efficient Rare Earth Element Recovery from Contaminated Waters: A Response Surface Methodology Approach

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The increasing demand for Rare Earth Elements (REE) in advanced technologies, coupled with their limited availability from traditional mining, has intensified the search for sustainable recovery methods [1]. Magnetic nanomaterials, such as spinel ferrite nanoparticles, offer an efficient solution for REE extraction from contaminated waters, with the added advantage of magnetic separation. However, optimal operating conditions for these materials, especially in mixed REE systems, remain underexplored [2]. This study employs Response Surface Methodology (RSM) to investigate the sorption efficiency of $MnFe_2O_4$ nanoparticles under varying conditions of pH (4–8) and sorbent mass (20–180 mg/L), for a mixture of 9 REE (Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, with individual concentrations of 1–5 µmol/L), in water samples with differing salinity levels (NaCl: 0–30 g/L). Response surfaces for all REE were elaborated and the example for Nd is given in **Fig. 1**. The sorption of behavior of this element is representative of most other elements tested. Results indicate that a higher pH (6–8) enhances REE uptake due to favorable surface charge interactions. Total removal was observed for lower REE concentrations using 151 mg/L of sorbent, with Y being the least effectively removed. At higher concentrations (5 µmol/L), near-complete removal was achieved, except for Y and La. Salinity had a minimal impact (<10 %) on sorption efficiency, attributed to the large sorbent mass employed. Additionally, increasing both sorbent mass and initial REE concentration led to faster sorption kinetics. Desorption studies showed that the material can be used up to 5 times without loss in efficiency. These findings highlight the potential of $MnFe_2O_4$ nanoparticles for practical applications in REE recovery, paving the way for future work in real-world settings.

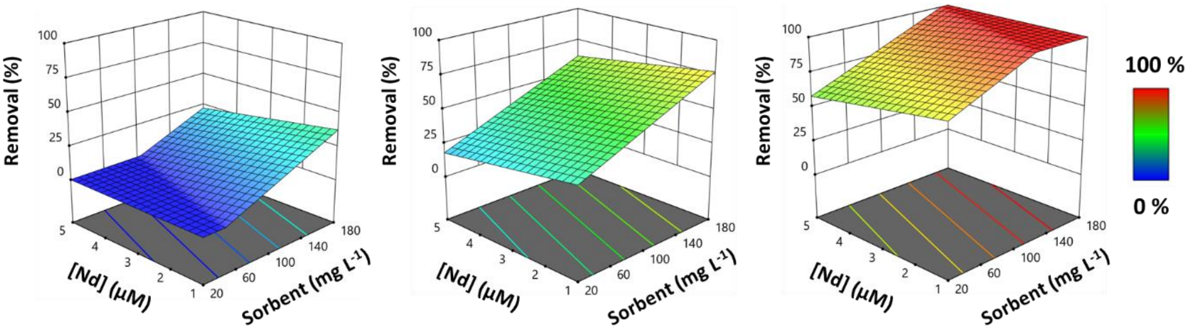

Fig.1. Removal (%) of neodymium (Nd) in a mixture of 9 Rare Earth Elements by $MnFe_2O_4$ nanoparticles. Results obtained show the removal for a pH of 4 (left), 6 (center) and 8 (right).

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Application of magnetic Nanoparticles for the removal of Microplastics from aquatic systems

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Plastics are one of the most widely used materials in society, with a rapid exponential increase in global production since 1950, according to the World Health Organization (2019), making them one of the biggest threats to ecosystems due to inappropriate disposal [1,2]. The effects of natural processes that plastics undergo in the environment, such as UV radiation, physical abrasion, chemical reactions, and biodegradation, lead to the formation of tiny plastic particles (size less than 5 mm) known as microplastics (MPs), which are widespread in the environment [2,3].

The physical and chemical alterations in MPs due to weathering agents enhance their capacity to interact with various pollutants (*e.g.*, pesticides, pharmaceuticals, heavy metals, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons), increasing their ability to adsorb and transport these contaminants, raising concerns about their presence in the environment [2]. In recent years, reports of MPs presence in marine environments have significantly increased. Also, their interactions and deposition in surface waters, freshwater, and wastewater, alongside their presence in bottled water have been documented [1].

Wastewater treatment plants are a significant MP pollution source. Despite the high removal rates of MPs (between 64 to 94%, depending on the treatment), conventional treatments have proven insufficient to fully address this issue [1,4]. Researchers have focused on exploring different approaches to developing an efficient, sustainable, and cost-effective quaternary treatment to tackle the MP problem. The application of magnetic particles to remove MPs has emerged as a promising approach [5] due to its fast processing time, low investment, efficiency, sustainability, and the possibility of reusing magnetic particles [6]. Preliminary studies were conducted with 3 types of MPs (polyamide nylon 6, polymethylmethacrylate, polytetrafluoroethylene) and magnetic iron oxide nanoparticles (NPs) with different coating layers. This approach reveals promising, as removal efficiencies higher than 80% were obtained for most of the MP/NPs systems.

Acknowledgements

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Advanced Functional Materials for Water Pollutants Adsorption

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The rapid expansion of industrial activity and global population growth has led to the continuous discharge of pollutants, mainly from mining, refining and pharmaceutical industries, into the environment.[1] Water pollution by inorganic pollutants, including metal ions, oxyanions/cations, and radioactive substances, poses a significant threat to the environment, aquatic organisms, and human health. The toxicity, carcinogenicity, and persistence of these pollutants highlight the urgent need for efficient water remediation strategies.[2]

Adsorption has emerged as one of the most promising methods, offering simplicity, cost-effectiveness, and energetic efficiency.[3] Among the recent advances in this field is the development of MOF-Derived Porous Carbons (MDPCs), a novel class of materials obtained through the carbonization of Metal-Organic Frameworks (MOFs) under inert atmosphere resulting in uniform metal/metal oxide nanoparticles distributed in the ligand-derived carbon matrix. MDPCs feature high specific surface areas, tunable porosity, non-toxicity, and ease of preparation. Their potential as adsorbents is further enhanced when prepared with superparamagnetic properties, enabling magnetic separation for practical use in water treatment systems.[4]

In parallel, there is growing interest in valorising industrial waste as part of Circular Economy strategy. Solid wastes are potential recyclable resources with enormous economic value and their valorisation into value-added products is highly needed. Chars, obtained from the thermal decomposition of wastes, have attracted the scientific community due to its low cost, sustainable preparation, wide availability of feedstocks and excellent adsorption capacities for water pollutants. Magnetic waste-derived chars offer considerable promise due to their availability, eco-friendly synthesis, and effective pollutant removal capabilities.[5]

This work focuses on the development of porous carbon-based materials derived from MOFs and industrial wastes from cork industry for the removal of inorganic water pollutants. The materials were characterised by solid-state techniques, namely FTIR, SEM/EDS, PXRD, N_2 adsorption-desorption isotherms, and zeta potential analysis, allowing to confirm the successful preparation of the materials. The adsorptive performance of these materials was evaluated, demonstrating their potential for sustainable water remediation applications. The durability of the adsorbents was investigated through consecutive cycles by adsorption-desorption procedures.

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Estudio del Análisis de Ciclo de Vida

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Mediante el Análisis del Ciclo de Vida (ACV) se evalúa el impacto ambiental desde las materias primas hasta el final de proceso, pasando por diferentes etapas del producto, fabricación, uso y fin de vida. Es una herramienta para evaluar y mejorar el impacto ambiental tanto de procesos como de productos. Este estudio se realiza con el software SimaPro que hace una comparación de los aspectos medioambientales de un producto según la norma ISO 14040. [1]

El nuevo reglamento europeo 2024/573 sobre los gases fluorados de efecto invernadero [2] introduce nuevas restricciones en el uso de refrigerantes, de forma que los gases refrigerantes deberán tener un PCG inferior a 150. Este trabajo analiza la influencia de diferentes refrigerantes, más concretamente R4 (R410A) y R5 (R454B), que se utilizan en bombas de calor geotérmicas (BCG). El primero tiene un potencial de calentamiento global (PCG) elevado de 2088, mientras que el segundo es de 466. La composición de estos refrigerantes está formada por distintos porcentajes de otros compuestos (Tabla 1), que se basan en las siguientes reacciones químicas:

Refrigerante R1 : $CH_3Cl + 2\ HF \rightarrow CH_2F_2 + HCl + H_2$

Refrigerante R2 : $2\ CHCl_3 + 5\ HF \rightarrow C_2HF_5 + 6\ HCl$

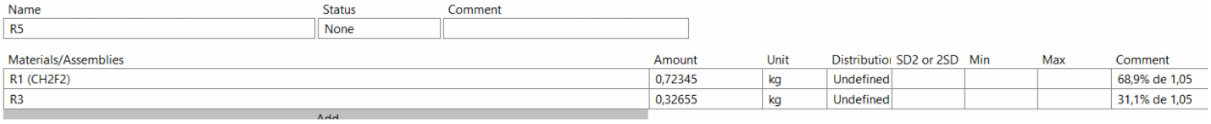
Refrigerante R3 : $C_3H_5Cl + 4\ HF \rightarrow C_3H_2F_4 + HCl + 3\ H_2$

Tabla 1. Composición refrigerantes

Composición	R1	R2	R3
R410A (R4)	50.0%	50.0%	-
R454B (R5)	68.9 %	-	31.1%

Algunas alternativas transitorias al uso del R410A han pasado por refrigerantes como el R454B. La figura 1 define en SimaPro el refrigerante R5, que se corresponde con este último, en función de los refrigerantes R1 y R3. El primer paso del ACV es definir el análisis de inventario tanto de los componentes de la BCG como de los refrigerantes estudiados, y después de evaluar las diferentes fases (funcionamiento, desmantelamiento,…) se procede al análisis de distintos sistemas. Finalmente, se lleva a cabo el análisis de impacto en función o bien de las diferentes categorías intermedias o bien de los daños finales.

Fig.1. Definición de R5 en SimaPro



Name	Status	Comment
R5	None	

Materials/Assemblies	Amount	Unit	Distributioı	SD2 or 2SD	Min	Max	Comment
R1 (CH2F2)	0,72345	kg	Undefined				68,9% de 1,05
R3	0,32655	kg	Undefined				31,1% de 1,05

A partir del estudio de los diferentes refrigerantes en la bomba de calor geotérmica, se ha concluido a través del análisis de ciclo de vida que el menos contaminante es el R5 (R454B), especialmente en términos de agotamiento de la capa de ozono, con una diferencia del 200%. En otros ámbitos como el impacto en la ecotoxicidad marina y terrestre, la acidificación o la eutrofización también se observan ligeras mejoras entorno al 1%.

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Green processes to valorize Paulownia wood based on deep eutectic solvent (DES)

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In recent decades, biofuels from renewable biomasses have gained attention, leading to a focus on biorefineries. [1]. Within this framework, lignocellulosic biomass, mainly composed of polysaccharides and lignin, offers several advantages like abundance, renewability, ubiquity, and non-competition with food resources [2]. Notably, Paulownia is a fast-growing tree species (up to 50 t/ha/year) known for its high tolerance to abiotic stress [3]. However, due to the recalcitrant nature of this biomass, pretreatment methods are essential for effectively separating its main components. In this regard, deep eutectic solvents (DES) have emerged as a promising alternative to traditional methods (such as organosolv or alkaline treatments) for lignin removal from lignocellulosic biomass, owing to their high selectivity for polyphenolic compounds while preserving cellulose in the solid phase [4].

This study focuses on the evaluation of various DES for the effective fractionation of Paulownia wood within a multi-product biorefinery framework. To this end, different DES formulations containing choline chloride were created by incorporating formic acid, acetic acid, lactic acid, glycerol, or ethylene glycol. The most effective DES, a combination of choline chloride and lactic acid, was selected, and extraction conditions—including temperature, residence time, molar ratio, and liquid-to-solid ratio—were optimized to achieve high glucan retention in the solid phase while maximizing lignin solubilization. Under the optimized conditions, the cellulose-rich solid underwent presaccharification and simultaneous saccharification and fermentation (PSSF) to produce bioethanol, achieving a yield of up to 43.61 g ethanol/L (nearly 90% yield). Additionally, the extracted lignin was characterized for purity using techniques such as FTIR, 1H NMR, TGA, and SEM. The liquid phase following lignin precipitation was analyzed for its content of oligomers and monomers, total phenolic content (TPC), antioxidant capacity (DPPH, ABTS, FRAP), and phenolic profile using HPLC-MS-ESI.

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Macroalgae for a circular economy: Recovering critical elements from acid mine drainage

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Technology-critical elements (TCEs) such as rare-earth elements (REEs) are considered critical raw materials for many emerging technologies [1]. Mining remains the largest source of TCEs, and its activities are well-known for their significant environmental impact, generating various wastes such as tailings, sludges, slimes, flue dust, and acid mine drainage (AMD). In particular, AMD poses severe threats to the environment and negatively affects marine and terrestrial ecosystems due to its considerable amount of toxic elements, its acid character and persistence (thousands of years) [2], remaining a global environmental challenge. Yet, AMD has a prominent concentration of TCEs, which recovery would promote the valorisation of AMD [3]. Among potentially low-cost sorbent materials, macroalgae are considered a greener, cost-effective and environmentally friendly alternative with a high potential for recovering TCEs from aqueous solutions [4].

The present work investigates for the first time the macroalgae potential to remove, concentrate, and recover TCEs from raw AMD, while improving water quality, thus contributing to Sustainable Development Goals No. 6, 12 and 14.

AMD samples were collected from a closed Portuguese mine and characterized using Inductively Coupled Plasma Mass Spectrometry, selecting the elements of economic interest. The results revealed the presence of concentrations in the order of 1000 – 2400 µg/L of ΣREEs, Co and Ni. A comparative study of living (bioaccumulation) and dried (biosorption) macroalgae species (*Ulva* sp., and *Gracilaria* sp.) under the original physicochemical conditions of AMD (pH 2.5, salinity 2.6 PSU) was performed and showed a negligible removal of TCEs for both processes and severe toxic effects such as chlorosis were observed. Adjusting the pH of AMD with NaOH successfully separated unwanted elements with minimal REEs loss. When in contact with the pH-adjusted AMD after 24 h, the bioaccumulation process showed superior performance against biosorption. The macroalgal dosage (0.08-0.3 ratio V/m) was evaluated for both *Ulva* and *Gracilaria* species. Overall, *Gracilaria* sp. stood out and accumulated up to 494 µg/g of ΣREEs, corresponding to bioconcentration factors between 470 - 532. FTIR and SEM-EDS analysis identified sulphonate, and carboxyl groups as key in binding elements to *Gracilaria* sp. biomass.

Overall, these results support the use of living macroalgae as the basis of an efficient, greener, and sustainable technology, easily incorporated in the current passive treatment systems, to value AMD-containing REEs.

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Selective Copper Removal from Multi-Element Solutions with Thiourea Formaldehyde-Graphene Oxide Composite

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Copper (Cu) is essential to renewable technologies, particularly in wind energy, due to its high electrical conductivity and durability. Wind turbines rely on 4.7 tonnes of Cu per MW for power generation, transmission, and control systems [1]. It can be estimated that about 270,000 wind turbines are currently operating worldwide [2], considering an average output of about 3 MW it can be estimated that 3.8 million tonnes of Cu are being currently used. Also, 1.18 million tonnes of material can be considered to manufacture wind turbine blades in 2017. Based on this it is predicted that more than about 600,000 tonnes of waste from wind turbine blades will exist in 2034 [2]. Copper is listed as a critical raw material, but its finite supply and increasing demand make efficient resource management crucial [3]. The recovery of Cu from end-of-life wind turbines is poorly explored and most studies regarding its removal from solution were conducted in mono-element assays. Moreover, despite the evolution on recycling technologies, such as automatic disassembly and chemical leaching, the selective separation and recovery of individual elements, such as Cu, from complex mixtures remains a challenge. To reduce dependence on primary mining and its environmental impact, it is important to develop technologies that enable the selective recovery of Cu from wind turbine waste.

The present work aims to evaluate the ability of thiourea formaldehyde graphene oxide (G3DTF) to remove Cu from complex mixtures simulating a wind turbine waste leachate.

The evaluated mixture simulated the nacelle component composition (Cu, B, Ni, Co, Nd, Dy, Pr, Gd) at two concentrations (100 µM and a 10-fold diluted real concentration). Results indicated that G3DTF selectively removed Cu after 24 h (82% and 68% removal with increasing concentration), while other elements were minimally removed (2–15%), as shown in Fig. 1. Optimization of Cu removal using response surface methodology studied sorbent dosage (0.2, 1.1, and 2 g L^{-1}), salinity (0, 15, and 25), and pH (4, 6, and 8), revealing that sorbent dosage was the most significant factor, with salinity and pH having negligible effects. The material also showed Cu selectivity in a real solution mimicking magnet leachate, removing 55% of Cu with negligible removal of other elements.

Overall, the results support the use of graphene-based materials as alternative sorbents to efficiently recover Cu from complex mixtures.

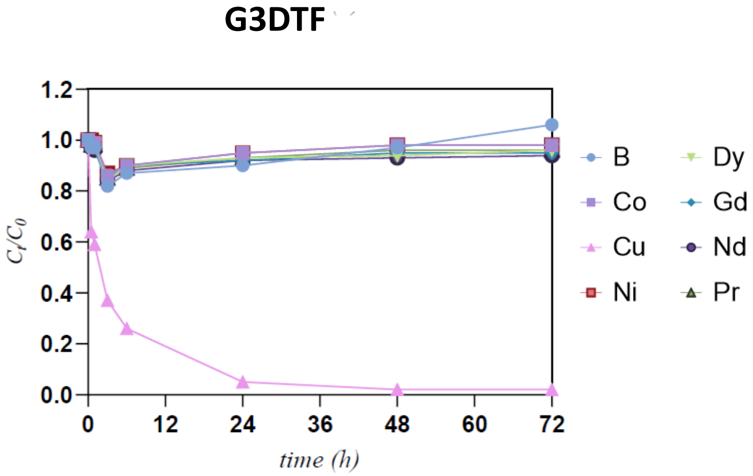

Fig.1. Normalized concentrations (C_t/C_0) of Cu, B, Ni, Co, Nd, Dy, Pr, and Gd as a function of contact time by G3DTF.

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Cork Boiling Wastewater: a promising sustainable water source for cosmetic application

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Global water scarcity, driven by population growth, economic development, and climate change, is a critical challenge [1]. The cosmetics industry, with products containing 60-85% water (up to 95% in rinse-off), greatly impacts water demand. Meanwhile, the cork industry produces large amounts of cork boiling wastewater (CBW)—an acidic effluent posing environmental risks—at 140 to 1200 litres per ton of cork during high-temperature processing. [2]. This study aimed to investigate CBW as a potential source of water for cosmetic application, focusing on its safety, physicochemical properties, and suitability for typical formulations. The CBW sample was water collected after boiling cork planks for 48 hours in the cork industry. CBW was treated with adsorbent powder to reduce toxic contaminants, and human keratinocyte viability was assessed after 24 hours. The main physicochemical properties (pH, conductivity, refractive index, density, turbidity, DPPH scavenging activity, and total phenolic content (TPC)) were compared between treated and untreated samples, along with chromatographic profile and metal content Treated CBW was then incorporated at 40% into an oil-in-water cream and characterized for pH, droplet size, preliminary stability, rheological behaviour, and texture properties. CBW decreased the viability of human keratinocytes compared to control water, but after treatment viability improved by approximately 20 percentage points. The treated CBW exhibited neutral pH (≈7), electrical conductivity > 500 µS/cm, refractive index > 0.5% Brix, density of 1.00, turbidity > 5 NTU, a DPPH radical inhibition of about 30% and TPC > 150 mg GA/L. The treatment minimally impacted properties, although reducing phenolic compounds as indicated by lower DPPH scavenging activity and TPC, confirmed by high performance liquid chromatography. Certain metals like lead decreased, while others slightly increased remaining within cosmetic safety limits. The cream with treated CBW was homogeneous, brownish, woody-scented, had uniform droplet size, and passed the centrifuge stability test. The consistency index and apparent viscosity (for shear rates of 0.1 to 100 s^{-1}) were higher in the formulation containing treated CBW, and the firmness was similar to the base formulation. Treated CBW, a cork industry by-product, could be a sustainable water source for cosmetic products due to its low toxicity to human keratinocytes (between 5-40%), suitable physicochemical properties, and ability to be incorporated in a typical cosmetic formulation, maintaining its physicochemical stability.

Acknowledgements

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Synthesis and evaluation of a pine cone-derived adsorbent for remediation of recalcitrant pollutants in water

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The noticeable generation of forest residues poses a significant risk to the environment, therefore, the pursuit of alternatives for managing these residues and providing them with a second life has become a priority. These wastes, characterized by their polymeric composition and high content of cellulose, hemicellulose and lignin, have emerged as a valuable raw material in the production of biochars through thermochemical treatments [1], which can be subsequently used in adsorption processes for the removal of recalcitrant pollutants from aquatics environments.

In this study, a biochar derived from pine cones was synthesized and evaluated for the removal of three model pollutants: fluoxetine (FLX), sulfamethoxazole (SMX) and sulfamethizole (SMZ). The material was initially carbonized and characterized through the analysis of its physicochemical properties, such as Fourier-transform infrared spectroscopy, elemental analysis, surface morphology or zero charge point. Then, preliminary adsorption tests were carried out with SMX to ascertain the optimal adsorbent material dosage and particle size. Subsequently, the removal capacity of the three pollutants was evaluated both individually (Fig. 1) and in mixtures, followed by the kinetic characterization of the process and an analysis of the adsorption mechanism involved [2].

The obtained results indicate a high capacity for the removal of FLX, SMX and SMZ when pine cone was used as an adsorbent, being this process primarily governed by chemisorption phenomena. Consequently, it was established that this biochar can be effectively used in environmental applications, being feasible to explore alternatives aimed at improving the adsorption process efficiency and extending its useful life.

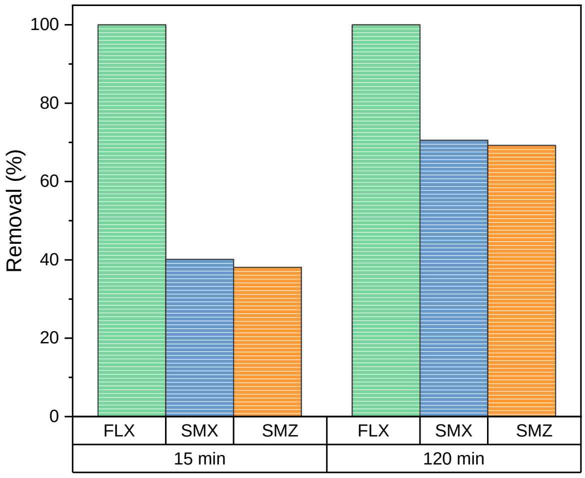

Fig.1. Removal values in the pine cone adsorption process for FLX (green), SMX (blue) and SMZ (orange) at 15 and 120 min

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Remoção de fluoxetina de efluentes aquosos usando adsorventes à base de casca de noz

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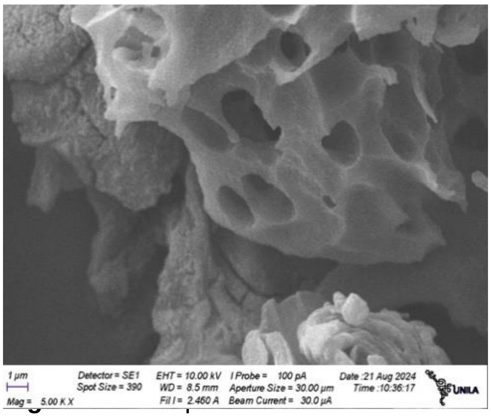
A fluoxetina, um antidepressivo amplamente utilizado, representa um contaminante emergente em efluentes, levantando preocupações sobre seu impacto na saúde pública e no meio ambiente [1],[2],[3]. Este estudo investiga a eficiência da remoção de fluoxetina de efluentes aquosos utilizando adsorventes à base de casca de noz, um resíduo agroindustrial. A metodologia inclui a preparação do adsorvente com ativação física e química, utilizando cloreto de zinco, seguida por um processo de carbonização de 1,5 horas a 500°C, e a posterior caracterização do adsorvente através da avaliação e medição de: rendimento de carbonização, pH_{pzc}, sítios ácidos e básicos, e a utilização das técnicas FTIR, TGA, MEV, EDS, DRX, e BET. Procedeu-se igualmente à análise de resultados relacionados com a cinética e equilíbrio de adsorção em regime descontínuo.

Os resultados demonstram que é possível produzir um adsorvente com características promissoras, apresentando uma formação de poros bem definida (vd. Fig. 1), com pH_{PZC} de 9,83 ± 0,48, e grupos funcionais ácidos e básicos com concentrações de 1,1461 e 0,8766 $mmol.g^{-1}$, respetivamente. A análise de DRX indica uma estrutura amorfa. O material apresenta uma isoterma favorável para a adsorção do fármaco (vd. Fig. 2), sendo capaz de remover mais de 95% da fluoxetina. Esta investigação sugere que a casca de noz pode ser uma solução eficaz e sustentável para a remoção de fluoxetina de efluentes, contribuindo para a mitigação dos impactos ambientais associados a contaminantes farmacêuticos. Concluí-se que a utilização de resíduos agroindustriais, como a casca de noz, não apenas auxilia na purificação da água, mas também promove uma abordagem mais ecológica na gestão de resíduos, alinhando-se com os princípios da economia circular.



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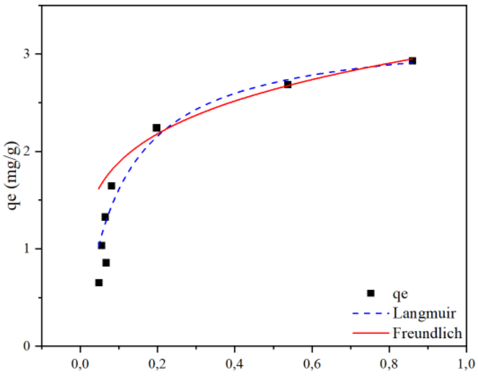

Fig. 2. Isoterma para o carvão com ativação física

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A Sustainable Approach to Cellulose Extraction from Wood Waste

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This research presents a novel, environmentally friendly method for extracting cellulose from eucalyptus and pine tree waste products. The proposed protocol utilizes microwave-assisted radiation, avoiding harsh chemicals and high temperatures, making it a more sustainable alternative to traditional extraction methods.

Initially, the methodology comprised three main steps: (i) alkaline treatment, (ii) bleaching with hydrogen peroxide (H_2O_2), and (iii) acidic bleaching. Characterization techniques (Fourier-transform infrared spectroscopy, powder X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry) revealed that cellulose was retained throughout the extraction process, while hemicellulose and lignin were primarily removed in the final step [1].

To enhance sustainability, an improvement to the firstly developed protocol was optimized for eucalyptus wood waste using deep eutectic solvents (DES). DES, known for their solubility capabilities, are promising for sustainable pulping technologies [2,3]. The novel approach replaced the alkaline treatment with alkaline DES, eliminated the need for H_2O_2 bleaching, and substituted the acidic treatment with acidic DES. Characterization results demonstrated that alkaline DES can effectively replace the traditional alkaline treatment and initial bleaching steps. While the optimization of acidic DES is ongoing, preliminary findings suggest that they may not offer significant advantages in this context.

In conclusion, this research provides a more sustainable and efficient approach to cellulose extraction from tree waste. The proposed methodology, combining microwave-assisted radiation and DES, offer promising alternatives to traditional processes, contributing to a more environmentally friendly and resource-efficient pulp and paper industry.

Acknowledgements

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Defect engineering of UiO-66 using a mixed-ligand strategy via microwave-assisted synthesis to enhance CO_2 capture and conversion potential

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The daily release of high levels of carbon dioxide (CO_2) into the atmosphere is a serious threat for the sustainable future of the Earth, contributing to catastrophic climate changes. The capture of CO_2 and, subsequent, its conversion into added-value chemicals, is a valuable and cost-effective solution for the reduction of the CO_2 levels. However, bifunctional materials that can conciliate CO_2 capture and conversion simultaneously under sustainable conditions are scarce and needed.[1, 2] Metal-organic frameworks (MOFs) are highly crystalline and porous structures formed by the junction of metallic center by organic ligands. A great number of metal-organic frameworks (MOFs) have shown promising results in either CO_2 capture or conversion, for example, the cycloaddition of CO_2 with epoxides into cyclic carbonates.[2, 3] Defect engineering, i.e. the deliberate creation of defects in MOFs structures increases the number of active sites, enhancing catalytic efficiency. UiO-66 is a strong candidate for defect induction, since its frameworks presents structural integrity even containing uncoordinated centers.[3, 4]

In this work, we successfully synthesized a series of defective UiO-66-based materials to enhance the catalytic activity of the parent UiO-66, with reported potential for CO_2 capture and conversion. The defects and improved catalytic potential were achieved through a mixed-ligand strategy, based on the mixture of different BDC-based ligands to introduce amine and halogen groups, that theoretically facilitate the opening of the epoxide rings. The materials were synthesized via conventional (solvothermal) and microwave-assisted methods, with the latter demonstrating a significantly lower environmental impact, as confirmed by a LCA study. Characterization techniques such as FTIR, PXRD, SEM-EDS, N_2 sorption, NMR and TGA were employed to confirm the engineered defects. This approach potentially enhanced the catalytic performance of UiO-66 in the cycloaddition of CO_2 with epoxides to produce cyclic carbonates, without significant loss of CO_2 adsorption-desorption abilities and through a “greener” synthetic process.

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Avaliação da Atividade Antioxidante de Extratos de Borra de Café: Comparação de Métodos de Extração para Aplicação Cosmética

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O café é uma das bebidas mais consumidas no mundo e apresenta uma cadeia produtiva complexa, a qual resulta na geração de subprodutos, de entre os quais se destaca a borra de café. Apesar de ser frequentemente descartada como resíduo, a borra de café é rica em compostos antioxidantes, que possuem elevado potencial bioativo. Esses compostos desempenham um papel essencial na neutralização de radicais livres, os quais estão relacionados ao envelhecimento celular e a génese de doenças crónicas [1]. A incorporação desses antioxidantes em produtos cosméticos pode conferir benefícios tanto para a saúde quanto para a estética. O presente estudo teve como objetivo investigar a atividade antioxidante de extratos de borra de café utilizando diferentes métodos de extração, a fim de identificar o mais eficiênte e aplicá-lo em formulações cosméticas. A borra de café utilizada, proveniente de grãos 100% arábica, foi obtida num café localizado em Bragança, Portugal. Para a análise da atividade antioxidante, foram empregues os métodos de sequestro de radicais livres 2,2-Difenil-1-Picrilhidrazilo (DPPH) [2] e o ensaio de poder redutor [3]. Os valores de EC_{50} (concentração necessária para reduzir 50%) foram calculados para cada amostra e estão expostos na **Tabela 1**. O extrato obtido pelo método de ultrassom apresentou os menores valores de EC_{50}, indicando maior eficiência. Esse desempenho superior pode ser atribuído ao fenómeno de cavitação ultrassónica, que promove a ruptura das células vegetais, libertando uma maior quantidade de compostos bioativos. Em acréscimo, o ultrassom é um método de extração que não utiliza altas temperaturas, o que o torna mais eficaz na preservação de compostos com elevada atividade antioxidante.

Tabela 1**.** Valores de EC_{50} de DPPH e poder redutor de diferentes extratos

Método de Extração	**Poder Redutor EC_{50} mg/mL**	**DPPH EC_{50} mg/mL**
Ultrassom	0,22±0,004	0,0060 ± 0,0008
Maceração	0,30± 0,06	0,0075 ± 0,0005
Decocção	0,27± 0,08	0,0092 ± 0,0019
Infusão	0,34±0,08	0,0211 ± 0.0024
p-value[a]	>0,05	<0,001

[a] Valores foram expressos como média ± D.P. (n=3). O valor do p calculado a partir da análise ANOVA.

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Estrogen Removal through Adsorption by Carbon Materials Prepared from Biomass Wastes: A Review

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Environmental impacts are an ever-growing concern in various industrial and economic sectors that produce wastes such as heavy metals, pharmaceuticals, pesticides, surfactants, and petroleum derivatives. These substances can be classified as emerging pollutants due to their increasing concentration in water bodies and living beings [1]. Since many of these substances can only be found in very low concentrations, in micrograms per liter (µg/L) or nanograms per liter (ng/L), they can also be classified as micropollutants [2].

One type of micropollutant that has been especially concerning are endocrine disruptors, composed of natural hormones, such as estrone (estrogen E1) and 17β-estradiol (estrogen E2), and synthetic hormones, such as 17α-ethinylestradiol (estrogen EE2). Endocrine disruptors can deregulate the endocrine system of both humans and animals and, due to their nature as micropollutants, are not effectively removed by conventional processes in wastewater treatment plants [3].

To establish a state-of-the-art in the particular field of alternative treatment methods based on adsorption, previous studies were selected with topics such as estrogen molecules removed, adsorbent activation type, adsorption capacity, and best fit for isotherm and kinetic models. Hence, a few relevant literature studies concerning biomass waste-based materials are summarized in Table 1.

Table 1. Selected adsorption studies from the literature and the respective main results

Estrogens	Adsorbent	Activation	Adsorption capacity (mg/g)	Isotherm Model	Kinetic Model	Ref.
E1, E2	Banana peal	No activation	0.387 – 0.420	Freundlich	PSO	4
EE2	Palm kernel shell	Steam carbonization	1.68	Langmuir	PSO	5
E1, E2, E3	Walnut shell	Pyrolysis	0.80 – 2.80	Freundlich	PSO	6
E2, EE2	Coffee waste	$Ca(OH)_2$ + pyrolysis	7.584 – 7.833	Sips	General	7
E2	Rice husk	NaOH + pyrolysis	32.41	Langmuir	PSO	8
E2	Corn straw	Pyrolysis	99.8	Langmuir	PSO	9
E2	Wood sawdust	K_2FeO_4 + pyrolysis	99.67 – 133.45	Langmuir	PSO	10

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Recyclable 3D Spongin Scaffold for Enhanced Recovery of Rare Earth Elements from Aqueous Waste Streams

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In April 2024, the European Union (EU) adopted the final Critical Raw Materials Act (CRMA) with the aim of ensuring self-sufficiency in raw materials vital to the EU's industrial ecosystem, particularly those necessary for the green and digital transition, like rare earth elements (REEs). The EU aims to shift the paradigm from the current reliance on importing REEs from countries like China to a circular economy where REEs can be obtained from secondary sources such as industrial and mining wastewater or e-waste leachate. The development of sustainable and efficient technologies to extract REEs from these aqueous waste streams is essential to achieving the CRMA goals [1]

Here, we propose the use of a 3D spongin scaffold from marine sponges [2] as an effective and sustainable biosorbent for REEs. This natural material has a porous structure with high mechanical resistance and the ability to return to the original shape after compression, being insoluble in both acidic and basic conditions. The Response Surface Methodology with a Box-Behnken design [3] was applied to optimize the biosorption of a mixture of 9 REEs (Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy) in water at different concentration (1–5 µM), pH (4–8) and material dose (20–180 mg/L). The desorption of the REEs and subsequent reuse of the sorbent was studied in four cycles.

Despite the presence of naturally occurring other cations and anions in water, such as Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, $SO_4^{2-}$and NO_3^-, the 3D spongin scaffold (180 mg/L) achieved 99 % REEs removal in 6 h, at pH 8. The concentrations of REEs in the sorbent were up to 19 times higher than those in common apatite ores (primary source of REEs), and with a small volume of dilute acid (0.1 M HNO_3) 100 % of the REEs were successfully recovered from the material. FTIR and SEM analysis confirmed that the structure and properties of the 3D spongin scaffold were preserved after acid regeneration, enabling constant sorption performance after four reuse cycles.

Overall, the results support the application of the 3D spongin scaffolds in the recovery of REEs from actual contaminated water and highlight the advantages of their use, including efficiency, recyclability, and ease of separation from water since no special infrastructures are required.

Agradecimientos
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Remoção de cloridrato de sertralina com carvão ativado produzido a partir de casca de noz ativada com $ZnCl_2$

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Entre 1990 e 2017, houve um aumento de 49,9% nos casos de depressão no mundo [1]. A sertralina, um inibidor seletivo de recaptação de serotonina, é amplamente usada no tratamento de depressão, ansiedade, TOC e outros transtornos [2]. Contudo, a presença desse fármaco em corpos hídricos e águas residuais tem sido identificada globalmente, e a sua remoção pelos métodos convencionais de tratamento de água é limitada [3],[4],[5]. O processo de adsorção surge como uma solução eficiente para a remoção de micropoluentes em águas residuais [6]. Este estudo teve como objetivo identificar e quantificar a sertralina em solução aquosa, assim como explorar a sua remoção por adsorção usando como adsorvente carvão ativado com $ZnCl_2$ produzido a partir de casca de noz.

A identificação da sertralina foi realizada por cromatografia líquida de alta eficiência, utilizando água com TFA e acetonitrila (40:60 v/v), a um comprimento de onda de 220 nm. O carvão ativado (vd. Fig. 1) foi produzido pela moagem da casca de noz, ativação com $ZnCl_2$ na proporção de 1:1:8 (casca de noz: $ZnCl_2$: água – proporção mássica) e carbonização em mufla a 500 ºC por 1,5 hora. Os resultados obtidos incluem valores de rendimento, pH_{PZC}, análise de grupos funcionais, termogravimetria, difração de raios X e MEV-EDS.

O rendimento de carbonização foi de 52,4% e o pH_{PZC} encontrado foi de 7,5. A análise de FTIR permite verificar a presença na superfície do adsorvente de grupos funcionais como álcoois, estiramentos de C=O, comuns em compostos com celulose e lignina, C=C presentes em composto aromáticos. O carvão ativado apresenta concentração de 0,06 mmol/g de grupos básicos e 0,43 mmol/g de grupos ácidos. Nos testes cinéticos, o carvão ativado removeu 97% da sertralina em solução aquosa, comprovando sua eficiência e destacando uma alternativa sustentável para o tratamento de água e a economia circular pela reutilização de resíduos.

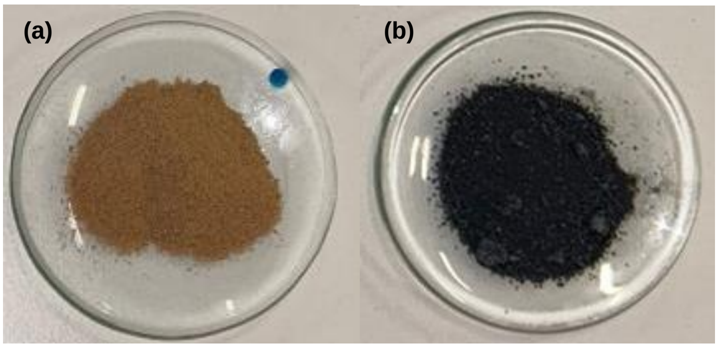

Fig.1. (a) Casca de noz moída; (b) carvão ativado com $ZnCl_2$

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Purificação a seco do biodiesel etanólico através de adsorção utilizando materiais à base de casca de amêndoa

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A demanda global de energia continua crescendo, devido, principalmente, ao crescimento populacional, ao desenvolvimento econômico e a urbanização acelerada, ocorrendo majoritariamente nas economias emergentes [1]. Os combustíveis baseados em petróleo e fontes não renováveis continuam dominando a fonte de energia global. Porém, a distribuição desigual dos recursos de combustíveis fósseis pode resultar em tensões geopolíticas, além de que o uso destes combustíveis promove uma grande emissão de poluentes na atmosfera, incluindo gases com efeito de estufa como o dióxido de carbono [2]. Nesse contexto, o biodiesel é uma possível alternativa para satisfazer a demanda de energia global em substituição dos combustíveis não renováveis, já que é considerado uma das melhores alternativas para substituir o diesel, devido a suas propriedades compatíveis, biodegradabilidade e origem renovável [3].

O biodiesel é produzido, normalmente, através da reação de transesterificação, utilizando, principalmente, óleos vegetais comestíveis como fonte de triglicerídeos. Por outro lado, o óleo alimentar usado (OAU) é uma ótima alternativa de matéria prima, já que é um resíduo produzido em grandes quantidades por indústrias alimentares, sendo descartado, geralmente, de maneira incorreta prejudicando o meio ambiente. Dessa maneira, o uso de OAU na produção do biodiesel, além de ser benéfico ambientalmente, por ser um resíduo doméstico ou industrial, possui um custo mais baixo em relação aos óleos vegetais [4]. A purificação do biodiesel é uma etapa importante do processo, já que os contaminantes presentes no biodiesel bruto, como o glicerol, trazem prejuízos aos motores, sendo necessário retirá-los, possibilitando, assim, a comercialização do combustível. Diversos métodos de purificação podem ser aplicados, sendo o mais comum a lavagem com água, que implica a geração de grandes quantidades de efluentes aquosos. Porém, a fim de solubilizar o glicerol e outras impurezas contidas no biodiesel, métodos mais sustentáveis como a lavagem a seco, envolvendo a utilização de materiais adsorventes, são atualmente objeto de estudo, nomeadamente através do aproveitamento de resíduos agrícolas como precursores na produção dos materiais adsorventes, tornando o processo ainda mais significante ambientalmente [5].

Na primeira etapa deste trabalho, o biodiesel foi produzido por meio do processo de transesterificação utilizando óleo alimentar usado (OAU) como matéria-prima e hidróxido de sódio (NaOH) como catalisador da reação. O processo foi conduzido via rota etanólica com uma razão molar óleo/etanol de 1:7,5 e uma proporção de catalisador de 0,5% (m/m) em relação ao óleo. Posteriormente, o estudo continuará com a produção e a caracterização de carvões ativados derivados de casca de amêndoa, analisando a sua capacidade na remoção de glicerol do biodiesel etanólico bruto, com o objetivo de atingir o padrão de qualidade especificado pela norma EN 14214, de um conteúdo máximo de glicerol livre de 0,02% (m/m).

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Remoção de Metformina de Matrizes Aquosas por meio de Adsorventes à base de Cortiça

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As atividades antrópicas associadas ao desenvolvimento industrial desenfreado, à urbanização e ao crescimento populacional exponencial resultaram na presença alarmante de diversas substâncias, consideradas poluentes, em corpos hídricos. Tornou-se crucial implementar medidas de controlo e monitoramento desses compostos para mitigar os impactos ambientais e preservar a qualidade dos recursos hídricos para as futuras gerações [1], [2].

Entre as substâncias preocupantes estão os micropoluentes emergentes, um grupo de contaminantes que inclui produtos de higiene, fármacos, hormônios e pesticidas. A deteção e quantificação desses micropoluentes exigem técnicas analíticas avançadas, já que são encontrados em concentrações muito baixas (µg/L a ng/L). Apesar disso, esses poluentes representam riscos consideráveis ao meio ambiente e à saúde humana [3], [4], [5], em especial os fármacos, já que são parcialmente metabolizados pelo corpo humano, e o restante é excretado nos sistemas aquáticos [6].

A metformina, amplamente prescrita para o tratamento da diabetes tipo 2, é um exemplo de fármaco encontrado cada vez mais nos ambientes aquáticos devido ao seu metabolismo incompleto e seu uso generalizado. Relata-se que a metformina pode estimular a expressão de genes ligados às vias hormonais endócrinas, e seus subprodutos clorados na água potável têm efeitos tóxicos no ambiente aquático [7], [8].

Diversos métodos de tratamento têm sido explorados na remoção de fármacos em águas residuais, com a adsorção se destacando como uma técnica eficaz. O carvão ativado, especialmente derivado de biomassa renovável, por exemplo a cortiça, tem atraído atenção devido à sua eficiência e baixo custo na remoção de poluentes orgânicos da água residual, apresentado uma estrutura com alta área superficial e porosa [9]. Essa abordagem não só oferece uma solução sustentável, como também se alinha aos princípios da economia circular pela utilização de materiais orgânicos descartados [10], [11].

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Neodymium extraction and recycling from magnet leachates using magnetic nanoparticles

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Neodymium, a vital element in the technology sector, plays a key role in the production of green energy and in emerging technologies, such as catalysts and permanent magnets used in mobile phones, wind turbines, and electric vehicle motors [1]. Given the high demand for neodymium, increasing prices, supply constraints from neodymium-exporting countries, and, most importantly, the environmental and energy challenges associated with its extraction, there is an urgent need to identify and optimise secondary sources of this element. Permanent magnets are a valuable source of neodymium as they are found in hard disk drives (HDDs), air conditioning units, and cars, among other devices, all of which have a limited lifespan. These magnets, commonly referred to as NdFeB magnets, are named after their primary components [2]. As such, the development of new processes for the removal and recovery of Nd is crucial.

Sorption using various sorbents presents a promising alternative to traditional methods of metals removal from waters [3]. Nanoparticles, especially magnetic ones, are excellent candidates for this purpose due to their large surface area and ease of separation.

This study explores the use of manganese ferrite nanoparticles ($MnFe_2O_4$) for extracting neodymium from contaminated water. By applying response surface methodology (RSM) with the Box-Behnken design (BBD), statistical analysis revealed that higher nanoparticle doses positively impact removal, while salinity has a detrimental effect. The optimal conditions for removal were determined to be an initial neodymium concentration of 20 µmol/L, low salinity, a nanoparticle dosage of 1000 mg/L, and a pH of 6. Experimental validation under these conditions achieved a removal efficiency of 90 %. A synthetic solution, simulating magnet dissolution, demonstrated removal rates above 70 % and desorption tests confirmed the complete recovery of neodymium from the nanoparticles.

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Development of an extraction method for the multiresidue analysis of 40+ pharmaceuticals in biota (mussels and red mullets) using QuECHeRS – LC-MS/MS

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Pharmaceutical compounds have been reported to have effects on mussels and fish [1,2], but the confirmation of their presence in environmental samples remains unclear due to the limited number of methods available for determining various therapeutic classes in biota. The methods are mainly focused on food regulation, which includes only few compounds from specific families. Many pharmaceutical belonging to different therapeutic classes have been found in the environment; thus, the aim of this work is to develop a multiresidue method for the determination of seven therapeutic classes of pharmaceuticals in mussels and red mullets.

The method studied is based on QuECHeRS (Quick, Easy, Cheap, Effective, Rugged & Safe) extraction. In order to improve the extraction, several approaches were tested: Matrix solid phase dispersion (MSPD) previous to the QuECHeRS extraction or use sonication instead of vortex agitation to perform the extraction. Moreover, different mixtures of solvents were studied. Lastly, for the clean-up step QuECHeRS and solid phase extraction were assayed. The proposed method involves QuECHeRS extraction assisted by sonication with HLB SPE column clean-up, and determination of the compounds by LC-MS/MS (QqQ).

This method allows the simultaneous analysis of pharmaceutical compounds in mussels and red mullets, including antibiotics, NSAIDs, cardiovascular drugs and psychiatric drugs among others therapeutic classes. It achieved good accuracy (70-125%) and precision (<20%) with method quantification limits (MQL) <0.1 ng/g for most of the analytes.

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Polystyrene recycling with green solvents using a dissolution-precipitation method

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Plastics have been a revolutionary material since the 19th century and remain highly relevant in several sectors, such as medical advancements, food preservation and packaging. They are an industrial alternative due to their cost-effectiveness, versatility, and wide range of properties [1].

With annual growth exceeding 400 million tons, of which 5.2% corresponds to polystyrene (PS), plastic recycling, which currently represents less than 10% of total production, emerges as the primary solution to mitigate environmental impacts. To achieve this, recycling processes must become increasingly optimized, sustainable, and accessible, ensuring the quality of recovered polymers. One promising alternative is dissolution-precipitation recycling, which traditionally employs organic solvents but has been seeking eco-friendly alternatives, such as green solvents [2].

In this context, terpenes and their eutectic mixtures have gained importance as promising options for the dissolution method. Terpenes are natural compounds found in essential oils, while eutectic solvents are mixtures of two or more compounds with a melting point lower than that of each pure component. In the plastic dissolution field, pure terpenes and terpene-based eutectic solvents have recently gained significant attention due to their dissolution potential. Among them, limonene has been reported as an attractive alternative for polystyrene solubilization. Also, turpentine, a mixture of monoterpenes derived from the pine industry, has been used as a solvent for polyethylene and polypropylene [3].

This study aims to develop a sustainable alternative for plastic dissolution using environmentally friendly terpene-based bio solvents (and their mixtures). To make the process more efficient, a pre-screening based on the Conductor-like Screening Model for Realistic Solvents (COSMO-RS) and the Hansen solubility parameters is used to identify the best solvents from the vast amount available. Based on these results, experimental dissolution-precipitation studies are carried out, and the quality of the recovered polymer (Fig. 1) is investigated through DSC, TGA and FTIR analysis.

The obtained results are of the utmost importance for plastic recycling and good contributions to future studies.

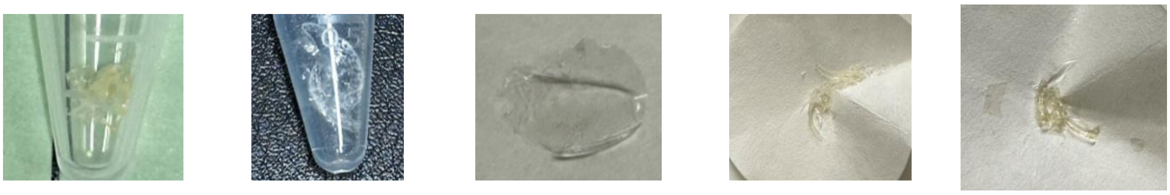

Fig.1. PS obtained after dissolution-precipitation with terpenes and their mixtures.

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Affectation of Galician beaches by microplastic pellets after the spillage from the Toconao ship

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On the 8th of December of 2023 the Toconao vessel lost part of its cargo during a storm in front of the Northern Portuguese coastline. Six containers fell overboard carrying, among other products, over 1000 sacks with polyethylene (PE), each with ca. 25 kg of preproduction pellets (also known as "nurdles", ~4mm white translucent beads). PE was additivated with ca. 10 % of Tinuvin 622, a UV-protector. The adverse weather caused many bags to open in the water. The buoyancy of the pellets allows their transport arriving in Galician beaches and affecting the entire coastline. The spill even reached neighbouring Asturias and, as the currents dispersed the spill, they arrived as far as Cantabria and the Basque country.

Even though this accident released a large quantity of pellets in a small timeframe pollution by plastic pellets has been prevalent for decades, not only in Galician beaches but worldwide. After the spillage, a state-owned company (grupo Tragsa) was tasked with cleaning the affected Galician beaches and collecting samples, some of which were sent to the Group of Applied Analytical Chemistry (Universidade da Coruña). There it was objectively assessed whether the pellets at a given beach were specific to the Toconao ship. Visual appearance was deemed inaccurate due to pre-existing pellets in the beaches that looked very similar to those of the Toconao, thus causing widespread confusion.

An infrared spectrometer (Spectrum 400 FTIR, Perkin-Elmer) with a horizontal, one-bounce diamond ATR accessory (Specac´s Golden Gate) was used to investigate the chemical composition of a high number of pellets that looked very similar to those of the Toconao. Of most relevance was the presence of the Tinuvin 622 additive in the polymeric mixture, which allowed for a fast differentiation of the Toconao´s pellets from other PE nurdles present in the samples, likely from other pollution episodes. Other polymers were also found, like polypropylene and polystyrene nurdles. **Figure 1** shows the beaches with confirmed arrivals. A total of 42 beaches were surveyed, finding Toconao´s nurdles in 26 (62%) of them.

Also, pristine pellets were weathered for 4 months under simulated sunlight conditions, either under dry and seawater conditions in order to ascertain the environmental transformations they might suffer. The pellets weathered in dry conditions showed no relevant results. However, in seawater conditions the pellets shed small, powder-like secondary microplastics and, after roughly 3 months, their spectral profile changed, with the appearance of new peaks, associated with various oxygen functional groups.

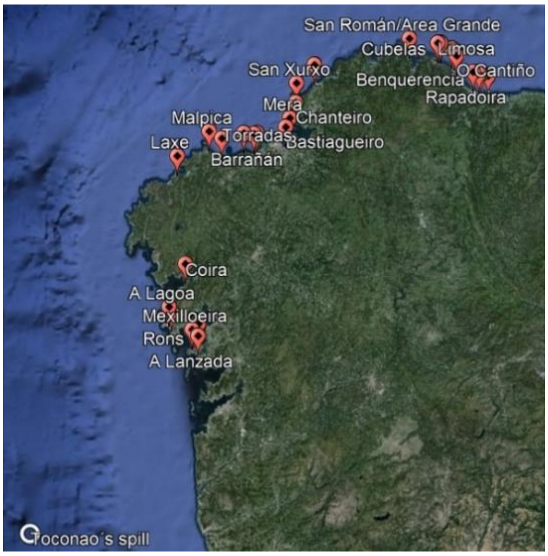

Fig.1. Sampled beaches with positive identifications of Toconao pellets .

Acknowledgements
The Galician Government (Xunta de Galicia, Programa de Consolidación y Estructuración de Unidades de Investigación Competitiva) is acknowledged for a Grant supporting partially this work (Grant ED431C 2021/56) partially financed by FEDER/ERDF funds.

RECOVERY OF ALL THE RAW MATERIALS FROM THE WASTE LIGHT-EMITTING DIODES

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This work presents a novel and efficient methodology for the complete recovery of the major raw materials: copper (Cu), aluminium (Al), and fibreglass from discarded light emitting diodes (LEDs). Unlike existing methods, which often result in significant tertiary wastes and inefficiencies (not all the raw materials are recovered), this process emphasizes both environmental and economic viability by recovering the major raw materials that constitute the LEDs. Our approach optimizes the total delamination of LED frames, utilizing Hansen solubility parameters to select the most effective solvents. Five solvents were tested [dimethyl acetamide (DMAc), dimethyl formamide (DMF), methyl ethyl ketone (MEK), dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP)] under heating conditions. Results have proven that NMP was the most efficient solvent, originating full delamination of the LED frame. The total delamination of the LED frame represents a noteworthy achievement since it allows the separation of all the raw materials and their further recovery. Subsequently, we implemented a cost-effective two-stage air-flow separation process, which selectively recovered 100% of Al, 80.9% of Cu, and 88.4% of fibreglass, surpassing recovery rates obtained in traditional methods [1]. The quality of the final products recovered (**Figure 1**) showed good thermal and chemical properties, demonstrating that the delamination process does not alter the properties of the secondary raw materials achieved and can be reused for other applications. Moreover, this innovation not only maximizes material recovery but also minimizes environmental impacts, such as dust and wastewater generation.

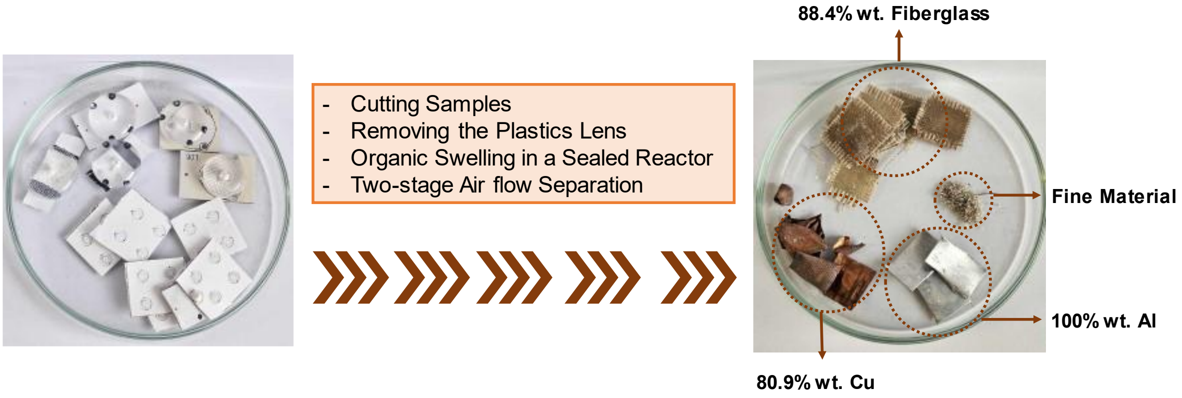

Figure 1. Original LEDs frames treated and the outputs products and their recovery rate after applying the proposed methodology.

The proposed method offers a faster, simpler and more sustainable alternative recycling strategy to LED waste, highlighting its potential for large-scale industrial practises due to its simplicity and scalability. By focusing on the recovery of high-value materials, this work contributes to the circular economy and supports sustainable practices in electronic waste management.

Acknowledgments
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Extração Eficiente de Compostos Fenólicos: Aplicação de Métodos Assistidos por Calor e Ultrassons em Partes Aéreas de *Crithmum maritimum* L. e *Scolymus hispanicus* L.

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As Plantas Silvestres Comestíveis (PSCs) crescem sem intervenção humana, utilizando exclusivamente os recursos naturais disponíveis no ecossistema em que se encontram. O *Crithmum maritimum* L. (funcho marinho) e o *Scolymus hispanicus* L. (cardo dourado) são exemplos de PSCs amplamente consumidos na zona do Mediterrâneo sobretudo em saladas e sopas [1-2]. Recentemente, a comunidade científica tem-se concentrado nos estudos destas PSCs, nomeadamente em trabalhos que avaliam as suas propriedades terapêuticas e nutricionais. O consumo destas plantas tem aumentado gradualmente à medida que os consumidores procuram por fontes de alimentos saudáveis e funcionais [3]. Uma das estratégias de valorização destas espécies é a otimização da extração de compostos fenólicos, frequentemente associados às suas propriedades bioativas, utilizando para isso métodos sustentáveis.

O objetivo deste estudo foi otimizar as variáveis independentes de tempo, temperatura/potência ultrassónica e percentagem de etanol para a extração assistida por calor (EAC) e assistida por ultrassons (EAU). Foram realizados 20 ensaios randomizados, com 30 g/L como proporção sólido/líquido, com três variáveis de resposta: rendimento de extração, compostos fenólicos totais (TPC) e flavonoides totais (TFC). As condições de extração foram para a EAC foram de 0 – 100% de etanol, de 20 – 90 °C durante 2 – 90 min; e para a EAU foram de 0 – 100% de etanol, de 5 – 500 W durante 2 – 45 min [4].

Para ambas as plantas, funcho marinho e cardo dourado, a EAC proporcionou rendimentos de extração mais elevados, demonstrando também maior eficácia na extração de TPC (6,88 e 5,60 mg GAE/g de extrato, respetivamente) em comparação com o EAU (5,61 e 4,02 mg GAE/g de extrato, respetivamente). Para a recuperação de TPC, a percentagem de solvente apresentou a variação mais significativa para o método de EAC, sendo necessário 16,2% e 49,4% de etanol para o funcho e cardo, respetivamente. No método EAU, obtiveram-se maiores teores de TPC com percentagem intermediária de etanol 38,4% e mesmo de 0% (ou seja, 100% de água), em ambas as amostras. Relativamente aos TFC, os processos de extração exigiram temperaturas ou potências ultrassónicas mais baixas, enquanto uma maior percentagem de etanol foi considerada necessária para a EAC.

O modelo matemático revelou-se eficaz para a otimização do rendimento de extração e do conteúdo total de fenóis totais no cardo dourado utilizando a EAC. No entanto, as condições específicas do funcho marinho influenciam os valores previstos pelo modelo para esta metodologia de extração, requerendo assim ajustes nas condições do modelo para obter previsões mais precisas.

Agradecimentos

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Optimized Ultrasound-Assisted Extraction of Bioactive Compounds from Raspberry and Blueberry Pruning Residues for Sustainable Cosmetic Applications

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Increased berry production has led to bioresidue buildup [1]. In this context, berry plant leaf extracts and other aerial components can be used to prepare cosmetics ingredients due to their unique chemical composition and functional properties [2][3][4].
This study aimed to optimize ultrasound-assisted extractions from raspberry (RB) and blueberry (BB) pruning residues using Response Surface Methodology (RSM). The analysis involved three factors: solvent concentration (0% to 100% ethanol/water), extraction time (5 to 30 min), and ultrasound probe power (20% to 100%, max 500 W). The experiment used a Box-Behnken design with 17 randomized runs.

The optimization maximized the extract yield (dry form). For RB, the optimal conditions were 32.9% ethanol:water, 15.2 minutes, and 95.7% power. For BB, the optimal conditions were 63.6% ethanol:water, 29.5 minutes, and 72.2% power. RB contained hydrolyzable tannins, while blueberry extract presented more flavonoids. Both extracts showed strong antioxidant, antibacterial, and anti-inflammatory activities and low cytotoxicity on non-tumor cell lines. Raspberry revealed a higher antioxidant activity (IC_{50} = 6.70 μg/mL) than trolox (IC_{50} = 21.50 μg/mL) through the OxHLIA assay, making it ideal for an interesting potential cosmetic.
The results obtained showed that the pruning residue extracts could have commercial interest for their potential application in the cosmetic industry.

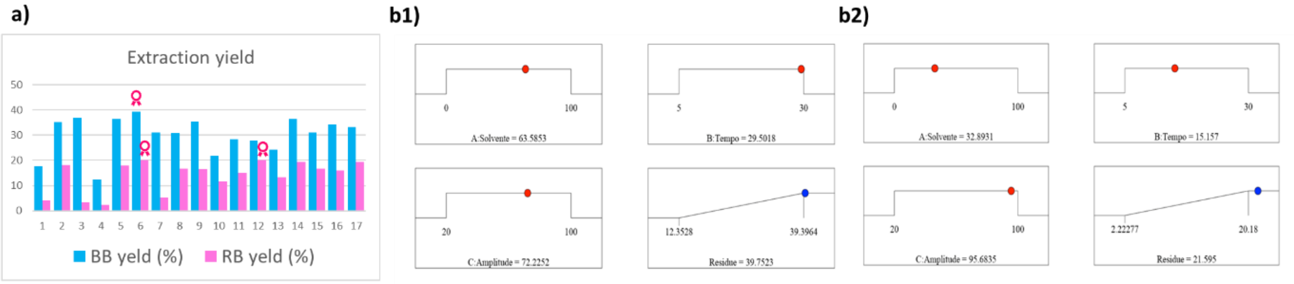

Fig.1. a) mass yield results (%), b) 1 and 2, optimum extract conditions for BB and RB, respectively.

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This work was supported by national funds through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); and SusTEC, LA/P/0007/2020 (DOI:10.54499/LA/P/0007/2020). M. Carocho thanks FCT for his individual employment program–contract (CEEC-IND/00831/2018). The contract of T.C.S.P. Pires (VIIAFOOD project nr. C644929456-00000040).

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Integrated Circuits: proposal of a closed recycling method for the recovery of gold

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Technological progress has been remarkable in the recent decades; however, this progress has significantly impacted the Earth's finite mineral resources. Since it is not possible to stop the advance of the technological progress, one alternative is to recover crucial metals from the products already discarded.

Integrated circuits (ICs) correspond to one of these vast streams of electronic waste generated every year containing significant amount of gold (Au). ICs are composed mainly by silica (SiO_2, 62% wt.) reinforced with brominated epoxy resin (14% wt.), alongside with various metals, including copper (Cu, 22% by wt.), iron (Fe, 1% wt.), and precious metals like gold (Au, 0.3% wt.) and silver (Ag, 0.7% wt.) [1-2]. Given its high content of Au, recycling ICs presents both an economic opportunity and an environmental necessity. In this study, we propose a hybrid method (combining mechanical, physical, and chemical processes) to efficiently recover Au from ICs.

The physical pre-treatment proposed consists in a three-step process—fragmentation of the ICs using a hydraulic press, homogenization of the fragmented material, and magnetic separation—to enhance the exposure of Au by removing its encapsulating silica shell. This process resulted in an Au-enriched fraction with 80% wt. of the total Au content, while other metals, such as, Fe and nickel (Ni) were concentrated in the magnetic fraction.

The Au-enriched fraction undergoes to a hydrometallurgical step using 2.5 M HCl and 0.34 M NaClO at 40°C for 3 hours, which resulted in an Au extraction rate of 88.6%. The resulting multi-metal leachate solution contained Ag, Al, chromium (Cr), Cu, Fe, Ni, lead (Pb), tin (Sn), and zinc (Zn) alongside with Au. To purify Au from this mixture, continuous-mode adsorption-elution assays using an ion-exchange resin (Purogold™ A194) were optimized. After a 26-hour adsorption process at a flow rate of 0.225 mL/min, the resin demonstrated high selectivity for Au over the other impurities ($Au >> Zn > Sn > Pb > Cr >> Fe > Cu \approx Ni \approx Al$), with 91% of the Au being successfully eluted from the resin during the elution phase, achieving a purity grade of 85% (20 carats). The primary contaminants in the final product were Sn (7.5% by weight) and Pb (4.3% by weight).

A preliminary economic analysis indicated that the method developed is economically feasible, highlighting its potential for industrial-scale application due to its simplicity and the high revenue of recovering Au from electronic residues in accordance with the circular economy concept. Moreover, this study demonstrates a sustainable and economically viable approach for recycling gold from ICs, contributing to the resource conservation and environmental protection.

Agradecimientos
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Optical Setups for Monitoring Nitrates, Carbon Dioxide and Turbidity in Macroalgae Production Tanks

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In the scope of the European project, INNOAQUA, two optical sensors are being developed to monitor the concentration of dissolved CO_2, nitrate and turbidity in macroalgae production tanks since these compounds are essential for algae growth.

The exploration of the optical absorption by dissolved nitrogen allowed to create an affordable, low-maintenance setup capable of performing automated and periodic measurements over extended periods. The absorption spectrum of nitrates and nitrites in the UV range was analyzed to decide which LEDs and photodetectors would be adequate for the sensing function. Several tests were done to optimize different sensor parameters, including the optimal optical path, which allowed the detection of nitrogen concentration with higher resolution. After testing the system in a controlled environment, within a nitrogen range of 5 to 30 ppm, a resolution of 0.01 ppm was achieved. The sensor was validated in an approximate real usage scenario by performing experiments in an aquarium with Ulva-algae.

The detection of CO_2 was achieved through the development of a prototype colorimetric sensor, whose working principle is based on the measurement of the absorbance of a colorimetric membrane through optical methods. This membrane suffers pH variations caused by CO_2, which induce its color change and, as a result, its light absorbance decreases/increases. This property was achieved through specific chemical modifications of the membrane matrix. The sensor presented high accuracy and short response times – 6 minutes in stagnant water and only seconds in flowing water – attaining a detection limit of 1.7mg/L in a concentration interval ranging from 1 to 100mg/L. Both the sensor presented, and the commercial sensor were placed in natural marine water and the comparison of the concentration values obtained allowed to conclude that the developed prototype is suitable for the aquaculture environment [1].

Turbidity is evaluated taking advantage of the scattering phenomenon. However, the considered approach is distinct from others because, additionally, it allows to obtain the absorbed light spectrum of the sample. Making use of a spectrometer, a photodetector and two LEDs, the sensor is able to measure forward-scattered light and 45º, 90º and 135º degree scattering. After testing the sensor in solutions of several turbidity levels, the results suggested that absorption, forward scattering and nephelometric measurements are suitable for lower turbidity measurements, at least up to 300 NTU. On the other hand, backscattering measurements are only effective for higher turbidities, above 150 NTU.

Aknowledgements

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Breakthrough Curves for the Continuous Adsorption of Micropollutants on Activated Carbon/Geopolymer Mixtures

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Breakthrough curves are key for designing continuous flow adsorption systems, typically obtained experimentally or through modeling [1]. In this study, a mixture of activated carbon (AC) and geopolymers (GP) was tested in a continuous treatment system for the removal of model contaminants from waters in a single-component system composed of sulfamethoxazole (SMX), acetaminophen (ACT), or gallic acid (GA). In addition, the adsorbent materials were also tested in a multi-component water matrix to evaluate the interactions between adsorbates and adsorbents. Adsorption tests were conducted using 1g of GP and 0.5g of AC, filled with glass beads. The experiments were carried out at room temperature, considering 100 mg/L for all contaminants and natural pH of the solutions. The flow was set to 1 mL/min and controlled by a peristaltic pump. The breakthrough curves are shown in Figure 1. Based on the experimental data, the useful operating times were calculated, assuming that the effluent concentration should not exceed 5% of the initial concentration [2], yielding 228 minutes for ACT, 46 minutes for SMX, and 53 minutes for GA in the multi-component system. A reduction in time was observed when compared to the single-component system due to faster saturation caused by competition for active sites. The useful adsorption capacities were also calculated, with values of 45.7 mg/g for ACT, 9.2 mg/g for SMX, and 10.7 mg/g for GA in the multicomponent system. The overall results indicated that the column was efficient, as the contaminating compounds were removed up to the system breakthrough. In conclusion, this preliminary study suggests that these materials can be effectively combined and applied in tertiary wastewater treatments, as permeable reactive barriers.

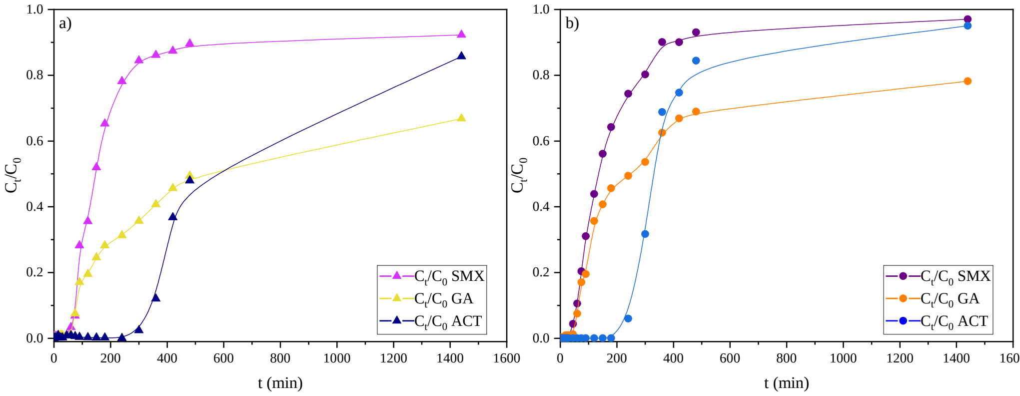

Figure 1. Breakthrough curve for a) single-component system and b) multi-component system

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AMB32

Synthesis and Characterization of Activated Carbons, Geopolymers, and Carbon Nanotubes from Waste-Derived Sources

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Circular Economy implies strategies for waste valorization and reuse to produce higher-value products [1]. In this context, exhausted olive pomace, a waste biomass derived from olive industry was used to synthesize activated carbon (AC) through slow pyrolysis, followed by activation with CO_2 to optimize the adsorbent's porosity. The pyrolysis furnace was initially maintained under an inert atmosphere with a nitrogen flow rate of 100 NmL/min, considering three different temperature stages reached through the application of a heating ramp of 5ºC/min up to 400°C and 600°C (maintained 1 hour each) and up to 800°C. Activation with CO_2 occurs in the first hour at this temperature, followed by 3 hours in a nitrogen atmosphere, completing the process in 9 hours. The geopolymer (GP) was synthesized using 10 g of fly ash, a byproduct of the combustion of municipal solid waste, mixed with an alkaline solution, a mixture of 5,67g of sodium silicate and 2,27g of sodium hydroxide (10M), to initiate the geopolymerization reaction. The synthesis of carbon nanotubes (CNTs) was based on the methodology of Díaz de Tuesta *et al.* [2], by chemical vapor deposition with plastic waste as the precursor. The results obtained for textural characterization are presented in Table 1. AC showed the highest surface area (527 m^2/g) and a pore volume of 0.318 cm^3/g, can be advantageous for adsorption, while CNT functions effectively as a catalyst despite its lower surface area. Acid-base characterization showed that AC possesses high basicity (1250 µmol/g), enhancing its ability to adsorb acidic contaminants, while CNT and GP demonstrated balanced acid and basic properties, with point of zero charge (pHpzc) values of 9.86 for AC, 6.9 for CNT, and 7.6 for GP. Elemental analysis (CHNS) revealed that AC contained 63.0% C, 0.8% H, 18.0% O, and 16.4% ash. CNT, in contrast, had a higher carbon content of 92.5% and 6.0% ash.

Table 1. Textural properties analysis for the materials

Sample	S_{BET} ($m^2 g^{-1}$)	$S_{Langmuir}$ ($m^2 g^{-1}$)	S_{ext} ($m^2 g^{-1}$)	S_{mic} ($m^2 g^{-1}$)	V_{mic} ($mm^3 g^{-1}$)	W_{mic} (nm)	V_{total} ($cm^3 g^{-1}$)
AC	527	782	33	749	269	1.43	0.318
GP	30	232	6.7	23	0	0	0.068
CNT	66	596	17.3	48.7	0	0	0.172

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Microplásticos en Sistemas Estuarinos: Interacciones con Mejillones e Implicaciones Ambientales

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En las próximas décadas, se espera un aumento en los residuos plásticos anuales que ingresan a los ecosistemas acuáticos [1], junto con un incremento en la transferencia de microplásticos (MP) a la biota [2]. Los MP se han vuelto omnipresentes en los océanos, infiltrándose en la cadena alimentaria de especies marinas y potencialmente llegando a los seres humanos [3]. En los entornos estuarinos, donde las actividades urbanas e industriales interfieren con la acuicultura de mejillones, estos podrían estar sometidos a presiones antropogénicas significativas y afluencias de agua dulce [4]. Las dinámicas de los MP en estas áreas están influenciadas por los flujos de mareas, los patrones de viento oceánico y el escurrimiento de áreas urbanas, que son las principales vías de entrada de residuos plásticos en los estuarios [5]. Debido a su naturaleza transicional, los estuarios juegan un papel importante en la concentración y transporte de MP, de manera distinta a otros cuerpos de agua. Además, el conocimiento del comportamiento estuarino es necesario para comprender y cuantificar el transporte de MP desde la tierra hacia el océano [6].

El objetivo de este trabajo es analizar el comportamiento de los MP en ambientes estuarinos y comprender sus interacciones con los mejillones. El caso de estudio se basa en una revisión exhaustiva de la literatura y en un análisis del sistema real para identificar los orígenes, fuentes y sumideros de MP en los estuarios, proporcionando ideas clave sobre su dinámica.

Los resultados destacan cómo los mejillones en los estuarios contribuyen a la movilización de MP, arrojando luz sobre cómo estos entornos influyen en el transporte y la distribución de los MP. Esta investigación amplía el conocimiento actual sobre los MP y proporciona nuevas perspectivas al identificar áreas propensas a la acumulación de MP, lo que puede orientar futuras estrategias de intervención en las regiones estuarinas. Sin embargo, abordar la contaminación por microplásticos sigue siendo un desafío, en gran parte debido a la limitada disponibilidad de datos cuantitativos, lo que dificulta las comparaciones regionales significativas. La estandarización de las definiciones y métodos de evaluación de microplásticos es esencial para mitigar eficazmente los impactos antropogénicos de esta contaminación.

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AMB34

Exploring Lignin Valorization as a Sustainable Modulating Agent: Impact on the Physicochemical Properties of Port Wine

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Wine is a complex matrix that undergoes multiple processes from grapes to the bottle, where physicochemical instabilities and sensory defects may arise [1]. The wine industry looks to develop safe and sustainable technologies to address these issues while preserving their organoleptic properties [2]. Lignin has physicochemical features that are useful for removing colloids, contaminants, and other unwanted particles from aqueous systems, including higher molecular weight, the presence of diverse functional groups, and a structure with high porosity. This study explores the potential of lignin as a novel clarifying agent for Port wine. Three types of lignin - lignosulfonates (LS), kraft lignin (KL), and organosolv lignin (OL) - were tested at concentrations of 25 and 100 g/hL over 7 and 30 days. The results reveal that the type of lignin and the time of treatment significantly affect wine composition. KL showed the highest potential for protein removal, decreasing protein content by 13 % at 25 g/hL and 37 % at 100 g/hL. LS and OL at 100 g/hL also significantly reduced to 90 % and 50 %, respectively, the protein content from day 7 to day 30. LS reduced tannin content (maximum 13 %) and the interaction of salivary acidic proline-rich proteins with wine phenolic compounds, related to the astringency perception. Interestingly, both LS and KL slightly increased anthocyanin levels. Related to the colorimetric properties, none of the types of lignin promoted significant color changes ($\Delta E < 2$), though KL and OL at 100 g/hL slightly increased the b* color coordinate, contributing to a more yellowish hue. In terms of aroma, LS had the most positive impact, reducing undesirable volatiles such as isoamyl alcohol (cheesy and fusel notes) and 1-hexanol (resinous) by approximately 30%. Simultaneously, LS increased fruity and brandy-like compounds like ethyl octanoate and decanoate by up to 60%. This study proposes a sustainable approach by repurposing a by-product, offering the wine industry a new, environmentally friendly alternative for clarification.

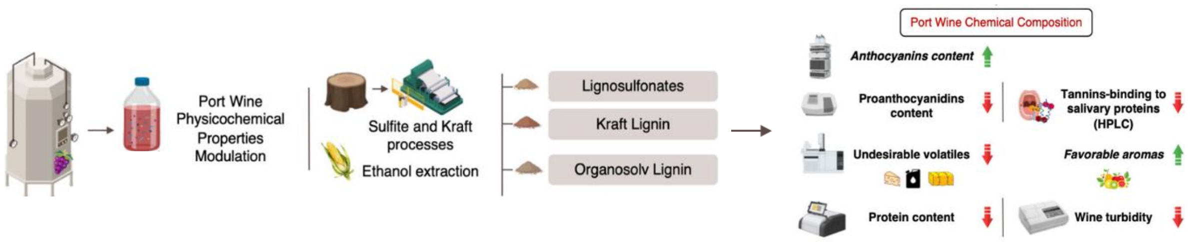

Fig.1. Application of lignin in wine samples with determination of chemical composition effects.

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Production and characterization of different green adsorbents for the removal of free glycerine in the biodiesel purification process

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There is environmental concern due to the high use of oil as a primary fuel, which results in a significant emission of polluting gases, and one of the most promising solutions involves replacing it with biodiesel. Biodiesel is a fuel that can be produced using waste cooking oil (WCO) and has become an excellent alternative to ordinary diesel. A crucial stage in the production of biodiesel is the purification process. Among the various methods used, there are two main ones: the wet purification method, which uses water, and the dry purification method, which uses ion exchange resins or adsorbents. Dry purification using adsorbents removes contaminants such as water, soap, and traces of glycerine based on their chemical polarities and acidic and basic properties. Also, it avoids the generation of high volumes of effluents, and the adsorbents can be reused [1][2].

The use of green adsorbents is a viable alternative for purification through adsorption processes, as they are biodegradable and are generally derived from agro-industrial waste, proving to be a more sustainable alternative since it allows cost reduction and environmental impacts. One way of using natural adsorbents is through the production of activated carbon. Even though it does not have a specific morphology, these adsorbents present a high surface area and porosity [3].

This work aims to produce, characterize, and study the potential use of four different activated carbons produced from almond shells (CA), rice husks (CR), olive stones (CO), and walnut shells (CW), for the adsorption purification process of removing free glycerol from crude biodiesel produced from WCO. The adsorbents were produced through physical activation at 800 °C, and characterization includes determining the point of zero-charge, texture properties, elemental composition, and thermogravimetric analysis. Afterwards, adsorption studies were carried out to identify the adsorbent with the best purification performance. Selected results for the materials characterization are shown in Table 1. The removal of free glycerol from biodiesel was studied at the temperatures of 25, 35, and 45 °C. The mass removal percentages were 25.10%, 18.79%, and 15.85% (for CA); 23.99%, 11.79%, and 16.59% (for CR); 37.26%, 33.12%, and 33.47% (for CO); and 17.69%, 21.17%,14,81% (for CW), respectively.

Table 1 – Selected results for the characterization of prepared adsorbents.

Adsorbent	pH_{PZC}	Texture properties			
		Surface area (m^2/g)	Micropore area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
CA	7.78 ±0.21	418.38	373.57	0.24	1.73
CR	9.02 ±0.12	277.53	240.66	0.17	1.81
CO	7.24 ±0.34	379.26	354.17	0.21	0.88
CW	8.25 ±0.18	301.33	301.33	0.22	0.88

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Development of a multi-phosphor system from *Chlorella pyrenoidosa* for luminescent solar concentrators

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Luminescent solar concentrators (LSCs) provide a simple and cost-effective approach to harvesting sunlight. By effectively reducing the number of photovoltaic modules required to be installed in urban landscapes, these devices are pivotal in today's much needed energy regulation context and the transition to future energy-efficient buildings and smart cities. [1] Among the most promising luminophores for LSCs are carbon dots (CDs) and organic colorants. The first are known for their excellent photoluminescence features, photostability, high aqueous dispersibility, good thermal stability, chemical inertness, and environment friendliness; the latter, for their large absorption coefficient, a broad emission band, and high quantum yields. [2]

In our recent work, we used biomass from the microalga *Chorella pyrenoidosa* to develop an unprecedented system that combines both CDs and chlorophyll pigments. The resulting CDs present excitation and emission maxima at 472 and 526 nm, respectively, while the chlorophyll centers provide a secondary photoluminescence process, thus ensuring that the as-prepared system can also interact with the farther red region of the visible spectrum. Details on the preparation of this system as well as its optical properties will be discussed, as well as preliminary tests regarding its application in LSCs.

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Valorización de *Salmo trutta*: Caracterización nutricional, fitoquímica y antioxidante para el desarrollo de productos sostenibles

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El pescado, fuente de proteínas y ácidos grasos, representa actualmente el 17% de la ingesta mundial de proteínas animales, y su consumo se compone de pescado fresco o procesado/en conserva. Las especies de pescado más consumidas en Portugal son la caballa, la sardina, el jurel, el pulpo, el bacalao, el atún y el sable negro, lo que pone de manifiesto un importante vacío de mercado para los productos a base de trucha. La producción de trucha en viveros se realiza principalmente para proteger la especie y repoblar los ríos. Este estudio se centra en la promoción, valorización y reutilización de la trucha marrón de la Estación de Acuicultura de Boticas Parque Naturaleza y Biodiversidad (BPNB), con el objetivo de gestionar de forma sostenible y añadir valor a un recurso endógeno de gran riqueza cultural y patrimonial.

Muestras de *Salmo trutta* (trucha marrón) fueran recogidas en BPNB y disecados en sus partes constituyentes, lomos, cabezas, piel, vísceras y espinas. Para evaluar el perfil nutricional de las muestras de trucha, incluyendo la composición en macronutrientes (proteínas, grasa total, cenizas y carbohidratos), humedad y valor energético, se utilizaron los métodos de análisis oficiales descritos por la AOAC. También se llevó a cabo una caracterización fitoquímica, centrada en el contenido en compuestos lipofílicos (ácidos grasos y tocoferoles), el contenido en sales (NaCl) y la actividad antioxidante mediante el método DPPH.

La proteína es el macronutriente más abundante en este pescado, seguido de la grasa. Entre los compuestos individuales, se detectó un predominio del α-tocoferol y de los ácidos oxálico y cítrico en todas las muestras. La fracción lipídica, bastante abundante, estaba constituida principalmente por ácidos grasos poliinsaturados. El filete de pescado presentaba el mayor contenido de NaCl y las cinco partes del pescado demostraron actividad antioxidante en el ensayo DPPH.

Este trabajo facilitará la aportación de valor añadido a este recurso endógeno mediante actividades de I+D dirigidas al desarrollo de nuevos productos alimentarios basados en la trucha, así como a la reutilización de los subproductos resultantes de su procesado. La caracterización detallada de cada parte del pescado permitirá la creación de otros productos de valor añadido para nuevas aplicaciones en nutrición, salud y otras áreas, con un impacto regional demostrable.

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Materiales carbonosos a partir de materiales lignocelulósicos para baterías ion litio

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Materiales como el grafito, los nanotubos de carbono (CNT) o el grafeno, son materiales carbonosos de uso habitual en baterías ion litio e ion sodio. Aunque presentan una buena reversibilidad electroquímica, se enfrentan a retos críticos asociados a sus métodos de síntesis y a los elevados costes de producción, lo que dificulta su producción a gran escala [1]. En consecuencia, los estudios entorno a la obtención de materiales carbonosos basados en recursos sostenibles ha ido en aumento. Entre los precursores estudiados, se encuentran aquellos derivados de la biomasa, debido a su abundancia, reducida toxicidad y facilidad de modificación, lo que permite adaptar sus propiedades a las requeridas por su aplicación, como es el caso del almacenamiento energético en baterías, como porosidad, grupos funcionales en su superficie o conductividad, entre otros.

Uno de los objetivos de las líneas de investigación impulsadas desde CETIM es la obtención de materiales carbonosos de alto valor añadido a partir de subproductos o residuos de biomasa. Para ello, se focaliza en identificar fuentes de materiales generados por sectores tractores a nivel local. Sectores como el agrícola, forestal, maderero, papelero o alimentario, tienen una gran importancia no solo en Galicia, sino en España y Europa, por lo que a través de esta estrategia se potencia el tejido industrial entre regiones dentro del continente europeo.

Algunos de los materiales en estudio son materiales lignocelulósicos, serrín procedente de madera local, y algas, preferentemente invasoras, que suponen un problema para el ecosistema de la costa gallega al impedir el crecimiento de otras especies autóctonas. Para la obtención de materiales electroquímicos, en función del origen del material, se aplicaron procesos de acondicionado (tratamientos mecánicos, lavados, etc.) con el objetivo de obtener un material de inicio homogéneo y con el mínimo grado de impurezas que implicasen reacciones electroquímicas no deseadas al introducirlas en la batería. Tras ello, se llevó a cabo la aplicación de tratamientos de activación (mecánicos y/o químicos) para la formación de estructuras porosas y favorecer la transferencia del iones durante la carga y descarga de la batería. Los materiales activados y sin activar se sometieron a tratamiento térmicos, priorizando aquellos que permitiesen un equilibrio entre el consumo energético del proceso de obtención del material poroso, y las propiedades que el material obtenido puede aportar. Estos materiales se caracterizaron físico-químicamente, y electroquímicamente mediante la preparación de electrodos y montaje de celda tipo botón.

Fig.1. (a) Celulosa previa carbonización, (b) celulosa carbonizada y (c) resultados electroquímicos para semicelda ion litio, con ánodo con un 90% material carbonoso procedente de celulosa

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Synthesis of choline-amino acid ionic liquids and application to the extraction of biomolecules and pharmaceuticals

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Choline-Amino Acid Ionic Liquids (CAAILs) offer a greener alternative to traditional ionic liquids, such as those derived from the imidazolium cation, due to their easy synthesis from natural materials and high biodegradability [1]. Additionally, their limited solubility in aqueous salt solutions creates favourable conditions for extraction in Aqueous Two-Phase Systems (ATPS), enabling the efficient recovery of valuable biomolecules such as antioxidants and vitamins [2] and dangerous contaminants such as Active Pharmaceutical Ingredients (APIs) [3].

This study focuses on synthesizing novel, environmentally friendly ionic liquids based on choline, characterising their thermophysical properties in pure state and in aqueous solution (including liquid density, dynamic viscosity, electrical conductivity, pH, ionicity and refractive index), and conducting ternary liquid-liquid equilibria assessments alongside partition studies for pharmaceutical contaminants (amoxicillin and acetaminophen) and valuable biomolecules (antioxidants and vitamins), at 298.15 K and 0.1 MPa. Specifically, CAAILs derived from L-alanine, glycine, leucine, and L-serinate were synthesized and their chemical structures were validated through Fourier-Transform Infrared Spectroscopy (FTIR) and computational predictions from Density Functional Theory.

Acknowledgments
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BIOQUÍMICA Y BIOTECNOLOGÍA

Biosensing platforms for exosome detection in liquid biopsies. Applications in cancer diagnostics

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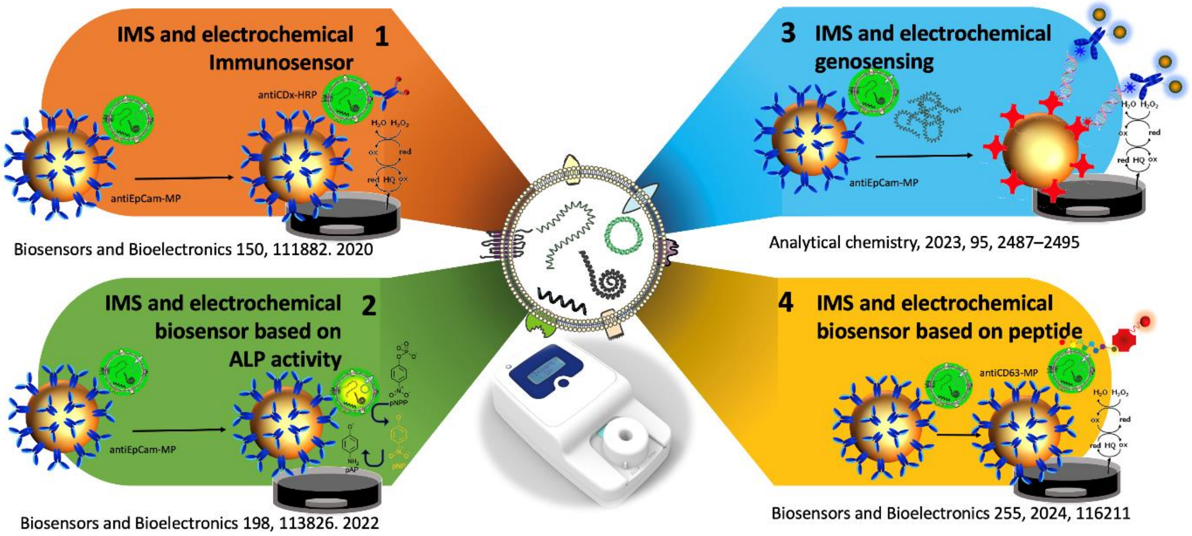
Exosomes, nanometric vesicles secreted by various cell types, are present in all biological fluids and reflect the state of their originating cells, making them valuable tools for early, non-invasive diagnosis through liquid biopsies. However, their small size and low concentration in complex biological samples pose challenges for detection, requiring advanced technological solutions. This study presents different approaches of biosensing devices for the detection and quantification of exosomes, focusing on their application as biomarkers for non-communicable diseases such as cancer.

Four different electrochemical biosensing platforms are detailed in this work (as illustrated in Figure 1), each combining immunomagnetic separation (IMS) with electrochemical detection in a portable biosensing device. In the first approach, IMS is used in an electrochemical immunosensor, where exosomes are captured and quantified using cancer-specific receptors and tetraspanins, achieving high sensitivity for exosome detection. The second approach employs an IMS-based biosensor taking advantage of the intrinsic alkaline phosphatase (ALP) activity of exosomes for their detection without secondary antibodies. In the third case, IMS is integrated with electrochemical genosensing to amplify exosome transcripts, such as GAPDH, enabling the sensitive detection of exosomes derived from cancer cells. Finally, the fourth platform uses IMS combined with a peptide-based biosensor, offering enhanced sensitivity and specificity by employing a biotinylated peptide with streptavidin-polyHRP for detection. These biosensor designs demonstrate the potential of exosomes as biomarkers for liquid biopsies in cancer diagnosis and monitoring. By providing cost-effective, scalable, and sensitive solutions, these platforms offer significant advantages for point-of-care diagnostics, especially in low-resource settings. The approaches described also highlight the versatility of the IMS-electrochemical biosensing platform for future applications in other disease diagnostics.



IMS and electrochemical Immunosensor 1

Biosensors and Bioelectronics 150, 111882. 2020

IMS and electrochemical biosensor based on ALP activity 2

Biosensors and Bioelectronics 198, 113826. 2022

3 IMS and electrochemical genosensing

Analytical chemistry, 2023, 95, 2487–2495

4 IMS and electrochemical biosensor based on peptide

Biosensors and Bioelectronics 255, 2024, 116211

Fig.1. Schematic of four electrochemical biosensing platforms for exosome detection

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Características de la superficie celular asociadas a la virulencia de mutantes de *Mycobacterium tuberculosis* defectivos en los transportadores de membrana CtpF y MmpL7

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La tuberculosis (TB) es una enfermedad infecciosa causada por el bacilo ácido-alcohol resistente *Mycobacterium tuberculosis* (*Mtb*) y es la principal causa de muerte en humanos por un único patógeno bacteriano (1.3 millones de muertes en 2022) [1]. El surgimiento de cepas de *Mtb* resistentes a múltiples fármacos y extremadamente resistentes (MDR y XDR), así como la coinfección de *Mtb* con VIH, ha convertido a la TB en una preocupación significativa para la salud global. Actualmente, la única vacuna autorizada contra la TB es el Bacilo de Calmette-Guérin (BCG) cuya eficacia es muy variable contra la TB pulmonar en adolescentes y adultos (entre 0-80 % de protección) [2]. Por lo tanto, el descubrimiento de blancos para la atenuación de *Mtb* es crucial en el desarrollo de nuevas vacunas vivas atenuadas. Algunos estudios han resaltado la importancia de las proteínas y transportadores de membrana en la interacción patógeno-huésped y la fisiología micobacteriana. Específicamente, MmpL7 está involucrado en la biosíntesis del conocido lípido factor de virulencia dimicocerosato de phtiocerol (PDIM) y su translocación a la pared celular [3]. Por otra parte, CtpF es una ATPasa tipo P de membrana involucrada en la desintoxicación del calcio que se activa en respuesta al estrés oxidativo, y posiblemente en la composición de la envoltura de *Mtb* [4].

En el presente trabajo, se evaluaron algunas características asociadas a la virulencia, de mutantes de *Mtb* en los genes *ctpF* y *mmpL7* (*MtbΔctpF* y *MtbΔmmpL7*, respectivamente). Así, los mutantes *MtbΔctpF* y *MtbΔmmpL7* mostraron variación en su morfología colonial rugosa en comparación con la cepa tipo salvaje *Mtb*H37Rv, lo que sugiere un cambio en su perfil lipídico de envoltura. Además, células completas de los mutantes (*MtbΔctpF* y *MtbΔmmpL7*) presentaron menor hidrofobicidad relativa en comparación con la cepa salvaje (*Mtb*H37Rv), indicando una menor proporción de compuestos hidrofóbicos en la envoltura celular, lo que para el caso del mutante *MtbΔmmpL7* puede ser asociado a la ausencia de PDIM. El posible cambio en la composición lipídica de envoltura alteró la motilidad de las células mutantes sobre una superficie hidrofílica de agarosa, en comparación con las células de la cepa salvaje. Por otra parte, el mutante *MtbΔmmpL7* mostró un contenido de PDIM en citosol similar a la cepa salvaje, lo que indica su biosíntesis y acumulación al interior celular, a ser traslocado a la pared celular. Finalmente, la no tinción citoquímica de colonias de los mutantes (*MtbΔctpF* y *MtbΔmmpL7*) con el colorante básico rojo neutro (rojo a $pH < 9.8$) sugiere una menor acidez en la superficie de las células mutantes, asociada con un menor contenido de lípidos metil-ramificados (como PDIM) en la pared y la pérdida de su virulencia.

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ChemSensing – A biosensor to detect human sensitizers

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Conjugation of chemicals and peptides represents the well-established molecular initiating event (MIE) in skin sensitization to low molecular weight chemicals. This MIE has been successfully exploited in the development of in chemico peptide reactivity assays, with the Direct Peptide Reactivity Assay (DPRA) being validated as a screening tool for skin sensitization hazard as well as an OECD test guideline [1,2]. DPRA is based on the use of a high-performance liquid chromatography (HPLC)/ultraviolet (UV) detection method to quantify the conjugation of chemicals and peptides [3]. However, this method has some limitations including the requirement of peptides in high concentrations and some chemicals may interfere with the UV detection method, leading to false positive/negative results. Moreover, the HPLC method is labor-intensive, time-consuming, and requires equipment that is not readily available in many laboratories, always requiring expert personnel. To overcome such limitations, this work presents the development of a novel colorimetric photonic-based sensor capable of detecting skin and respiratory allergens based on a fast, simple, and cost-effective method.

The biosensor is composed of a photonic crystal (PC) and a biopolymer-based hydrogel. The PC is first developed by dip-coating deposition of colloidal silica particles, and is then embebbed in the hydrogel obtained by photopolymerization of the biopolymer-based precursors. When the sensitizers are introduced, those react with specific chemical groups present in the photonic hydrogel, leading to an observable color change from green to red, visible to the naked eye. This is due to shift in the reflectance peak of the PC structure caused by interaction of the analyte with the hydrogel. The ARE-Nrf2 luciferase method (KeratinoSens) approved by the OECD as a test guideline to detect skin sensitizers was used to validate the obtained results.

Stability tests were performed by monitoring the reflectance peak of the photonic hydrogel and the colorimetric sensor expired in 20 days.

The constructed photonic hydrogel was successfully used to detect skin and respiratory sensitizers, showing good analytical performance. This finding provides a proof-of-concept for a colorimetric sensor for visual detection of sensitizers and demonstrates the great potential of the photonic hydrogels for visual detection of this type of allergenic chemicals.

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Application of adjuvant factors in differentiated intestinal epithelial cell systems: assessment of gluten-induced perturbation in cells' homeostatic and inflammatory states

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Celiac disease (CD) is a chronic enteropathy triggered by an immune response to an external stimulus – gluten, found in wheat, rye, barley, and other cereals – causing changes in the intestinal mucosa and a perturbation of the homeostatic state of cells, in genetically predisposed individuals [1]. In most recent years, CD has begun to be seen as a relevant public health problem, independently of age, and recent studies estimates that 1.4% of world's population has CD [2]. Although multiple studies have explored the immune response associated with CD, the exact onset of the disease and the factors that trigger gluten intolerance in susceptible patients remain largely unknown.

Recent studies have shown that specific gluten peptides, which are rich in glutamine and proline residues - causing high resistance to digestion by gastric, pancreatic, and intestinal enzymes – can directly promote structural and functional changes in intestinal cells, by influencing the pro-inflammatory gene expression and oxidative stress. Many studies regarding the inflammatory and oxidative stress changes in cells associated with CD are performed using human intestinal epithelial cell lines, such as the Caco-2, showing interesting results regarding the pro-oxidative effects of gluten protein digests. Previously we evaluated the gluten-induced redox perturbations in two intestinal epithelial cell systems (Caco-2 monoculture and Caco-2/HT29-MTX co-culture) [3] and these results confirmed the necessity to increase the complexity of the cell systems used, either through the addition of pro-inflammatory cytokines or use of immune cells, with the main goal of achieving a more biologically representative model to use in CD-related studies.

Therefore, in the presented work we performed experiments in Caco-2 and Caco-2/HT29-MTX co-culture models with either an external cytokine pre-treatment (IFNγ) - representative of the adaptive immune response - or implementing innate immune-related cells into our cell model, in a non-differentiated state (THP-1 cells in suspension) and differentiated into macrophage-like cells, accessing the integrity and redox state perturbations in cells challenged with gluten protein digests. The results obtained indicate that (1) adding innate immune-related cells in epithelial cell models can be an important upgrade for in vitro CD-related studies, (2) the incubation with gliadins resulted in transient perturbations in the cell redox state and (3) the epithelial disruption caused by gliadins is a key aspect to account for, allowing immunogenic peptide to enter the lamina propria, which in turn propagates the inflammatory response in cells (through the innate and adaptive pathways).

Agradecimientos
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Severity Scale of post-COVID condition using advanced spectroscopy

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The COVID-19 pandemic has resulted in a persistent health challenge known as Post-COVID Condition (PCC) [1], characterized by symptoms lasting at least three months after the initial SARS-CoV-2 infection and potentially persisting for several years. While studies on PCC using lipidomics and proteomics have been conducted, these methods are costly and time-consuming. The comprehensive analysis of UV-VIS-NIR-MIR spectroscopy [2] is explored here as an alternative for the rapid and cheap diagnosis and quantification of the severity of PCC. Blood samples from 65 PCC patients, previously analyzed in lipidomic and proteomic studies, along with samples from 65 new patients, were examined to develop a model that quantifies the severity of PCC based solely on spectrophotometric data.

Significant spectral variability was observed in the UV-VIS region, particularly between 297-600 nm, correlating strongly with patient symptoms. Unsupervised clustering algorithms of the spectra performed on this region effectively differentiated between asymptomatic and symptomatic patients, aligning well with clinical symptom severity. Comparative analysis with proteomic and lipidomic studies indicated that UV-VIS spectroscopy captures clinically relevant biochemical information. The results of the model developed to quantify the severity of PCC demonstrated robustness with new patient data, underscoring the method's potential as a rapid, non-invasive, and cost-effective diagnostic tool. This study highlights the strengths of spectroscopic techniques, suggesting their suitability for widespread clinical application in diagnosing and monitoring PCC, and emphasizes the need for further refinement and integration of these methods into healthcare practice, particularly for their potential implementation in portable devices.

Fig.1. Schematic of the spectroscopy workflow for diagnosis and assessing PCC severity.

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Deben usarse los siguientes ejemplos para su formato: [Arial 9 pt]

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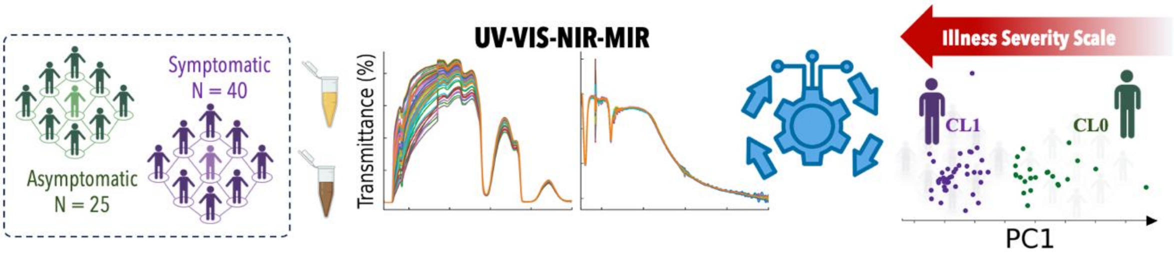

Evaluation of the Cytotoxicity Profile of Prebiotic Biosurfactants Produced by Lactic Acid Bacteria for Dermal Applications

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Many efforts have been made throughout history to maintain healthy skin, particularly in the field of cosmetics. Personal care products often include chemical surfactants, which can cause allergic reactions and skin irritations in humans [1]. This issue, combined with growing environmental awareness, has highlighted the interest in biosurfactants, natural compounds with several advantages over their synthetic counterparts, including lower toxicity, biodegradability and compatibility with human skin [2,3]. Recent studies have demonstrated the potential of prebiotic biosurfactants produced by certain lactic acid bacteria in skin care applications [4]. Therefore, the goal of this work is to study the cytotoxic effect of biosurfactants obtained from two different *Lactobacilli* strains for dermal applications. First, biosurfactants of *Lactobacillus pentosus* were produced by fermentation under two different synthetic culture media: one in MRS broth and the other in a cost-competitive culture media based on corn steep liquor (10 g/L) and yeast extract (10 g/L) supplemented with glucose (11 g/L) and xylose (18 g/L) at 31°C, pH 5.85, for 48 h. On the other side, *Lactobacillus paracasei* was fermented in a simulated MRS broth, replacing glucose with lactose (20 g/L) at 37°C, pH 7, for 72 h. After fermentation, the biomass of *Lactobacilli* strains was recovered by centrifugation, and the biosurfactant extracts were obtained following the protocol described in previous works [5]. Then, to determine the cytotoxicity profile, human dermal fibroblasts were treated with the biosurfactant extracts at different concentrations (0.01, 0.1, 0.5, 1 and 3 g/L) for 24 h, and cell viability was assessed using the MTT assay, which measures the reduction of 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide to formazan [6]. These measurements were normalized against an untreated control to assess the cytotoxicity profile of each sample. The results revealed that treatment with 1 g/L and 3 g/L of the biosurfactant extract from *L. pentosus* and *L. paracasei* growing in hexoses did not exhibit any cytotoxic effects, with cell viability greater than 90% and 80%, respectively, for each concentration. In contrast, the biosurfactant extract from *L. pentosus* grown on hexoses and pentoses showed a decrease in cell viability below 80% at a concentration of 0.1 g/L. These findings indicate a strong potential for integrating the prebiotic biosurfactants from *L. pentosus* and *L. paracasei*, produced in MRS broth media, into cosmetic products at the concentrations tested in this study.

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Engineered Defensosomes: Quantifying and improving the cytoprotective efficiency of extracellular vesicles (EVs) against Staphylococcus aureus Alpha Hemolysin (Hlα)

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Methicillin-resistant S. aureus (MRSA) infections are a major public health concern, particularly in the context of hospital-acquired infections, being associated with high rates of mortality. The production of bacterial pore forming toxins (PFT) such as alpha hemolysin (Hlα) plays an important role in MRSA pathogenicity. Notably, a role of extracellular vesicles (EVs) as part of the innate immune system, and more specifically as decoys to sequester and inactivate bacterial toxins has been recently proposed [1].

In this work we aimed to quantify the efficacy of EVs in inhibiting the toxicity of S. aureus alpha hemolysin (Hlα). Cytotoxicity assays were carried out against the L-929 mouse fibroblast cell line, employing commercially available *S. aureus* Hlα, and LC50 values were determined. *S. aureus* Hlα was found to have an LC50 of 174 nM in complete medium and 72 nM in EV-depleted medium, confirming that EV depletion promoted Hlα mediated cell death.Then, EVs secreted from HEK 293T cells were isolated using weak anion exchange chromatography and caracterized through biophysical and biochemical methodologies.

Isolated EVs were found to dramatically inhibit the pore forming activity of Hlα, using permeabilization assays of both L-929 cells and giant unilamellar vesicles (GUV). Importantly, modification of lipid composition of isolated EVs was found to potentiate the Hlα neutralization efficacy of these vesicles, further validating the potential of EVs in the framework of antivirulence therapeutic strategies for drug-resistant bacterial infections.

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Extraction of hydrophilic cell bound surface active compounds from biomass contained in olive residual sludge

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The European Union is the leading producer, consumer, and exporter of olive oil, producing 67% of the world's olive oil, being Spain, Italy, Greece, and Portugal the main producers [1]. This high production rate of olive oil generates huge amount of olive mill wastewater sludge (OMWS) that should be treated to reduce its environmental impact. In addition, in previous works, it has been proven that corn mill wastewater sludge (CMWS) is an interesting source of biosurfactants [2], which opens the door to evaluate other food industry residues, rich in nutrients and spontaneously fermented, as a direct source of bioactive compounds. In this sense, due to the high content of nutrients in OMWS, that can promote the growth of microorganisms, it is evaluated as direct source of biosurfactants. For that, OMWS was centrifuged, and the biomass was washed twice with deionized water and subjected to a cosmos extraction process carried out using phosphate buffer saline (PBS) (see Fig.1), using the protocol established by Bustos et al. [3], and subsequently subjected to dialysis with membranes. Surfactant properties of the biosurfactant extract under evaluation were measured in terms of surface tension water reduction, using a tensiometer K20 EasyDyne, with a 1.9 cm platinum Wilhelmy plate, from KRÜSS Scientific. These results were compared with the TS and CMC values of the cell-bound biosurfactants of lactic bacteria [4], and the extracts obtained from CMWS with chloroform following the protocol established by Vecino et al. [5]. Results showed that biosurfactant extract was able to reduce the surface tension of water in more than 20 units with a critical micellar concentration (CMC) of 0.27 g/L. These results were comparable with the values provided by the biosurfactant extract produced from CMWS in previous works [5], but, in the case of biosurfactants produced by lactic acid bacteria, better CMC results were achieved, reducing it from 0.4 g/L to 0.27 g/L [4]. Based on this preliminary study, it can be concluded that OMWS can be a potential source for obtaining more environmentally friendly biosurfactants contributing to reduce the carbon footprint of chemically synthetized surfactants.

Fig.1. Pictures corresponding to: A) OMWS sample before extraction; B) Dialysis of biosurfactant extract with membranes; C) Biosurfactant extract dissolved in water.

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Engineered Defensosomes: Quantifying and improving the cytoprotective efficiency of extracellular vesicles (EVs) against *Staphylococcus aureus* alpha hemolysin (Hlα)

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Methicillin-resistant *Staphylococcus aureus* (MRSA) infections are a major public health concern, particularly in the context of hospital-acquired infections, being associated with high rates of mortality. The production of bacterial pore forming toxins (PFT) such as alpha hemolysin (Hlα) plays an important role in MRSA pathogenicity. Notably, a role of extracellular vesicles (EVs) as part of the innate immune system, and more specifically as decoys to sequester and inactivate bacterial toxins has been recently proposed [1].

In this work, we aimed to quantify the efficacy of EVs in inhibiting the toxicity of *S. aureus* alpha hemolysin (Hlα). Cytotoxicity assays were carried out against the L-929 mouse fibroblast cell line, employing commercially available *S. aureus* Hlα, and LC50 values were determined. *S. aureus* Hlα was found to have an LC50 of 174 nM in complete medium and 72 nM in EV-depleted medium, confirming that EV depletion promoted Hlα mediated cell death. Then, EVs secreted from HEK 293T cells were isolated using weak anion exchange chromatography and characterized through biophysical and biochemical methodologies.

Isolated EVs were found to dramatically inhibit the pore forming activity of Hlα, using permeabilization assays of both L-929 cells and giant unilamellar vesicles (GUV). Importantly, modification of lipid composition of isolated EVs was found to potentiate the Hlα neutralization efficacy of these vesicles, further validating the potential of EVs in the framework of antivirulence therapeutic strategies for drug-resistant bacterial infections.

Acknowledgements
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Development of a nanoplatform for a vaccine against toxoplasmosis

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Toxoplasma gondii is a parasite that affects approximately one-third of people worldwide [1]. This pathogen is responsible for toxoplasmosis, posing significant health risks to certain populations, namely immunocompromised individuals and pregnant women [1]. Despite the widespread nature of this infection, an effective vaccine for human use remains elusive. Recent research has shown encouraging results using nanotechnology, a cutting-edge approach, for the creation of an effective immunization against toxoplasmosis [2].

This research aimed to develop an optimized nasal vaccine against *T. gondii* using polylactic-co-glycolic acid (PLGA) nanoparticles (NP) containing *T. gondii* sonicates (NP-TgS) for intranasal administration. A single emulsion method was used to synthesize the NP, and their physical and chemical properties were characterized by NP tracking analysis and dynamic light scattering. The encapsulation efficiency of TgS by NPs (NP-TgS) was determined by lowry assay and UV-Vis spectroscopy. Several *in vitro* tests were conducted to assess the biosafety and biocompatibility of the nanoformulation. Cell viability and permeation were evaluated using a mouse fibroblast cell line (L929) and a human nasal epithelial cell line (RPMI). The cellular uptake and activation markers (MHCII, CD80, and CD86) expression were determined, using mouse bone marrow-derived dendritic cells (BMDCs).

The NP-TgS characterization showed a size of 207 nm, a polydispersity index of 0.227, indicating a relatively uniform size distribution, a zeta potential of -14 mV, suggesting moderate stability, and an encapsulation efficiency of 55%. No toxic effects were evidenced below 0.25 mg/ml for BMDC, or below 7.5 mg/ml for RPMI and L929. Permeation assay demonstrated that 66% of the NPs successfully permeated a monolayer of RPMI cells, suggesting a good potential for intranasal delivery. Further, an increasing uptake of the NPs by BMDC was shown over 24 h. Additionally, NPs treatment induced a significant increase in the MHCII expression but not of CD80 or CD86. These data indicate that the developed NP present appropriate chemical and physical characteristics, biosafety, and biocompatibility, and were able to cross an *in vitro* model of the nasal epithelium and be internalized by antigen-presenting cells, which is determinant for the development of an effective immune response against *T. gondii* infection.

Acknowledgments
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Integrated glucose oxidase biocatalyst and Fenton-based system for cancer therapy

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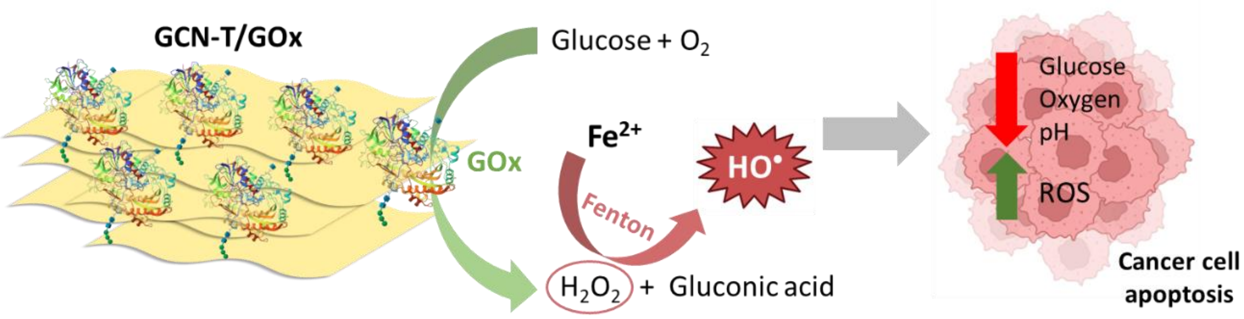
The burden of cancer on society is a significant concern, causing massive pressure on individuals, families, and health systems. Developing alternative strategies for enhanced therapeutic efficacy is of utmost urgency [1]. By combining different single-strategy treatments [2, 3], namely Starvation Therapy (ST) and Chemodynamic Therapy (CDT), this work involves the H_2O_2 production and glucose consumption using glucose oxidase (GOx) immobilised onto thermally exfoliated graphitic carbon nitride (GCN-T), followed by the generation of highly toxic hydroxyl radicals via Fenton reactions. This synergetic system will allow the creation of a suitable acidic microenvironment and the formation of reactive oxygen species (ROS) to promote cancer cell apoptosis.

In this work, the influence of the amount of GCN-T/GOx, initial pH and Iron concentration on the glucose degradation rate was studied using the Central Composite Design (CCD) of experiments. Under the optimal conditions (16 mg of GCN-T/GOx, initial pH of 4.9, and 10 mM of Iron), the glucose degradation rate was 0.17 mM min^{-1}. In addition, through the CCD methodology, the amount of GCN-T/GOx was considered the most significant variable. Compared with the experimental trial without added Iron, combining the two therapies revealed a higher glucose degradation rate, highlighting the synergetic effect between ST and CDT. Considering the promising results obtained, GCN-T will be further directly modified with Iron precursors to create a novel and integrated biocatalyst for the treatment of cancer (Figure 1).

Figure 1. Schematic representation of GCN-T/GOx bioconjugate for the combined use in ST and CDT.



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CATÁLISIS Y FOTOCATÁLISIS

Iron-based metal organic framework as a suitable catalyst in photo-PMS activation for venlafaxine degradation

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Pharmaceutical compounds are often resistant to traditional biological degradation processes and consequently, advanced oxidation processes (AOPs) have arisen as a treatment alternative. The present study validates the usage of the metal organic framework (MOF) NH_2-MIL-101(Fe) as a suitable catalyst for AOPs, highlighting the positive properties of these materials such as catalytic activity due to metal content and high stability [1]. This MOF attained an excellent performance on venlafaxine degradation using peroxymonosulphate (PMS) as an oxidizing agent, defeating the degradation performance when compared to peroxydisulphate (PDS), hypochlorite (HC) and hydrogen peroxide (H_2O_2). Moreover, the degradation rate synergistically increased by coupling visible-light radiation.

The process was further studied in terms of PMS concentration and MOF load, with complete degradation of venlafaxine (5 ppm) being achieved in 5 minutes. The process was validated by treating surface water and urban wastewater, causing a detriment of less than 16 % due to the complexity of the matrixes. Moreover, NH_2-MIL-101(Fe) also exhibited high stability, withiron leaching below 0.03 ppm, and remained reusable for up to five batches, with only a 20 % decrease in performance in the final batches (Figure 1). A deep characterization of NH_2-MIL-101(Fe) was performed, being possible to explain its good catalytic performance, and its high crystallinity, the presence of active functional groups homogeneously distributed throughout the surface, a high electrochemical active area (447 mF/cm^2) and an acidic point of zero charge (3.03) that avoided a strong venlafaxine (neutral) adsorption. This work opens a path for the efficient application of AOPs to real scenarios.

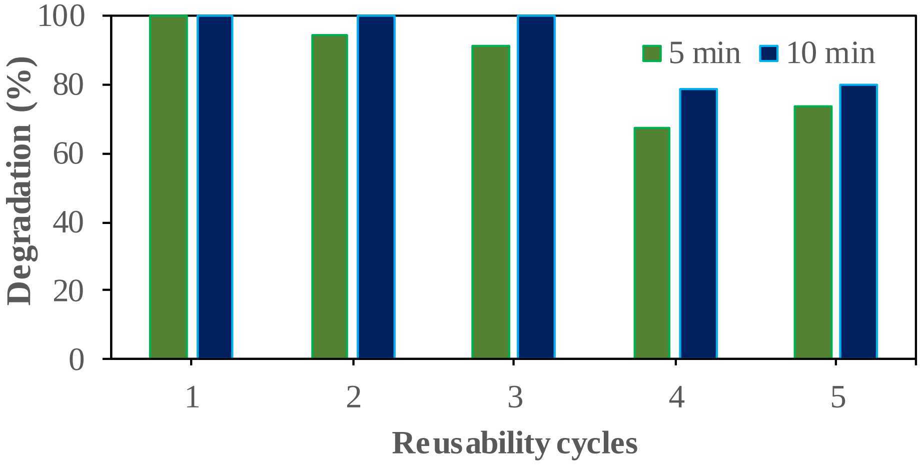

Figure 1. Venlafaxine degradation after 5 and 10 min of the photo-PMS process with 2.5 mM of PMS and 0.1 g/L of NH_2-MIL-101(Fe).

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β -Ketoenamine linked Covalent Organic Frameworks as photocatalyst for direct sulfonilation of anilines

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Finding new strategies for the synthesis of sulfonylaniline compounds is crucial for drug development, as these molecules play an important role in the pharmaceutical industry. The most common method for preparing these compounds involves photoredox-catalyzed reactions using iridium complexes,[1] which present certain disadvantages, such as lack of recyclability. Covalent Organic Frameworks (COFs), a class of crystalline porous polymers, are gaining significant attention in the field of (photo)catalysis due to their exceptional performance and recyclability in organic transformations.[2] In this work, we evaluate, for the first time, the use of different COFs as photocatalysts to synthesize sulfonylaniline compounds under different wavelengths. We synthesized a family of β-ketoenamine COFs derived from TFP (*2,4,6*-triformylphloroglucinol) with BTD (*4,7*-bis(*4*-aminophenyl)-*2,1,3*-benzothiadiazole) or TD (*4,4'*-diamino-*p*-terphenyl). In the case of **TFP-BTD**, three different isomers with different packing (AA, AB, and ABC) were obtained.[3] The catalytic activity of **TFP-BTD** with packing AA surpassed that of the other TFP-BTD isomers, achieving up to 90% yield and complete selectivity for the formation of *N,N,4*-trimethyl-*2*-tosylaniline under blue LED light (centered at 465 nm). In contrast, the AB isomer produced a 35% yield, and only trace amounts were observed with the ABC stacking form. The photocatalytic performance of this COF was further evaluated under green (525 nm) and orange (595 nm) light, achieving yields of up to 93% and 87%, respectively. In comparison, TFP-TD (AA) exhibited photocatalytic activity under blue and green light, with yields of 89% and 93%, respectively, but only 23% under orange light. Additionally, we studied the recyclability of **TFP-BTD** (AA), which maintained consistent yields over five cycles at all wavelengths employed, highlighting its potential as a sustainable and efficient catalyst for these types of compounds.

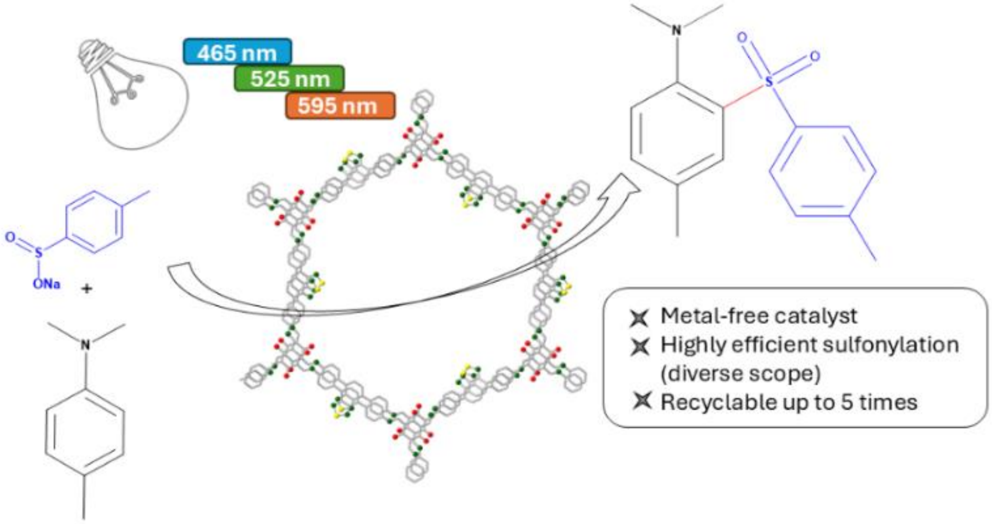

Fig.1. Schematic representation of the photocatalytic reaction using **TFP-BTD** (AA) COF as catalyst.

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Modificaciones y optimización del nitruro de carbono grafítico y sus técnicas de inmovilización para la eliminación de contaminantes coloreados en agua

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La contaminación ambiental, y en particular la contaminación del agua por diversos procesos industriales se ha convertido en una de las mayores preocupaciones de la ciudadanía lo que contrasta con los beneficios que proporcionan las industrias. De hecho, con el tiempo, esta problemática ha ganado un reconocimiento cada vez mayor. Entre las principales fuentes de contaminación hídrica se encuentra la industria textil, debido al vertido de efluentes de sus fábricas. Estos efluentes contienen numerosos agentes contaminantes, siendo los colorantes uno de los más prevalentes en las aguas residuales. La Rodamina B, entre otros colorantes, está despertando especial interés en los últimos años debido a su carácter nocivo [1].

Para tratar estos efluentes y combatir esta contaminación, en las últimas décadas se han desarrollado diversas tecnologías, entre las cuales destacan los procesos de oxidación avanzada. Estos métodos de oxidación química se postulan como una solución eficaz para el tratamiento de aguas residuales, superando las limitaciones de los métodos convencionales. Entre los procesos más prometedores se encuentra la fotocatálisis, combinando la radiación con catalizadores y donde en los últimos años se ha prestado especial atención a catalizadores no metálicos como el nitruro de carbono grafítico (GCN).

Este estudio se centró en optimizar las propiedades del GCN con el objetivo de mejorar su eficiencia como fotocatalizador en la eliminación de colorantes, específicamente la Rodamina B. Durante la síntesis del GCN, se investigaron distintos precursores, como la urea y la melamina, así como su combinación, y se aplicaron tratamientos ácidos para mejorar sus propiedades. Los resultados mostraron que el uso de urea como precursor, junto con un tratamiento ácido posterior, mejoró notablemente las características del GCN y su estabilidad química. Este enfoque permitió eliminar completamente la Rodamina B y su reutilización en ciclos sucesivos, con una ligera reducción del rendimiento (solo un 5%) en el décimo ciclo.

Uno de los principales desafíos en el uso de estos fotocatalizadores es su pequeño tamaño de partícula, que dificulta su retención en los sistemas de tratamiento. Para superar este problema, se exploró la inmovilización del GCN utilizando varias técnicas como la encapsulación, el electrohilado y la formación de composites. Los materiales obtenidos tras la inmovilización del GCN fueron caracterizadas mediante técnicas como FTIR y microscopía, confirmando la retención efectiva del GCN. De entre las técnicas evaluadas, el método más eficaz fue el electrohilado con poliacrilonitrilo, debido a su flotabilidad y alta hidrofilicidad, lo que permitió que el GCN estuviera disponible y retenido, logrando una eliminación del 90% de la Rodamina B en 90 minutos. Además, este material demostró una gran estabilidad, manteniendo su actividad catalítica casi inalterada durante múltiples ciclos de uso.

Agradecimientos

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High-performance Fe-modified black tea biochar as electrocatalyst for water splitting applications

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Energy demand have experienced a huge increase in the last years due to the population growth. As a result, carbon dioxide emissions from fossil fuels and other greenhouse gas emissions have exacerbated global warming [1]. In response to this issue, water splitting technologies have been proposed as a potential solution to replace fossil fuels as the primary energy source [1].

Water splitting consists in the division of water molecule in its main elements, O_2 and H_2, in the reactions known as Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER), respectively. This process is remarkable for being environmentally friendly and simple [1]. Nonetheless, the thermodynamics of water splitting emerge as a difficulty due to the high overpotential that must be overcome, increasing the cost of the process [2]. Thus, several authors have synthesized different catalysts to accelerate the reaction rate and reduce the overpotential, focusing on OER catalysts as this reaction is the rate-determining step, implying 4-electron exchange [2,3].

On this basis, our study was focused not only on finding a catalyst that can facilitate the thermodynamics, but also a noble metal-free option, to make the process profitable and environmentally friendly. For that, biochar (after pyrolytic treatment) and hydrochar (after hydrothermal synthesis) were obtained from black tea waste. Considering the promising activity of the biochar synthetised at 400ºC for 2 h under 2L/min of N_2, it was used for further modifications. Fe addition resulted in the obtention of a high-performant electrochemical OER catalyst due to its capacity to defeat the benchmark catalyst: IrO_2. Different percentages of Fe (5, 10, 15 and 20 wt%) were added to the black tea to optimize the catalyst activity of the attained biochar (Fe-biochar). Results have shown that this parameter is crucial, affecting the OER performance. The best catalytic activity was observed for 10 wt% Fe-biochar, which loading into Ni-foam support was studied between 0.1 and 1 mg/cm^2. Additionally, the working pH effect was evaluated. Additionally, the application of several cyclic voltammetry (CV) cycles ensured catalyst activation by removing surface impurities and the generation of oxygen-functional groups [4]. Under optimal conditions (0.25 mg/cm^2 of 10 wt% Fe-biochar under alkaline OER, after 360 CV activation), only 354.9 mV were required for a response of 10 mA/cm^2 with a minor Tafel slope of 44.9 mV/dec. Furthermore, this novel catalyst presents a good stability, showing only 20% of activity loss after 30h at 10 mA/cm^2 and 30 h at 50 mA/cm^2. Physical-chemical characterizations explained this slight detriment is caused by 10 wt% Fe-biochar surface oxidation, typical after OER [3].

In conclusion, these impressive results demonstrate that it is possible to attain good results without the usage of expensive and scarcity precious metals as catalysts. The 10 wt% Fe-modified biochar, thanks to the increase in the number of surface-active sites created during the catalyst synthesis, leads to a competitive OER performance as a result of the superior electronic transfer kinetics.

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Implementation of novel Zn-MIL53(Fe) catalyst in Advanced Oxidation Processes to degrade pharmaceuticals in wastewater

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In the present research, the potential of a novel one-step synthesised bimetallic Metal-Organic Framework (MOF), Zn-MIL53(Fe), for activating PeroxyMonoSulfate (PMS) and its catalytic activity in an Electro-Fenton process, as promising improvement to Advanced Oxidation Processes, was evaluated. After a deeply material characterization, crystal structures as depicted in Fig. 1 by SEM technique confirmed the correct synthesis of the MOF. Initially, the adsorption capacity of Zn-MIL53(Fe) for removing Rhodamine B was assessed through kinetic and isotherm studies. The bimetallic MOF exhibited superior performance than other monometallic catalysts [1], showcasing enhanced adsorption capabilities, particularly in the context of its physical interaction under natural pH. After that, the catalytic activity of the material was evaluated to generate sulphate radicals by activating PMS. It was also demonstrated that Zn-MIL53(Fe) exhibited the best catalytic activity being optimized using response surface methodology for Rhodamine B degradation (0.11 mM PMS and 4.32 mg/L Zn-MIL53(Fe)). Under optimal conditions, favorable outcomes were attained, facilitating the degradation of Rhodamine B, Fluoxetine, and Sulfamethoxazole by 93, 99, and 75 %, respectively.

After that, the evaluation of Zn-MIL53(Fe) as electro-Fenton catalyst was performed and improved outcomes were reached by electro-Fenton regarding anodic oxidation. Then, electro-Fenton treatment optimization was carried out using response surface methodology assays considering different catalyst dosages (7.2-43.2 mg), current intensities (5-45 mA) and treatment time (30-90 min) in a volume of 0.1 L. Under optimal conditions, a degradation rate over 90% for Fluoxetine and Sulfamethoxazole in synthetic wastewater [1][2] was achieved within 90 min, using graphite sheet as anode and nickel foam as cathode (25 mA), with a catalyst dosage of 43.2 mg in a volume of 0.1 L. Additionally, its application in the pathogen inactivation was evaluated using different gram-negative (*E. coli and P. aeruginosa)* and gram-positive (*L. crispatus)* bacteria [2]. Complete eliminations of both types of bacteria were reached in 5 min using the optimal conditions for Electro-Fenton process.

In the end, Zn-MIL53(Fe) was proven as a reusable material, capable of performing 3 complete cycles of electro-Fenton treatment, or 3 complete cycles to activate PMS, to degrade both types of pollutants pharmaceuticals, which makes it a promising candidate for more efficient wastewater treatment applications which involve the Fenton reaction.

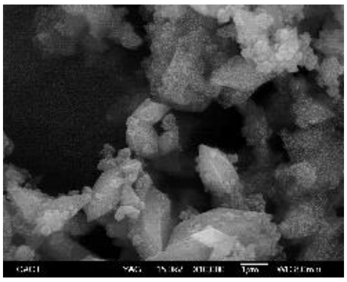

Fig.1. SEM image of the novel Zn-MIL53(Fe) MOF catalyst.

Acknowledgments
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Empleo de materiales organometalo-silíceos de iridio (III) en procesos fotocatalíticos de transferencia electrónica

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Las reacciones fotocatalíticas están experimentando un gran avance en los últimos años, como consecuencia de su empleo en el descubrimiento de rutas sintéticas novedosas, en condiciones suaves, con excelentes resultados. Sin embargo, los fotocatalizadores utilizados tradicionalmente se basan en complejos organometálicos de iridio (III) o rutenio (II), con escasa recuperabilidad y reutilización [1]. El creciente precio de estos metales ha obligado a explorar métodos de heterogeneización que faciliten su reutilización en diversos ciclos catalíticos.

En esta comunicación presentamos la síntesis de un nuevo tipo de material de ionosílice, basado en la autocondensación de un complejo catiónico ciclometalado de iridio (III) funcionalizado con grupos trietoxisilano, que ha sido previamente descrito por nuestro grupo (Figura 1) [2]. La eficiencia de este material como fotocatalizador heterogéneo, junto con su reusabilidad, han sido estudiadas en dos tipos distintos de reacciones de transferencia electrónica (SET), con desactivación tanto reductora como oxidante. Los prometedores resultados obtenidos hacen de este método de heterogeneización una buena alternativa para los fotocatalizadores basados en metales de transición.

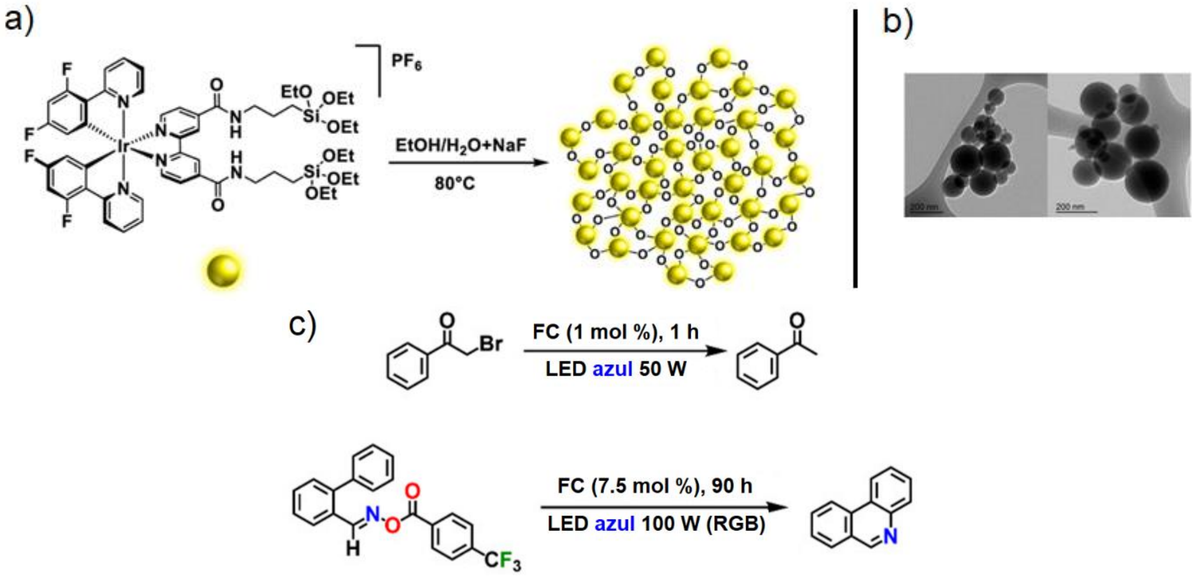

Fig.1. a) Complejo de iridio (III) y síntesis de la ionosílice; b) Imágenes TEM representativas del material; c) Reacciones fotocatalíticas estudiadas.

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Molybdenum oxide hybrid catalysts with bipyridine ligands as heterogeneous and RISS catalysts in olefin epoxidation

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Molybdenum catalysts have been industrially recognized, for decades, for liquid phase catalytic epoxidation, which is an important chemical reaction, since epoxides are used for many industrial applications. In this work, two molybdenum oxide hybrid catalysts with the general formula [MoO_3(L)], specifically, a chain-like polymer (**1**) with L= 4,4'-dimethyl-2,2'-bipyridine (DMB) and a discrete di/tetranuclear complex (**2**) with L= 4,4′-dinonyl-2,2′-bipyridine (DNB), were synthesized by a green aqueous-based reflux methodology and characterized by various complementary techniques (Fig. 1). The hybrids promoted *cis*-cyclooctene (Cy) epoxidation with H_2O_2 or tert-butylhydroperoxide (TBHP) as oxidants, under mild reaction conditions. While **2** acted as a homogeneous catalyst (HO) with TBHP, **1** presented heterogeneous (HE) catalytic features. On the other hand, using H_2O_2 as oxidant, both compounds acted as reaction-induced self-separating (RISS) catalysts and are (to the best of our knowledge) the first reported cases of Mo-based RISS epoxidation catalysts with bipyridine-type ligands. The hybrids were easily separated as RISS or HE catalysts and reused without significant loss of activity. Catalyst **1** was further evaluated in the conversion of biobased olefins, namely fatty acid methyl esters (70 °C) and lignin-derived isoeugenol (50 °C) to useful bioproducts. Specifically, the yields of epoxide product were 100% and 79-81% for the reactions of *DL*-limonene and FAMEs, respectively, with TBHP. On the other hand, the reaction of isoeugenol in the presence of **1** gave 80% Licarin A selectivity at 40% conversion; to the best of our knowledge, this is the first report of a molybdenum catalyst for this reaction (targeting Licarin A).

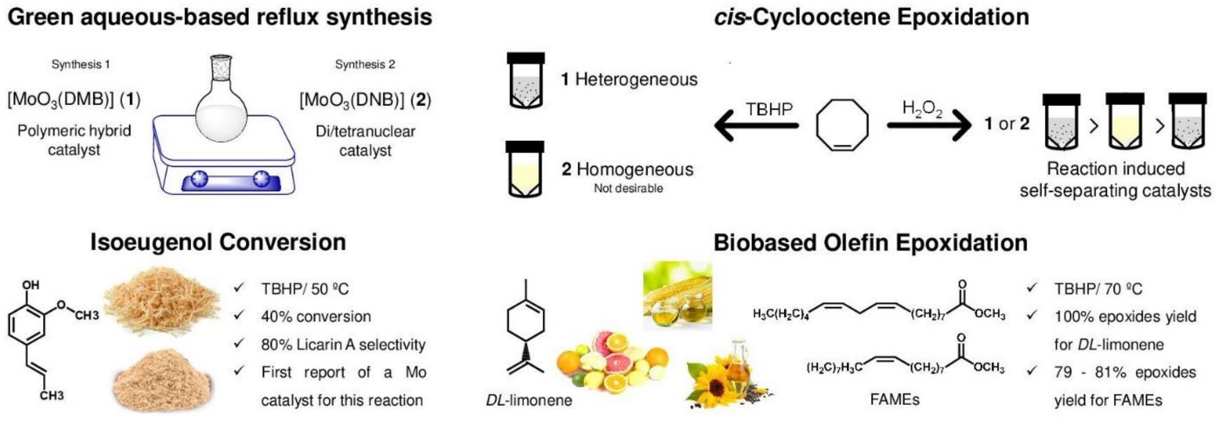

Fig.1. Synthesis and oxidation catalytic tests of Mo-bipyridine compounds.

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Síntesis de organometalo-titanias híbridas y su aplicación en la fotodegradación de colorantes con luz visible

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Actualmente, el dióxido de titanio es uno de los materiales más prometedores en el campo de la fotocatálisis, gracias a su amplio rango de aplicaciones y a sus excelentes propiedades, tales como su abundancia, baja toxicidad y alta fotoestabilidad. Sin embargo, presenta un salto electrónico elevado entre las bandas de valencia y conducción (aproximadamente 3,2 eV). Con el objetivo de conseguir materiales estables basados en la titania que sean activos con luz visible, nuestro grupo ha desarrollado un método *in-situ* basado en la *Química de Coordinación Sol-Gel* [1] (Figura 1.a). De esta forma, se han sintetizado dos materiales híbridos organometalo-titania nanoestructurados, **[1]-TiO_2** y **[2]-TiO_2**, utilizando dos complejos de Ir(III): $[Ir(ppy)_2(3,3'\text{-}H_2dcbpy)](PF_6)$ (**1**) [2] y $[Ir(ppy)_2(4,4'\text{-}H_2bicinchoninic)](PF_6)$ (**2**), respectivamente. Estos materiales han demostrado ser fotocatalizadores altamente estables y eficaces bajo irradiación de luz visible en la degradación de Rodamina 6G en medio acuoso. Ambos materiales híbridos son fotocatalizadores más eficaces utilizando luz azul y luz blanca (Figura 1.b) que la titania (TiO_2) de control, destacando que **[2]-TiO_2** presenta constantes cinéticas más elevadas que **[1]-TiO_2**. Esta diferencia es especialmente notable con irradiación de luz blanca, donde **[2]-TiO_2** es seis veces más eficiente que **[1]-TiO_2**.

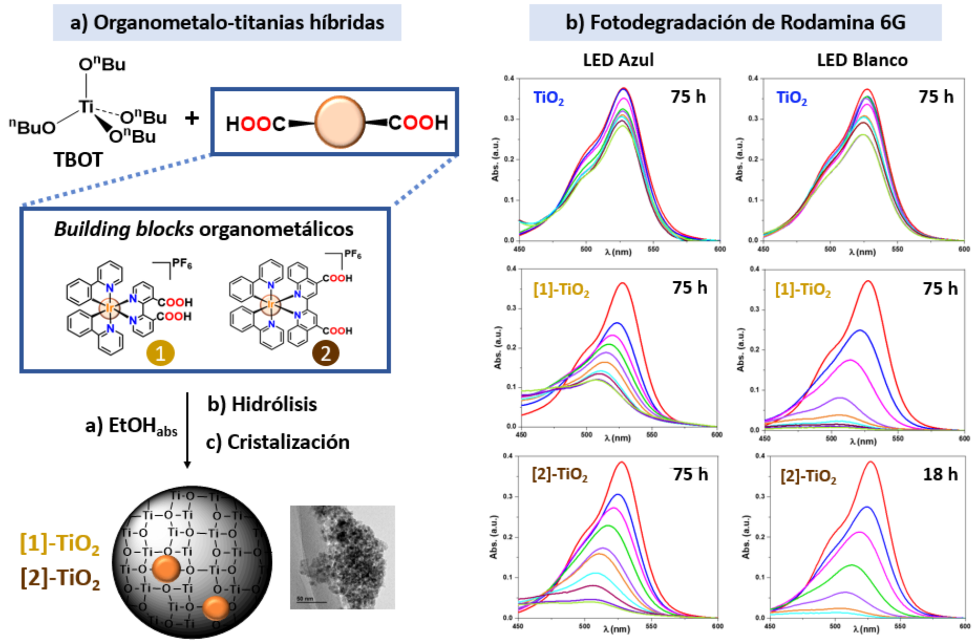

Figura 1. a) Materiales híbridos obtenidos mediante *Química de Coordinación Sol-Gel. b) Fotodegradación de Rodamina 6G en disoluciones acuosas utilizando los materiales nanoestructurados bajo iluminación de luz visible.*

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Electrospun Fe-MOF nanofiber membranes: Synthesis and catalytic application in the Electro-Fenton process

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In recent years, pharmaceutical pollution in water has become a serious environmental concern, driving the need for innovative remediation technologies. Advanced oxidation processes (AOPs) stand out as a promising solution. Among them, heterogeneous electro-Fenton processes have received significant attention for their high efficiency. These processes leverage electrochemistry to generate highly reactive hydroxyl radicals on the surface of solid catalysts, that effectively degrade pharmaceuticals in water. One of the key parameters in these processes is the proper selection of the catalyst and Metal-Organic Frameworks (MOFs) stands out due to their exceptional properties. MOFs are a class of porous crystalline materials composed of groups of metal ions coordinated with organic linkers. They exhibit clear advantages, including a highly adjustable porosity, vast surface areas and many functional groups. However, their powder form limits their application in continuous flow system, making efficient immobilization techniques essential. Electrospinning has emerged as a versatile fabrication method for the immobilization of MOFs. By this method, nanofibers are produced, forming an interconnected pore matrix by applying an electric field to a jet of a polymer solution [1].

In this study, an iron MOF (Fe-MOF) was synthesized and immobilized by electrospinning technique to obtain a nanofiber membrane composed of this material (Fe-MOF nanofiber membrane). The physicochemical characterization confirmed both the correct synthesis of Fe-MOF and its effective retention within the elaborated membranes. The usefulness and effectiveness of the Fe-MOF nanofiber membrane as a catalyst for the electro-Fenton process was evaluated by performing sulfamethoxazole degradation tests. Different parameters were explored, such as the current intensity (25 and 100 mA), the initial concentration of drug (10-50 mg/L) and the reusability of membranes. After evaluating the effect of the operational conditions, the degradation of a drug mixture formed by sulfamethoxazole and antipyrine was evaluated, reaching a degradation of 92.10 % and 87.43 % respectively for each drug in 4 h at 25 mA. In addition, the study of the main reactive species involved in the degradation process, the identification of the generated intermediate products was also carried out and their toxicity was predicted by ECOSAR program, concluding that the environmental toxicity would disappear with mineralization. Finally, given the good results obtained in batch tests, the behavior of the process was studied in a continuous flow system, achieving a stable degradation of 83.10 % in the case of treatment with a mixture of drugs.

The attained results confirmed the stability of the Fe-MOF nanofiber membrane, as well as, its catalytic activity, making it suitable for batch and flow treatments on long-term.

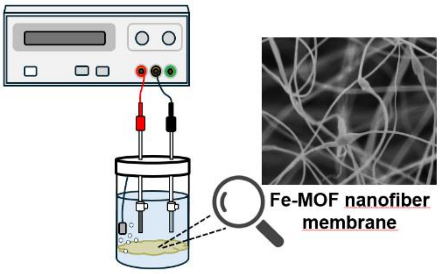

Fig.1. Graphic summary illustrating the experimental set-up with the membrane in detail.

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COMUNICACIÓN DADA DE BAJA

Hybrid nanomaterials based on semiconductor–metal sulfides/oxides; synergetic promotion of photocatalytic activity

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The infiltration of pollutants in water bodies is a course of concern as they seriously threaten water security. Synthetic dyes used in various industries, including textile and paper, can either alter the chemistry of water (pH, turbidity) or introduce harmful chemicals into wastewater [1]. Emerging pollutants or contaminants (*e.g.*, pharmaceutics) also pose potential risks to human health and the environment ecological balance [2]. Catalytic advanced oxidation processes (AOPs) have been among the most effective strategies for contaminants degradation. In particular, solar light-promoted photocatalysis has shown great promise for wastewater treatment [3].

In this work, new hybrid nanomaterials based on multiwalled carbon nanotubes (MWCNTs) functionalized with semiconductor Bi_2S_3 (BS) and magnetic $MnFe_2O_4$ (MF) nanoparticles were developed and applied as photocatalysts for the degradation of Rhodamine B (RhB) dye, and Tetracycline (TTC) antibiotic, Figure 1. The BS and MF nanoparticles were *in situ* grown onto the previously oxidized MWCNTs (CNT-ox) surface to produce the three-component nanohybrids. The structure, morphology, and composition of all prepared nanomaterials were characterized by several techniques, namely Xray-Diffraction (XRD), Scanning Electron Microscopy (SEM-EDS), Transmission Electron Microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. The adsorption (in the dark) and photocatalytic (under visible light irradiation, 150 W) performance of the hybrid materials and their individual counterparts were evaluated in the removal of RhB and TTC in the absence and the presence of H_2O_2 by UV-Vis spectroscopy and Ultra-High Performance Liquid Chromatography with tandem mass spectrometry (UHPLC-MS/MS).

The BS@MF@CNT-ox material generated reactive oxygen species under visible light irradiation (confirmed by EPR spectroscopy) and degraded 97% of RhB (confirmed by UV-Vis and Nuclear Magnetic Resonance (^{1}H NMR) and 93% of TTC (confirmed by UHPLC-MS/MS) in 30 min. The photocatalyst could be re-used at least 3 times without activity loss. The XRD pattern of BS@MF@CNT-ox remained unchanged after the last catalytic cycle, suggesting the stability of the catalyst structure.

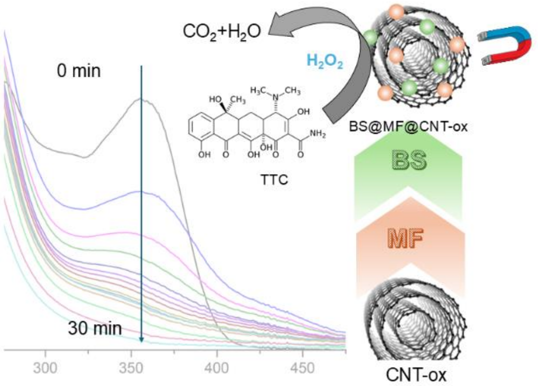

Fig.1. Photocatalytic degradation of tetracycline (TTC) by BS@MF@CNT-ox.

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Heteropoly acids @PVA membranes for glycerol acetalization

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Biodiesel production has surged in recent years, resulting in a significant amount of glycerol waste, a common by-product in biodiesel formulation. Approximately 10% of the total biodiesel produced is glycerol, with a purity ranging from 50 to 55% [1]. However, the market cannot absorb this excess glycerol in its crude form, and purification on a large scale can be prohibitively expensive [2,3]. Despite this, it is crucial to convert glycerol into high-value compounds due to its immense potential as a raw material for generating value-added products. Various catalytic reactions have been explored for glycerol valorization, with acetalization gaining significant interest. The products derived from this reaction can support a circular economy model linked to the biodiesel industry.

Keggin heteropoly acids (HPAs) are an attractive group of acid catalysts, highly active in oxidative processes or acid-catalyzed reactions [4]. Despite the efficiency that HPAs have demonstrated in acetalization reactions to produce solketal [5], the best solution for recovery and reuse is to immobilize HPAs on inert support materials. For the first time, single-layer membranes that exhibit only catalytic behavior due to catalyst immobilization (i.e., heteropoly acids, HPA) have not been applied in glycerol acetalization reactions. This work aims to introduce innovation in this area.

Thus, the HPA as active centres were incorporated in a polymeric material, polyvinyl alcohol (PVA), forming the catalytic membranes HPA@PVA. These were prepared based in the active centres (H_3PW_{12} and H_3PMo_{12}). Two different procedures were followed, one containing the functional group 3-aminopropyltriethoxysilane (APTES): H_3PW_{12}@APTES-PVA and H_3PMo_{12}@APTES-PVA, and the other without APTES: H_3PW_{12}@PVA and H_3PMo_{12}@PVA. All the materials were characterized by various techniques: FTIR-ATR, SEM-EDS, ICP-OES and potentiometric titration. Finally, all the membranes were applied in glycerol acetalization reactions with acetone. Membranes with APTES exhibited absence of catalytic activity. Polymeric membranes without APTES were also applied in glycerol acetalization reactions, with H_3PW_{12}@PVA demonstrating superior catalytic efficiency (95% of conversion with 98% of solketal selectivity, after 60 min at 60 °C). Catalytic membrane stability of H_3PW_{12}@PVA was studied during ten consecutive reutilization cycles, without loss of catalytic performance.

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Effective Porous Metal-organic Frameworks catalysts for ring-opening reaction

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Nowadays the synthetic pathway on the production of β-aminoalcohols has been widely investigated, crossing various scientific disciplines, such as medicinal chemistry and synthetic organic chemistry [1]. This class of compounds play an important role due to its importance as building blocks for bioactive substances and therapeutic agents, especially in antimalarial drugs [1,2]. The common approach in the production of β-aminoalcohols is by the ring-opening of epoxides with amines; however, these processes use high temperatures and high excess of amines [2,3].

In order to overcome the typical issues associated with the synthetic path of these class of compounds, new composites materials were designed to act as heterogenous catalysts, specifically for the ring opening reaction between styrene oxide and aniline (Fig. 1.). The materials prepared were based on Metal-organic Frameworks and Polyoxometalates, namely ZIF-8 (Zeolitic Imidazolate Frameworks), that acts as a support material, and PMo_{12} (Phosphomolybdic acid), that acts as the active catalytic site, in the final composite denoted as PMo_{12}@ZIF-8. The preparation of this catalyst was made by impregnation approach. This method consists in the encapsulation of the active catalytic site (PMo_{12}) in the porous support material (ZIF-8), by diffusion. The prepared composite was then characterized by FTIR-ATR, Powder XRD, ICP-OES.

The designed composite was evaluated as catalyst for the ring-opening of styrene oxide with aniline using a solvent-free system and using ethanol as solvent. Both catalytic systems resulted in high conversion of styrene oxide (97%), confirmed by GC-FID. High selectivity was found for the 3-Anilino-3-phenylpropionitrile (identified by GC-MS): 87% using the solvent free process, and 81% using ethanol as a solvent. The recyclability of the catalyst was tested in both systems (solvent-free and ethanol), and no loss of activity was observed.

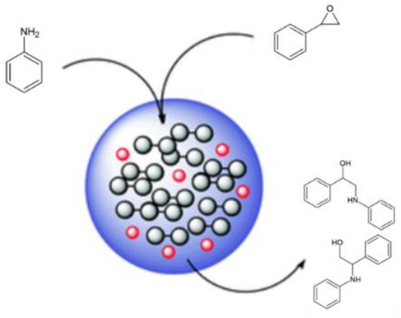

Fig.1. Representation of the catalytic process in the ring-opening of styrene oxide with aniline.

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Microwave-assisted ethyl levulinate production using as catalyst rice husk biobased materials

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The current energy consumption is rising as a result of industrialisation and population growth. Fossil fuels are also major contributors to several environmental concerns, including the release of toxic pollutants, acid rain, smog formation, and global warming. Consequently, the lack of a viable replacement for fossil fuels is a cause for alarm and has motivated researchers all over the world to find more sustainable alternatives. In this context, biomass has been explored to produce carbon-based fuels or chemicals. The production of alkyl levulinates has recently gained significant interest due to their unique physicochemical properties, making them suitable for applications in the petrochemical sectors.[1] Furthermore, because of its low sulfur content, excellent lubricity, improved flow properties, alkyl levulinates have shown substantial potential for use in gasoline blends and diesel engines. In this regard, ethyl levulinate (EL) has been suggested as one of the most promising fuel additives because it is soluble in diesel fuels, even with a higher aromatic content and is also less toxic, promoting a cleaner combustion. [2] 5-hidroxymethylfurfural (HMF) is recognized as one of the most promising platform chemicals. However, the use of HMF as feedstock for EL production is not a common procedure. Despite the apparent simplicity of this process, in reality, the occurrence of side-reactions, renders EL obtention from HMF challenging. To enhance the process efficiency, more active and selective catalysts are required. Agricultural and forestry biomass residues offer inexpensive and sustainable feedstocks. In this context, rice husk (RH), a common agricultural byproduct of rice production, stands out. Despite the vast global rice output, there are relatively few applications RH, leaving much of this resource underutilized. [3,4] In this work a series of -SO_3H functionalized rice husk-based materials were developed and their performance as catalysts was studied on the conversion of EL from HMF, under microwave irradiation.

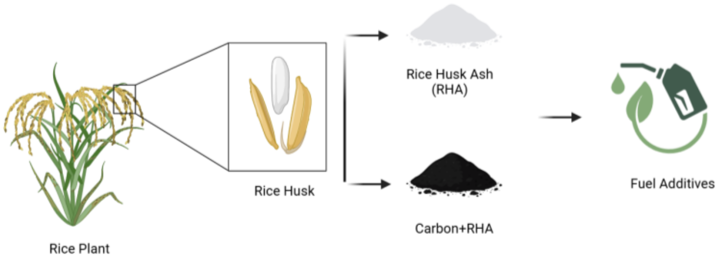

Fig.1. Rice Husk-based materials for fuel additives obtention.

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Evaluating the Impact of Thermal Treatment on the Catalytic Efficiency of Carbon Nanotubes as Catalytic Support in Fischer-Tropsch Synthesis

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Despite the push for cleaner energy, fossil fuels remain essential for electricity generation, transportation, and industry, serving diverse users from households to businesses. Gasoline and diesel continue to be the main fuels for vehicles, with demand driven not just by transportation needs but increasingly by the requirement for petrochemicals and specialized products like jet fuel [1]. Among emerging fuel production technologies, Fischer-Tropsch synthesis (FTS) is notable for its potential to create synthetic fuels that mirror the properties of gasoline, diesel, and jet fuel, but with a significantly lower environmental impact and lacking harmful compounds like sulfur and aromatics found in traditional fossil fuels, thereby reducing air pollution [2]. One of the keys to improving the efficiency of the FTS is in catalyst development since their properties can determine both the activity and selectivity towards specific hydrocarbon ranges [3]. Carbon materials, which are chemically and thermally stable under harsh conditions and have tunable surface area and surface chemistry, have been gaining interest as catalyst support for FTS [4].

This study aimed to investigate the effect of different temperatures used in thermal treatment on chemically functionalized carbon nanotubes (CNTs). The modified CNT were used as catalytic support and the catalysts were evaluated in the FTS. The tests were performed in a fixed-bed fully automated Microactivity Effi unit at T = 220 °C, P = 20 bar, GHSV = 4.0 $m^3 \cdot kgcat^{-1} \cdot h^{-1}$ and $H_2/CO = 2$. The effect of the treatment temperature on the CNTs was analysed regarding their stability, and catalytic performance, including CO conversion, specific yield, selectivity, and product distribution (paraffins/olefins/isomers). The results showed that by varying the thermal treatment temperatures of the supports, it is possible to select which range of hydrocarbons is the majority in the products, through the potential removal of functional groups. As the temperature increased, the selectivity shifted from the jet fuel and diesel range (C_{12-20}) to the gasoline range (C_{5-11}), and CH_4 formation decreased. However, at the highest temperature, the selectivity shifted back towards the jet fuel and diesel range (C_{12-20}), achieving the highest selectivity for this range and the lowest CH_4 selectivity.

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ENSEÑANZA DE LA QUÍMICA

El uso de los gráficos en la enseñanza de la química

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Las representaciones figurativas estáticas tienen una gran incidencia en el proceso de aprendizaje y enseñanza en los distintos niveles de la educación. Los gráficos, los diagramas, los íconos y cualquier otro tipo de representación permiten lograr una comprensión más completa de teorías, conceptos e ideas. (Pérez Echeverría et al, 2009:137) [1]. Todas las imágenes tienen en común la facilitación de forma integrada y sencilla de grandes cantidades de información y de conocimiento relacionados entre sí de manera compleja; dichas representaciones - en especial los gráficos- son muy importantes en las enseñanza-aprendizaje de la química; ellas le dan vida a la matematización del fenómeno de estudio y en el mismo momento lo constituye al brindarles visibilidad.

En coincidencia con el pensamiento de muchos autores manifestadas en distintas publicaciones, tales como Pérez Echeverría, el principal escollo que encontramos durante la práctica docente es la creencia de que no es necesario enseñar, aprender a leer y comprender dichos sistemas figurativos. Debido a nuestra experiencia docente, hemos detectado que muchos de nuestros colegas docentes frecuentemente suponen que durante la vida universitaria no hace falta trabajar en particular estos tópicos. No basta con presentar una imagen, un gráfico o un mapa; estas representaciones no son tan evidentes o transparentes, todos los alumnos necesitan un cierto nivel de “alfabetización gráfica”.

El campo de acción abordado consiste en la compresión de gráficos, que permita tanto su lectura como su escritura, muy frecuentemente utilizados en nuestra disciplina. Por ello, propusimos abordar el uso de gráficos como herramientas de pensamiento científico, centrándose en el análisis de cómo introducir esto a metodología, simultáneamente con los contenidos conceptuales de química del nivel secundario.

Tanto los diseños curriculares de la secundaria, como los programas de química de las materias de los primeros años de la universidad, requieren la enseñanza/uso de herramientas de pensamiento científico siendo mencionada en profusas oportunidades para introducirla en los contenidos conceptuales tradicionales de la disciplina.

La enseñanza de esta herramienta tiene sus propios desafíos desde lo didáctico, siendo una condición sine qua non la explicitación de objetivos a alcanzar o recorridos de enseñanza a implementar.

Es importante avanzar en un nivel de detalle en el análisis de este aspecto de la enseñanza para delimitar mejor qué enseñar y qué no, con qué nivel de profundidad y precisión, con qué objetivos finales.

Implementamos diversos talleres con docentes en busca de iniciar este tipo de debate alrededor de una herramienta de pensamiento científico, tratando a la vez de ofrecer recursos que puedan ser implementados críticamente en las aulas. Detectamos que los docentes utilizan muy poco los gráficos, solo en ocasiones en aquellos contenidos donde está especificado en el diseño curricular la lectura, producción e interpretación de gráficos, siendo esas ocasiones muy pocas como para que el alumno adquiera destreza en la lectura, interpretación y construcción de gráficos. Si solamente utilizamos los gráficos en los contenidos habituales como: leyes de los gases, soluciones, solubilidad y cambios de estado; resulta un inconveniente a la hora de generar en el alumno estas competencias, coincidimos con Blubaugh y Emmons, 1999 [2] y Ainley, Nadi y Pratt, 2000 [3] cuando afirman que una de las causas por las cuales los estudiantes tienen dificultades para comprender las gráficas cartesianas es la ausencia de prácticas en las que ellos puedan construirlas e interpretarlas.

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Reacciones microquímicas:
Un interesante recurso para el ahorro de reactivos y residuos.

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En el trabajo de un laboratorio de Química existen diferentes técnicas que permiten separar y/o identificar compuestos de manera cualitativa. Incluso a veces esas técnicas pueden ser el método principal para determinaciones analíticas.

Un grupo de estas técnicas se denominan auxiliares, que como su nombre indica, sirven de ayuda en el transcurso del análisis. Un ejemplo de técnica auxiliar es la Microscopía Química. Ésta generalmente consiste en la identificación de la estructura cristalina de un precipitado formado en el transcurso de una reacción mediante un microscopio. También puede utilizarse para mostrar procesos de cualquier tipo de reacción siempre que se produzca una modificación notable en las características físicas de los productos con respect a los reactivos.

Como ejemplo, presentamos la reacción de reducción del ion Ag(I) por un simple alambre de cobre de los cables conductores de electricidad comerciales (Fig. 1) y la reacción de precipitación del $MgNH_4PO_4$ (Fig. 2.).

La microscopía química clásica posee varias ventajas que la convierten en una técnica ideal para su aplicación:

- Una prueba microquímica puede ser realizada en menos de cinco minutos
- No es necesario ninguna preparación previa.
- Las cantidades de reactivos son pequeñisimas.
- El material es mínimo y muy barato.
- La cantidad de residuos generados es extremadamente pequeña.
- Los microscopios USB tienen un precio muy bajo y su utilidad permanece indefinidamente.
- Es una metodología muy sencilla y fácil de usar para alumnos de cualquier nivel.
- Pueden utilizarse para sustancias como minerales, metales, aleaciones, alimentos, etc.
- La conexión del microscopio USB a dispositivos audiovisuales permite la apreciación de la experiencia a multitud de alumnos.

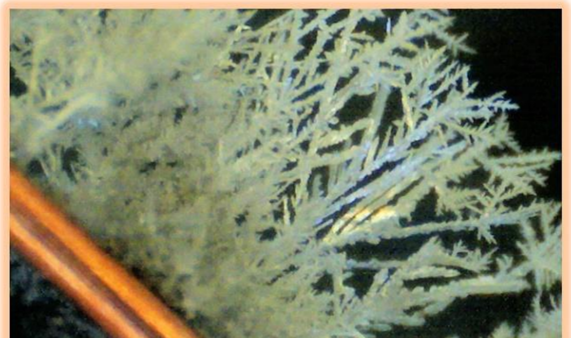

Fig.1. Cristales de plata generados por reducción de Ag^+ con cobre metal

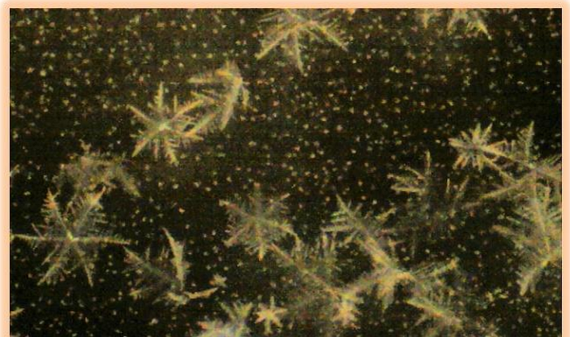

Fig. 2. Reacción de precipitación de $MgNH_4PO_4$.

El color que te puede salvar la vida: una aproximación experimental a la química de fármacos en el aula de Educación Secundaria Obligatoria, Bachillerato y Formación Profesional

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En un mundo en constante cambio, donde la incertidumbre es la norma y la velocidad de los acontecimientos nos abruma, la idea de que “todo cambia y nada permanece” resuena con fuerza. Nuestra sociedad, definida por su inestabilidad, requiere que el conocimiento científico sea un pilar fundamental para afrontar las complejidades de la vida contemporánea. La ciencia está integrada en todos los ámbitos de nuestra vida: desde la tecnología que empleamos hasta los tratamientos médicos que recibimos y las decisiones cotidianas que enfrentamos. Así, la alfabetización científica se convierte en una herramienta esencial, no solo para entender y enfrentar nuevos desafíos, sino también para empoderar a las personas a participar activamente en su comunidad.

Un claro ejemplo de las peligrosas consecuencias de la falta de conocimiento científico es el incidente nuclear de Goiânia. En 1987, dos chatarreros encontraron una máquina de radioterapia en desuso en un hospital y, sin comprender los riesgos, decidieron desmantelarla, ignorando la presencia de una fuente de Cesio-137 altamente radiactivo. La diseminación de este isótopo entre la población tuvo efectos nefastos en términos de contaminación ambiental, además de causar enfermedades graves a casi 250 personas y la muerte de 5 individuos. Hoy, tras 37 años de este suceso, surge una pregunta inquietante: si un incidente similar ocurriera en la actualidad, ¿qué medidas y opciones de tratamiento podrían implementarse para reducir los efectos dañinos de la radiación?

Este proyecto educativo, que puede ser realizado en diferentes niveles de enseñanza, desde los últimos cursos de Educación Secundaria Obligatoria, hasta ciertas familias de Formación Profesional, trata de dar respuesta a la pregunta anterior, empleando la experimentación como recurso metodológico. A lo largo de diferentes trabajos prácticos se explorará el fenómeno de la radiactividad y sus efectos a nivel corporal. Así mismo se analizarán las posibilidades terapéuticas existentes hoy en día y se sintetizará en el aula un fármaco efectivo para el tratamiento del envenenamiento por radiación. ¿Alguna vez te habías planteado que un color te podría salvar la vida?

Agradecimientos
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De las chicas del Radio al enemigo invisible: aprendizaje experimental de la radiactividad en el aula de ciencias experimentales

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¡Embárcate en un viaje que te llevará a descubrir el intrigante mundo de la radiactividad a través de diferentes contribuciones de destacadas mujeres científicas! Este proyecto fusiona conceptos de ciencias experimentales con la creatividad artística, para poner de relieve el impacto crucial que estas investigadoras han tenido en el avance del conocimiento. Al explorar sus logros, se desafían mitos arraigados y se revelan historias inspiradoras de mujeres cuyas aportaciones, a menudo pasadas por alto, han moldeado nuestra vida cotidiana y nuestra comprensión de la ciencia.

Los objetivos de este proyecto son:

- Integrar conceptos de científicos y elementos estéticos para diseñar y crear una obra de arte que represente simbólicamente la vida y el trabajo de diversas científicas e investigadoras en el campo de la radiactividad.
- Evaluar la contribución al desarrollo de una disciplina científica de diversas mujeres investigadoras, valorando los logros y descubrimientos atendiendo al contexto social en el que se produjeron para determinar el impacto real en el desarrollo de la ciencia moderna y la vida cotidiana.
- Diseñar y realizar experimentos que demuestren los principios fundamentales de la radiactividad, utilizando los descubrimientos, materiales y técnicas que representen las investigaciones de mujeres científicas clave en este campo.

Para evitar que los estudiantes desarrollen una percepción distorsionada del proceso científico, se incluyen en el currículo de las materias de ciencias experimentales menciones a la historia de las disciplinas. La historia se convierte en un recurso pedagógico crucial, articulando un proyecto de aula que explora el fenómeno de la radiactividad. A partir del estudio de las vidas y obras de diversas investigadoras, emergen distintos trabajos prácticos donde la experimentación se utiliza para abordar temas como el decaimiento radiactivo y la radiactividad de fuentes naturales. Además, se potencia la perspectiva de género, indagando sobre las protagonistas de muchos avances en este campo, mediante componentes artísticas y lúdicas.

Los resultados indican que, a través de este proyecto interdisciplinar, los estudiantes desarrollan habilidades prácticas en la experimentación científica y artística, adquiriendo simultáneamente sólidos conocimientos sobre los principios que rigen la radiactividad y la historia de la disciplina. La combinación de ciencia y arte en las actividades finales no solo captura la esencia de las contribuciones científicas de las mujeres investigadoras, sino que también constituye una base fundamental para crear nuevos materiales didácticos que se pueden emplear en el propio centro educativo.

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QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA

Produción de ácido biosuccínico mediante estratexias fermentativas a partir de peles de pataca: optimización do proceso

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O ácido succínico (AS) é unha molécula de plataforma de base biolóxica considerada un composto clave no contexto das biorrefinerías [1]. A importancia deste ácido neste campo xustifícase grazas a propiedades como son a súa renovabilidade e a funcionalidade, ademais de presentar unha ampla gama de derivados de interese. Por outro lado, o AS emprégase de forma extensiva como produto químico especializado en diversos sectores entre os que se atopan a industria alimentaria, médica, cosmética, agrícola e farmacéutica [2]. Na actualidade, a súa principal síntese é a vía petroquímica, o cal ocasiona a xeración de gran cantidade de residuos químicos e presenta altos costes [3]. Por todas estas razóns, cada vez préstase máis atención á biosíntese de AS mediante fermentacións microbianas como vía alternativa á produción convencional [2,3].

A pataca (*Solanum tuberosum* L.) é un dos principais cultivos producidos a nivel mundial, concretamente, producíronse ao redor de 370 millóns de toneladas no ano 2022. Pola contra, o seu procesamento industrial xera unha gran cantidade de subprodutos que poden contribuír á contaminación ambiental; entre eles, destacan as peles, que supoñen aproximadamente un 10% do peso total da pataca. Estas peles presentan gran interese coma materia prima de baixo custo. De feito, a súa composición, rica en amidón, posibilita a valorización biotecnolóxica, polo que presenta potencial como materia prima en biorrefinerías enfocadas na produción de biocombustibles e produtos bioquímicos de valor agregado, incluído o AS [4].

Este estudo aborda a optimización da produción de AS a partir de peles de pataca empregando o microorganismo *Actinobacillus succinogenes* 22257. Na fermentación compararónse os esquemas fermentativos de hidrólise e fermentación separadas (HFS) e de pre-sacarificación e sacarificación e fermentación simultáneas (PSFS). Ademais, optimizáronse parámetros como a relación líquido-sólido (con valores de 6, 10 e 15 g/g), a porcentaxe de sal ($MgCO_3$) engadida (80 e 100%) e os nutrientes.

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Synthesis of novel Carboxymethyl Cellulose-Coated Metal-Organic Framework and its use in heterogeneous Electro-Fenton

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The treatment of wastewater is a critical process for ensuring the safety and quality of water resources. Conventional wastewater treatments have limitations in effectively removing pathogens and other micropollutants, leading to the need for innovative approaches. One promising approach is the use of innovative technologies based on Advanced Oxidation Processes, such as Electro-Fenton, which requires a suitable catalyst for its effectiveness. Thus, a bimetallic Metal Organic-Framework (MOF) Zn-MIL53(Fe)[1] was successfully one-step synthesised and embedded in a CarboxyMethyl Cellulose polymer (CMC) matrix, resulting in a novel bio-based hydrogel (Figure 1). Its performance and stability as a heterogeneous catalyst were tested in an Electro-Fenton process to generate hydroxyl radicals which completely removed 10 mg/L of Rhodamine B from wastewater in 120 min. Several assays were done in order to optimise working conditions using the model organic pollutant Rhodamine B.

Under optimal dosage of 15 g/L of hydrogel, which contains 0.29% (m/m) of MOF and 0.71% (m/m) of CMC, using a current intensity of 25 mA, 50 mL/min of bubbled air and using graphite sheet as anode and nickel foam as cathode, pharmaceuticals such as Fluoxetine and Sulfamethoxazole, reached over 99 and 92% removal from wastewater in 150 min, respectively.

Moreover, it was also tested for the inactivation of pathogens, gram-positive (*L. crispatus)* and gram-negative (*E. coli and P. aeruginosa)* bacteria, reaching complete inactivation for both types of bacteria in 15 min. Finally, the hydrogel was proven as a reusable material, capable of undergoing 6 complete cycles of Electro-Fenton process, which makes it a promising candidate for more efficient wastewater applications.

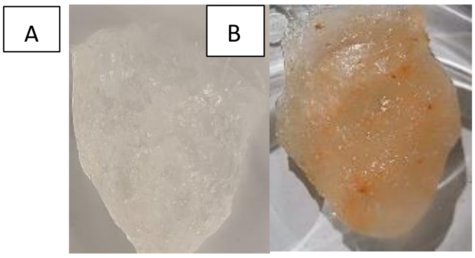

Fig.1 (A) CMC hydrogel and (B) Zn-MIL53(Fe) embedded in CMC hydrogel.

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Extraction of Hydroxyapatite at Moderate Temperature Using Ionic Liquids

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Tuna scales are one of the residues produced by the canning industry, currently discarded as waste. Their composition, similar to that of fish bones, consists mainly of hydroxyapatite combined with organic material. Hydroxyapatite is an interesting mineral composed of phosphorus and calcium ($Ca_{10}(PO_4)_6(OH)_2$), which offers beneficial properties as fertilizer. It can help alleviate the global shortage of phosphorus in agriculture, as each kilogram of human food requires the addition of between 4 and 13 kilograms of phosphorus. Current reserves are estimated to last a maximum of 100 years [1-4]. Furthermore, hydroxyapatite is being investigated in an orthopedic context, due to its ability to accelerate bone regeneration and enhance the adherence of dental implants [5].

The production of hydroxyapatite from fish scales involves removing the organic material they contain. The conventional process accomplishes this through calcination at high temperatures (> 600 ºC), which is energy-intensive. Recent studies have reported the extraction of hydroxyapatite at significantly lower temperatures by using alkaline solutions to dissolve the organic fraction [6]. However, these methods require hard solvents, which are environmentally unfriendly. In this context ionic liquids, known for their high solvation capacity, are proposed as a greener alternative to conventional solvents.

In this work, several ionic liquids were investigated for the extraction of hydroxyapatite from fish scales. Thermostated glass cells were used to put in contact 5 mL of ionic liquid (or aqueous solution of ionic liquid) per gram of scales, ensuring proper mixing through gentle stirring. With a fixed treatment time of 12 hours, several ionic liquids were tested at temperatures ranging from 25 ºC to 100 ºC. The solid recovered by filtration was washed with water, dried, and identified as hydroxyapatite using X-ray diffraction and FT-IR analysis. The recovery yield was determined through thermogravimetric analysis. This procedure provides an environmentally friendly method that outperforms the use of alkaline media at elevated temperatures.

Acknowledgements
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Rheological measurement of corn starch gel hydrolysis rate at different α-amylase concentrations

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Introduction: Rheology is a widely used technique to determine starch transformations during gelatinization processes [1], but starch digestion is usually monitored by biochemical methods, which is a long process. Furthermore, the amount of enzyme used per substrate is important for the digestion rate, so it is proposed to monitor the hydrolysis of gelatinized starch by measuring the decrease in apparent viscosity of the samples in a rheometer. In this way, this method is much faster and simpler.

Materials and Methods: The corn starch gel (20% w/w) was gelatinized in boiling water for 20 min. It was then tempered to 37ºC and then a constant amount of gel was taken and different amounts of α-amylase dissolved in maleate buffer were added. In the literature, 0.14 U α-amylase/mg starch [2] is normally used. A wide experimental range from 0.01 to 20 U/mg starch of enzyme concentration was evaluated. Enzyme was dispersed for 2 min in a homogenizer and an aliquot was added to the rheometer where the viscosity was measured at constant shear rate (10 s^{-1}). The viscosity drop is modelled with the Equation (1):

$$\mu = \mu_\infty + (\mu_0 - \mu_\infty)e^{(-k\,t)} \tag{1}$$

where μ (Pa s) is the apparent viscosity, μ_∞ (Pa s) is the final viscosity, μ_0 (Pa s) is the initial viscosity, k (min $^{-1}$) is the kinetic constant and t (min) is the time.

Results and discussion: As the amount of enzyme increases, the kinetics are faster. In fact, k increased from 0.06 to 0.35 min^{-1} with the addition of 0.01 and 20 U/mg starch, respectively. In the **Figure**, the values of k vs the enzyme concentration per mg of starch can be observed. It can be observed equilibrium is reached and the data obtained were modelled following Equation (2) that expresses the saturation of the substrate by the enzyme:

$$k = k_{max}\frac{[E/S]}{K_S+[E/S]} = 0.36\frac{[E/S]}{0.97+[E/S]} \tag{2}$$

where k is the kinetic viscosity constant, k_{max} and K_s are the maximum kinetic constant and saturation constant, respectively, and their values were obtained after non-linear fitting of experimental data, finally, [E/S] is the enzyme/substrate ratio (Enzyme units/mg starch).

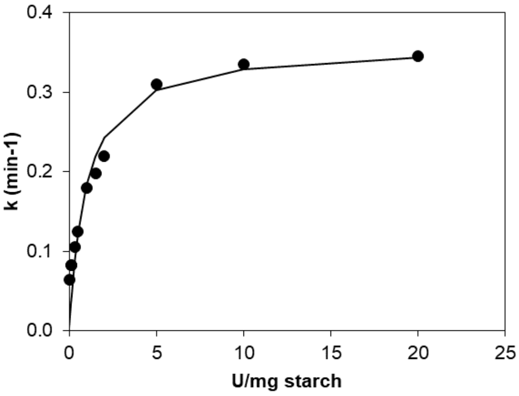

Figure. Plotting of k vs enzyme concentration: experimental data (dots) and modelled values, Equation (2), (line)

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PEG/Sodium Citrate Aqueous Two-Phase Systems: Phase Diagrams

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Abstract.

Aqueous two-phase systems (ATPS) have been investigated for about half a century as mild biphasic systems for extraction processes in biotechnology and wet metallurgy. Polymer/polymer and polymer/salt combinations in water are the conventional formulations, with polyethylene glycols (PEG) being the most commonly used polymers. Inorganic salts, such as phosphates and sulphates, are the most common, but in recent years organic salts (such as citrates, tartrates, oxalates, etc.) have been investigated due to environmental concerns on effluents with high concentrations of inorganic salts [1]. Furthermore, the effect of sulphate and phosphate salts on the environment, animals and humans is well known [2,3]. Ionic liquids (as new salts) and organic solvents (carbohydrates and other chemicals) have also been proposed as ATPS forming agents in the last 20 years [4].

A key piece for the characterisation of an ATPS is the phase diagram, together with some physical properties of interest (such as density and viscosity). Moreover, knowledge of the complete envelope of the liquid-liquid equilibrium region is essential for extraction processes, as it indicates the compositional limits that can be used for extraction, as well as the compositions of both phases at equilibrium. In this work, the complete liquid-liquid equilibrium region of ATPS formulated with PEG/sodium citrate, with PEG molecular weights of 6, 10 and 20 kDa, has been determined at different temperatures (283.15 K, 298.15 K and 313.5 K). The analysis of the equilibrium phases has been done by combining two physical properties (density and refractive index) to obtain the concentrations of the components in each phase. A total of nine phase diagrams (three polymers, three temperatures) were generated, and the study was extended to cover all the different solid-liquid equilibrium regions, allowing the complete phase diagram to be presented across the full range of compositions.

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Fish Protein recovery using Aqueous Two-Phase Extraction

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Abstract.

Aqueous two-phase systems (ATPS) have been widely used for the separation of enzymes, proteins, nucleic acids, cells, organelles, viruses and even living cells [1]. Although different types of systems exist, the PEG (polyethylene glycol)/dextran and PEG/salt ATPS are the most employed [2]. In the latter case, their main disadvantage is the relatively high ionic strength in the salt-rich phase for protein recovery [1]. On the other hand, PEG/dextran systems despite offering higher protein purification efficiency than PEG/salt systems, are also significatively more expensive [3]. Two-phase polymer/salt systems use typical inorganic salts such as phosphates or sulphates [1,4]. To avoid their drawbacks, in recent years, there has been increasing interest in salts of organic origin, such as citrates, as they degrade rapidly under natural conditions [5].

This work evaluates the possibility of using ATPS formulated with PEG and sodium citrate to recover proteins from aqueous effluents from the canning industry. Fishmeal (kindly supplied by Jealsa Foods, Boiro, Spain) has been used to simulate effluents from the canning industry, and the partition coefficients of the total protein in various selected ATPS were determined. The concentration of total protein in both equilibrium phases of the ATPS was quantified using the BCA method. For each ATPS and tie-line investigated, different protein concentrations were tested to confirm that the partitioning was independent of protein concentration, thus ensuring that thermodynamically meaningful partition coefficients were obtained. The results obtained show the preference of fish proteins for the PEG-rich phase, where they can be concentrated.

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Optimisation of pectin extraction from inner lime peel using succinic acid aqueous solutions

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The processing industry of citrus fruits generates copious volumes of organic waste [1]. A significant portion of this waste is constituted by citrus peels, where the biopolymer pectin represents as much as 20-30%. Pectin is a valuable substance extensively used in the food, pharmaceutical, and cosmetic sectors for its texturizing, gelling, and emulsifying properties. The efficient recovery of pectin from citrus peels will add economic value to an underutilised resource while simultaneously contributing to a reduction of the environmental footprint associated with the citrus processing industry [2]. Conventional extraction methods to obtain pectin from this source do typically involve the use of strong mineral acids, posing environmental hazards and limiting their sustainability. An interesting alternative with greener credentials may be the use of biobased and biodegradable organic acids. One good example of the latter is succinic acid, that can be produced from renewable resources and is recognised for its low toxicity and environmental compatibility, making its aqueous solutions a promising candidate for a more sustainable pectin extraction process [3].

One of the most representative citrus fruits is lime. In this work, powdered inner lime peel (particle size: 0.125-0.250 mm) was selected as raw solid substrate for the study of aqueous succinic acid solutions as solvent for pectin extraction. A Box–Behnken design of experiments was performed to evaluate the effect of four variables: the pH of the extracting solution (range: 2.3-3.3), which is directly associated with the concentration of succinic acid; the extraction time (30-120 min); the temperature (40-100 °C); and the liquid-to-solid ratio (10-40, in volume/weight) [4]. The results revealed that the highest yield, 18.2 % was achieved with pH 2.3 at 100 °C for 70 minutes, with a liquid-to-solid ratio of 40 (v/w). The pH was found to be a particularly relevant variable in the maximisation of the extraction yields. An initial assessment of the chemical identity of the extracted pectin and of its degree of esterification characterisation (a key characteristic in determining the set of applications for which it would be particularly useful) was performed by Fourier-transform infrared spectroscopy. The extracted pectin extracted at the optimal conditions was found to have a degree of esterification of 78 %, thus classifiable as low methoxy pectin. Thermal stability was confirmed by thermogravimetric analysis. Additional characterisations included ash content, moisture content, galacturonic acid content, and rheological studies, confirming the purity and quality of the extracted pectin.

The results demonstrate that aqueous solutions of succinic acid can be an efficient and biobased alternative for pectin extraction processes, offering a viable route for the valorisation citrus fruit peels. Future studies will expand on this work by applying the method to other citrus peels and exploring additional organic acids to further advance sustainable pectin production practices in the industry.

Acknowledgements
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A comparative study of leather dyeing with different colourants: synthetic *versus* natural mordant

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Synthetic dyes harm water bodies by contaminating effluents, which affects aquatic life [1]. Natural dyes derived from plants and insect secretions have emerged as a more sustainable alternative [2]. Combined with natural mordants, like tannic acid, these dyes offer a safer and more eco-friendly solution for the leather industry. In this study, leather dyeing tests were conducted using five different natural dyes sourced from various plants and insects, namely: Kareel – Myrobalan (*Terminalia chebula*) fruit, Mallow – Pomegranate (*Punica granatum*) fruit rind, Nimbus – secretion of *Kerria lacca* insect, Rubia – *Rubia cordifolia* root, and Yeliona – a blend of Marigold (*Tagetes erecta*), Tesu (*Butea monosperma*), and Kamala (*Mallotus philippensis*) plant. A natural mordant, tannic acid, was compared with a metallic mordant, potassium aluminium sulphate.

The results showed that tannic acid performed similarly to the synthetic mordant in some cases (especially with Rubia and Yeliona extracts), suggesting that natural alternatives could replace metallic mordants in the leather industry (Table 1). Notably, the Nimbus dye produced a distinct purple hue with the metallic mordant, highlighting the influence of mordants on the final colour of the leather piece. These findings emphasise the potential of natural mordants to promote sustainable dyeing practices without compromising leather quality, offering an eco-friendly alternative to synthetic mordants.

Table 1. Comparative results of leather dyeing with natural dyes and different mordants.

	Dyed leather				
Mordants/Dyes:	Kareel	Mallow	Nimbus	Rubia	Yeliona
Tannic acid					
Aluminium sulphate					

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Leather natural dyeing with Mulberry (*Morus alba*) leaf extract: a comparative study with different natural mordants

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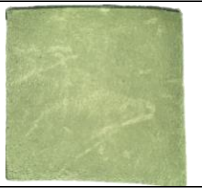
The demand for sustainable and non-toxic dyeing systems has increased in recent years [1]. In the tanning industry, the widespread use of synthetic dyes has led to significant environmental pollution, with discharged effluents causing carcinogenic effects and allergic reactions [2]. As a result, natural dyes and pigments have emerged as a crucial alternative to potentially harmful synthetic counterparts.

In this study, wet-white leather samples were dyed using an extract from Mulberry (*Morus alba*) leaves using various natural mordants, including an aloe vera extract, chitosan, mimosa extract, and tannic acid. A synthetic mordant, potassium aluminium sulphate, was selected as a reference for comparison purposes. The main objective was to investigate the dyeing capacity of the natural colourant face to the used natural mordant, focusing on the colour quality and intensity (measured using a colourimeter) and uniformity (visual inspection). Performance parameters such as colour fastness to light, perspiration, and rubbing were determined to validate the applied colouring system's effectiveness.

Overall, aloe vera extract, mimosa extract, and tannic acid achieved uniform leather dyeing, surpassing the synthetic mordant, which resulted in non-uniform dyeing with some stains (Table 1). Furthermore, because of the moisturising properties of aloe vera, the leather samples treated with this mordant demonstrated enhanced texture and softness, making the leather more pleasant to the touch.

Table 1. Leather dyeing results with *Morus alba* dye: Mordant comparison.

Undyed	**Dyed**				
					
Mordants:	Aloe vera extract	Chitosan 85%	Mimosa extract	Tannic acid	Aluminium sulphate

Acknowledgements

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Enhanced Gelatine Extraction from Tuna Skin Using a Non-Dissolution Ionic Liquid Pretreatment

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The fishing industry generates a large amount of discards, and their management is a current concern with both environmental and economic implications. These discards are usually considered waste. However, they contain valuable materials, such as the collagen found in fish skin. This skin constitutes one of the largest components of the waste in this industry, accounting for up to 30% of it [1]. Consequently, methods for producing gelatine from this collagen are being developed in favour of a circular economy.

The conventional process for collagen extraction involves strong acidic and alkaline solutions, which limit its environmental compatibility [1,2,3]. Ionic liquids present a greener alternative due to their generally lower toxicity and negligible vapour pressure, which facilitate recyclability. Ionic liquids based on basic anions are widely used in the pretreatment of lignocellulosic biomass. It is expected that these salts, with the ability to weaken hydrogen bonds, will facilitate the extraction of collagen from fish skin [4].

In this study, the extraction of collagen was tested using several ionic liquids. The process consisted of two steps. In the pretreatment step, the skin (cut into 5 x 5 mm^2) is macerated with the ionic liquid. The maceration is conducted at a reduced temperature with gentle stirring, to prevent the solubilisation of collagen and the disintegration of the skin. The ionic liquid is then separated by filtration, resulting in minimal residue, which allows for recycling. The skin is washed three times with cold water to remove any remaining salt. In the second step, the skin is immersed in warm water, with gentle stirring, to dissolve the gelatine. The water enriched with protein is centrifuged to decant and remove solids, and the gelatine is recovered by adding acetone to the water to induce precipitation.

High quality gelatine is obtained, exhibiting different rheological properties according to the ionic liquid used. In this way, the process can be designed to produce a gelatine with the specifications required for its final use.

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Enhancing Grid Stability and Sustainability Through Battery Storage Systems Integration with Renewable Energy Sources

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Abstract

The transition to a sustainable energy future is driven by the need to reduce greenhouse gas emissions and combat climate change. One of the most promising approaches to achieving these goals is the integration of renewable energy sources (RES) with Battery storage systems (BSS). Combining RES, such as solar and wind power, with BSS addresses the inherent variability and intermittency of renewable energy, ensuring a more reliable and stable electricity supply [1-3].

This research explores the integration of BSS with RES systems to store surplus energy generated during peak periods and release it during lower production times, thereby addressing these challenges. This study evaluates various types of BSS with a focus on key performance. Additionally, it examines the environmental impact of integrating the BSS with RES systems. By comparing these technologies, the research identifies the strengths and limitations of different BSS solutions in mitigating the intermittency of renewable energy.

The results hihglights the broader environmental advantages of BSS integration, including lower carbon emissions. The study also demonstrates how BSS can smooth out energy supply fluctuations, decrease energy noise, and enhance the reliability of power output, contributing to both grid stability and the long-term sustainability of energy systems.

In conclusion, the research highlights the vital role of energy storage solutions in supporting renewable energy's viability while minimizing the environmental footprint of electricity generation.

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Engineering of Chemically Resilient FTO Current Collectors for Stable and Efficient Upscaled Photovoltaics and Photoelectrochemical Devices for Water Splitting

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The chemical engineering of fluorine-doped tin oxide (FTO) current collectors offers a pathway to overcoming the challenges of scaling third-generation photovoltaics and photoelectrochemical (PEC) devices[1,2]. This work highlights the development of FTO collectors that exhibit exceptional chemical stability, particularly in aggressive environments like highly alkaline solutions used in PEC water-splitting applications and triiodide electrolytes in dye-sensitized solar cells (DSSCs). Through a novel, less corrosive spray pyrolysis method, FTO current collectors were deposited with improved chemical compatibility, addressing corrosion issues associated with traditional Sn(II) chloride precursors. A specialized thermally resistant mask capable of withstanding 500°C enabled the deposition of precisely patterned FTO for efficient current collection without compromising chemical stability.

Multiphysics simulations and experimental studies (**Fig.1**) demonstrated that these chemically engineered FTO collectors maintain electrical performance and resist chemical degradation, leading to significant efficiency gains. Single-cell DSSCs and PEC-WS devices with a 25 cm^2 active area, both integrated with FTO current collectors, demonstrated a 110% and 30% improvement in photocurrent conversion efficiency under AM1.5G, respectively, compared to control devices, while maintaining stable operation during tested 1000 h. An impressive 130% of photocurrent improvement was achieved in PEC-WS devices under concentrated sola light (3Sun), for the first time successfully addressing FTO substrate-originated limitations of concentrated solar light conversion in PECs.

The presentation will discuss future prospects, including the potential for further optimization of chemical formulations and grid designs, which could drive the commercialization of robust, large-area PV-cells and PEC devices for solar energy conversion and hydrogen production.

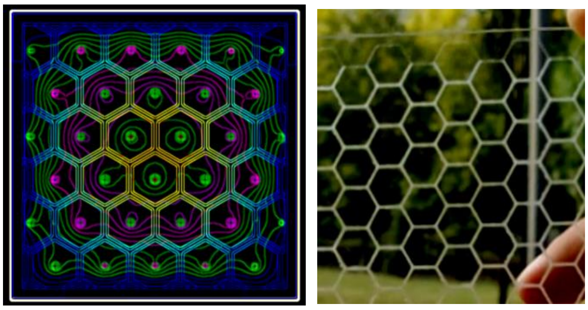

Fig.1. (a) Multiphisics simulation of current distribution and (b) produced collectors on FTO-glass

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Phosphomolybdic acid as a high-capacity electrolyte in aqueous redox flow cell

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Redox flow batteries emerged as a prominent technology for energy storage where energy and power are decoupled metrics, especially suitable for stationary applications. The all-vanadium redox flow battery (VRFB), the most developed and widely commercialized flow technology, has limitations inherent to vanadium chemistry: low volumetric capacity (43 Ah/$L_{negolyte}$ for a 1.6 M electrolyte, 1.37 V is the nominal potential difference), narrow working temperature range (between 5 ^{o}C and 50 ^{o}C), sluggish kinetics, to mention a few. Novel energy storage materials are needed to develop the RFB further.

Polyoxometalates (POMs), with their fascinating ability to reversibly store multiple electrons, reasonable aqueous solubility, and fast kinetics, hold a strong promise for active materials in aqueous RFBs. Despite these attractive features of POMs, only a few works have demonstrated the high-storage capacity of POM-based aqueous RFBs; the most interesting redox species are Dawson type $Li_6P_2W_{18}O_{60}$ and $H_6P_2W_{18}O_6$ [1,2], which can accommodate up to 18 electrons per cluster [2]. The Keggin-type redox species $H_4SiW_{12}O_{40}$ exchange two electrons [3], and four electron transfer is reported for $Na_{4.75}H_{4.25}[PV_{14}O_{42}]$ [3] and $H_6ZnW_{12}O_{40}$ [4].

This study presents for the first time the use of phosphomolybdic acid (PMA), a Keggin-type POM available commercially, for high-capacity negative electrolytes in aqueous RFBs. This work comprehensively examines the impact of PMA concentration on negolyte discharge capacity, limiting current and power density. The impressive high discharge capacity achieved (126 Ah/$L_{negolyte}$) outperforms commercial vanadium electrolytes due to the multiple electron transfer enabled by the POM structure. The developed research includes cyclic voltammetry showing numerous redox events and galvanostatic flow tests, which confirm the multielectron storage ability of PMA (*ca.*10-12, depending on POM concentration); the exchanged number of electrons was further confirmed using titration measurements. The roots for the high capacity of PMA are discussed. Summarizing, the PMA-based electrolyte offers the potential for aqueous flow systems with superior energy and power densities compared to VRFB, particularly when paired with a complementary counter-electrolyte with comparable or higher capacity.

Acknowledgment

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NANOQUÍMICA Y NANOTECNOLOGÍA

Preparation, characterization and stability evaluation of self-assembled anthocyanins-loaded zein/polysaccharide nanoparticles

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Anthocyanins (ACNs) are crucial water-soluble bioactive flavonoid that not only provide bright colors to fruits and vegetables, but also have many functional activities, such as scavenging free radicals, suppressing inflammation and tumors, inhibiting fat oxidation, preventing metabolic disorders, and protecting eyesight [1]. However, the sensitivity of ACNs to external factors, such as temperature, pH, light, and presence of metal ions has led to low bioaccessibility and restricted their widespread application in food industry during a host of processing procedures [2].

Nanoencapsulation is viable alternative strategy for the delivery and to overcome the instability of environmentally sensitive bioactive compounds [3]. Owing to the high biocompatibility, biodegradability, food-grade proteins and polysaccharides are considered high-quality raw material to prepare nanoparticles for ACNs delivery. Zein contains more than half of non-polar amino acids and has a special structure consisting of hydrophilic upper and lower surfaces and hydrophobic outer surfaces. The amphiphilic nature of zein makes the resultant microspheres an ideal form for the delivery of hydrophilic (e.g. ACNs) [4] and hydrophobic (e.g. curcumin) molecules [5]. However, zein particles have poor aggregation stability when exposed to certain pH, salt, and temperature conditions. In addition, they can be quickly hydrolyzed in the stomach by pepsin thereby releasing any encapsulated ingredients into gastric fluids, which may cause the degradation of pH- or enzyme-sensitive ingredients such as anthocyanins [6]. To date, a strategy to reduce these limitations is the incorporation of polysaccharides as a second polymer matrix that provides stability to zein-based nanoparticles [7].

In this study, anthocyanins-loaded nanoparticles comprising zein and three different anionic polysaccharides (pectin, chondroitin sulfate, λ-carrageenan) were formed using a combined antisolvent precipitation/electrostatic deposition method in pH 4.0. Based on the results of SEM, TEM and DLS, anthocyanins-loaded nanoparticles showed spherical morphology with an average particle size of 102.6-360.4 nm, polydispersity index of 0.214-0.415, zeta potential of -(26.7-42.6) mV and the total ACNs encapsulation efficiency of 68.03-80.55%, depending on the type of polysaccharides and the different adding sequences of the raw materials. Encapsulation efficiency of each ACNs monomers being influenced by their chemical structure. FT-IR spectrum indicated hydrogen bond, hydrophobic and electrostatic interaction showed to be the dominant forces for the stabilization of ACNs. In addition, the anthocyanins-loaded nanoparticles had good colloidal stability to different pH, ionic and storage condition due to the electrostatic and steric repulsion from the polysaccharide coating on the nanoparticle surface.

Agradecimientos
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Interplay Between Spin-Spin Interactions and Molecular Conductance in Boron-Doped GNRs

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Nanoelectronics is progressing towards the creation of smaller and more functional devices. This evolution is currently reaching sizes of just a few nanometers, at which it becomes difficult to prepare and implement certain technological components. In this context, molecules seem to be a plausible alternative to traditional silicon-based systems. In terms of chemical structure, molecular candidates for this purpose must present a delocalized π-conjugated system that facilitates electron transport. An example of such molecules are graphene nanoribbons (GNRs), which can display an outstanding performance as molecular wires [1]. Furthermore, some GNRs exhibit localized spin density at their periphery [2], that provide an extra degree of functionality with potential implications for technology.

Here, we present a clear strategy for synthesizing conjugated GNRs that contain unpaired electrons at the center of their structure. We investigate their molecular conductance and demonstrate how they can be utilized as technological components [3,4].

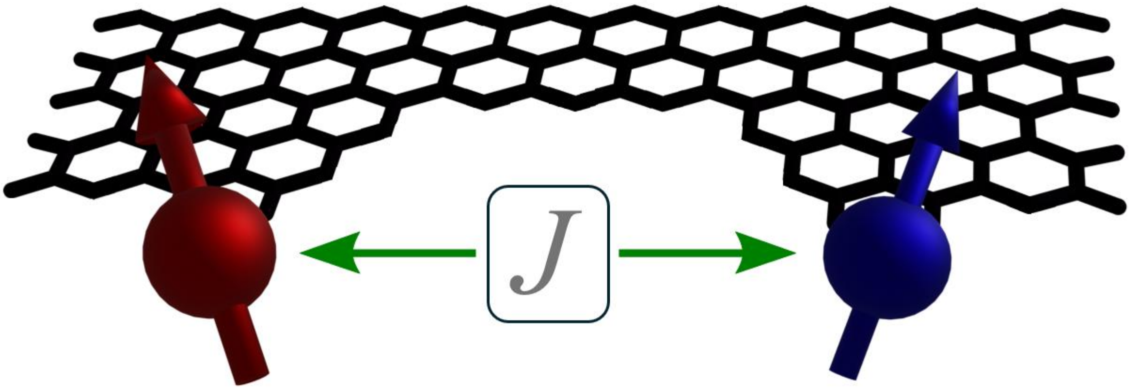

Fig.1. Two spins connected by a graphenoid scaffold.

Agradecimientos

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Emprego de carbon dots como material sensor fluorescente para a detección de nanopartículas de titanio en auga

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As Nanopartículas Inorgánicas (NPs) estanse a incluír nunha gran variedade de produtos, principalmente cosméticos, alimentos e útiles médicos, e existe un certo grao de preocupación en como se liberan esas NPs no medio ambiente [1]. Xunto cos avances nas técnicas nanometrolóxicas para a determinación/caracterización de NPs, o desenvolvemento de métodos analíticos rápidos, de baixo custe e *in situ* son o obxectivo a marcar nestes momentos. Os Carbon Dots (CDs) son un nanomaterial moi axeitado para ser empregado como sensor *in situ* debido a que exhibe un comportamento óptico excelente (propiedades luminescentes), unha baixa toxicidade, e poden ser obtidos mediante varios procesos de síntese moi simples [2, 3].

Nesta investigación, estúdanse as posibilidades dos CDs como un material sensor para a detección de nanopartículas de dióxido de titanio (TiO_2 NPs) en auga. Estudáronse dous procesos distintos para a detección de TiO_2 NPs. O primeiro basease no desprazamento da lonxitude de onda de emisión fluorescente dos CDs debido a aglomeración dos mesmos en presenza de TiO_2 NPs. O segundo método baséase na diminución da fluorescencia dos CDs debido a fotodegradación dos mesmos en presenza de TiO_2 NPs baixo radiación UV (254 nm).

Resultados preliminares amosaron que en ambos os dous procedementos conseguimos unha resposta fluorescente lineal ó incrementar a concentración de TiO_2 NPs nun rango de 25-300 µg/L.

Agradecimientos
Os autores agradecen o financiamento do Ministerio de Economía e Competitividade (FOODNANORISK, referencia PID2021-125276NB-I00) e a Xunta de Galicia (Grupo de Referencia Competitiva, referencia ED431C 2022/029)

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Sol-Gel Coordination Chemistry for sustainable applications

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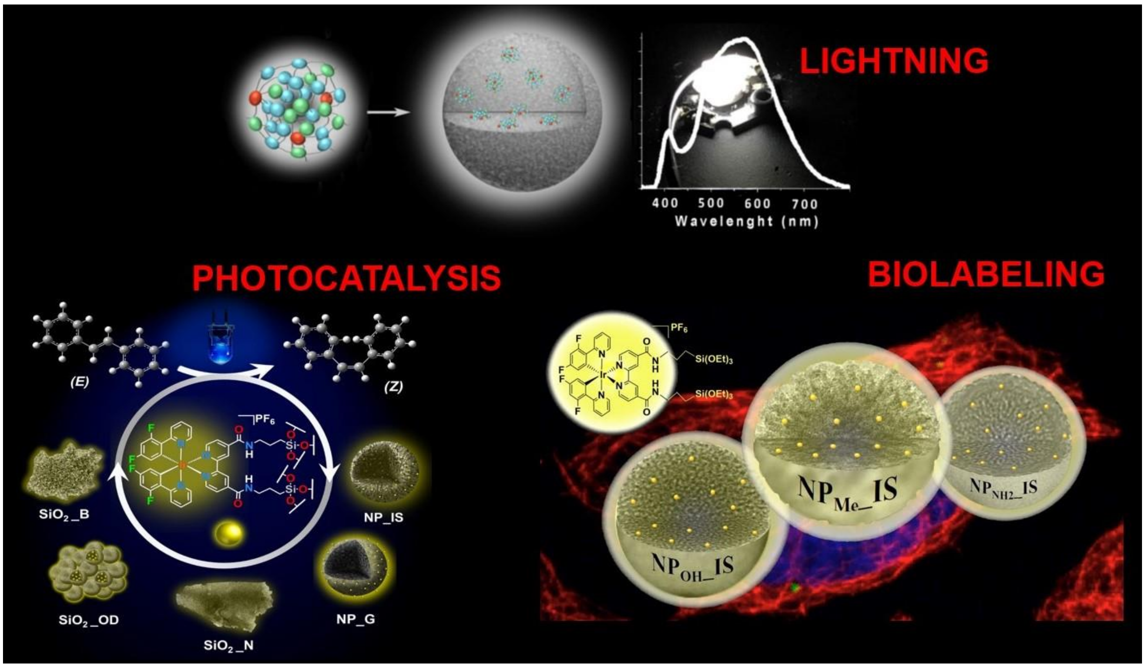
The search for new, efficient photonic materials that comply with the principles of green chemistry (sustainable synthesis, recyclability, etc.) and can be used in energy or biological applications represents one of the major challenges facing chemistry today. In this sense, emissive silica-based nanomaterials have emerged as a particularly promising type of material. [1] In the last years, our research groups have developed an environmentally-friendly one-pot synthetic route, Sol-Gel Coordination Chemistry, for the preparation of highly stable hybrid silica-based materials, containing different types of chromophores (organometallic complexes, perovskite nanocrystals or proteins), which exhibit enhanced luminescence. In this communication, we present part of this synthetic strategy, as well as the applications of these materials as photocatalysts, [2] bioimaging, [3] and in the development of highly stable and efficient HLED. [4]



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MoS_2-Fe_3O_4 nanomaterials for effective water treatment: A study on acetamiprid removal

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Contaminated water remediation has been a subject of extensive study over the past decades due to the limitations of current technologies in ensuring good water quality. Techniques such as photocatalysis and adsorption have been proposed as potential solutions to address the inefficiencies of conventional wastewater treatment processes, particularly in the removal of persistent contaminants, such as pesticides. [1,2] Acetamiprid, a neonicotinoid t pesticide widely used to control *Hemiptera spp.* proliferation in fruit, vegetables and ornamental plants and flowers, poses significant environmental risks upon release.

Molybdenum disulfide (MoS_2), a transition metal dichalcogenide, holds significant promise for use in adsorption and photocatalysis. [2] Additionally, incorporating magnetic nanomaterials into MoS_2 allows for simple, rapid, and cost-effective separation of the catalyst from water, while also potentially improving its effectiveness in photodegrading pollutants.

In this study, MoS_2-Fe_3O_4 nanocomposites were synthesized using the solvothermal method. The nanostructures were analyzed through transmission electron microscopy, powder X-ray diffraction, BET analysis, FTIR spectroscopy. These materials were subsequently applied in the photocatalytic degradation and adsorption of acetamiprid in water samples, with the concentration of acetamiprid monitored using HPLC. The photocatalytic and adsorption efficiency of the MoS_2-Fe_3O_4 nanocomposites and their regeneration potential are discussed, providing insights into innovative strategies for reducing pesticide contamination in aquatic environments.

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Energy monitoring by color change in electrochromic textile supercapacitors using PEDOT:PSS and nitrogen-doped porous carbon from glucose

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A sustainable future requires energy transition, which involves moving away from systems that rely on fossil fuels and towards the development of clean energy technologies. Supercapacitors (SCs), with their extended cycle life and fast charging, show potential as an energy storage solution. The development of multifunctional SCs with sensing capabilities for real-time energy usage monitoring is a current challenge. Electrochromic supercapacitors (ECSCs), which combine energy storage with the capacity to change color reversibly when an applied potential is applied, are being developed as a solution.[1]

In this work, cotton textiles screen-printed with the electrically-conductive polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and N-doped glucose-derived carbon/multi-walled carbon nanotubes (CNT) hybrid as electrode materials and a gel polymer electrolyte were used to develop symmetric and asymmetric ECSC devices with planar structures. The hybrid material presented high specific surface area (1381 m^2 g^{-1}) and micropore volume (0.56 cm^3 g^{-1}). All the flexible devices that were developed successfully stored energy. In terms of electrochromic performance, the asymmetric device and the symmetric device based on PEDOT:PSS presented the greatest color change upon the application of potentials higher than |±1.2| V. In particular, the asymmetric device showed the most significant total color difference (ΔE) of 16 between the reduced and oxidized states of PEDOT:PSS-based working electrode. Concerning the electrochemical outputs, the asymmetric ECSC afforded 4.6 mF cm^{-2} capacitance, 3.4 µW h cm^{-2} energy density, and 610.7 µW cm^{-2} power density, which were respectively 31%, 69%, and 40% higher than the outputs of the symmetric ECSC based on PEDOT:PSS.

This work provides new opportunities for the development of textile-based stimuli-responsive devices with electrochromic and supercapacitive properties for wearable electronics.

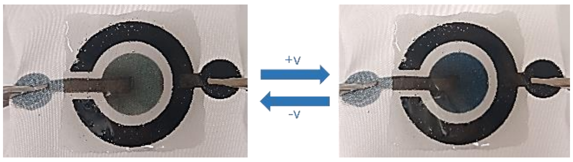

Fig.1. Asymmetric textile ECSC device.

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Magnetic CNT@MnFe$_2$O$_4$-based Thermally-Chargeable Textile Supercapacitor with Glow-in-the-Dark Properties

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The rise of real-time sensing technologies in Society has heightened the demand for efficient energy storage and harvesting systems, which is leading to the development of autonomous smart multifunctional textile devices [1]. Thermoelectric devices convert wasted heat from sources, such as industrial processes or body heat, into electricity, but they generate energy intermittently. Supercapacitors (SCs) complement this technology by storing energy and managing the fluctuations in energy production. The hybridization of both these technologies into thermally-chargeable supercapacitors (TCSCs) opens new avenues for highly efficient, flexible, and lightweight wearable devices – Fig.1 [1].

In this work, multifunctional asymmetric hybrid TCSCs were fabricated using carbon nanotubes (C) and a hybrid nanomaterial composed of manganese(II) ferrite magnetic nanoparticles (~5 nm) immobilized on C (C@Mn) as electrode active materials. Asymmetric devices were constructed with sandwich-like configuration, using PVA/H$_3$PO$_4$ (P) or a glow-in-the-dark doped PVA/H$_3$PO$_4$ (GID) as electrolytes (C//C@Mn_P and C//C@Mn_GID cells). A symmetric CNT-based SC (C//C_P) was also prepared for comparison.

The glow-in-the-dark C//C@Mn_GID device exhibited expanded potential window relative to C//C_P from 2.0 to 2.6 V, as well as enhancements of 153%, 99% and 234% in specific capacitance (40.66 mF cm^{-2}), power density (929.06 µWh cm^{-2}) and energy density (10.26 µWh cm^{-2}), respectively, due to the combination of pseudocapacitive and non-Faradaic mechanisms. Moreover, it presented an excellent cycling stability of 100% after 14000 *i*-*V* cycles. The hybrid TCSC also showed the capability to convert thermal into electrical energy, reaching 17.34 mV under a small temperature gradient of 2.25 K.

These hybrid devices present an innovative solution for thermal energy harvesting and storage, making them ideal for powering low-energy electronics in low-light or dark environments.

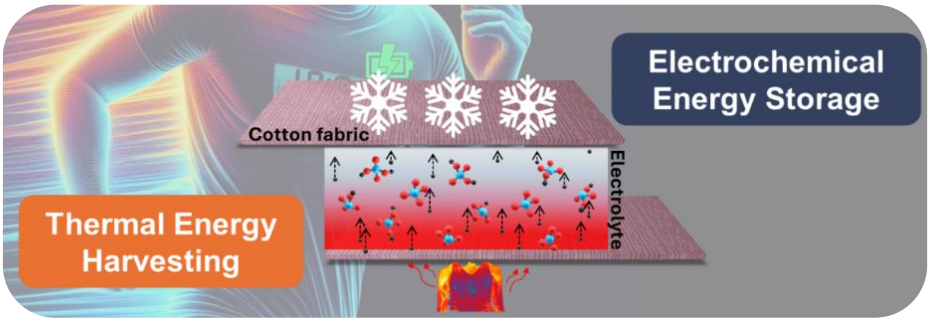

Fig.1. Soret effect in textile TCSC: diffusion of electrolyte ions under a temperature gradient.

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Quantum-dot mediated fluorescence detection of miRNAs

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Variations of microRNA (miRNA) expression can be correlated with several pathologies, making their monitorization essential for clinical diagnosis and prognosis [1]. While promising targets, miRNA characteristics like small size, high sequence homology and degradation proneness are challenges that need to be addressed when developing new precise quantification techniques.

Nanomaterials have been widely employed for new sensing approaches, with quantum dots (QDs) emerging as interesting alternative vehicles for nucleic acid detection. QDs are semiconductor crystals at the nanoscale, with distinctive chemical and optical properties, like inherent fluorescence [2]. In contrast with typical organic fluorophores, QDs have high quantum yields, narrow emission peaks and resistance to photobleaching [3].

In this work, we developed a miRNA sensing scheme utilizing the intrinsic fluorescence of QDs for the detection of miR-122, via Förster resonance energy transfer (FRET)-based interactions with signaling oligonucleotide probes, specifically QDs-ssDNA and Black Hole Quencher 1-ssDNA (BHQ1-ssDNA).

Thioglycolic-acid capped CdTe-QDs, with mathematically projected emission wavelength [4], were obtained via microwave hydrothermal synthesis, and thoroughly characterized. Bioconjugation with ssDNA probes was achieved via carbodiimide chemistry using EDC/NHS (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride/ N-hydroxysuccinimide), with conditions like activation time, incubation time and QD:DNA ratio being optimized, and stability of the conjugates evaluated through absorbance, fluorescence and zeta-potential tracking.

Detection of target miRNA was achieved employing QDs-ssDNA and BHQ1-ssDNA, with nucleotide complementarity to the target miRNA. Upon hybridization, the forced proximity of the two signaling probes creates the necessary Förster's distance to meet FRET requirements. QDs with emission in the 556 nm region and BHQ-1 acted as the FRET donor/acceptor pair, with concentration-dependent quenching of QDs emission, indicating the presence of the target.

Due to the versatility of nucleic acids as molecular recognition probes attached to fluorescent QDs, this detection scheme can be tailored to other potential nucleic acid biomarkers.

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Quantum Dot-Based Nanosensors for Early Detection of Cancer Biomarkers via TR-FRET Technology

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Quantum dots (QDs) possess exceptional optical and chemical properties, making them ideal candidates for use as fluorescent probes in cellular imaging and biosensing. In biomedical research, there is a growing focus on developing new methods that enable rapid and reliable detection of cancer biomarkers, enhancing clinical diagnostics and offering accurate results at early disease stages [1]. Prostate Cancer Antigen 3 (PCA3) is a long non-coding RNA (lncRNA) that is overexpressed in prostate cancer cells, making it a valuable biomarker for non-invasive prostate cancer diagnosis [2].

This study introduces a nanosensor designed to detect circulating PCA3 lncRNAs, addressing the limitations of traditional diagnostic methods, by exploiting time-resolved Förster Resonance Energy Transfer (TR-FRET) between the terbium complex Lumi4-Tb (Tb) and CdTe/ZnS core/shell QDs. The QDs were functionalized with a peptide-DNA through metal-affinity coordination between the hexahistidine tag (His_6) and the ZnS shell of QDs. His_6-DNA on the QD surface can hybridize with Tb-labeled DNA, enabling efficient Tb-to-QD FRET. In the presence of the target DNA, a PCA3 lncRNA analog, the Tb-DNA hybridizes with the target, displacing it from the QD-DNA complex. This results in the QD-DNA becoming unbound, restoring fluorescence by interrupting the FRET process, as Tb-DNA is no longer in proximity to the QDs. The developed sensor achieved detection limits of 0.65 nmol L^{-1} using a benchtop plate reader (SPARK, Tecan) and 0.32 nmol L^{-1} using a clinical plate reader (KRYPTOR compact plus, Thermo Fisher Scientific).

These results highlight the nanosensor's potential for clinical prostate cancer diagnosis, providing a promising tool for early, non-invasive PCA3 detection.

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Análise de glóbulos vermellos expostos a AgNPs mediante single-cell ICP-MS

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A resposta celular á exposición ás nanopartículas é de gran interese para a nanotoxicoloxía e a nanomedicina. As interaccións que presentan as NPs nun medio biolóxico, así como a súa localización e internalización dentro das estruturas celulares, son clave para elucidar o comportamento e os mecanismos das nano-bio-interaccións.

Neste estudo investigouse a exposición dos glóbulos vermellos (Red Blood Cells) a nanopartículas de prata de 40 nm (AgNPs). Os glóbulos vermellos (tamén coñecidos como eritrocitos) son as células máis abundantes do corpo humano e desempeñan un papel fundamental en moitas funcións biolóxicas esenciais, tales como o transporte de osíxeno e dióxido de carbono. Teñen forma de disco bicóncavo e un diámetro aproximado de entre 6 e 8 µm. Durante 8, 12 e 24 horas os glóbulos vermellos foron expostos a dous niveis de concentración de NPs nunha relación 1:1 célula/NP e 1:50 célula/NP. A determinación e cuantificación de AgNPs levouse a cabo mediante single-cell (SC) ICP-MS. Logrouse unha correcta introdución da suspensión celular no plasma utilizando unha cámara Asperon. Debido á heteroxeneidade celular, un método que sexa capaz de proporcionar información a nivel celular individual e non unha información media sobre a poboación celular é moi útil para comprender a diversidade celular. En condicións óptimas de exposición (39 °C, 94,5 % de humidade relativa e 5,0 % de CO_2), os resultados amosaron un aumento da asimilación de NPs por parte das células co aumento do tempo de exposición e concentración.

A técnica de análise SC-ICP-MS demostrou ter un potencial prometedor na determinación de células a nivel individual, proporcionando información célula a célula e axudando así a comprender a diversidade e heteroxeneidade propias dunha poboación celular.

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Breaking bAD: using chemistry, biophysics and biotechnology to unburden Atopic Dermatitis

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Atopic dermatitis (AD) is a worldwide spread common skin condition characterized by skin barrier dysfunction and allergic inflammation. It affects a considerable percentage of children and adults worldwide and can significantly impact their quality of life [1]. Current treatments often involve a baseline topical emollient therapy, but mild, moderate and severe forms require potent corticosteroids and immunomodulators, which can have several limitations, side effects and high associated costs. Being a heterogeneous disease, AD clinical manifestations can vary widely from one individual to another. This raises the awareness for necessary personalized medicine approaches shared by international guidelines, to be applied globally for affordable treatments regardless of the healthcare financial situations.

Chemistry and nanotechnology offer promising solutions for AD. Marine-derived polysaccharides can be used to create hydrogels with enhanced drug delivery, skin retention, and anti-inflammatory properties [2, 3, 4]. These hydrogels can be loaded with active compounds, in this case betamethasone, to target specific aspects of the disease. These systems can be tested through biophysical determinations to study what happens in the skin biological system, and through biotechnology, by creating *in vitro* relevant models of the disease to predict the treatment outcomes.

This research aimed to develop multipurpose hydrogels combining marine polymers and bioactive compounds for AD treatment, to improve skin barrier function and reduce inflammation. Among the key findings, it is highlighted that different hydrogels were successfully developed using marine polysaccharides and loaded with betamethasone, or betamethasone-loaded lipid nanoparticles, with the purpose to achieve enhanced drug delivery and reduced systemic side effects. After physicochemical evaluation the anti-inflammatory effects the designed formulations were demonstrated *in vitro*, cytocompatibility was confirmed in keratinocyte and fibroblast cell lines, improved skin barrier function and drug retention was evident in the porcine ear skin model after analysis of synchrotron-based Fourier Transform Infrared microspectroscopy and Franz cell permeation, respectively. Lastly, when tested in human skin equivalent models of AD, there was an increase in the expression of barrier proteins and decrease in inflammation markers.

Overall, this research demonstrates the combined potential of chemistry, biophysics and biotechnology to break AD symptoms, by designing multipurpose nanoplatforms to unburden this disease.

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Biodispoñibilidade de nanopartículas de Ag e TiO_2 en organismos mariños

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As nanopartículas de prata (AgNPs) e dióxido de titanio (TiO_2NPs) empréganse moito na industria debido as súas aplicacións. Estas partículas, as cales as veces poden ser tóxicas, acaban nos océanos, onde poden ser asimiladas por diferentes organismos mariños consumidos polo ser humano.
As algas e os mexillóns, que son moi consumidos ao redor do mundo, son bioconcentradores da contaminación. Estes organismos poden, por tanto, asimilar diferentes tipos de contaminantes e incluso nanopartículas presentes no medio.
Os fenómenos de bioacumulación de nanopartículas e efectos adversos nestes tecidos demostráronse en estudos previos. Por tanto para garantir a seguridade alimentaria e necesario estudar tamén a biodispoñibilidade destas partículas.

Para isto, estudouse a bioaccesibilidade e a biodispoñibilidade das nanopartículas de Ag e TiO_2 en algas crúas e cociñadas (*Ulva* sp. e *Palmaria Palmata*), e en mexillóns cociñados (*Mytilus edulis*). Todas as mostras foron expostas a 1,0 mg L^{-1} de nanopartículas de TiO_2 de 25 e 5 nm ambas recubertas con citrato, e a nanopartículas de Ag de 15 nm recubertas con polivinilpirrolidina, onde todas as exposición duraron 28 días.
As mostras expostas foron sometidas a un proceso de dixestión gastrointestinal *in vitro*. A biodispoñibilidade estudouse a través do transporte celular das partículas dun intestino simulado ao torrente sanguíneo. Para isto recorreuse ao uso dunha monocapa celular de células de adenocarcinoma humano (Caco-2) que simulaba a parede intestinal. Determinouse o contido total de Ag e Ti empregando o plasma de acoplamento inductivo acoplado a espectrometría de masas (ICP-MS), e o contido de nanopartículas de Ag e TiO_2 empregando o modo de detección individualizada de nanopartículas-ICP-MS (SP-ICP-MS). Ademais, tamén se estudou a presenza das nanopartículas provintes das algas crúas e cociñadas na parede intestinal simulada, empregando para iso, o modo de detección individualizada de células-ICP-MS (SC-ICP-MS).

Os resultados dos porcentaxes de bioaccesibilidade das nanopartículas de TiO_2 situáronse entre o 17-81% no caso das algas e entre o 76-100% no caso dos mexillóns. Os porcentaxes de bioaccesibilidade das nanopartículas de Ag foron entre o 22 e o 98% no caso das algas e o 30% no caso dos mexillóns.
A pesar disto, os transportes celulares das nanopartículas de Ag e TiO_2 foron en todos os casos inferiores ao 1%. Non obstante, as porcentaxes de internalización da prata como NP e do titanio como NP nas células Caco-2 para as algas crúas e cociñadas foron do 9 e do 7%, e do 20% e do 6%, respectivamente.

Cationic polyurea (PURE) dendrimers an Escape from antimicrobial resistance

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Millions of people worldwide face significant risks due to the growing societal impact of complex microbial infections such as biofilm infections. This issue has become even more urgent with the rise of new resistant strains and infectious diseases, demanding swift action. As a result, there is a critical need for the development of antimicrobial drugs with innovative mechanisms of action. The World Health Organization (WHO) has emphasized that the development of new antimicrobial agents should be a top priority for research and development (R&D) programs.

In light of this, we created a unique class of antimicrobial and antibiofilm nanodrugs called engineered polyurea (PURE-OEI) dendrimers [1], which are highly positive charged core-shell nanoparticles that resemble antimicrobial peptides (AMPs). Following a sustainable methodology, the new cationic core-shell PURE dendrimers were synthesized.

Using a variety of multidrug resistant (MDR) bacteria and candida cells, the antimicrobial capacity (MIC, MBC values, and colony count kinetic assay) was evaluated. The outcomes indicate that dendrimers are highly effective in treating multidrug resistant illnesses including having an impact in biofilm adherence and cell density. Using coarse-grained molecular dynamics simulations and electron imaging we were able to show that PURE-OEI exhibit a disruptive activity at the membrane level.

Interestingly, we observed that administering biocompatible doses of PURE-OEI accelerates wound closure in an adapted *in vitro* wound infection model.

With infectious diseases becoming more resistant, cationic core-shell PURE dendrimers represent a breakthrough in the creation of efficient antimicrobial and anti-biofilm drugs.

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Development of Gold NanoProbes for detection of DNA mutations

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Gold nanoparticles (AuNPs) can be used in a great variety of applications in diagnostics, including diseases associated with DNA/RNA mutations due to their atractive optical and spectral properties [1].

The current work focuses on the (i) to synthesize and characterize of spherical-AuNPs; (ii) to functionalize these AuNPs with specific oligonucleotide to obtain stable Au nanoprobes; (iii) development and optimization of a nanotechnology-based colorimetric assay for detection of a DNA deletion mutation of the epidermal growth factor receptor (EGFR) [3,4].

Forty nm spherical AuNPs were successfully synthesized, based on a citrate-reduction method, and further characterized by Ultraviolet-visible spectrophotometry, Dynamic Light Scattering (DLS), Electrophoretic Light Scattering (ELS) and Nanoparticle Tracking Analysis (NTA). Their functionalization was further performed using a pH method, and a thiol-modified oligonucleotides. The pH method afforded Au nanoprobes with good colloidal stability. The optimized nanoprobe was further used in colorimetric assays, when nanoprobes were incubated with target DNA and upon salt induced aggregation, the color of nanoprobes visibly changes from red (negative) to blue (positive) depending on the type of DNA present (Complementary/normal, Mutated or Noncomplementary). In conclusion, we propose an innovative, fast, and simple colorimetric molecular assay for one of the most frequent mutation in exon 19 of EGFR, an important mutation associated with non-small cell lung cancer.

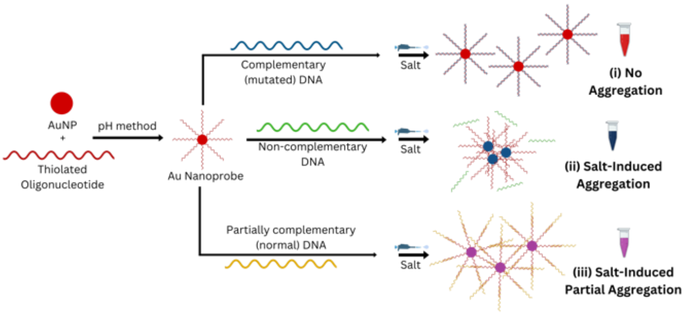

Fig.1. Au nanoprobes for DNA detection based on a Non-Cross linking approack

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Science Inspired by Nature: Milk-Based Delivery Systems

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Delivery systems based on nanotechnology offer wide applications, from nutritional enrichment to therapeutic interventions, and represent an innovative approach, where substances of natural and biological origin have been gaining attention, due to their biocompatibility and efficiency. Within these substances, milk is widely recognized for its role in nutrition and biological functions, which are due to the presence of unique structures such as milk fat globules, casein micelles, small proteins, and extracellular vesicles. [1] Among the various sources of milk, goat, and cow milk are easy sources to obtain and rich in these elements that occur naturally and provide advantages in terms of biocompatibility, low immunogenicity, and ability to cross biological barriers, making them candidates promising for the development of nutrient and drug delivery systems.

The unique properties of milk exosomes, including their natural composition and structural integrity, make them particularly suitable for encapsulating therapeutic agents. Their ability to mimic biological vesicles enhances their compatibility with cellular membranes, facilitating the delivery of drugs directly to target cells. This characteristic is crucial for brain tumor treatments, where effective drug delivery across the blood-brain barrier is a significant challenge. In order to avoid this hurdle, the direct drug delivery to the brain can be achieved by intranasal administration, mainly through the sensory neuronal pathway or indirectly by the passage across the BBB from the systemic circulation.

In this sense, the essential focus of this work is using exosomes derived from bovine milk to treat brain tumors, through targeted delivery of mitoxantrone (EXO-MTX), intranasally. EXO-MTX was evaluated *in vitro* for cell viability and permeability in RPMI-2650 cells, indicating that milk exosomes were not cytotoxic. Additional studies on the SF-268 cell line show the anti-tumor capacity of EXO-MTX as well as a more efficient cellular internalization of EXO-MTX compared to MTX.

Funding

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Acknowledgments

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Engineered liposomes as an efficient strategy for enhancing the treatment of Mycobacterial infections

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Infections caused by nontuberculous mycobacteria, particularly *M. avium*, are becoming increasingly relevant due to their rising prevalence and significant impact on public health, especially among immunocompromised individuals. *M. avium* primarily targets antigen-presenting cells, such as macrophages, where it can survive and replicate, resulting in persistent infections. This persistence leads to considerable morbidity and complicates treatment strategies amid growing concerns about drug resistance [1]. Consequently, there is a rising demand for new anti-mycobacterial therapies that offer improved efficacy and fewer side effects.

Nanoparticle-mediated drug delivery systems are a promising strategy in the management of mycobacterial infections, by addressing issues of non-specific tissue distribution and toxicity, allowing for lower doses, higher selectivity and controlled drug release. In this work, different liposomal formulations were carefully engineered to target antigen-presenting cells, where *M. avium* resides. These include pH-sensitive liposomes that allow for higher drug release at acidic pH and mannose-functionalized liposomes that target mannose receptors, which are overexpressed in phagocytic cells such as macrophages and dendritic cells. The liposomes were loaded with sutezolid (STZ), an antimycobacterial drug currently in clinical trials for extremely drug-resistant tuberculosis, which also shows efficacy against *M. avium* [2]. The liposomal formulations exhibited over 80% of encapsulation efficiency, and controlled drug release at physiological pH, with increased release in acidic environment. All the nanoformulations were efficiently internalized and did not cause cytotoxicity in bone marrow-derived macrophages. Moreover, the encapsulation of STZ did not compromise its antimycobacterial activity against *M. avium* 2447 *in vitro*.

Overall, this research contributes to the development of an effective, host cell-targeted therapeutic modality, with great potential to tackle mycobacterial infections.

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Nanocellulose for Applications in Strategic Sectors: Production, Modification, and Application

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Accelerating the transition towards a regenerative growth model that gives back to the planet more than it takes is the goal of the green transition. Two key aspects are then considered as fundamental: the bioeconomy and bio-based products. Cellulose is the most abundant renewable resource on the planet, making it a key material with great potential. It comes from renewable sources such as wood pulp, cotton, or agricultural by-products, which is highly relevant in the current context of finite resource depletion, particularly those derived from petroleum, and the environmental impact of plastics and microplastics. The development of novel materials, such as nanocellulose derived from cellulosic fibers, and its applications has recently sparked significant interest. Subjected to a mechanical shearing process, nanometric-sized crystalline or fibrillar particles (~10^{-9} meters) with high technical properties are obtained. These cellulose nanoparticles, derived from natural sources, non-toxic, and with high technical properties, are a formidable alternative to several synthetic compounds [1]. Its large surface area, high reactivity, hydrophilicity, excellent mechanical and barrier properties, and chirality, makes it an ideal raw material for a wide variety of high-value-added applications: enhance the strength, stiffness, and other properties of paper and cardboard, the production of highly resistant and lightweight composite materials, the replacement of carbohydrate-based food additives, water remediation, alternative to non-biobased coatings for textiles, among others. Nanocellulose provides three types of advantages: those new functionalities, the potential for reducing production costs (due to its already noted abundance), and sustainability (biodegradable and bio-based).

However, the process of obtaining nanocellulose involves several steps with high energy and time consumption, which affects its final price and, therefore, limits its commercialization at an affordable price. Research on simple and cost-effective production processes is of great interest. Likewise, the modification of its functional groups is important to achieve suitable reactivities for specific applications

In this context, the production of cellulose nanoparticles has been proposed through an innovative process that reduces both energy and time costs, while achieving high properties. Additionally, their chemical and physical modification have been carried out to give them hydrophobic and antimicrobial properties. The nanoparticles and modified nanoparticles have been characterized in terms of fiber size using electron microscopy, viscosity, and functional groups. The results have demonstrated adequate performance in both production and modification for use in high-interest applications.

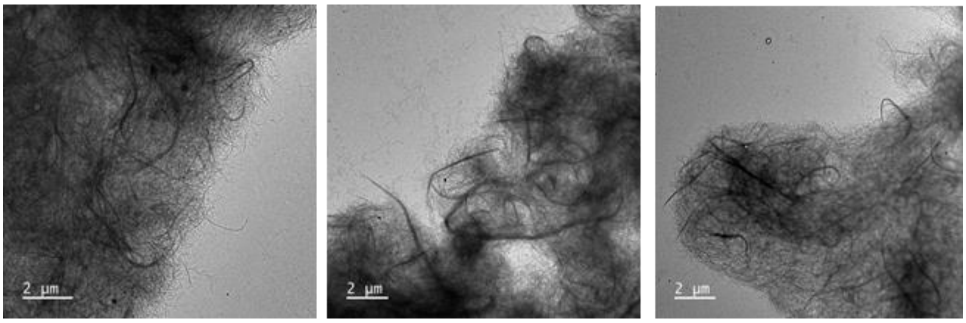

Fig.1. Microscopy image of cellulose nanoparticles obtained using different mechanisms

Acknowledgments
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Plan de Recuperación, Transformación y Resiliencia
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Lipid Nanoparticles in Action: Powering Hyaluronic Acid Production in Skin Cells

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Hyaluronic acid (HA) plays a vital role in skin health, supporting nutrient exchange and protecting against free radicals through multiple signalling pathways [1]. It is imperative in combating the effects of ageing [2], as it helps retain moisture and maintain skin elasticity [3]. To stimulate HA production in skin cells [4], we developed solid lipid nanoparticles (SLNs) composed of lipids and surfactant, loaded with β-carotene, a compound known for its potent antioxidant and photoprotective properties [5].

Our study focused on optimising SLN formulations using two lipids: Glycerol Monostearate (commercial name: Imwitor 900K) and cacao butter. We characterised these nanoparticles in terms of storage stability, size, polydispersity index, zeta potential, encapsulation efficiency, and loading capacity. The SLNs were then evaluated in vitro using fibroblasts and HaCaT cells to determine their ability to enhance HA production via AlphaLISA assays. Additionally, we assessed the photoprotective and antioxidant effects of the nanoparticles.

Our findings suggest that β-carotene-loaded SLNs have the potential to stimulate HA production and may offer enhanced photoprotection and antioxidant capacity, indicating their possible promise as an innovative approach to anti-ageing skin care.

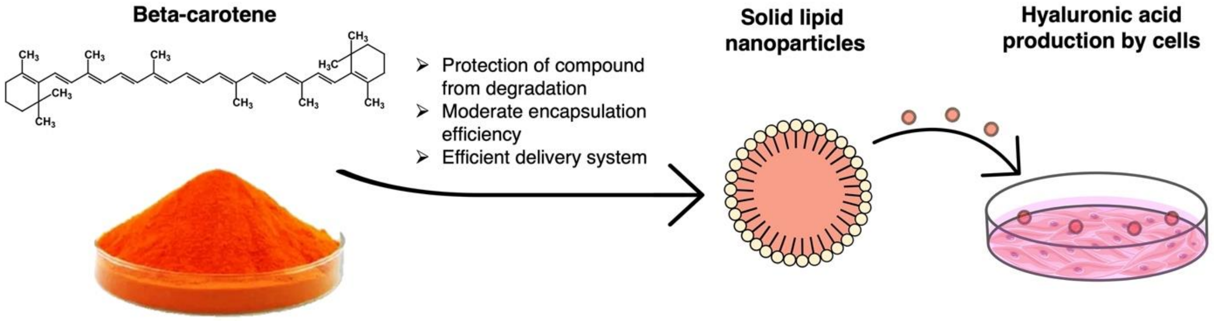

Fig.1. Schematic overview of encapsulation of β-carotene in solid lipid nanoparticles for enhanced hyaluronic acid synthesis in skin cells.

Acknowledgements
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Engineering Efficient Energy Transfer in DNA Hybrid Systems

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The exploration of energy transfer mechanisms is crucial for understanding the efficiency of light harvesting in both natural and artificial systems. In photosynthetic organisms, light absorption and transfer occur through highly organized pigment assemblies within light-harvesting complexes (LHCs), where exciton transport is facilitated by the structural arrangement of pigments. J-aggregates, known for their excitonic properties, exhibit strong coupling among dye aggregates, resembling the behavior of natural pigments.[1]

Recent advancements in the use of DNA as a programmable scaffold have opened new avenues for integrating directional energy transfer with photonic components. DNA hybrids have been shown to effectively mediate energy transfer between donor and acceptor molecules positioned at the ends of the DNA strands, allowing for the efficient relay of energy from an excited donor dye through multiple identical transmitter dyes to a single acceptor fluorophore.[2]

To replicate and understand the natural processes of light harvesting, constructing artificial systems that can efficiently control light transfer is essential. This communication presents an investigation into the energy transfer properties of synthesized hybrid DNA wires comprising 30 and 50 base pairs, with strategically selected donor and acceptor fluorophores attached to their termini. We employed a cyanine dye based on quinoline, known for its ability to form J-aggregates, that served as effective energy bridge and transmitter dye. The mechanisms of energy transfer within these hybrid systems are critically analyzed, providing insights into their potential applications in advanced light-harvesting technologies.[3]

Acknowledgements
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Rosamine-Loaded Metal-Organic Framework: A Bright Sensor for Cu(II) Detection

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Copper (Cu) is an essential trace element with critical roles in various biological processes within the human body. However, an excess of this metal is linked to several neurodegenerative disorders, such as Wilson's, Menkes, Alzheimer's, and Parkinson's diseases. This makes the development of effective sensors for detecting Cu in different contexts (e.g. industrial waste, water systems, and drinking water) a priority [1].

Metal-organic frameworks (MOFs) have gained significant attention in recent years as versatile platforms for applications as selective and sensitive sensors for a wide range of analytes [2]. Their high porosity and tunable structures make MOFs excellent candidates for chemical sensing.

This study focuses on developing fluorescent materials that address the limitations of traditional organic dyes, such as rosamines, which suffer from issues like self-quenching due to aggregation and poor water stability, while maintaining the ability to selectively and accurately detect harmful substances.

To achieve this, a series of new composites were prepared by integrating the rosamine dye, RosCOOH, into the UiO-66 MOF using either physical adsorption or *in-situ* synthetic methods. Our results demonstrate that the *in-situ* incorporation of RosCOOH within the MOF structure produced an efficient nanoplatform for Cu(II) sensing. Environmentally friendly heating techniques, including microwave and ohmic heating, were explored during synthesis [3]. The synthetic approaches and the sensor's performance in detecting Cu ions will be presented and discussed.

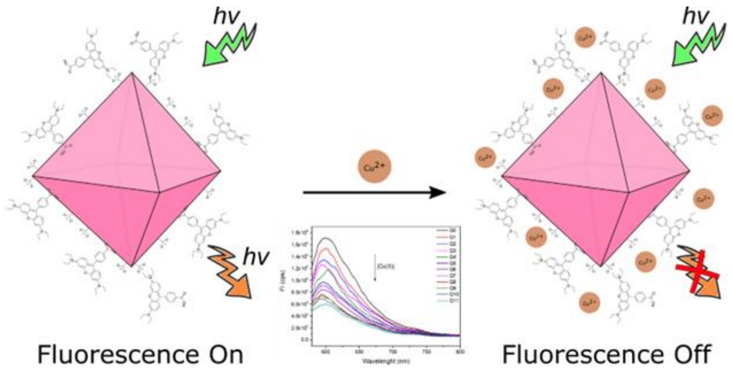

Fig.1. Schematic diagram of the fluorescence detection mechanism.

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Formulation of Ethosomal Suspensions Loaded with *Rubus idaeus* Leaf Extract for Cosmetic Application

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Plant extracts, long valued as active ingredients in cosmetics, have seen increasing adoption by professional cosmetic laboratories in recent decades due to their remarkable bioactivity and potential for innovative formulations [1]. In this context, the use of plant-based by-products, such as those from fruit production, to create new functional ingredients has become especially attractive, given the large generated volumes [2]. Building on the group's previous research and recognising both the potential of *Rubus idaeus* waste and the rising interest in waste reduction in recent years [3], the optimal conditions for producing ultra-deformable liposomes, known as ethosomes, were investigated. A commercial raspberry leaf extract was used as a model extract to determine the optimal encapsulation conditions through response surface methodology (RSM). The ethosomes were produced according to a Central Composite Rotational Design (CCRD 2^2) comprising 11 experimental runs, including 3 replicates in the central point. The CCRD was applied to study the effect of the extract concentration and the ethanol concentration on the size, entrapment efficiency, colour, and zeta potential of the ethosomes. The mass of soybean phosphatidylcholine (lipidic carrier) was maintained constant.

The different suspensions loaded with raspberry extract were characterised by laser diffraction, revealing a mean particle size in volume (D4:3) ranging from 2.48 to 10.80 µm. The entrapment efficiency (EE%) was between 51.79 to 72.25%. The zeta potential ranged from -40.06 to -30.93 mV, while colour parameters L* (lightness), a* (red vs green), and b* (yellow vs blue) ranged from 70.49 to 83.79, -1.17 to 2.39, and 7.89 to 20.52, respectively, Results revealed that vesicle size and colour depend significantly on the defined variables. Further investigation into long-term stability is essential for ensuring formulation effectiveness. Encapsulating plant-based biowaste extracts presents a sustainable solution for the cosmetics industry, decreasing environmental impact while improving product efficacy.

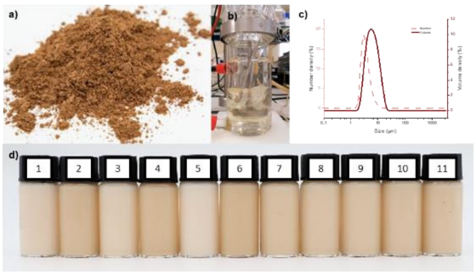

Fig.1. a) Raspberry commercial extract, b) encapsulation system, c) size distributions ethosomal formulation number 3, and d) final visual aspect of the 11 different formulations.

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QUÍMICA DE POLÍMEROS

Proyecto REGATEX: Escalado de un proceso de reciclaje químico de residuos textiles

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De acuerdo con la Orden TED/167/2024, de la Fundación Biodiversidad para el impulso de la economía circular en los sectores del textil y la moda y confección y del calzado en el marco del Plan de Recuperación, Transformación y Resiliencia, para el año 2024, ENCE está llevando a cabo un proyecto de reciclado químico de residuos textiles para incentivar la transformación del sector hacia un modelo sostenible con especial énfasis en la reducción de la generación de residuos e incremento de las tasas de reciclaje. Este proyecto pretende construir, arrancar y operar una planta piloto de reciclado químico de residuos textiles, para escalar un proceso novedoso, que aporta importantes ventajas respecto a los procesos actuales y en desarrollo. En este proceso se revalorizan las fracciones obtenidas con las tecnologías más adecuadas, fomentando la sostenibilidad y circularidad de los procesos industriales y empresariales para mejorar la competitividad y la innovación en el sector textil que nos permita reducir la huella de carbono en el marco de una economía circular, que supere el anterior modelo de producción lineal.

El reciclaje mecánico de residuos textiles está ampliamente establecido en el mercado, pero solo ofrece soluciones para cierto tipo de productos como materiales monocomponente (principalmente, residuos textiles preconsumo, 100% algodón). Por ello, ENCE propone el escalado de una tecnología innovadora desarrollada por ShareTex A.B. para el reciclaje químico de materiales multicomponente (principalmente, residuos textiles posconsumo, de poli algodón), dando salida a otros tipos de residuos a través del proceso de sales iónicas hidratadas desarrollado por ShareTex. La propuesta de ENCE supone un primer paso en el escalado del proceso de reciclaje químico de textiles (TRL de 3-4 a 5-6), el cual ha sido identificado como una de las principales barreras y retos a superar para cumplir con los objetivos medioambientales en este sector. La magnitud de dicho reto queda perfectamente ejemplificada en el hecho de que hoy en día no existe ninguna planta comercial de reciclaje químico de textiles en el mundo.

Esta novedosa tecnología destaca por permitir una amplia versatilidad tanto en las materias primas utilizadas como en el segmento de productos obtenidos. El proceso permite la extracción de celulosa de diferentes tipos de productos textiles (mono o multicomponente), por lo que no depende de un tipo de fibras en particular, además de ofrecer la posibilidad de modificar las propiedades de la celulosa en el producto final, adaptándose a las necesidades de los clientes. Esta capacidad de adaptación permite reintroducir las fibras de celulosa con el máximo valor añadido posible, ya sea como nuevas fibras textiles u otro tipo de aplicaciones. Además, las fibras sintéticas presentes en la materia prima se obtienen de forma controlada y purificadas, permitiendo establecer sinergias con recicladores de este tipo de materiales.

Agradecimientos
El proyecto es producto de un acuerdo de colaboración entre la start-up sueca, ShareTex, A.B.y la empresa ENCE energía & celulosa, S.A.

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Isocyanate-terminated prepolymer synthesis targeting cork composites for the footwear cluster

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Acknowledging the growing demand in the footwear industry for more sustainable production processes, the substitution of synthetic raw materials with bio-based raw materials has emerged [1]. This study focuses on developing polyurethane prepolymers as binders for cork composites to manufacture eco-friendly shoe insoles. The polyurethane prepolymers were formulated with different commercial polyester polyols, with bio-based content between 80 – 100% through the prepolymer process, which generates a polymer containing free isocyanate groups [2]. A reference formulation based on synthetic polyol was also prepared for comparison purposes. The resulting prepolymers were used as binders for cork composite formulation.

Chemical and physical characterisation of the prepolymers were performed to check the stability of the isocyanate groups throughout time by the standard method for determining the NCO content (ASTM D2572-97) and Fourier transform infrared spectroscopy (FTIR). Mechanical tests were carried out to determine the mechanical properties of the cork composites prepared with the best-produced pre-polymers (stress at break "σ", strain at break "ε" and modulus of elasticity "E"), as shown in Fig.1. It was possible to conclude that the synthesised prepolymers showed stability with time and were successfully applied in cork composites, exhibiting promising flexibility and resistance for use in shoe insoles application.

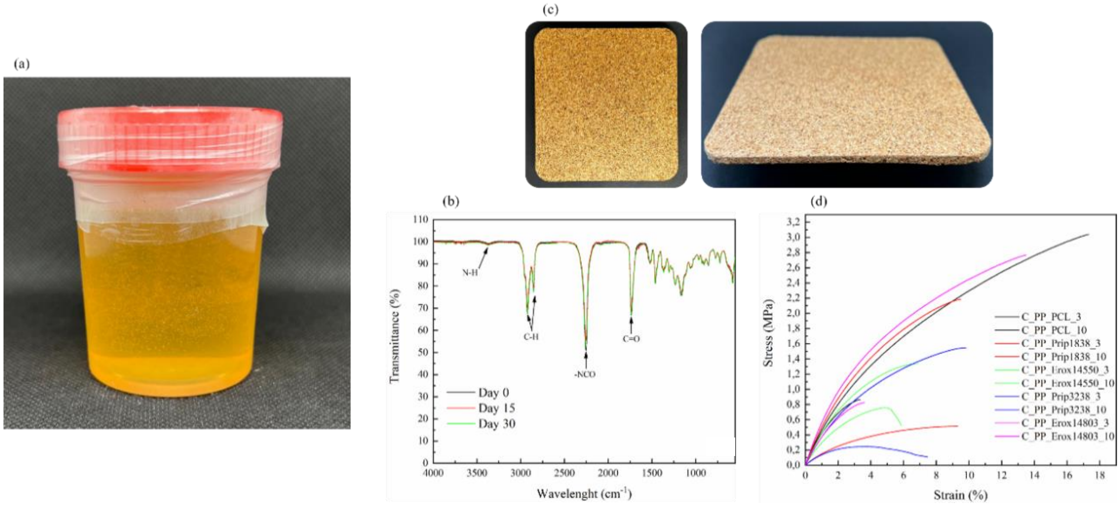

Fig.1. (a) Prepolymer synthesised with 10% NCO Content; (b) FTIR spectra of the synthesised PP with 10% NCO content; (c) Cork composite; and (d) Stress-strain curves at break of cork composites.

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Water-based Polyurethane-urea dispersions as adhesives for the footwear industry: Developing high biobased content solutions

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Waterborne polyurethane-urea (WBPUU) dispersions are versatile polymer systems used in a wide range of applications. Due to their low flammability and toxicity, there is great interest in developing and applying WBPUU as adhesives in the footwear industry, adhering to existing regulations regarding the emission of organic solvents into the atmosphere [1]. To innovate while ensuring sustainable and ecological production methods, new approaches are directed at using renewable raw materials and applying low environmental impact technologies to synthesise these systems [2].

In the present work, WBPUU dispersions were formulated using five commercial polyester polyols featuring biobased content ranging from 80% to 100%. This was achieved through a modified pre-polymer method developed in the research group, adhering to EU regulations [3]. Additionally, a reference formulation using a synthetic polyol was prepared for comparison. The produced dispersions (solids content, particle size, viscosity, and pH) were characterised. Moreover, the adhesiveness performance was checked by evaluating the adhesion strength. Once the dispersions were ready, films were made using Teflon® moulds. Films produced with the dispersions were examined regarding morphology, physicochemical properties, and thermal properties. In conclusion, effective water-based polyurethane-urea adhesives with a biobased content of nearly 70% were successfully developed, showing promising attributes to be used as effective alternatives to current synthetic counterparts.

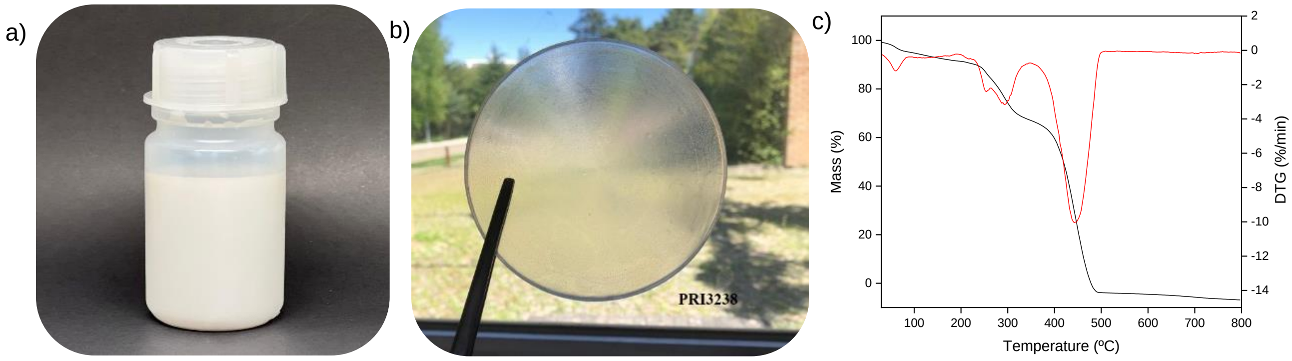

Fig.1. a) WBPUU dispersion bio-based; b) Film obtained; c) Thermogravimetry analysis.

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NIPUs a partir de lignina kraft de ENCE

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Con la creciente conciencia sobre la protección del medioambiente y las preocupaciones de seguridad, la preparación de sustitutos no peligrosos de los PU convencionales bajo el concepto de química verde está ganando mayor interés tanto en el ámbito industrial como en el académico. Entre los candidatos, la síntesis de poliuretanos sin isocianatos (NIPUs -Non Isocianate Poly Urethanes-) se considera una estrategia más eficiente, ecológica y altamente aplicable.

La ruta de mayor viabilidad técnica y medioambiental es la poliadición de diaminas y carbonatos cíclicos de cinco miembros, que incluye la ventaja de no sólo eliminar los isocianatos del proceso de producción, sino también el uso de diferentes tipos de recursos naturales y renovables. [1]

Se ha considerado que la introducción de grupos amino en la estructura de la lignina resulta ser la transformación química más factible, puesto que puede llevarse a cabo a través de una única reacción, conocida como reacción de Mannich, para conseguir una lignina aminada como precursor para la síntesis de NIPUs mediante la vía de poliadición con carbonatos cíclicos.

Se presenta la investigación desarrollada al respecto dentro del proyecto DICKENS (Investigación y optimización integral de composites a partir de fuentes naturales), entre los años 2020 y 2024, y que ha contado con la financiación de CDTI.

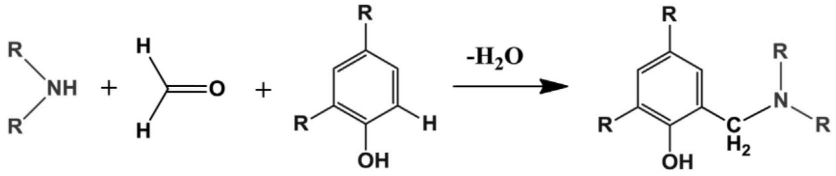

Fig.1. Esquema de la reacción de Mannich.

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QUÍMICA ANALÍTICA

Portable electrochemical biosensing device for point-of-care diagnostics. Applications in communicable diseases

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This study presents the development of a portable biosensing device designed for early and accurate disease identification through the quantification of various biomarkers. The device integrates magnetic actuation and electrochemical biosensing within a battery-operated portable reader (Figure 1, Panel A), offering a versatile and agnostic platform capable of detecting a wide range of biomarkers, including proteins, exosomes, transcripts, DNA, and miRNA (Figure 1, Panel B) [1,2]. This adaptability allows the device to address emerging diagnostic challenges with minimal technological adjustments. The method significantly reduces the time to results, enabling the detection of biomarkers at low concentration ranges using a simplified analytical procedure, making it particularly valuable in low-resource settings and high-income countries where rapid turnaround times and cost-efficiency are essential. The device has been validated for its ability to detect pathogens in both immunosensing and genosensing formats. By combining magnetic actuation with electrochemical biosensing, it can analyze complex specimens without compromising analytical performance or accuracy. Applications include the rapid detection of *Streptococcus agalactiae* in pregnant women and their newborns, the stratification of infectious diseases like sepsis based on fever biomarkers, and the detection of respiratory pathogenic bacteria as *Legionella* or *Mycobacteria* [3]. This flexibility positions the device as a powerful tool for personalized medicine and timely clinical decision-making across diverse healthcare settings.

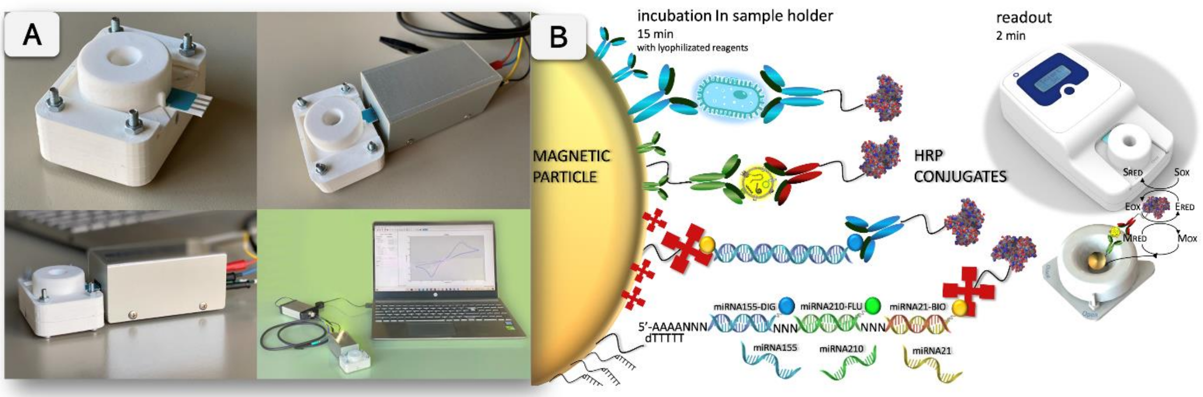

Fig.1. Panel A. Laboratory proof of concept of the biosensing device, containing a cartridge for the magnetic actuation, connected to a portable commercial bipotentiostat. **Panel B.** Molecular strategies integrated in the core of the technology, involving magnetic particle reaction and HRP labelling, and the electrochemical readout on the biosensing platform, which is common for all kind of targets, regardless of their nature. The figure shows the two components (PCT/EP2022/071078): i) Disposable cartridge and ii) Digital reader for the readout. Data may be collected directly from the display of the digital reader and sent by Bluetooth to an App.

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Screening y determinación de plaguicidas en aguas superficiales y subterráneas mediante cromatografía líquida acoplada a espectrometría de masas con analizador de tiempo de vuelo.

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La agricultura convencional emplea diferentes tipos de compuestos fitosanitarios (herbicidas, insecticidas, fungicidas) para el control de plagas que afectan a la calidad y productividad de las cosechas. En el Noroeste de la Península Ibérica, la viticultura hace un uso intensivo de diferentes pesticidas, entre los que destacan los fungicidas. Dependiendo de las características de cada compuesto, y las condiciones ambientales en las zonas de aplicación, una fracción de estos compuestos puede alcanzar las aguas superficiales debido a derivas durante su aplicación y/o transporte asociado a partículas del suelo. Adicionalmente, en función de su estabilidad en el suelo y polaridad, algunos de estos compuestos podrían llegar a contaminar las aguas subterráneas.

Evaluar el impacto de fitosanitarios en las matrices anteriores requiere la combinación de una etapa de concentración con una técnica de determinación, con unas características adecuadas en cuanto a su sensibilidad y selectividad. Habitualmente, estos estudios se llevan a cabo empleando sistemas de tipo LC-QqQ-MS [1]. Aunque resultan imbatibles desde el punto de vista de sensibilidad, estos equipos son ciegos ante cualquier pesticida no seleccionado a priori, es decir, para el que no hayan definido sus correspondientes transiciones. Este hecho representa una limitación relevante debido a la volatilidad del mercado de fitosanitarios, con la introducción continua de nuevos principios activos y la pérdida de autorización de otros. Los analizadores de masas exacta, tales como *Orbitrap* y tiempo de vuelo (TOF), resultan más apropiados en procesos de *screening*. Sin embargo, su sensibilidad se ve afectada por el registro simultáneo de varios canales, tales como la combinación de los modos MS y MS/MS en la misma inyección.

En esta presentación, se discuten las posibilidades, y las limitaciones, de los sistemas LC-QTOF-MS, operados en el modo *Allions*, para la cuantificación de una selección de fungicidas e insecticidas en muestras de agua tomadas en las proximidades de viñedos. El protocolo analítico empleado, incluye una etapa de preparación de muestra combinada en línea con el sistema LC-QTOF-MS. De esta forma, la preparación previa de las muestras se reduce a una etapa previa de filtración y la duración del proceso analítico se reduce a 30 min. Además de la evaluación de los límites de cuantificación de método, se investiga como afecta el modo de pseudo masas-masas a la selectividad asociada al ión cualificador, registrado en el canal de alta energía.

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Identificación de sustancias orgánicas peligrosas en residuos de aparatos eléctricos y electrónicos

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A nivel mundial, los residuos de aparatos eléctricos y electrónicos (RAEE) constituyen uno de los desechos de más rápido crecimiento, impulsados principalmente por los rápidos avances tecnológicos y la obsolescencia programada [1]. Estos residuos comprenden una mezcla compleja de materiales como vidrio, plástico y metales, incluyendo sustancias valiosas y peligrosas. Por esta razón, las Naciones Unidas incorporaron en sus Objetivos de Desarrollo Sostenible un nuevo plan de acción de economía circular que prioriza la reducción de RAEE. Hasta la fecha, el reciclaje de RAEE se centra en componentes reutilizables como el Cu y los metales preciosos [2]. Sin embargo, debido al número limitado de instalaciones especializadas y a los altos costes asociados, el depósito en vertederos, la incineración y la exportación a países en desarrollo siguen siendo las principales alternativas, lo que conlleva riesgos ambientales y sanitarios debido a la presencia de sustancias tóxicas.

Los plásticos constituyen aproximadamente el 20% de los RAEE y contienen altas concentraciones de aditivos diseñados para prolongar su vida útil. Una de las principales barreras para alcanzar una verdadera economía circular sostenible es la falta de información detallada sobre los aditivos químicos utilizados en los distintos plásticos y sus aplicaciones. Por ello, el primer paso hacia un reciclaje seguro es investigar la presencia de estas sustancias.

En este trabajo se investigó la presencia de compuestos orgánicos peligrosos (HOCs) en plásticos de RAEE mediante la cromatografía de gases acoplada a la espectrometría de masas (GC-HRMS). Se desarrolló una nueva metodología análisis de cribado no dirigido (*non-target screening*) para obtener una visión global de los HOCs presentes en estos residuos. Como resultado, se identificaron tentativamente más de 300 sustancias pertenecientes a diferentes familias utilizadas habitualmente como aditivos plásticos, retardantes de llama, PAHs, plastificantes y filtros UV. Se creó una nueva base de datos que incluye los *m/z* y los espectros obtenidos para 339 compuestos, la cual se aplicó para la semi-cuantificación de 52 sustancias. Las concentraciones totales medias obtenidas variaron entre 14,3 $\mu g\ g^{-1}$ y 10.062 $\mu g\ g^{-1}$, siendo el polipropileno (PP) y el acrilonitrilo butadieno estireno (ABS), los polímeros que contienen las concentraciones más bajas y altas, respectivamente. Entre las sustancias detectadas, bisfenol A, tetrabromobisfenol A (TBBPA) y triphenyl phosphate (TPhP) presentaron las concentraciones más altas en las muestras analizadas. Por primera vez, se hace un análisis de HOCs en RAEE y se informa de la presencia de residuos de TBBPA en la cubierta de plástico de los dispositivos de router, lo que apunta a la necesidad de abordar las implicaciones con enfoques integrales, que incluyan la mejora de las prácticas de gestión de residuos, medidas reguladoras y el desarrollo de alternativas más seguras a los HOCs en los productos electrónicos.

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Simultaneous detection of human neutrophil elastase and Cathepsin G on a single substrate using a fluorometric quantum dots probe and chemometric models

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Human neutrophil elastase (HNE) and cathepsin G (Cat G) are crucial proteolytic enzymes involved in the pathophysiology of chronic wounds. High levels of these enzymes indicate prolonged inflammation and impaired healing processes, making their discrimination and quantification essential for effective wound management and treatment strategies [1]. In this study, we propose a novel method combining distinctly sized CdTe quantum dots (QDs) as a fluorescent probe to implement a platform for simultaneous discrimination and quantification of HNE and Cat G, applying chemometric analysis.

The fluorometric response was acquired using two different methods: kinetic and excitation/emission matrices (EEM). These second-order data were processed using various chemometric models, including unfolded partial least-squares with residual bilinearization (U-PLS/RBL), radial basis function artificial neural network (RBF-ANN), and partial least squares-discriminant analysis (PLS-DA), to guarantee a detailed and precise analysis [2]. The results showed that the kinetic method, when processed with the aforementioned models, accurately quantified Cat G in the presence of HNE with a relative error of prediction (REP) of around 20%. This method also successfully discriminated the two enzymes both together and individually, achieving a sensitivity and specificity of 1. In contrast, the EEM method only allowed for the discrimination of the two enzymes both together and individually.

Our groundbreaking approach proved to be accurate for both the discrimination and quantification of one of the enzymes, offering the advantage of being simpler and faster than other reference procedures. This method paves the way for more effective therapeutic interventions and could initiate a path toward the simultaneous discrimination of multiple enzymes.

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Nanosensores Ópticos para la Detección de Iones y Compuestos Volátiles en Muestras Ambientales y Alimentarias

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El desarrollo de nanosensores ópticos presenta un gran interés en el ámbito analítico, ya que estos sistemas simplifican y reducen el tiempo necesario para la detección de los analitos de interés. Concretamente, la interacción/reacción de moléculas e iones con las nanopartículas (NPs) puede producir modificaciones de las propiedades ópticas de las NPs, ofreciendo una gran versatilidad para el desarrollo de sensores químicos. Sin embargo, estos sistemas presentan ciertas limitaciones, entre las que se pueden incluir sensibilidad y selectividad mejorable, consumo relativamente elevado de nanopartículas (NPs) por muestra analizada, así como la posible incompatibilidad de las NPs con las muestras objeto de análisis. Recientemente se han descrito estrategias miniaturizadas que permiten incrementar la sensibilidad y selectividad de los ensayos con NPs mediante su implementación en sistemas de microextracción y su combinación con sistemas instrumentales portátiles [1]. Sin embargo, sería conveniente alcanzar una integración completa de las etapas de preconcentración y detección. Además, el empleo de sistemas de detección no convencionales de alta implantación, tales como los dispositivos de telefonía móvil [2], podría favorecer la aplicabilidad de los nanosensores desarrollados.

En la presente contribución se propone el desarrollo de nanosensores ópticos para la determinación de analitos (o derivados) volátiles mediante la integración de las etapas de preconcentración, reconocimiento molecular y detección. El empleo de sustratos de celulosa hidrofobizados hace posible la exposición de un microvolumen de NPs a la fase gas sobre la muestra para la captación y preconcentración de los analitos (o derivados) volátiles, así como la obtención de imágenes digitales de la gota de NPs mediante el empleo de la cámara de un teléfono móvil sin necesidad de transferir la gota de NPs al compartimento de muestra del sistema de detección correspondiente.

Los métodos desarrollados en base a la estrategia propuesta permitieron la determinación de especies iónicas y compuestos orgánicos presentes en muestras ambientales y alimentarias. Por un lado, las NPs núcleo@corteza de Au@Ag se aplicaron a la determinación colorimétrica de sulfuro en aguas ambientales previa generación *in situ* de sulfuro de hidrógeno, en base al cambio de color experimentado por la gota de Au@AgNPs en presencia del volátil [3]. Además, se desarrolló un nanosensor dual basado en *nanoclusters* de plata (AgNCs) para la determinación de bromuro y sulfito en aguas residuales, siendo posible la detección fluorimétrica y/o colorimétrica de ambos aniones dependiendo de sus niveles de concentración [4]. Finalmente, se diseñó un nanosensor luminiscente basado en *nanoclusters* de cobre (CuNCs) para evaluar la frescura del pescado a partir del contenido de trimetilamina y de las bases volátiles totales nitrogenadas, en base a la disminución de intensidad de fluorescencia de los CuNCs tras la captación de estos volátiles [5]. Los tres métodos descritos se caracterizan por presentar factores de preconcentración elevados (153-181), una excelente sensibilidad y selectividad, y precisión aceptable. Además, se demostró la aplicabilidad de los nanosensores descritos mediante la comparación con métodos de análisis de referencia y estudios de recuperación.

Agradecimientos
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Innovative strategies for trapping metals and metalloids using noble-metal nanoparticles immobilized onto cellulose substrates

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Cellulose paper has been widely used in the past, mainly as pH indicator, in chromatography or in spot tests. At present, cellulose has undergone a revival in the analytical field due to its interesting properties, i.e., high abundance, porosity, biodegradability, excellent sorption capability and the possibility of surface modification [1]. Recently, nanostructured materials such as silver nanoparticles (AgNPs) have been used in cellulose substrates for the preparation of antibacterial papers [2].The present contribution reports on the modification of cellulose filters with noble metal nanoparticles (Ag, Au, and Pd) for enhanced trapping of metals and metalloids and their application in trace and ultra-trace chemical analysis. Different modification procedures, namely physical adsorption, thermal reduction and *in situ* chemical reduction, were extensively evaluated for cellulose decoration with Ag, Au and Pd. *In situ* chemical reduction using sodium tetrahydroborate was finally selected for the preparation of the Ag NPs modified nanosorbents. Cellulose filters modified with Ag NPs were employed for the enrichment of a) Hg (as Hg^0) [3], b) Cd and Pb (after complexation with pyrrolidine dithiocarbamate) [4] and c) As, Sb and Bi (as volatile hydrides) [5]. Two detection techniques were used for analysis, namely a direct mercury analyzer (DMA) and inductively-coupled plasma mass spectrometry (ICP-MS). Particularly, trapped Hg was determined by the direct mercury analyzer (DMA) [3], which allowed the direct combustion of the enriched cellulose substrate followed by atomic absorption spectrometry (AAS). In addition, the determination of Cd, Pb, As, Sb and Bi was performed by ICP-MS [4,5], even though desorption/elution of the elements was required prior to ICP-MS determination. The related variables were carefully evaluated in each application. The developed approaches were applied to the analysis of water samples and reference materials, and their accuracy and precision were assessed. Characterization of modified filter papers was performed by Scanning Electron Microscopy (SEM) combined with energy dispersive X-ray spectrometry (XRS) that showed spherical Ag NPs of 30-60 nm. The developed nanosorbents are affordable and easy to prepare, and a wide range of applications involving noble metal NPs can be envisaged.

Acknowledgements

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DESIGN OF PAPER-BASED ANALYTICAL DEVICES FOR CHEMICAL AND BIOCHEMICAL ASSAYS OF BIOMARKERS IN BIOLOGICAL FLUIDS OF NON-INVASIVE COLLECTION

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Microfluidic paper-based analytical devices (µPADs) are innovative diagnostic tools that combine microfluidic principles with paper substrates to offer simple, portable, and cost-effective solutions. Because they use capillary action, µPADs do not require external pumps or power sources. Colorimetric reactions can be performed directly on paper, allowing for the immediate visual detection and quantification of chemical and biochemical parameters, as health biomarkers. The coloured product can be scanned and quantified through digital image processing, converting colour intensity into absorbance units. These measurements then correlate with the concentration of the individual biomarkers, like glucose and urea, among others, enabling real-time, quantitative analysis with no need for complex equipment. These features make µPADs ideal for point-of-care applications as low cost, portable, ease to use and disposable devices. Recently there also has been an increased interest in the use of saliva and urine as a biological sample for diagnosis and monitorization of several health conditions, since they are more convenient and reduce patient discomfort compared to traditional blood sampling. Non-invasive sample collection is also easier to handle in field settings. It lowers infection risk, making it highly valuable for low-resource environments, remote areas, and situations where rapid, on-site diagnosis is crucial.

This work aimed to combine µPADs' strengths and the benefits of non-invasive sample collection to develop disposable microfluidic devices for rapid, real-time diagnosis of biomarkers in saliva and urine. The designed devices are intended to be an alternative diagnosis tool to complement, not replace, conventional blood analysis. The developed work, focused on optimizing these devices to cover the dynamic concentration ranges of target analytes and minimize matrix interferences in the diagnostic fluids, aiming for high accuracy and reproducibility. Such innovations could significantly improve personalized medicine, early disease detection, and preventive healthcare by making diagnostics more accessible and efficient, especially where traditional laboratory facilities are unavailable or impractical.

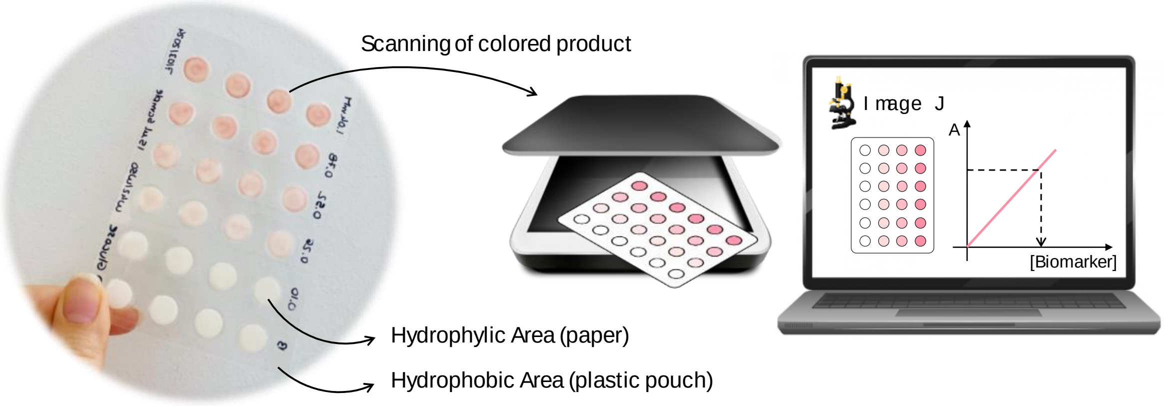

Fig.1. Schematic representation of a microfluidic paper-based analytical device and determination procedure.

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Análise elemental e isotópica de alta precisión de metais para o estudo da metalómica de peixes infectados por parasitos

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Aínda que a investigación das variacións isotópicas naturais de metais esenciais en organismos vivos comezou fai só uns anos, obtívose información reveladora na comprensión do metabolismo e capacidades de diagnóstico. As variacións na composición isotópica de metais, coma o Cu, Fe ou Zn, aínda non están claras, pero parecen estar gobernadas por alteracións na súa captación, metabolismo e/ou excreción. Sábese que o fraccionamento isotópico está relacionado ca cinética e coas diferencias nas enerxías de enlace, polo que se ven afectadas pola coordinación do ligando e das condicións redox.[1]

Neste traballo, avalíase un método analítico para determinar a composición elemental e isotópica do Cu, Fe e Zn en tecidos de peixe mediante espectrometría de masas con plasma acoplado indutivamente de tempo de voo (ICP-TOF-MS) e espectrometría de masas con plasma acoplado indutivamente de multicolector (MC-ICP-MS) e o estudo das variacións intra-individuo da palometa (*Brama brama*) e a do parasito (*Gymnorhynchus gigas*), comunmente presente neste peixe.

O método baseouse na dixestión ácida das mostras e a purificación dos analitos de interese empregando unha resina de intercambio aniónico. Obtivéronse recuperacións cuantitativas (entre 89 e 103 %) para o Cu, Fe e Zn despois da separación, garantindo que non se produce fraccionamento isotópico na columna, e unha pureza das fraccións axeitada para a medida das relacións isotópicas mediante MC-ICP-MS. As concentracións de Cu, Fe e Zn en materiais de referencia certificados (CRMs) de peixes estiveron en concordancia cos valores certificados e as relacións isotópicas de Fe e Zn en concordancia cos valores publicados. [2] Ademais, as liñas de fraccionamento isotópico obtidas cos CRMs, tecidos da palometa e parasito coinciden cas liñas de fraccionamento teóricas dependente da masa. A mostra de parasitos presentou unha maior concentración de Cu, Fe e Zn en comparación co tecido onde se encontra (músculo adxacente) e a tendencia seguida nos tecidos da palometa foi Zn > Fe > Cu. A variabilidade isotópica intra-individuo foi de 0,5 ‰ para o δ^{56}Fe e de 1,6 ‰ para o δ^{66}Zn. O parasito mostrou unha composición isotópica de Fe lixeira debida potencialmente a unha acumulación preferente do isótopo ^{54}Fe do hóspede no parasito e unha composición isotópica do Zn pesada que podería relacionarse ca absorción do Zn do músculo polo parasito.

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Cytochrome P450 Testosterone Biosensor using Modified Carbon Screen-Printed Electrodes

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Cytochrome P450 (CYP450) enzymes, particularly CYP3A4, are essential in phase I drug metabolism and responsible for the biotransformation of around 50-70% of pharmaceuticals. The catalytic cycle of CYP450s typically relies on electron transfer from redox partners. Thus, the use of electrochemical techniques enables direct electron transfer from the electrode to the enzyme, bypassing the need for natural electron donors and simplifying the catalytic mechanism [1,2].

Important factors for CYP450 biosensor development and response include enzyme orientation, immobilization on the electrode surface, and substrate, oxygen and cofactors accessibility. Cross-linked hydrogels are commonly used for enzyme immobilization as they stabilize proteins and create a microenvironment that enhances enzyme activity and nanomaterials as carbon nanotubes can further improve performance, due to fast electron transfer kinetics, and high sensitivity [3].

This study presents the development of a CYP3A4 biosensor for detecting its natural substrate, testosterone. The biosensor employed a commercial carbon screen-printed electrode, modified with a mixture comprising 70 µL of a 5 $mg.mL^{-1}$ synthesized pyrene-linear poly(ethyleneimine) solution, 5 $mg.mL^{-1}$ multiwalled carbon nanotubes, 30 µL of a 10 $mg.mL^{-1}$ CYP3A4 enzyme solution, and 3.75 µL of 13% v/v ethylene glycol diglycidyl ether.

This modification significantly enhanced the electroactive surface area, with a 150% increase and the catalytic system presented a formal potential of -0.274 ± 0.008 V vs. Ag pseudoreference. The sigmoidal shape of the current response as a function of testosterone concentration confirmed the homotropic positive cooperativity in CYP3A4-catalyzed substrate conversion, with a Hill coefficient of 2.4 ± 0.2, an apparent Imax of 2.6 ± 0.1 µA, and a Km of 7 ± 4 $\mu mol.L^{-1}$.

This study highlights the critical role of a correct enzyme immobilization in facilitating substrate metabolization and focuses how enzyme degradation, oxygen concentration and substrate levels significantly impact the biosensor's performance.

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Flow-based method for total protein content monitoring in by-products hydrolysates

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In the past few years, the interest in protein hydrolysates has been growing exponentially due to their nutritional and functional benefits for both human food and animal feed. In this context, total protein content is a key parameter for characterizing by-products, monitoring hydrolysis processes, and hydrolysates. This study aims to develop an accurate and expeditious flow-based spectrophotometric method for total protein quantification in food samples and hydrolysates (Fig.1).

For this purpose, the conventional and reliable Biuret method was used. This method was chosen for its ease of preparation and the use of reagents with associated low toxicity [1]. The flow-based approach consisted of a double injection of the sample and reagent in a continuous stream, resulting in the reduction of the reagent consumption. For the development of the flow injection analysis (FIA) system, essential parameters, including reagent concentration, flow rate and reactor length, were optimized. The method was validated across various matrices, addressing potential interferences, and demonstrated repeatability and reproducibility. This optimized protocol offers a robust, efficient tool for the food industry, enhancing quality control and nutritional assessments.

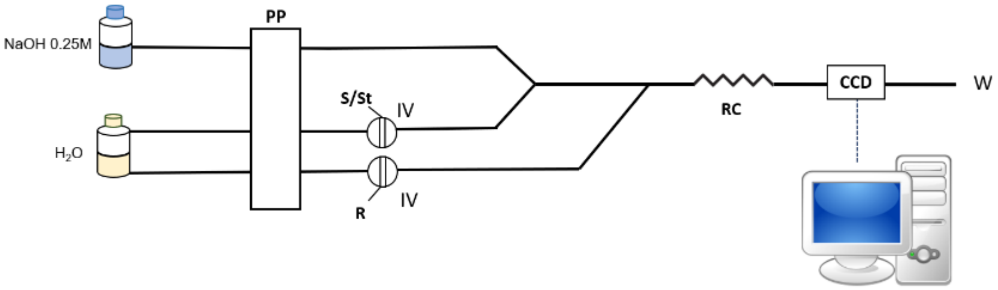

Fig.1. Flow injection manifold for the quantification of total protein content; PP, peristaltic pump; S/St, sample/standard; R, Biuret reagent ($CuSO_4$ 0.028 mol/L; $Na_3C_6H_5O_7$ 0.17 mol/L; Na_2CO_3 0.24 mol/L); RC, reaction coil 100 cm; IV, injection valve with a 400 µL loop; CCD, detector (λ= 554 nm); W, waste.

Acknowledgements

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Utilização de diferentes dados de segunda-ordem para a determinação de tiamina explorando a reversão de um processo FRET entre Pontos Quânticos de Carbono e Nanopartículas de Prata

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A monitorização precisa e seletiva dos níveis de tiamina em suplementos multivitamínicos é essencial para prevenir deficiências e garantir a qualidade do produto final. O uso de nanomateriais como sondas fotoluminescentes para detetar e quantificar compostos de interesse farmacêutico tem ganho importância devido às suas excelentes propriedades óticas [1]. Entre os nanomateriais fluorescentes, os pontos quânticos de carbono (CDs) têm atraído atenção crescente como alternativas aos pontos quânticos à base de cádmio uma vez que oferecem baixa toxicidade, biocompatibilidade e custo reduzido [1]. Neste trabalho foi desenvolvido um sistema de transferência de energia por ressonância de Förster (FRET), utilizando os CDs como dadores de energia e nanopartículas de prata, estabilizadas com citrato (Cit-AgNPs), como aceitadores de energia. As plataformas de deteção baseadas em processos FRET têm sido cada vez mais utilizadas para melhorar a seletividade e a sensibilidade na implementação de metodologias analíticas [2].

A síntese aquosa das Cit-AgNPs com irradiação por micro-ondas foi otimizada para obter nanopartículas plasmónicas eficientes, visando uma intensidade de absorção máxima, estabilidade e para que o comprimento de onda máximo de absorção da nanopartícula coincidisse com a banda de emissão dos CDs. Usando um desenho composto central ortogonal (CCOD), as condições ideais foram estabelecidas: tempo de reação de micro-ondas de 12,5 minutos, razão molar de Ag de 0,72 e pH de 8,28.

Este sistema FRET foi aplicado para a determinação de tiamina, onde a presença da vitamina inibe o processo FRET, restaurando a emissão de fotoluminescência (PL) dos CDs de forma dependente da concentração. Para mitigar interferências de outras vitaminas, os espetros de fluorescência ao longo do tempo (cinética) e as matrizes de excitação-emissão (EEM) foram processados com análise de mínimos quadrados parciais não-dobrados (U-PLS), seguida de bilinearização residual (RBL), alcançando alta sensibilidade e especificidade na deteção de tiamina. Quando foram usados os dados de EEM o método demonstrou precisão e robustez, com um coeficiente de determinação (R^2) de 0,952 e um erro relativo de previsão (REP%) de 11%. Esta abordagem inovadora oferece uma deteção altamente sensível e livre de interferências, com grande potencial para uma ampla gama de aplicações analíticas.

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Innovative extraction procedure based on deep eutectic solvent and cellulose membrane for the determination of synthetic musks in surface waters

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Synthetic musks (SMs), a class of emerging micropollutants, have raised growing concerns due to their persistence in the environment and potential risks to human health and ecosystems. SMs such as Cashmeran (6,7-dihydro-1,1,2,3,3-pentamethyl-4(5*H*)-indanone or DPMI), Celestolide (4-Acetyl-6-tert-butyl-1,1-dimethylindan or ADBI), Galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8,-hexamethyl cyclopenta[*g*]benzopyran or HHCB) and Tonalide (6-Acetyl-1,1,2,4,4,7-hexamethyltetralin or HHTN) have been detected in various aquatic environments, including northern Portuguese rivers (Cunha & Fernandes, 2018), which highlights the challenges of removing these contaminants from water systems, especially with conventional purification methods.

This study introduces an innovative extraction procedure using cellulose paper impregnated with deep eutectic solvents (DES) for extraction of SMs followed by gas-chromatography mass spectrometry analysis (GC-MS). DES is a type of solvent formed by mixing two or more components, typically a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), which, when combined, create a liquid with a melting point much lower than either of the individual components. They are recognized for their exceptional chemical versatility, high selectivity, and permeability, making them excellent candidates for water purification technologies. Cellulose offers mechanical stability, porous structure and sustainability making it an ideal substrate for solvent and sorbent-based microextraction procedures. (López-Ruiz et al., 2023)

In this work, two distinct DES formulations—tetrabutylammonium bromide and hexanoic acid (1:3), and acetic acid and thymol (1:1)—were evaluated using three different cellulose papers (regular cellulose, cellulose nitrate, and cellulose acetate) in the extraction of DPMI, ADBI, HHCB and HHTN in waters. Several other parameters that can affect the extraction efficiency, such as volume of DES, time of impregnation of DES in the membranes, and extraction time, were optimized. Under the optimum extraction conditions, good linearity was achieved for all the tested compounds, DPMI, ADBI, HHCB and HHTN, with coefficients of determination (R^2) higher than 0.9956 for the linear ranges from 0,025 to 25 µg/L. The limit of detection ranged for HHCB and HHTN from 0.0075 to 7.57 ng/g, while for DPMI and ADBI ranged from 0.15 to 7.57 ng/g. The spiked relative recoveries were in the range of 87–103%. This method demonstrated excellent figures of merit and could find potential applications in routine analytical laboratories.

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Binding studies of synthetic cannabinoids to human serum albumin by high-performance affinity chromatography

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Since the early 2000s, the abuse of new psychoactive substances (NPS) has been rising, with synthetic cannabinoids being one of the most reported groups. This group of NPS primarily targets the endocannabinoid system, which plays a key role in various physiological functions. Additionally, their consumption has been linked to numerous reports of severe morbidity and mortality [1,2]. To better understand the behavior of these substances, further toxicodynamic and toxicokinetic studies are essential. Research on their interaction with human serum albumin, the most abundant plasma protein, to our knowledge, remains scarce [3].

This study aims to evaluate the binding affinity of five synthetic cannabinoids (5F-AMB, AB-PINACA, AMB-FUBINACA, AB-CHMINACA and ADB-FUBINACA) through zonal elution chromatography and obtain insights into their binding sites on HSA using displacement experiments. Competitors with well-characterized binding sites on HSA, such as warfarin, (*S*)-ibuprofen, and *L*-tryptophan were selected. Both these studies were performed using high-performance affinity chromatography (HPAC), which is a widely used and effective technique for evaluating intermolecular interactions between HSA and drugs [4,5].

For the binding affinity study, mixtures of potassium phosphate buffer (67 mM, pH 7.0) and acetonitrile were used as mobile phases in reversed elution mode. The binding percentages (%*b*) values ranged from 94 to 95%. AB-PINACA and AB-CHMINACA showed the highest binding affinity, both with a %*b* of 95%. The synthetic cannabinoids bounded to HSA with high affinity, which can interfere with drugs pharmacokinetics by increasing their free fraction in blood, as result of their eventual displacement from HSA or even by its saturation. For the displacement experiment, concentrations ranging 0-20 µM of the competitors were added to the mobile phase. Synthetic cannabinoids were found to bind to different sites on HSA, since direct and/or allosteric competition was observed between the five synthetic cannabinoids and the competitors. All compounds showed allosteric competition for the (*S*)-ibuprofen. Among them, four showed direct competition for the warfarin site. In addition, AB-CHMINACA also displayed direct competition for the *L*-tryptophan site.

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Ensuring food safety: Electrochemical genosensors for the authentication of plant honey origin

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Honey is a high-quality and natural ingredient often consumed because of its unique sweet taste and multiple therapeutic and nutritional benefits [1]. These properties are normally intrinsically connected to the regional flora from which the plant pollen is harvested. Hence, the botanical and geographical origins of honeys play a substantial role in the end product's composition [2].

With the recent interest in natural food products many businesses, including the honey industry, have observed a significant expansion in production and market value [2]. However, honey is susceptible to adulteration and, as more and more adulterated honeys are being found on the global market, it is difficult to monitor the safety and quality of all honey products, making honey fraud a serious problem for both consumers and the food industry [3]. Some of the most prevalent fraudulent acts include mislabeling the botanical and geographic origin of honeys and mixing pure honey with inferior honeys, processed sugars, syrups, and other substances [4]. Thus, there is a need to develop an analytical tool that can quickly, cheaply, and easily guarantee the quality and safety of honey.

In this study, an electrochemical genosensor, based on a sandwich format DNA hybridization reaction between two complementary probes, for the detection and quantification of two pollen producing plant species: *Erica arborea* and *Castanea sativa* were designed and optimized. Analyzing public databases, two synthetic DNA-target sequences capable of unequivocally detecting the pollen from *E. arborea* and *C. sativa* were selected and designed. Their complementary oligonucleotide probes were also designed and cut into two distinct sequences: the DNA-capture and DNA-signaling probes.

In order to recognize the two plant species in real honey and pollen DNA samples and optimize the hybridization procedure, a mixed self-assembled monolayer of each plant species' DNA-capture probe and mercaptohexanol was used. Then, the electrochemical signal was enzymatically amplified using chronoamperometric measurements. A concentration range of 0.03 to 2.00 nM for *E. arborea* and 0.03 to 1.00 nM for *C. sativa* were obtained. The developed sensors were successfully applied for the detection and quantification of the two plant species in real plant samples and, thus, indicate the botanic origin of honeys. Therefore, the developed electrochemical genosensors are a viable and affordable analytical tool to authenticate the botanical origin of honeys, ensuring honey quality and safety for consumers as well as the industries.

Acknowledgments
This work received financial support from national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through project MTS/SAS/0077/2020—"Honey+—New reasons to care honey from the Natural Park of Montesinho: A bioindicator of environmental quality & its therapeutic potential" and through the projects UIDB/50006/2020 and UIDP/50006/2020. MFB thanks Fundação para a Ciência e a Tecnologia (FCT) for the FCT Investigator (2020.03107.CEECIND). Stephanie Morais (2023.028929.BD) and Michelle Castanheira (2023.05159.BDANA) are grateful to FCT and the European Union (EU) for their grants financed by POPH-QREN-Tipologia 4.1-Formação Avançada, funded by Fundo Social Europeu (FSE) and Ministério da Ciência, Tecnologia e Ensino Superior (MCTES).

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N-hydroxyamides' pK_a determination by NMR spectroscopy

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The *N*-hydroxyamides are siderophores present in nature with impact on agriculture and medicine[1-2]. They form metal complexes, mainly with iron(III), which modify the overall concentration of such cations in the aqueous systems. For the building of predictive models where *N*-hydroxyamides are present, their acid behaviour in water, expressed by the pK_a value, must be considered.

We have measured the aqueous pK_a values of five different *N*-hydroxyamides, two *N*-hydroxyimides, and three reference compounds (succinimide, benzotriazole and vanillic acid). Some of them were synthesized in the laboratory, others had been purchased. Due to the impurities or degradation products in some compounds, the ^{1}H and ^{19}F NMR spectroscopy were the chosen pK_a measurement techniques. Measurements were carried out at 298 K. The NMR enabled the identification of the peaks corresponding to the actual measured compounds, even in the presence of impurities. The observed changes in the chemical shifts ($\Delta\delta$) with pH were very close to theoretical relations between $\Delta\delta$ and pH, both for monoprotic and diprotic acids. Both absolute (pK_a) and relative (ΔpK_a between an acid and a reference acid) values were calculated. The ΔpK_a values between different acids were compiled into a ladder scale and, together with the absolute pK_a, used for achieving higher self-consistency and accuracy of the results. The activity coefficients were calculated using the Debye-Hückel theory.

Because of the multiple repetitions and the inclusion of relative measurements against reference pK_a values, we concluded that our pK_a values were more reliable than some literature data. New experimental data were also acquired, such as for vanillic acid, 2,2,2-trifluoro-*N*-hydroxyacetamide and the second acidity constant of 2-(hydroxyamino)-2-oxoethan-1-aminium.

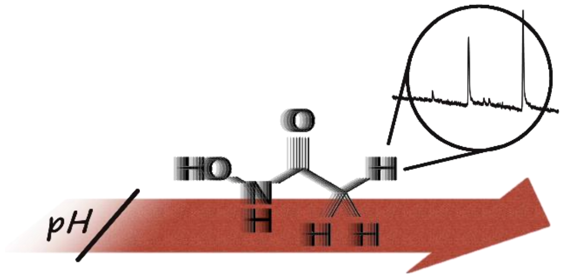

Figure 1. Graphical Abstract – The NMR heartbeat of N hydroxyacetamide running on a pH scale.

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Funding: This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020 and from the Estonian Research Council (grant PRG690).

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QUÍMICA-FÍSICA

Temperature-dependent photoluminescence of trioxoazatriangulenes

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Photoluminescent organic molecules have attracted great interest due to their efficient light absorption and emission, as well as their tunable electronic properties, and versatility in device fabrication. By fine-tuning the optical properties of these molecules, they have the potential to become important building blocks in optoelectronic applications [1,2]. Herein, we report the synthesis of a new trioxoazatriangulene (TOAT) derivative and the study of the temperature-dependent luminescence properties. The new TOAT derivative was functionalized with benzophenone-imine (BPI) moieties which prevent p-p stacking between the TOAT molecules due to steric hindrance, as revealed by the crystal structure. Solid-state temperature-dependent photoluminescence measurements were performed on TOAT-BPI (Fig.1) and the appearance of an intense emission band at 608 nm and the decrease in intensity of a band at 550 nm were observed at low temperature. The correlation of such emission bands was rationalized by theoretical calculations. With further structural and chemical tuning, TOAT derivatives have significant potential for use as luminescent molecular thermometers.

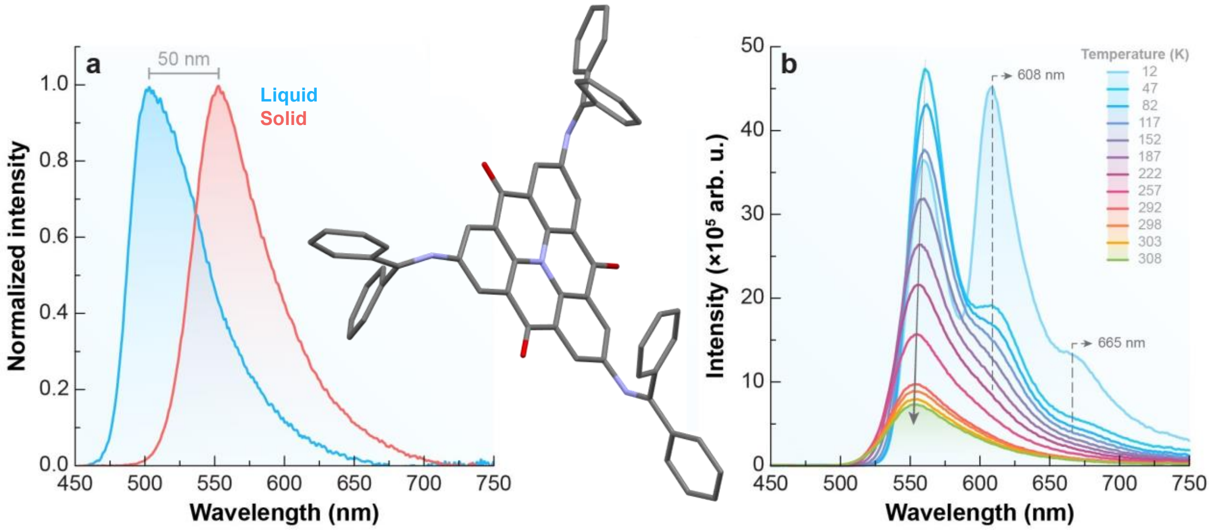

Fig.1. a) Comparison between the emission bands of the **TOAT-BPI** in solution and solid state. **b)** Temperature-dependent solid-state emission spectra of **TOAT-BPI**.

Acknowledgements

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Interaction of cationic gemini surfactants with lipid membranes: a study at the air/water interface

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A very important part of drug delivery is finding the best way to transport the drug to the specific site of action (drug targeting), as well as enhancing its bioavailability. One popular solution to this issue involves using colloids as drug carriers, with examples including vesicles like liposomes or niosomes [1]. One can exploit the varying physicochemical conditions of the specific location as a targeting approach. Among these, the existence of charges, frequently located on the outer layer of cells, leads to thinking of charged vesicles for delivering active ingredients.

To improve targeting and retention of the colloid in negatively charged biological environments, such as bacterial membranes, we suggest the use of vesicles with cationic gemini surfactants in their composition. This type of dimeric surfactants has two polar head/hydrophobic chain structures connected by their headgroups through a variable length alkyl spacer. In this characterization study, we examined a gemini surfactant consisting of two tetradecylammonium bromide monomers connected by an N-alkyl-N chain with twenty methylene groups (14-20-14, abbreviated as GS20) [2]. To achieve this, we spread it from a chloroform solution at the air/water interface in a Langmuir-Pockets trough, enabling them to spontaneously form a monolayer. After making 2 hysteresis cycles of compression-expansion of the monolayer at a constant speed of 15 cm^2/min, we generated the compression-expansion isotherm showing surface pressure (π) vs mean area occupied by each molecule, A [3]. We also made π-A measurements to analyze the interaction between the gemini surfactant and a membrane model consisting of DPPC (1,2-dipalmitoyl-sn-glycero-3-phosphocholine) and a second model with DPPC and cholesterol (100/10 mol/mol). Lastly, we calculated the compressional modulus of the systems studied, a modified derivative of the π-A isotherm which allow us to understand the compressibility properties of the studied monolayer, showing the resistance of the monolayer to further compression.

The resulting graphs highlight that this particular gemini surfactant undergoes a conformational change upon compression, which according to the hysteresis cycle is irreversible. Furthermore, there is an interaction between the GS20 and the studied membrane models, and this interaction is influenced by the presence of cholesterol at the membrane model: for the same values of area, the monolayer with the surfactant and the membrane model with DPPC and cholesterol registers higher surface pressure in comparison with the pure phospholipid membrane model, where the opposite is shown. These differences are also shown in the compressional moduli of the systems.

Our study proves that this gemini surfactant makes it well-worth to expand this study in order to characterize this surfactant more completely, which could facilitate the encapsulation of drugs and their targeting and diffusion through biological membranes.

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Risk of Dietary Supplements: DNA Alkylation by the Nitrosation Products of Amino Acids

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The concern of today's society to maintain good health means that the consumption of different types of dietary supplements is increasing; a very widespread example is amino acids (AA). The intake of leucine (Leu), isoleucine (Ile) and methionine (Met) occurs mainly among athletes seeking good physical performance and recovery/increase in muscle mass [1], although they are also indicated in diets deficient in amino acids and in different pathologies [2]. Ingested amino acids, in the acidic conditions of the stomach, can react with the nitrite used as a preservative in cured meats, giving rise to nitrosation reactions. In this work, the alkylating potential of the nitroso compounds formed from the aforementioned amino acids has been investigated by studying their reaction with 4-(*p*-nitrobenzyl)pyridine (NBP) - a model molecule for DNA bases and a trap for alkylating agents [3]- under biomimetics conditions, in order to evaluate the risk of their consumption as supplements in tumor formation.

Nitrosation mixtures were incubated at pH ≈ 3.5 and 298.15 K or 310.15 K. At different times ($t_{nitrosation}$), aliquots were remove and added to a NBP solution to form the alkylation mixture at neutral pH (as in the cells of the stomach lining into which such nitrosation products can diffuse) and constant temperature. Aliquots of the alkylation mixture were remove at different times ($t_{alkylation}$) and added to the spectrophotometer cuvette containing triethylamine, which stopped the alkylation reaction and stabilized the formed adduct whose absorbance was measured at the wavelength of maximum absorption. Since the nitrosation products are unstable, evidenced by the numerous bubbles formed in the nitrosation mixture, we evaluate the alkylation potential by measuring the absorbance adduct as a function of the nitrosation times, at different alkylation times. Under the working conditions, for Leu, Ile and Met, the $t_{nitrosation}$ to get maximum adduct concentration at 298.15 K were 120, 150 and 15 min respectively and, in the same order, 150, 45, 5 min at 310.15 K. The necessary $t_{alkylation}$ to obtain the maximum concentration of adduct from the nitrosation products of Leu, Ile and Met at 298.15 K were 10, 10 and 5 min and at 310.15 K were 5, 7 and 3 min respectively.

The following conclusion can be drawn:
i) All three amino acids are nitrosated in acidic media, but the rate of the nitrosation reaction of Met is approximately 10 times faster than that of Leu and Ile.
ii) The loss of N_2 in the nitrosation mixture is in agreement with the formation of a highly reactive α-lactone [4], which would be the effective alkylating agents.
iii) The nitrosation products of the three amino acids give rise to alkylation reactions with NBP. The alkylation times to obtain the maximum adduct concentration are quite short, but shorter in the case of nitrosation products of Met.
iv) The alkylating adducts obtained from Leu and Ile are quite unstable, despite this, at 310.15 K, after 150 min still remain the 30-40% of the maximum adduct concentration. In the case of methionine, the adduct is much more stable and at the same time 80% of the adduct remains.
v) The consumption of amino acids as food supplements, and their dosages, should be done with caution and under medical prescription due to the risk of their nitrosation.

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QUÍMICA INORGÁNICA

Luminescente Europium(III) complexes supported on Rice husk ash functionalized with pyridyl groups

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Rice is the second most consumed food item globally and its demand is expected to increase accordingly to the growth of world population.[1] From environmental and economic perspectives, the most logical solution is to utilize industry wastes directly in production. This strategy goes accordingly to the 2030 Agenda for Sustainable Development, that aims to balance three areas of sustainable development: economic, social, and environmental.

Rice husk (RH) is a very important residue composed of 70-80% organic substance (e.g. cellulose, lignin, etc) and 20% inorganic components (silica, alkalis and trace metals). The controlled combustion of RH leads to the formation of rice husk ash (RHA) its composition can vary, but for complete combustion of RH almost pure silica (> 95%) can be obtained [1]. RHA can be used in different sectors as cement and concrete industry, construction of lightweight materials, steel industry, agriculture [2].

Silica, which is transparent to light, and can be easily modified, allowing further functionalization with various functional groups making it an ideal matrix for the immobilization of luminescent complexes. Although there are several reports on silica luminescent materials, only few reports can be found in the literature on the use of silica derived from RHA.

In this work, rice husk ash (RHA) was used as silica support for luminescent Europium(III) complexes. An organic–inorganic hybrid material was prepared, by functionalization of RHA with a pyridyl type group (RHA-py), subsequent reaction with $Eu(btfa)_3(H_2O)_2$ [Hbtfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedione] resulted in a organic–inorganic hybrid material presenting luminescent properties $Eu(btfa)_3(H_2O)$@RHA-py. The characterization, of both inorganic and organic moieties, by a series of spectroscopic techniques, will be herein discussed. With special Photoluminescence studies will allow to analyse the interaction between the Europium(III) complexes and the RHA support, and the effect on the excited states of the organic ligands, and the sensitisation of the Europium(III) ions.

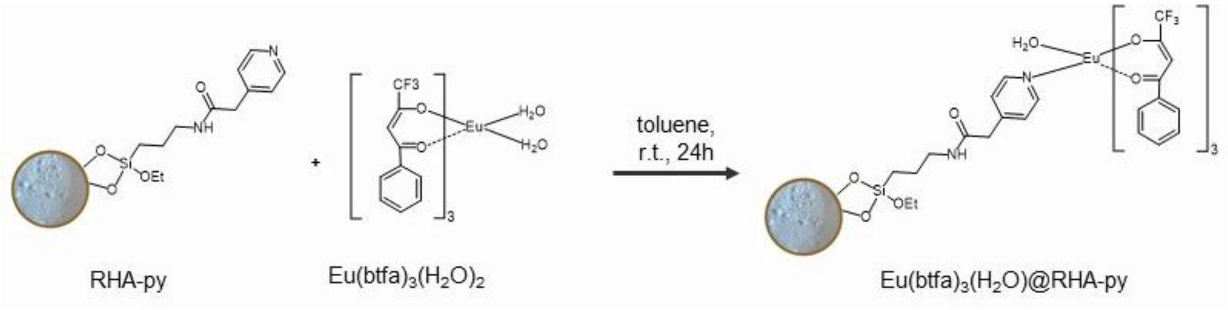

Fig.1. Schematic representation of the organic–inorganic hybrid material preparation.

Agradecimientos

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A dysprosium complex as a novel magneto-luminescent molecular material

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Multifunctionality represents a pivotal objective in the realm of smart materials, offering enhanced versatility and performance. Within this context, the field of magneto-luminescent molecular materials has garnered considerable attention and interest due to its potential for a wide array of applications. A significant challenge in this field is the development of single molecule magnets (SMMs) with temperature-dependent luminescence, enabling them to function as in situ thermometers.[1]

Despite recent progress in this field, several challenges remain unresolved. One such challenge is the development of air stable SMMs with high blocking temperatures (T_b). While milestones like the 80 K achieved with metallocenes are noteworthy,[2] their practical utility is hindered by their air instability. Therefore, there is a need for further research to explore air-stable alternatives.

In this way, we introduce a novel molecular magnet setting a new T_b record of up to 43 K for air-stable unencapsulated SMMs. Our air-stable hexagonal bipyramidal complex $\{[Dy(L)(OSiPh_3)_2](BPh_4)\}\cdot 1.5CH_2Cl_2$ (**1**$\cdot 1.5CH_2Cl_2$) is a single ion magnet (SIM), boasting an impressive energy barrier of 1528 K. However, its robust QTM contributes to a lower T_b, which is removed by dilution in $\{[Dy_{0.09}Y_{0.91}(L)(OSiPh_3)_2](BPh_4)\}\cdot 1.5CH_2Cl_2$ (**1@Y**$\cdot 1.5CH_2Cl_2$). Thus, **1@Y**$\cdot 1.5CH_2Cl_2$ functions serves a dual purpose, operating as a SIM up to the blocking temperature of 43 K and as a luminescent thermometer, for the first time allowing self-tracking the temperature of the magnet below T_b.

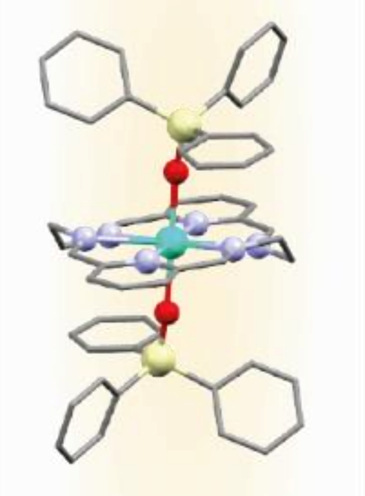

Fig.1. Crystal structure for cation $[Dy(L)(OSiPh_3)_2]^+$ in **1**$\cdot 1.5CH_2Cl_2$.

Acknowledgments

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Bifunctional lanthanoid-based molecular materials: exploring opto-magnetic properties of a mononuclear Yb complex

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Multifunctional molecular materials integrate multiple properties within a single molecule. Molecule magnets gained attention after the 2003 discovery of the first single-ion magnet (SIM), [Tb(Pc)$_2$], which demonstrated slow relaxation of magnetization in mononuclear lanthanoid (Ln) complexes. These Ln^{III} compounds also exhibit unique luminescence, but few have been studied spectroscopically. The first report of Ln complexes combining slow relaxation and luminescence appeared in 2009, but interest in bifunctional materials has grown since studies in 2012 and 2016 linked relaxation dynamics, light emission, and magnetic fields.[1] Lanthanoid-based magneto-luminescent complexes, especially with Dy^{3+} and Yb^{3+}, show potential for spintronics, single-molecule detection, and quantum readout. Although Yb complexes are less studied, they hold potential for optical temperature sensing.[2].

With these considerations in mind, in this study, we examine the opto-magnetic properties the mononuclear complex [Yb(L)Br(EtOH)] (**1**), which was isolated and structurally characterised (Fig. 1a). Besides, the opto-magnetic properties of **1** were investigated, revealing two coexisting functionalities: single-molecule magnetic behaviour induced by an external field (H_{dc}=1000 Oe), and temperature-dependent (11-336 K) Yb^{3+} centred NIR luminescence (Fig. 1b). The magnetic relaxation in this complex is of the Orbach-Raman-QTM type. Moreover, the substantial difference in the energy barrier determined from *ac* measurements compared to luminescence calculations suggests that the Orbach process is not the dominant relaxation mechanism.

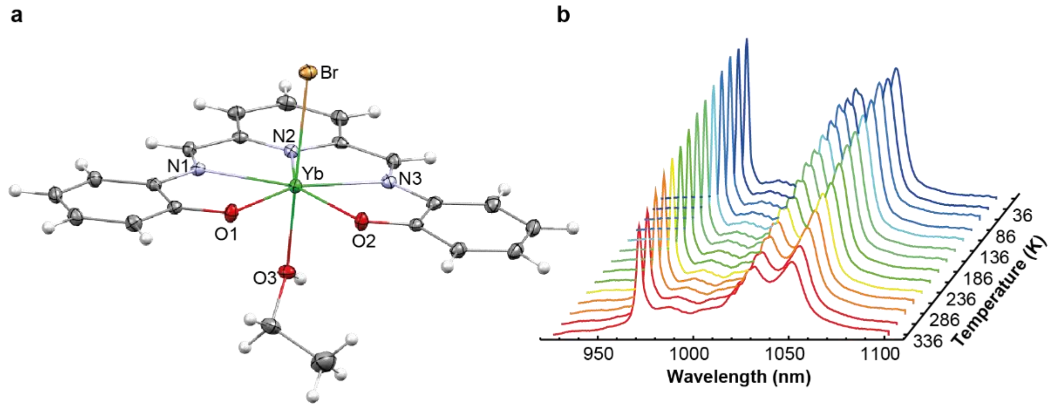

Fig.1. (a) Ellipsoid diagram (50% probability) for **1**. (b) Temperature dependence (11–336 K) of the emission spectra of **1** excited at 390 nm.

Acknowledgments
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Lanthanoid complexes with hexagonal bipyramidal geometry acting as SMMs induced by a magnetic field

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The field of molecular magnetism, in particular single molecule magnets (SMMs), is currently being widely studied in view of its promising applications. These magnets have quantum nature, which would allow them to store far more information than classical magnets, and at unprecedented speeds [1]. Research in this area has focused on lanthanoid SMMs, as they inherently have a high spin ground state and magnetic anisotropy, essential conditions for a compound to act as a magnet. In this sense, the introduction of the Rinehart and Long electrostatic model was a key development, because they established that the geometry surrounding lanthanoid ions plays a crucial role in determining the system's anisotropy [2]. Specifically, for prolate ions, such as Ho^{3+} or Tb^{3+}, maximal anisotropy occurs when ligands promote an axial geometry, such as hexagonal bipyramidal. One effective approach to achieve this geometry is the use of macrocyclic N_6 donors that are designed to occupy the equatorial plane, while anionic monodentate *O*-donors are situated in the apical positions [3].

With these considerations in mind, we present herein the synthesis, structural and magnetic characterization of the hexagonal bipyramidal holmium and terbium mononuclear complexes $\{[Ln(L^{N6})(OSiPh_3)_2](BPh_4)\}\cdot2CH_2Cl_2$ (Ln = Ho, **1**$\cdot2CH_2Cl_2$; Tb, **2**$\cdot2CH_2Cl_2$). As an example, the crystal structure for **1**$\cdot2CH_2Cl_2$ is shown in Fig.1a. The magnetic alternating current (*ac*) studies show that these compounds exhibit SMM-like behaviour induced by an external magnetic field (H_{dc}) of 2000 Oe, as it can be seen in Fig.1b for the Ho^{3+} complex.

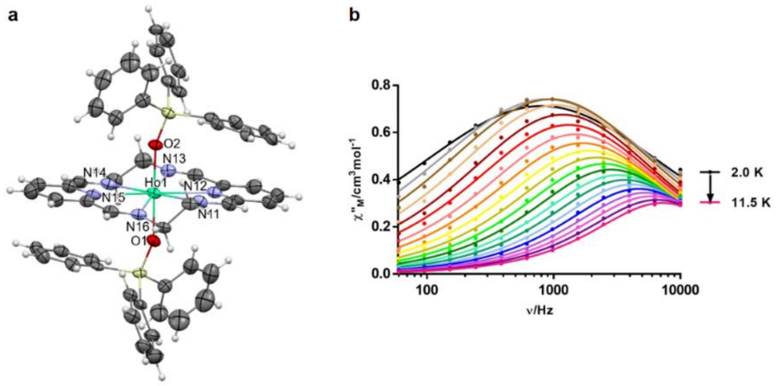

Fig.1. (a) Ellipsoids diagram (50% probability) for cation $[Ho(L^{N6})(OSiPh_3)_2]^+$ in **1**$\cdot2CH_2Cl_2$. (b) Frequency dependence of χ_M'' for **1**$\cdot2CH_2Cl_2$ in a H_{dc} of 2000 Oe at different temperatures.

Acknowledgements
This work was supported by Universidade de Santiago de Compostela (2024-PU027-1) and Consellería de Cultura, Educación, Formación Profesional e Universidades, Xunta de Galicia (convenio 2023-1298).

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QI05

A molybdenum(0)-tricarbonyl metal-organic framework for the storage and release of the gasotransmitter carbon monoxide

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Over the past twenty years, after the discovery of the biological role of carbon monoxide (CO) as a gasotransmitter molecule, metal carbonyl complexes have been intensively studied as CO-releasing molecules (CORMs) for therapeutic applications. To overcome some limitations of the low molecular weight CORMs, researchers have been studying the conjugation of several CORMs with macromolecular and inorganic scaffolds to produce CO-releasing materials (CORMAs). These materials should be capable of storing and delivering large payloads of the gasotransmitter. In the present study [1], a new type of CORMA was investigated, consisting of a crystalline metal–organic framework (MOF) formulated as $Mo(CO)_3(4,4'\text{-bipyridine})_{3/2}$ (**Mobpy**), with a structure based on $Mo(CO)_3$ metallic nodes and bipyridine linkers, which was prepared in near quantitative yield by a straightforward reflux method. This material revealed CO-release properties that mimic those typically observed for molybdenum carbonyl CORMs. **Mobpy** was characterized by several techniques (powder X-ray diffraction, thermogravimetric analysis, FT-IR, FT-Raman and diffuse reflectance UV-vis spectroscopies, and $^{13}C\{^1H\}$ cross-polarization (CP) magic-angle spinning (MAS) NMR. The CO release profile for **Mobpy** was determined by the standard myoglobin (Mb) assay, which uses UV-vis spectroscopy to follow the conversion of deoxy-Mb to carbonmonoxy-Mb. **Mobpy**, under simulated physiological conditions (10 mM PBS, pH 7.4, 37 ºC) and in the dark, led to a CO release of 1.3 mmol g^{-1}, after 1.5 h of incubation, with a half-life of 1 h.

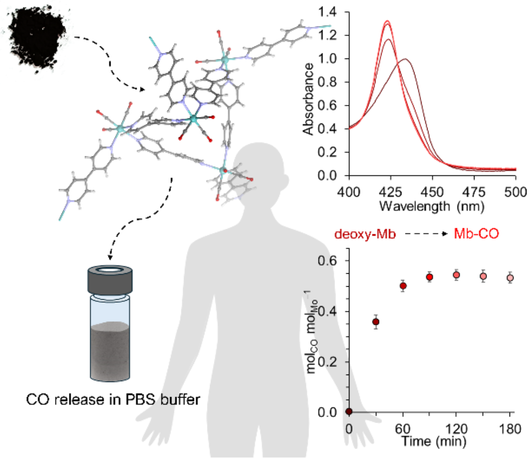

Fig 1. Structure of **Mobpy** and CO release behavior as determined by the Mb assay.

Acknowledgements

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Synthesis of a copper helicoidal architecture derived from an azine ligand

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Helicates are a class of metallosupramolecular architectures that have gained significant attention in recent years due to their potential applications in various fields, such as catalysis [1], materials science, and biomedicine [2]. These chiral structures are formed through the self-assembly of organic ligands and metal ions that are wrapped in an helical mode. Therefore, the design of the ligand and the precise selection of the metal ion are factors particularly important [3].

In this work, we present the synthesis and characterization of a copper helicate (Fig 1) derived from a symmetric azine ligand (H_2L) that exhibits hydroxyl and tert-butyl groups in its branches. Characterization techniques, including X-ray diffraction, mass spectrometry, and NMR spectroscopy, were employed to confirm the synthesis of both the ligand and the metal helicate.

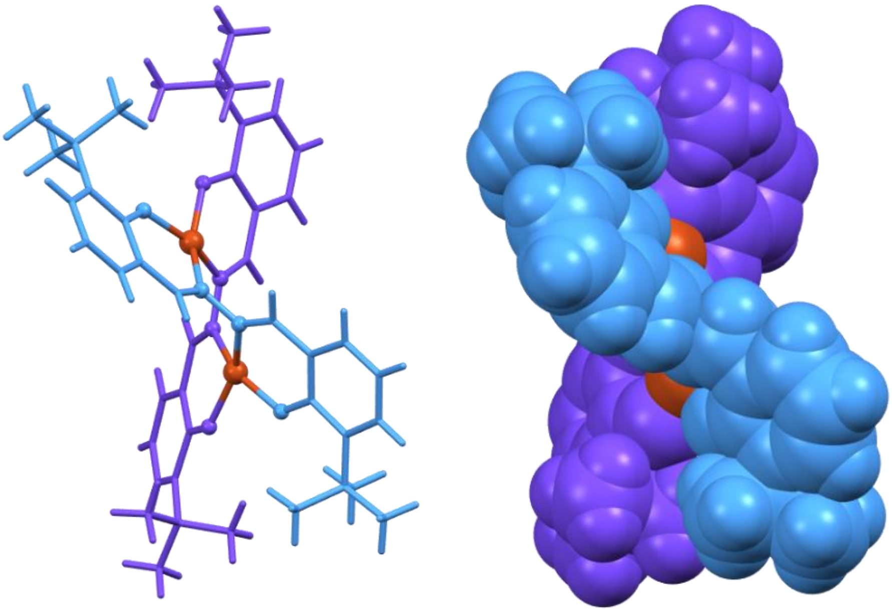

Fig.1. Representation of the copper helicate $[Cu_2(L)_2]$

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Estabilidade da estrutura *closo* de ligandos bidentados neutros derivados de B3-carborano

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Os sistemas coñecidos coma carboranos son clústeres moleculares formados por átomos de boro e carbono que presentan propiedades físicas e químicas especiais, polo que poden servir coma farmacóforos interesantes para o deseño e desenvolvemento de novos fármacos [1-3]. Ademais, recentemente demostrouse que existen diferenzas significativas na actuación dos fragmentos carborano segundo se se presentan na súa forma pechada, *closo*, con todos os vértices do clúster icosaédrico; ou na súa forma aberta, *nido*, coa perda dun destes vértices.

Desta maneira, nesta comunicación preténdese acadar a formación de dous ligandos iminofosforano-fosfina-*o*-carborano bidentados, isómeros estruturais de dous exemplos xa reportados [4]. Unha vez obtidos pode estudarse a estabilidade da caixa carborano a través da complexación dos ligandos, comprobando desta maneira que nestes dous novos ligandos presentados si se mantén a integridade do clúster (Figura 1).

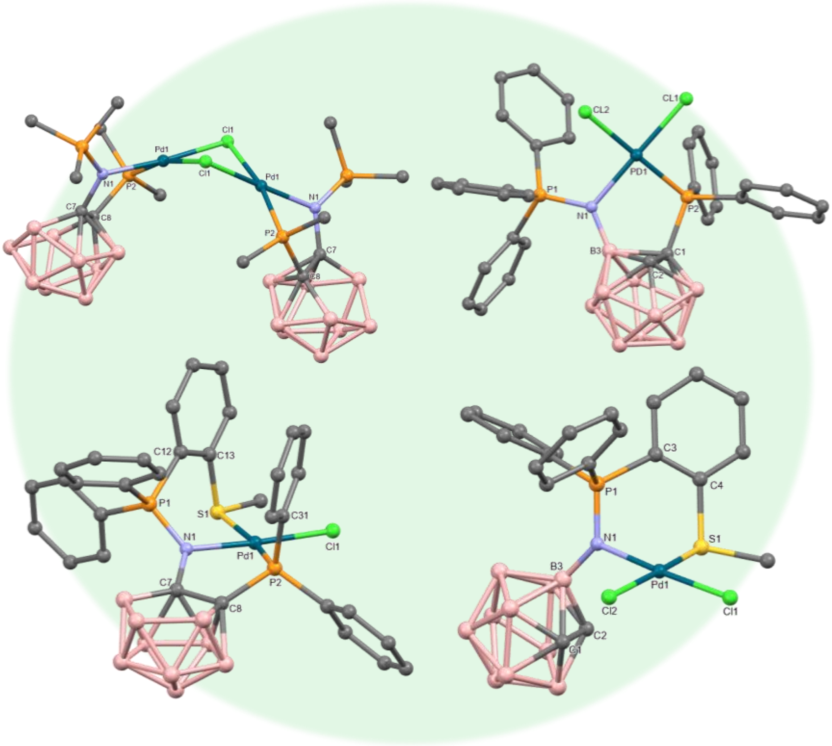

Fig.1. Ligandos iminofosforano-fosfina-*o*-carborano en forma *nido* (esquerda) e *closo* (dereita).

Agradecementos

Esta investigación recibiu financiación das seguintes axudas: Consellería de Cultura, Educación e Ordenación Universitaria (Xunta de Galicia) baixo o proxecto 2018GRCGI-1584 (ED431C2018/13), da rede MetalBIONetwork (ED431D2017/01) e do Ministerio de Ciencia e Innovación (Spain) baixo o proxecto PID2021-127531NB-I00 e RED2022-134091-T.

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Obtención de complexos derivados de ligandos *bis*carbamato e estudo da súa descomposición hidrolítica

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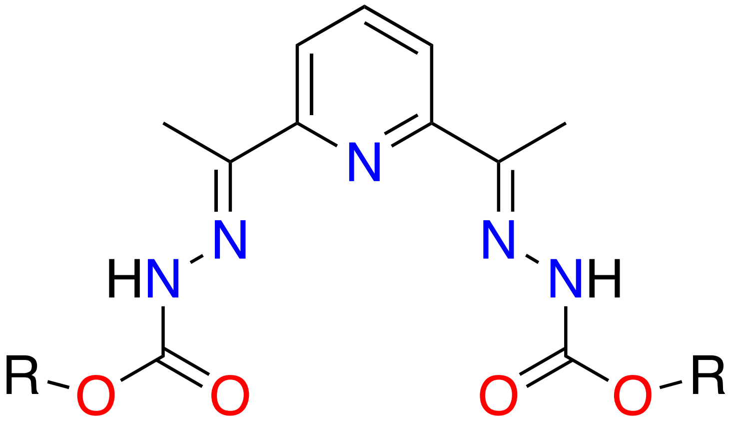
Nos últimos anos, o emprego de complexos derivados de carbamato atraeu a atención da comunidade científica debido á súa aplicación no campo da química médica.[1] O seu interese radica na posibilidade de preparar metalocompostos que actúen como profármacos, capaces de superar a resistencia e minimizar os efectos secundarios dos fármacos derivados de platino(II), que actualmente se empregan para tratar diferentes tipos de cancro. Polo tanto, é preciso estudar en que condicións se hidrolizan este tipo de ligandos, xa que un deseño adecuado dos mesmos podería abrir a posibilidade de liberar o profármaco a través dun proceso de hidrólise.[2, 3]

O noso grupo de investigación ten estudado o comportamento coordinativo dun ligando *bis*carbamato, derivado dunha piridina, fronte a ións metálicos, e o seu proceso de hidrólise.[4] Nesta comunicación afóndase neste estudo. Para isto, emprégase unha serie de ligandos *bis*carbamato funcionalizados con diferentes grupos R nas ramas, e analízase a coordinación aos ións metálicos e o efecto dos substituíntes sobre o proceso de hidrólise.

Fig.1. Estrutura xeral dos ligandos carbamatos empregados



Agradecimientos
Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia, 9 2023GRCGI-1584 (ED431C 2023/02). Ministerio de Ciencia e Innovación, Proxecto PID2021- 10 127531NB-I00 (AEI/10.13039/501100011033/ FEDER, UE) e METALBIO (RED2022-134091-T).

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Luminescent Tb^{3+}/Eu^{3+} complex as optical temperature sensor: design, synthesis, and thermometric properties

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Temperature is a fundamental parameter in science and technology. Traditional sensors, which require direct contact with the sample, face challenges in achieving the high spatial resolution required for applications such as sub-micron scale measurements. Early versions relied on single-transition measurements, but these were prone to errors caused by variations in sensor concentration, excitation power, and the detection system, among other factors. Ratiometric thermometers, which compare the intensity of two emissions, overcome these challenges by offering self-calibration.[1]

Lanthanoid (Ln) complexes are valued for their spectroscopic advantages, including narrow absorption/emission bands, long excited-state lifetimes, and high color purity. The *4f–4f* transitions have an atomic-like character due to shielding by the *5s* and *5p* subshells, minimizing the ligand field effect. Although these transitions are forbidden by Laporte's rule, chromophores act as sensitizers, transferring energy to Ln^{3+} ions *via* the antenna effect. Photoluminescence properties can be tuned by selecting specific lanthanoid ions and ligands. Recently, Eu^{3+}/Tb^{3+} co-doped complexes have gained attention in ratiometric luminescent thermometers, which rely on the luminescence intensity ratio (LIR) between the $^5D_4 \rightarrow {}^7F_5$ (Tb^{3+}) and $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) transitions for precise, sensitive temperature measurements.[2]

In this work, a series of lanthanoid complexes, $[Ln(L^{N6prop})(OAc)_2][BPh_4]$ (Ln = Eu (**1**), Tb (**2**), and $Eu_{0.1}Tb_{0.9}$ (**3**)), were synthesized using the macrocyclic ligand L^{N6prop}. The structures of complexes **1** and **2** were confirmed through by X-ray crystallography. Emission spectra revealed that both complexes exhibit strong luminescence properties. The thermometric behavior of complex **3** was investigated. Furthermore, the relative thermal sensitivity (S_r) and temperature uncertainty (δT) were evaluated.

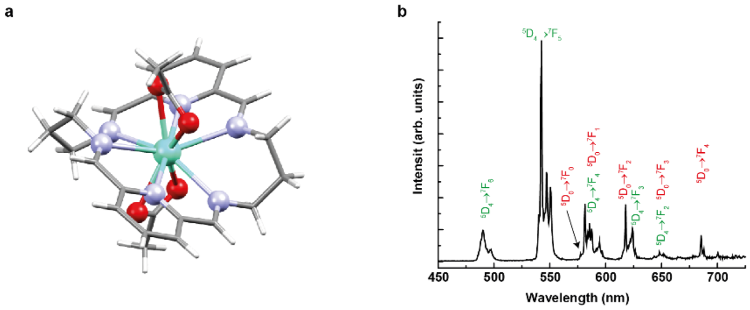

Fig.1. (a) Crystal structure for cation $[Eu(L^{N6prop})(OAc)_2]^+$ in **1**. (b) Emission spectrum for **3** recorded at 12 K under 380 nm excitation.

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This work was supported by Universidade de Santiago de Compostela (2024-PU027-1), Consellería de Cultura, Educación, Formación Profesional e Universidades, Xunta de Galicia (convenio 2023-1298). This article is based upon work from COST Action CA22131, supported by COST (European Cooperation in Science and Technology). J.C.V. thanks Xunta de Galicia for his postdoctoral fellowship (ED481B-2022-068). P.O.-M. also thanks the Fundación Segundo Gil Dávila for her PhD fellowship.

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Fe(III) helicates derived from *bis*hydrazone ligands

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The design of artificial helical compounds derived from metal ions, called helicates, is one of the main goals of metallosupramolecular chemistry. In recent years, these compounds have attracted great interest due to their interesting properties in various fields such as Biology[1], Pharmacology[2] or Material Chemistry[3]. In this context, several iron(II) helicates with the ability to interact with DNA and also with anticancer and antimicrobial properties have been published[4].

Taking into account these previous results, herein we report two iron(III) helicates derived from a family of *bis*hydrazone ligands with different terminal groups, $Fe_2(L^1)_2\cdot 2CH_2OH$ and $Fe_2(L^2)_2\cdot 2CH_3CN$. These helicates were obtained by an electrochemical methodology (Fig.1) and they have been fully characterized by different techniques, including X-ray diffraction studies.

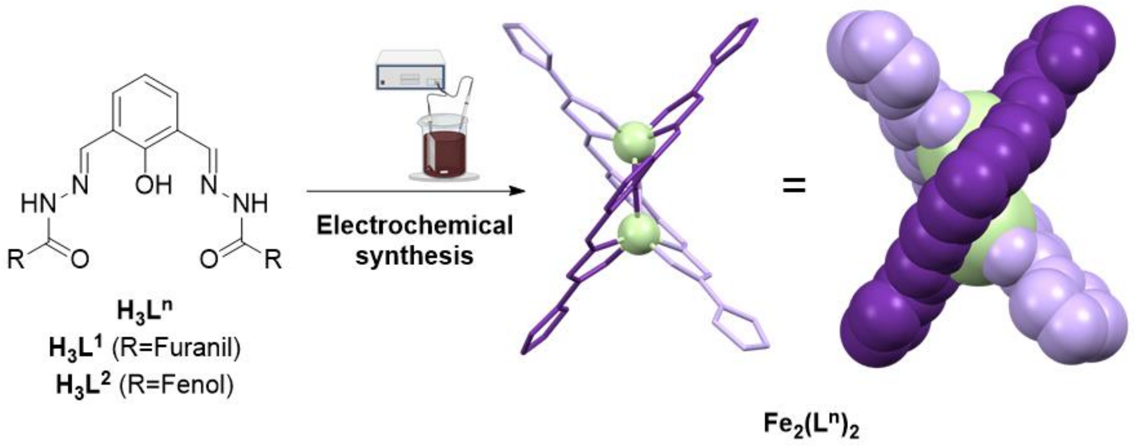

Fig.1. Synthesis of Fe(III) helicates derived from *bis*hydrazone ligands H_3L^n.

Acknowledgments

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QUÍMICA ORGÁNICA

Innovadores Análogos Tipo Gemini con Fragmentos Ciclopropano: Mellora da Eficacia Antitumoral a Través da Modulación do Receptor da Vitamina D

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Neste estudo, informamos do deseño, síntese e avaliación biolóxica de dous novos análogos tipo Gemini, **UG-480** e **UG-481**, que presentan un grupo ciclopropano nunha das súas cadeas laterais. A síntese destes compostos implicou unha reacción clave de ciclopropanación Simmons-Smith, que introduciu de maneira eficiente o fragmento de ciclopropano. Esta reacción foi crítica para mellorar a rigidez e a eficiencia de unión dos análogos ao receptor da vitamina D (VDR), co obxectivo de aumentar as súas actividades antitumorais [1]. As nosas simulacións de acoplamento e dinámica molecular revelaron que **UG-480** de configuración (20*S*), presentaba unha afinidade de unión superior ao VDR, interactuando especificamente con residuos clave como His397. Este composto demostrou unha interacción estable coa conformación activa do VDR, provocando maiores cambios conformacionais na rexión H6-H7 en comparación co seu análogo parental Gemini (**Fig.1.**). **UG-480** demostrou ser tan eficaz como a forma hormonalmente activa da vitamina D_3 (1α,25$(OH)_2D_3$) para inhibir a proliferación de células de adenocarcinoma de mama MCF-7. Por tanto, estes estudos suxiren que estes análogos tipo Gemini do calcitriol que portan un ciclopropano nunha das súas cadeas lateral poderían ofrecer unha vía prometedora para o desenvolvemento de agonistas VDR potentes e selectivos con propiedades antitumorais, abrindo novas vías na terapia do cancro [2].

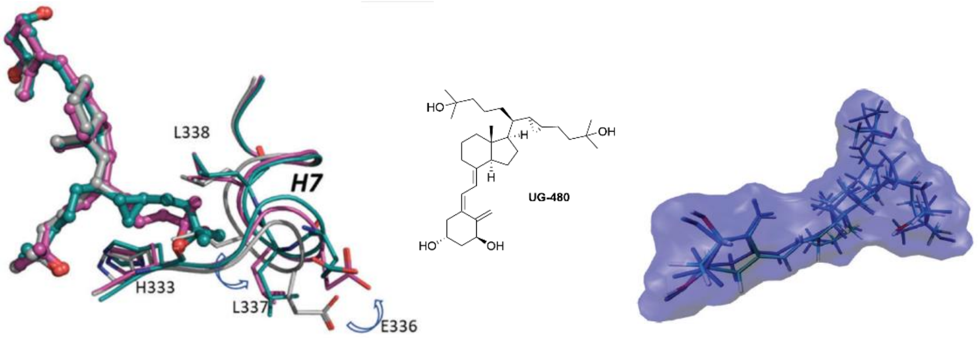

Fig.1. Estrutura cristalina do complexo VDR con **UG-480**.

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Improved synthesis of BODIPY dyes: Batch *vs* continuous flow chemistry

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BODIPY dyes are a class of pyrrolic compounds with many photosensitive applications, such as in photodynamic therapy, biological labelling and fluorescent sensing [1]. However, the synthesis of these compounds, particularly in large scale remains difficult, with much room for improvement [2,3]. In this work, we describe our recent results in the optimization of BODIPY batch chemistry synthesis, and its transposition to continuous flow chemistry, with a methodical analysis of the reaction parameters (temperature, reaction time, reagent concentration and solvents), comparing the specific advantages of batch and flow chemistry, with the objective of achieving gram scale synthesis of these molecules.

The continuous flow process used a microchip reactor for the condensation step, followed by the sequential introduction of oxidant into a coiled tubular reactor. Finally, the complexation of dipyrromethene **A** with boron is performed under batch conditions, giving the desired BODIPYs **B** in high isolated yields (Fig 1).

The developed methodology shown in this work shows promise for an improved and sustainable BODIPY synthesis with good prospects for scaled-up synthesis.

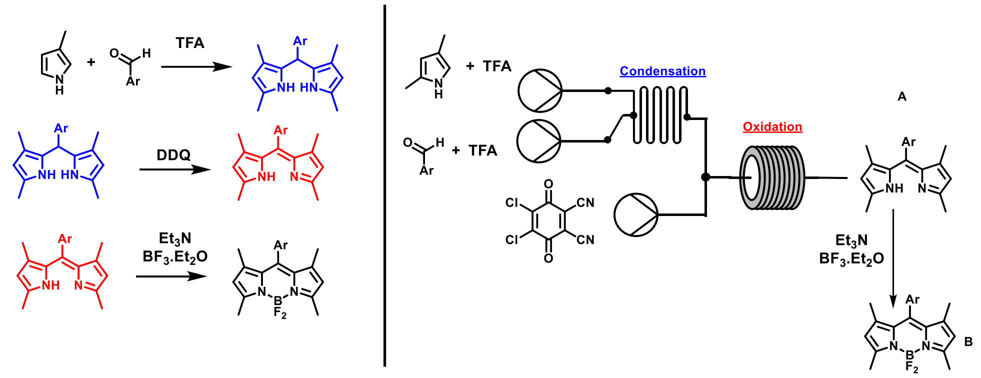

Fig.1. Synthetic route to *meso*-aryl-1,3,5,7-tetramethy BODIPYs.

Acknowledgements

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Derivados do Colesterol: Unha Nova Fronteira para Dirixir os Receptores Orfos Relacionados cos Retinoides Para as Terapias Inmunitarias e Contra o Cancro

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Os receptores orfos relacionados cos retinoides (ROR) son receptores nucleares que xogan un papel fundamental na regulación das respostas inmunitarias, os ritmos circadianos e o desenvolvemento de certos cancros [1]. En particular, RORγ captou especial atención pola súa implicación en enfermidades inflamatorias e de progresión tumorais [2]. Este estudo céntrase no deseño e síntese de novos análogos do colesterol destinados a modular a actividade RORγ. Mediante análises estruturais de cristalografía de raios X e fluorimetría de barrido diferencial, demostramos que estes análogos interactúan eficientemente co dominio de unión ao ligando (LBD) de RORγ, inducindo un cambio conformacional que os converte en agonistas inversos (**Fig.1.**).

Un dos descubrimentos clave é a reorientación dos residuos Trp317 e His479, que estabiliza a hélice H12 e crea un novo canal de unión para unha segunda cadea lateral, estendendo o LBD esteroidal. Este mecanismo inhibe a función de RORγ, suxerindo que estes análogos teñen un gran potencial terapéutico para o tratamento de enfermidades autoinmunes relacionadas con Th17 e cancro. Aínda que necesitan máis estudios para avaliar os efectos biolóxicos e a especificidade destes ligamentos, os resultados abren novas perspectivas na modulación de RORγ [3].

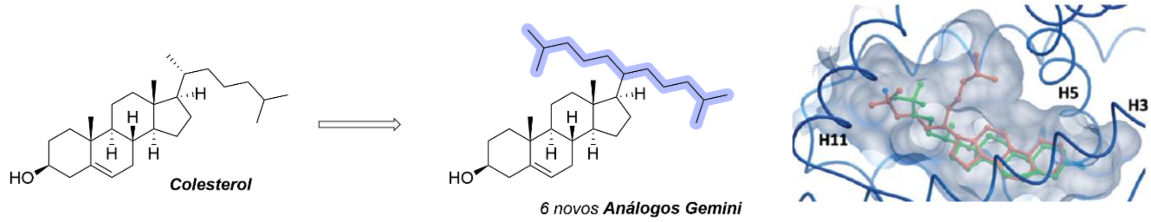

Fig.1. Estudio estructural dos novos análogos tipo Gemini do colesterol.

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A new porphyrin–rosamine conjugate as a potent singlet oxygen generator

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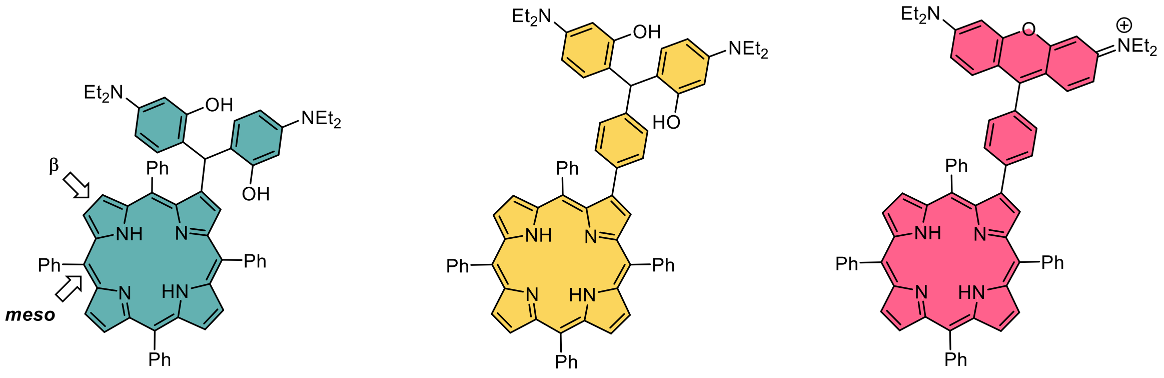
Designing novel molecular structures with tunable photophysical properties is crucial for applications in optoelectronics, sensing, and bioimaging. Porphyrin and rhodamine/ rosamine derivatives are widely studied as chemosensors and imaging probes due to their high absorption coefficients and long emission wavelengths [1, 2]. Recently, porphyrin–rhodamine conjugates have shown promise as photosensitizers for photodynamic therapy (PDT), with cationic rhodamines specifically targeting mitochondria and being able to potentiate the photophysical properties and the singlet oxygen generation [3].

This study introduces a new porphyrin–rosamine conjugate (**H2P3**) and its triarylmethane precursors (**H2P1** and **H2P2**). We evaluated their photophysical properties and ability to chelate iron(III) and copper(II) ions using absorption and emission spectroscopy. Electron paramagnetic resonance (EPR) confirmed the formation of copper(II) complexes and revealed an intense, stable radical signal for **H2P3**. This signal indicates **H2P3**'s strong capacity for singlet oxygen generation, suggesting its potential as an effective photosensitizer.



H2P1 **H2P2** **H2P3**

Fig.1. Porphyrin derivatives **H2P1**, **H2P2** and **H2P3**.

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Factorial design for optimization of tetra-substituted meso-aryl porphyrins synthesis through flow chemistry

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Flow chemistry is a specialized field within synthetic organic chemistry where reagents are continuously pumped to a reactor. Unlike traditional batch processes, often carried out in round-bottom flasks, flow chemistry offers multiple advantages, such as enhanced mass and heat transfer, increased safety, greater reaction efficiency leading to minimized waste production, improved scalability, and more reproducibility [1].

In this study, we explore the synthesis of tetra-substituted porphyrin families using the nitrobenzene method [2], their transposition to continuous flow chemistry and optimization of the reaction parameters (Figure 1). To determine optimal conditions for reactor temperature and residence time, we began the studies by performing a factorial design [3] to fine-tune the reaction parameters to boost optimized yields (up to 30%). Additionally, we performed a large-scale synthesis, maintaining consistent yields of the desired porphyrin over an 8-hour continuous run demonstrating the efficiency of the process.

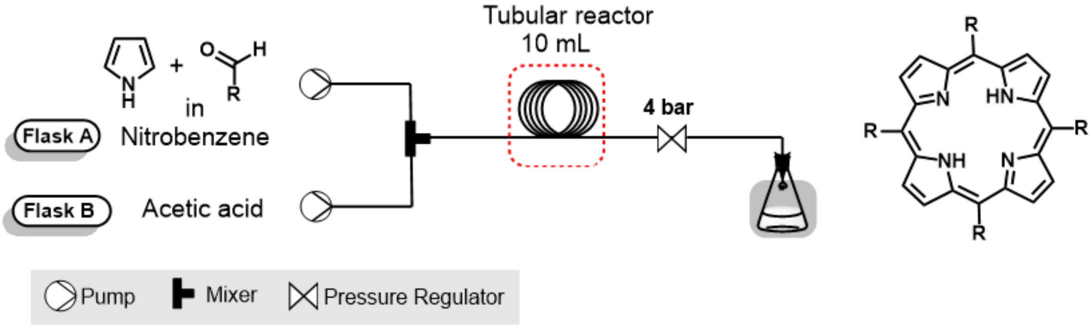

Figure 1: Continuous flow setup for the synthesis of tetra-*meso*-aryl porphyrins using the nitrobenzene method.

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Acidochromic free-standing multilayered chitosan-pyranoflavylium/alginate membranes towards food smart packaging applications

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Food smart packaging has been emerging as a promising technology addressing consumers that are concerned about food safety and quality while consciously committed to food waste issues. These smart packaging systems provide real-time visual information of the freshness state of food products: as the spoiling processes begin the development of organic acids and volatile amine-based compounds is promoted lowering or raising the pH of perishable foods such as dairy products, meat, and fish, among others[1]. Regarding this, the rational design of a novel azide-containing pyranoflavylium-based pH-sensitive dye for subsequent click-chemistry conjugation towards a chitosan-modified alkyne is reported in this work. The chitosan-pyranoflavylium conjugate was then characterized by Infrared (ATR-FTIR), Ultraviolet-Visible (UV-Vis), Nuclear Magnetic Resonance (NMR) spectroscopies and Dynamic Light Scattering (DLS), as well as its thermodynamic parameters related to their pH-dependent chromatic features. The fabrication of thin-films through electrostatic-driven interactions were performed by Layer-by-Layer (LbL) assembly technology and first screened by Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) onto gold substrates. Then free-standing (FS) multilayered membranes onto a polypropylene substrate were obtained using a home-made automatic dip coating robot. The membranes characterization included morphology analysis and thickness evaluation, assessed by Scanning Electron Microscopy (SEM)[2]. The developed membranes were subsequently submitted to pH-responsive color change performance tests using buffer solutions at different pH levels using and biogenic amines-enriched model solutions, demonstrating the feasibility and effectiveness of the multilayered chitosan-pyranoflavylium/alginate biomembranes for food spoilage monitoring [3].

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Preparation of A_2B_2-type porphyrins through C–N bond formation as useful components in perovskite solar cells

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Advancing methods for incorporating nitrogen-based groups into organic structures is highly relevant to synthetic chemistry research. Traditional strategies for forming carbon-nitrogen (C–N) bonds often involve multiple steps, but more efficient alternatives, such as metal-catalyzed C–N bond formation (e.g., Ullmann and Buchwald-Hartwig amination reactions), have emerged as highly effective and versatile tools. Over the past few decades, considerable advancements have refined these techniques and established them as the most efficient ways to form C–N bonds [1,2].

These approaches are particularly appealing for tailoring the physicochemical properties of porphyrins, such as enhancing π-electron delocalization, improving thermal stability, and optimizing electron transfer capabilities, which are critical for applications such as the development of photovoltaic devices [3,4]. In particular, 5,15-diarylporphyrins have shown great promise as hole-transporting materials (HTMs) in perovskite solar cells (PSCs), provided they are appropriately functionalized. As a result, many research efforts have focused on synthesizing and modifying these derivatives, with the goal of incorporating well-defined substitution patterns, including electron-donating groups, to create alternatives to the widely used spiro-OMeTAD HTM [2,4,5].

This work will explore the modification of the 5,15-diarylporphyrin core at the *meso*-positions using nitrogen-donor groups via transition metal-catalyzed methods. The aim is to synthesize *trans*-A_2B_2-type porphyrins containing *N*-donor heterocycles or arylamines. The efficacy of the resulting Zn(II)-based porphyrins as HTMs in PSC devices will also be briefly discussed [6].

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Click on Click: Unlocking the Potential of Click Chemistry in Drug Delivery and Small Molecule Synthesis

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Glioblastoma (GBM) remains the most common and aggressive form of brain cancer, contributing to over 189,000 deaths per year worldwide [1]. The complexity of treating GBM is attributed to the blood-brain barrier (BBB), which restricts drug penetration into the brain, and the tumour's heterogeneity, which complicates therapeutic targeting. Flavonoids, a class of polyphenolic compounds, have demonstrated anti-proliferative properties, and in our research group, synthetic flavonoids have shown promising activity against GBM cell lines [2,3].

In this work, three flavonoids were designed and synthesized with anti-proliferative potential, derived from 3,7-dihydroxyflavone with three different sugars linked through a triazole ring. The synthetic strategy followed click chemistry principles [4], which involved the modification of building blocks with azide and alkyne groups. The flavonoid, 3,7- dihydroxyflavone (**1a**), reacted with propargyl bromide to form 3,7-(prop-2-yn-yloxy)flavone (**1b**). Simultaneously, acetobromo-α-D-glucose (**2a**) reacted with sodium azide in order to be converted into 2,3,4,6-tetra-O-acetyl-β-glucopyranosyl azide (**2b**). Subsequently, a click reaction was performed via copper-catalysed cycloaddition (CuAAC) between the alkyne group of **1b** and the azide group of **2b**, as well as two other commercial sugars (**3b** and **4b**), resulting in three distinct flavone glycosides linked by triazole (**5**, **6**, and **7**).

Biocompatibility assays conducted on L929 fibroblast cell lines and human glioblastoma astrocytoma U-251 cell lines revealed limited activity at the tested concentrations (0-150 µM), suggesting the need for an optimized drug delivery system to improve therapeutic efficacy. To address this issue, the synthesized compounds were encapsulated in polymeric particles - polymersomes (PMs) - of polylactic acid-polyethylene glycol (**PEGPLA**). These were functionalized with azide or transferrin peptide (**T7-HAIYPRH peptide**), the later also by using click chemistry reactions [5].

The PMs were prepared by solvent displacement using varying proportions of **PEGPLA**, Azide-PEG-PLA (**N_3PEGPLA**), or Transferrin-PEG-PLA (**TRFp-PEGPLA**). Firstly, the resulting empty **N_3PEGPLA** PMs exhibited stability over 90 days, proving to be a suitable drug delivery system. Then, the resulting T7 peptide functionalised PMs (**TRFp-PEGPLA**) showed good encapsulation efficiency, and both mean size diameters of 100-140 nm. PMs offer numerous advantages, such as high stability, functionalization potential, a wide choice of drug encapsulation, bioavailability, biodegradability, and more [6].

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QUÍMICA Y SALUD

Surface-Active Ionic Liquids derived from Antimalarial Drugs and Natural Lipids That Display Multi-Stage Antiplasmodial Activity

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The use of Ionic Liquids (ILs) in Medicinal and Pharmaceutical Chemistry has been greatly evolving since they were first used as alternative solvents for the chemical synthesis of active pharmaceutical ingredients (APIs). ILs are now used with other purposes in this area, such as adjuvants in drug formulation and delivery, or even as bioactive compounds *per se*. New ionic structures with biologically relevant properties can be easily obtained through straightforward reactions, as nearly all APIs are ionizable and can be paired with counter-ions that could be either inert or offer additional beneficial biological effects. This efficient, cost-effective strategy for the rescuing and repurposing of drugs is particularly appealing for finding new options to combat "diseases of poverty" like malaria.

We implemented this approach to “recycle” classical antimalarial aminoquinolines, namely, chloroquine (CQ) and primaquine (PQ), by pairing them with natural acidic lipids through acid-base reactions. Our goal was to create novel ILs capable of targeting multiple stages of the *Plasmodium* parasite’s life cycle. Additionally, we were interested in that such ILs could act as surface-active ionic liquids (SAILs), able to self-assemble into nanostructures displaying adequate bioavailability. For this purpose, we paired the antimalarial drugs with either fatty acids or bile acids, due to their biocompatibility and amphiphilic nature.

The antiplasmodial activity and self-aggregation properties of the new SAILs were determined. PQ fatty acid salts preserved the liver-stage antiplasmodial activity of the original drug, while exhibiting significantly enhanced activity against blood-stage parasites. In the case of bile salts, those derived from PQ retained the efficacy of the parent drug, whereas the CQ-derived salts proved to be novel triple-stage antiplasmodial agents. The SAILs obtained from bile acids showed a remarkable ability to self-aggregate, with a notably lower critical micelle concentration compared to their respective sodium salts.

Overall, these findings open a new strategy for drug repurposing, extending beyond antimalarials and other anti-infective therapies.

Acknowledgements
The authors thank Fundação para a Ciência e Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior, (FCT/MCTES), for supporting the Research Units LAQV-REQUIMTE (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020), CIQUP (UIDB/00081/2020), and GHTM (UID/04413/2020 and LA-REAL-LA/P/0117/2020). ATS thanks both FCT/MCTES and Sociedade Portuguesa de Química (SPQ, Portugal) for her doctoral grant SFRH/BD/150649/2020. The following reagent was obtained through BEI Resources, NIAID, NIH: *Plasmodium falciparum*, Strain 3D7HT-GFP, MRA-1029, contributed by Andrew M. Talman and Robert E. Sinden.

Biomonitoring of Emerging Pollutants - The Problematic of Synthetic Musks and Organophosphate Esters

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Emerging pollutants are chemical substances that have recently been identified as hazardous to the environment, and human health. These might be new substances in the environment, or their effects were recently revealed as concerning. The lack of analytical methods has been a barrier to human biomonitoring studies due to the presence of many different chemical substances and the complexity of biological samples. Subsequently, there is a knowledge gap about the general population's exposure to emerging pollutants and the potential impact on health [1,2].

Synthetic musks (SMs) are known for their distinct and enduring scent, and therefore widely employed in personal care and household products. These were detected at high levels in human samples and classified as endocrine disruptors, with associated reports of cancer development, reproductive disorders, dermatitis, photosensitivity, and DNA damage. Despite the reported health effects, only the usage of nitro musks is forbidden or subject to EU use regulations in cosmetic products [3].

Organophosphate esters (OPEs) are flame retardants created as substitutes for brominated flame retardants and released into the environment through leaching, abrasion, or volatilisation. These have been found in human samples and linked to toxic effects (*e.g.,* carcinogenicity, hepatotoxicity, and reproductive toxicity), oxidative stress, obesity, low-birth-weight infants, DNA damage, amongst others. Even though these are categorized as a health and environmental hazard in European Union (EU) regulations and included in the HBM4EU initiative, OPEs are not bound by any usage restriction [4].

SMs and OPEs, as a great part of environmental pollutants, are lipophilic compounds. Hence, prone to deposit and persist in fat tissues, and adipose tissue is the main reservoir for these chemicals in the body. However, there is a shortage of analytical methods and biomonitoring studies of endocrine disruptors in adipose tissue. Sample preparation protocols that clean, concentrate, and pre-fractionate the sample without compromising the analyte within, are desirable for a better chromatographic analysis. Yet, sample preparation is at times a neglected step in the analytical procedure [2,3,4].

The research undertaken develops and validates an analyte method for the assessing of lipophilic compounds in adipose tissue by gas chromatography. The biomonitoring of SMs and OPEs was performed in Portuguese women. SMs were found in all the samples analysed and OPEs in 50% of the samples. Highlighting their bioaccumulative properties and the importance of raising public awareness for the growing problems surrounding these emergent pollutants [3,4].

Acknowledgements

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Enhancing DNA Gyrase Inhibition with Tunable Fluoroquinolone-Derived GUMBOS: A New Frontier in Antimicrobial Therapy

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Antimicrobial resistance is an urgent global health threat that requires the development of alternative therapeutic strategies [1]. One promising approach involves a class of tunable materials called Group of Uniform Materials Based on Organic Salts (GUMBOS), which share similarities with ionic liquids in their ability to modulate physicochemical and biological properties through the selection of cationic and anionic counterparts without engaging in intricate synthetic processes [2]. The incorporation of outmoded antibacterials as active pharmaceutical ingredients (APIs) [3] in GUMBOS represents an innovative strategy to rejuvenate these older antibiotics with diminished efficacies.

In this study, novel fluoroquinolone (FQ)-based GUMBOS were synthesized by through a simple metathesis reaction with five distinct bulky organic anions: bis(perfluoroethylsulfonyl)imide ([BETI]), bis(trifluoromethanesulfonyl)imide ([NTF_2]), tetraphenylborate ([TPB]), docusate ([Doc]), and deoxycholate ([Dxc]). Ciprofloxacin ([Cip]), lomefloxacin ([Lom]), and moxifloxacin ([Mox])-based GUMBOS were structurally characterized using NMR, FTIR and ESI-MS. GUMBOS were evaluated for their antibacterial properties, specifically targeting DNA gyrase, a type II topoisomerase crucial for bacterial DNA replication and a well-known target in drug development. A high-throughput screening (HTS) assay was employed to assess the inhibitory effects of these compounds on DNA gyrase activity, and half-maximal inhibitory concentration (IC_{50}) values were determined. Also, the cationic or anionic counterparts' influence on DNA gyrase's activity or inhibition was evaluated and compared with clinical precursors.

Notably, the choice of anionic or cationic counterparts significantly influenced the compounds' inhibitory potential. All [Cip] GUMBOS demonstrated enhanced inhibitory activity compared to the precursor, ciprofloxacin, with IC_{50} values ranging from 0.106 to 1.084 µM. Among the [Lom] GUMBOS, only [Lom][NTF_2] and [Lom][Dxc] exhibited stronger inhibition than the parent compound, lomefloxacin. [Mox][NTF_2] displayed the highest inhibition (IC_{50} 0.076 µM), outperforming moxifloxacin and all other GUMBOS evaluated. Overall, these results suggest that FQ-based GUMBOS, particularly those derived from ciprofloxacin and moxifloxacin, exhibit promising inhibitory profiles against DNA gyrase. These findings highlight the potential of GUMBOS as a new class of antimicrobial agents that warrant further investigation in both preclinical and clinical trials and more effective antibacterial therapies.

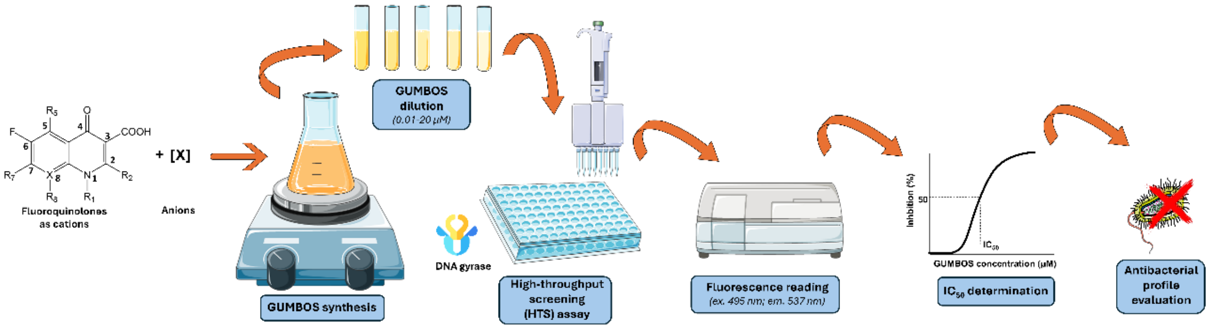

Fig.1. Synthesis of GUMBOS and evaluation of their inhibitory effects on DNA gyrase activity.

Acknowledgments

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Broad-Spectrum Photosensitive Materials for Photodynamic Inactivation of Multidrug-Resistant Bacteria

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Infections caused by multi-drug resistant (MDR) microorganisms are a major concern in modern medicine and place a tremendous strain on healthcare systems worldwide. These pathogens are currently linked to 1.3 million deaths each year, a number expected to increase significantly in the coming years.[1] A well-established factor contributing to the rise of MDR bacteria is the contact with contaminated hospital surfaces and medical devices, which can rapidly lead to life-threatening infections, especially in immunocompromised patients.[2] To address this challenge, it is vital to develop antimicrobial surfaces with broad-spectrum of activity, that can inactivate bacteria upon contact, limit their pathogenicity, and prevent biofilm formation. This can be accomplished by utilizing photosensitive materials,[3,4] that combine a polymeric matrix, ideally composed by biodegradable biopolymers, with photosensitizers (PS), Figure 1.

Porphyrins bearing cationic imidazolium groups are among the most promising classes of photosensitizers for developing photosensitive materials, thanks to their exceptional stability, strong photophysical and photochemical properties, as well as broad-spectrum antimicrobial activity.[5] In this study, we present our latest findings on the synthesis and characterization of a novel cationic mono-imidazolium porphyrin, used as a photosensitizer for creating innovative photosensitive materials, based on polylactic acid (PLA). These materials were thoroughly characterized using standard techniques. Additionally, their ability to photoinactivate both antibiotic susceptible and MDR Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria were conducted under blue light irradiation, with light doses ranging from 16 to 24 J/cm^2. Under these conditions, complete bacterial inactivation (7 log reduction) was achieved with the biopolymer-photosensitizer composite, highlighting how the amphiphilicity of the photosensitizer influences both material stability and antibacterial effectiveness.

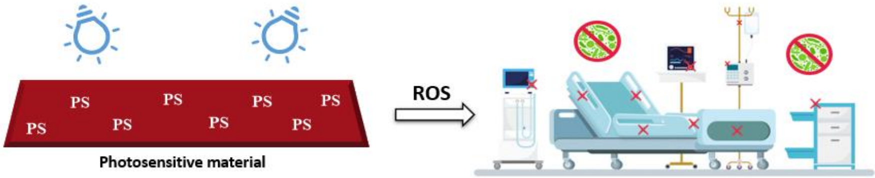

Fig. 1. Schematic overview of the process of photodecontamination of surfaces.

Acknowledgments
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Which compounds are behind the therapeutical properties of Dragon's Blood? Purification strategies for its identification

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The scarlet resin known by its traditional name, **Dragon's Blood**, is derived from over 20 different plant species that fall into 4 different genera, including *Dracaena*, *Daemonorops*, *Pterocarpus*, and *Croton*.[1] This traditional medicine source has been used for thousands of years to cure a wide range of conditions, including diabetes, cerebral infarction, coronary heart disease, diarrhea, internal ulcers, and many other health issues that have been reported in various cultures.[1-3]

Numerous polyphenolic compounds (including stilbenoids and flavonoids), terpenes, and sterols make up this complex resin. Many compounds are still unknown, nevertheless, because of their intricate matrix and challenging compound purification.[4] In order to get around this complexity, the resin was dissolved and separated into smaller fractions using a C-18 and *Toyopearl®* gel preparative column with different eluents. For the colored fragments that were recovered, a spectrophotometric analysis was conducted to check the pH dependence of the fractions, and the results revealed an intriguing range of color solutions at various pH values, including yellow, orange, pink, and colorless solutions.

Due to this pH dependence, it is possible to divide the Dragon's Blood sample more effectively. In particular, the yellow compounds, for the acidic pH yellow flavylium compounds can be separated from extract naturally yellow degradation products. This approach allowed to obtain fewer complex ESI-MS fragmentations, which made the HPLC-DAD/MS quantitative and qualitative analysis easier to perform.

With the simplification of this intricate resin matrix, this work provides a new avenue for the discovery and analysis of a wide spectrum of all the chemical compounds' potential therapeutic uses.

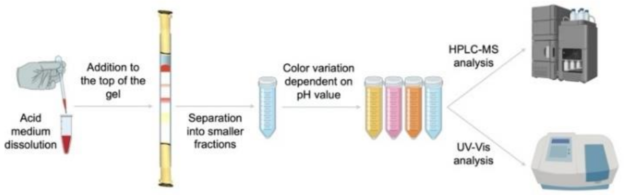

Fig.1. Schematic representation of the abstract.

Acknowledgments
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In vitro evaluation of new aminosquaraine dyes as potential photodynamic therapy photosensitizers for prostate cancer

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Squaraine dyes are a family of polymethine dyes consisting of a central four-membered ring derived from squaric acid, to which two heterocyclic units are attached. Depending on the structural modifications made to this scaffold, these dyes exhibit unique properties such as strong absorption at red and near-infrared wavelengths, moderate to high fluorescence quantum yields in organic solvents, and increased fluorescence intensity upon non-covalent interaction to specific ligands [1]. Additionally, the ability of squaraine dyes to produce reactive oxygen species and their general stability under light make them “ideal candidates” as photosensitizers in photodynamic therapy (PDT) [2].

Thus, in this communication, it will be presented the synthesis of four propylbenzene-bearing indolenine-derived squaraine dyes [three aminosquaraine dyes and the corresponding zwitterionic precursor dye (dyes **2**-**4** and **1**, respectively, Figure 1], their light stability, their ability to generate singlet oxygen and the half-maximal inhibitory concentration (IC_{50}) values against NHDF normal human dermal fibroblasts and PC-3 prostate adenocarcinoma cells, which was evaluated to determine their possible tumor selective effects, using the MTT assay. Light-emitting diode systems centered at wavelengths close to the dyes’ maximum absorption wavelengths were used for irradiation.
Despite its moderate capacity for producing singlet oxygen, but high stability to light, it was concluded that the unsubstituted squaraine dye **1** had the greatest photodynamic effect, with marked effects between irradiated and non-irradiated conditions. On the other hand, introduction of amines increased their intrinsic cytotoxicity, and the aminosquaraine functionalized with the pyrenemethylamine group **4** did not show any interest concerning this potential biological application.

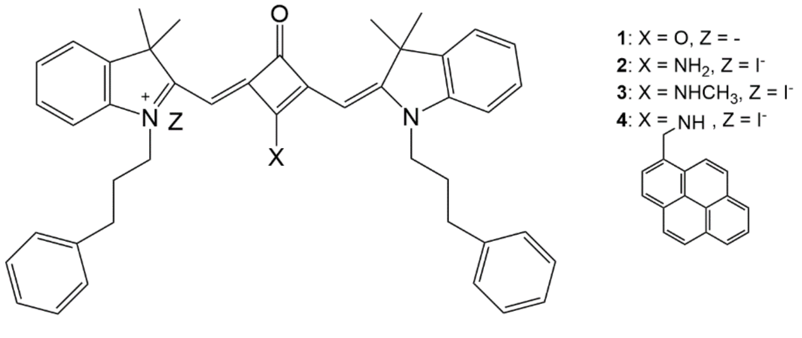

Figure 1. Structure of new squarylium dyes synthesized.

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Deciphering the Mechanisms Behind LUZ51 Cellular Internalization and Release

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Photodynamic therapy (PDT) is a minimally invasive and selective therapy for the treatment of solid tumors. It involves the use of a photosensitizer (PS), which ideally absorbs light within the phototherapeutic window (650-850 nm) in conjunction with molecular oxygen to generate reactive oxygen species (ROS) in target cells. However, ROS have a brief lifespan and can only diffuse over limited distances. As a result, the distribution of the selected PS across tissues and cell organelles, together with its unique physicochemical properties, will dictate the effectiveness of PDT [1]. The ability of therapeutic molecules to interact with and cross cell membranes is crucial for achieving effective intracellular bioavailability at therapeutic concentrations. A key factor influencing this internalization is the molecule's size and lipophilicity. Smaller, more lipophilic molecules typically enter cells through energy-independent mechanisms such as passive diffusion. Whereas, large and/or hydrophilic molecules require energy-dependent mechanisms, such as endocytosis [2].

LUZ51 is a carboxamide halogenated bacteriochlorin, of low molecular weight and relatively lipophilic (595 g/mol and $\log P_{o/w}$ 2.9) [3]. These physicochemical properties enable LUZ51 to be rapidly internalized by cells in substantial quantities, leading to high phototoxicity (IC_{50} = 6.88 nM, 4T1 cells) at a relatively low light dose (1 J/cm^2). For this reason, the mechanisms of LUZ51 influx and efflux were studied *in vitro* using the 4T1 cell line, in which the effect of temperature (4ºC versus 37ºC), ATP (adenosine triphosphate) depletion (by means of 2-deoxy-D-glucose), alongside a co-incubation of a series of inhibitors targeting endocytosis (chloroquine and chlorpromazine) were evaluated.

Our results demonstrate that the internalization of LUZ51 was notably decreased at 4ºC, yet remained unaffected by ATP depletion or the presence of endocytosis inhibitors. This indicates that LUZ51 is predominantly internalized by cells through passive diffusion. Interestingly, we also observed that LUZ51 can be released from cells into the extracellular environment. Our findings revealed that this efflux process was significantly inhibited at 4ºC and under ATP depletion, suggesting the involvement of active efflux pumps in the transport of LUZ51. Cells contain various types of active efflux pumps, with P-glycoprotein (P-gp) being one of the most extensively studied [2]. In contrast, the inhibitors of p-glycoprotein (cyclosporin A and verapamil) did not influence LUZ51 efflux, indicating that this pump is not responsible for its transport. Presently, we are exploring whether other efflux transporters, including MRP1 (MK-571) and BCRP (ko143 and fumitremorgin C), play a role in the cellular mechanisms governing LUZ51 release.

Agradecimientos
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Using multi-component reactions to synthesize structurally diverse novel antitubercular agents

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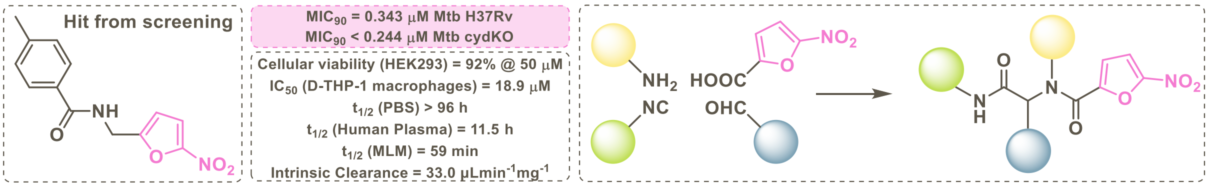
Tuberculosis (TB), caused by *Mycobacterium tuberculosis* (Mtb), remains one of the deadliest infectious diseases worldwide, with 1.3 million estimated deaths in 2022. [1] The most serious limitation to TB control is Mtb's ability to shut down its metabolism to a latent state, with a high natural resistance to most antibiotics, including traditional anti-TB agents. The limited efficiency of current pharmacological tools imposes prolonged treatment regimens, that result on low patient compliance, and the emergence and spread of drug-resistant (DR) TB, which are more lethal and have less treatment success. [2]

The mycobacterial energetic metabolism has received attention as a validated therapeutic target for TB therapy after the discovery of ATP synthase inhibitor bedaquiline, that displayed activity against latent and DR-TB. As Mtb requires a sustained supply of ATP, compounds targeting the energetic metabolism with multiple modes of action (MoA) have been considered an effective strategy to overcome the pathogen's metabolic adaptability. Currently, the only drug class with such MoA are the nitroimidazoles, delamanid and pretomanid, that target replicant Mtb through the inhibition of mycolic acid synthesis, and latent Mtb through the *in vivo* reduction of a nitro moiety and release of nitric oxide, which produces free radical species that can react with the bacterial biomolecules. [3]

Multi-component reactions (MCRs) are chemical reactions where three or more reactants successively combine in a single reaction vessel to make a novel product, that retains the majority of the starting material's atoms. MCRs reduce the necessary steps to generate chemical libraries with simple accessible starting materials, under green reaction conditions, with high efficiency and selectivity. [4]

In a screening performed at iMed against Mtb, a hit nitrofuranylamide (**Fig.1.**) emerged with sub-micromolar MIC value, low cytotoxicity, and a good pharmacokinetic (chemical, plasmatic and metabolic stability) and physicochemical profile. Here, we report the synthesis of a small library of derivative compounds containing nitro 5-membered ring heterocycles using MCRs.



MIC_{90} = 0.343 µM Mtb H37Rv
MIC_{90} < 0.244 µM Mtb cydKO

Cellular viability (HEK293) = 92% @ 50 µM
IC_{50} (D-THP-1 macrophages) = 18.9 µM
$t_{1/2}$ (PBS) > 96 h
$t_{1/2}$ (Human Plasma) = 11.5 h
$t_{1/2}$ (MLM) = 59 min
Intrinsic Clearance = 33.0 $\mu L min^{-1} mg^{-1}$

Fig.1. Hit nitrofuranylamide compound (left), biological and early pharmacokinetic profile (middle), and general scheme for library synthesis using MCRs (right).

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Enhancing Anticancer Activity in Osteosarcoma: Buchwald-Hartwig Amination of Flavonoids Directed by Biological Activity

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Osteosarcoma is the most common type of bone cancer in children, and its recurrent forms lack effective treatments, highlighting the need for new therapeutic options [1]. One approach to address this need is by exploring flavonoids, which are known for their wide range of biological effects, including anticancer activity [2].

This study aimed to identify flavonoids with the highest activity against osteosarcoma, determine the specific structural characteristics associated with this activity, and synthesize compounds with potentially improved efficacy (**Fig. 1**). Initially, we exposed four human osteosarcoma cell lines to five structurally related flavonoids for 48 hours and assessed cell viability and growth using WST-8 and sulforhodamine B assays, respectively. Myricetin and robinetin were the most active compounds, showing IC_{50} values below 20 µM in 143B cells. Subsequently, based on the structure-activity relationship data, we redesigned flavonoids by introducing amine derivatives at the C-7 position using Buchwald-Hartwig cross-coupling reactions. The newly synthesized flavonoid derivatives were thoroughly characterized by 1D and 2D NMR techniques as wells as HRMS. Following the cross-coupling synthesis, we obtained five new compounds in moderate yields (20–50%).

Further studies are required to fully elucidate the properties of these newly synthesized flavonoids and confirm their therapeutic potential as novel drugs for osteosarcoma.

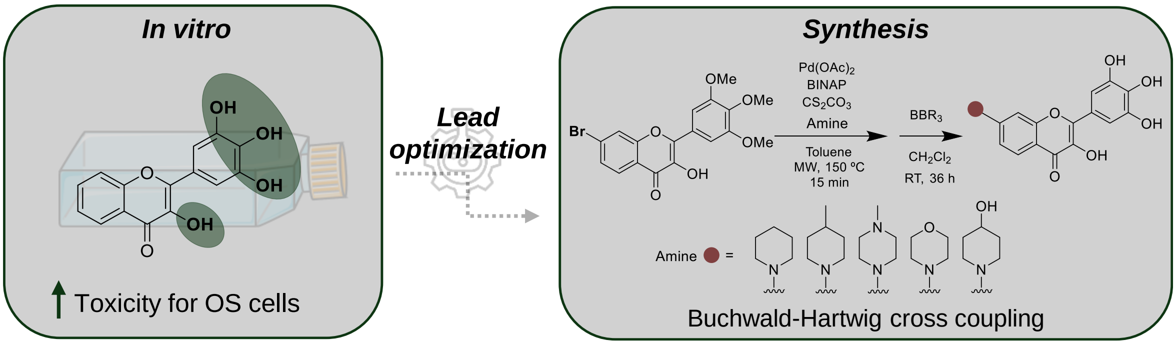

Fig.1. Workflow for identifying key structural features of the most bioactive flavonoids and redesigning them via Buchwald-Hartwig Cross-Coupling.

Funding
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Avaliação química do óleo essencial de *Foeniculum vulgare* para aplicação em aromaterapia

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O funcho também conhecido por fiolho, erva-doce, fionho, cujo nome científico é *Foeniculum vulgare* Mill é uma planta aromática, perene que pertence à família das *Umbelíferas* encontrada em Portugal continental e também na ilha da Madeira e Açores nos meses de Maio a Julho [3]. O óleo essencial de funcho possui diversas atividades biológicas entre elas na redução da ansiedade [1]. O objetivo deste estudo foi obter o óleo essencial das sementes de funcho através de hidrodestilação por arrastamento de vapor e avaliar a sua composição química através de GC e GC-MS para posterior aplicação deste óleo essencial em ensaios de aromaterapia. As sementes utilizadas são de origem certificada e adquiridas comercialmente a uma empresa portuguesa. O óleo essencial de sementes de funcho foi extraído através da hidrodestilação sendo realizadas diversas extrações e o rendimento médio teve o valor de 1,26%. Também na análise química por CG-MS do óleo essencial de sementes de funcho foram realizadas três injeções e esta análise demonstrou que o composto mais abundante presente foi o *trans*-Anetol com uma percentagem de 78,2 %, com quantidades muito inferiores para fenchona (9,3%) e Metil chavicol (4,7%) e outros compostos com percentagens mais baixas como p- Anisaldeído, Limoneno. Um estudo realizado por Kallelli et al., (2020) exibiu percentagens semelhantes nos constituintes maioritários como o *trans*-anetol, fenchona e Metil chavicol, com valores de 78,26 %, 10,64% e 4,67%, respetivamente [2]. Segundo Alvarado-Garcia et al., (2022) o composto maioritário *trans*-anetol pode ser o responsável pelo comportamento ansiolítico do óleo essencial [1].

Agradecimentos
Este trabalho foi suportado por fundos nacionais através da FCT/MCTES (PIDDAC): UIDB/00690/2020 (DOI:10.54499/UIDB/00690/2020) e UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); e SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020).

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Aromaterapia na redução da ansiedade, aumento da qualidade de sono e promoção do bem-estar

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A aromaterapia é uma forma de fitoterapia que utiliza os óleo essenciais extraídos das plantas como terapia complementar/alternativa com o propósito de melhorar a saúde fisica e emocional e o bem-estar do corpo [1]. O óleo essencial de sementes de funcho (*Foeniculum vulgare* Mill.) constituido por uma mistura de terpenos e terpenoides tem sido utilizado por reduzir a ansiedade, aumentar a qualidade de sono e bem-estar, sendo utilizado em aromaterapia nomeadamente na forma de massagem. Neste sentido, o objetivo do presente estudo foi avaliar o benefício da aplicação de óleo essencial de sementes de funcho, através de massagem, para diminuição da ansiedade, aumento da qualidade de sono e bem-estar. O ensaio consistiu na participação de 40 indivíduos divididos aleatoriamente em dois grupos: “Grupo Massagem” e “Grupo Aroma”. Os indivíduos do “Grupo Massagem” foram tratados com o óleo de amêndoas doces, enquanto que o “Grupo Aroma” recebeu a massagem com óleo essencial de sementes de funcho diluido a 1,6% no óleo de amêndoas doces.O ensaio teve a duração de 2 meses com cerca de 4 sessões de 15 em 15 dias (2 sessoões por mês). Os níveis de ansiedade, qualidade de sono e bem-estar foram avaliados aplicando respetivamente, o Inventário de Estado-Traço de Ansiedade, Qualidade de sono de Pittsburgh e Índice de bem-estar OMS antes da massagem (Questionário 1), após a 2º e 4º sessão (Questionário 2 e Questionário 3) e 1 mês após a última sessão (Questionário 4). De acordo com os resultados obtidos, no Índice de bem-estar observou-se que no “Grupo Massagem” o valor médio do Questionário 1 foi 13,3 ± 3,93 tendo aumentando gradualmente nos Questionários 2 e 3 para valores de 15,6 ± 4,72 e 16,5 ± 4,98, respetivamente, com um decréscimo para 14,5 ± 4,89 no questionário 4. Já no “Grupo Aroma” o valor médio no Questionário 1 foi de 16,05 ± 5,01 que diminui no Questionário 2 para 15,8 ± 4,95. No questionário 3 o valor médio aumentou para 17 ± 3,61 e no Questionário 4 voltou a diminuir para 16,4 ± 3,75. No “Grupo Massagem” e na ansiedade-E o valor médio do Questionário 1 foi de 41,7 ± 9,81 que diminui para 39,2 ± 11,89 no Questionário 2. Este valor aumentou para 41,8 ± 11,91 no Questionário 3 e diminui no Questionário 4 para 37,6 ± 10,50. Em relação à ansiedade-T o valor médio diminui desde o Questionário 1 até ao Questionário 4 com valores médios de 42,2 ± 9,56 e 38,5 ± 10,98, respetivamente. No “Grupo Aroma” e na Ansiedade-E ocorreu uma diminuição ao longo do tempo com valores de médios de 38,4 ± 11,45 para o Questionário 1, 35,5 ± 8,53 e 32,5 ± 7,86 no Questionário 2 e 3. O valor médio no Questionário 4 aumentou ligeiramente para 33,2 ± 9,07. Relativamente à ansiedade-T e no Questionário 1 o valor médio foi de 37,1 ± 10,10 e este valor diminui para 34,7 ± 10,08 e 34,6 ± 9,44 nos Questionário 2 e 3, respetivamente. No Questionário 4 o valor manteve-se próximo ao obtido no Questionário 3, 34,6 ± 9,29. Na qualidade de sono Pittsburgh, no “Grupo Massagem” os valores diminuiram até ao questionário 3 com valor inicial de 8,6 ± 3,94 (Questionário 1) que decresceu para 7,1 ± 2,97 (Questionário 2) e 5,7 ± 3,12 (Questionário 3), aumentando para 7,2 ± 4,31 no Questionário 4. No “Grupo Aroma” o valor médio do Questionário 1 foi de 7,2 ± 3,96 que teve um decréscimo no Questionário 2 e 3 para valores de 5,9 ± 3,57 e 5,5 ± 3,24, respetivamente. Este valor também teve um pequeno aumento no Questionário 4 para o valor de 5,6 ± 4,03. De uma forma geral, os níveis de ansiedade diminuiram de forma mais evidente no “Grupo Aroma” relativamente ao “Grupo Massagem”, assim como um aumento do índice de bem-estar e qualidade de sono.

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Synthesis and Pharmacological Characterization of Diversely Substituted Pyrazoles as Cannabinoid Receptor 1 Ligands

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The endocannabinoid system participates in the regulation of numerous physiological processes. It has been also involved in the pathophysiology of different diseases, highlighting the therapeutic potential of modulating this system.[1] Thus, cannabinoid compounds may be potentially useful as analgesics, antiemetics, antispasmodics, appetite stimulants, and in the treatment of epilepsy and glaucoma.[2] Therefore, developing new cannabinoids as drugs for the treatment of several diseases is a hot research topic nowadays. Pyrazoles are five-membered heteroaromatic compounds (**Fig. 1**) that exhibit diverse pharmacological activities, including cannabinoid activities, and serve as crucial intermediates in organic synthesis.[3,4]

In this context, thirty-four diversely substituted pyrazoles, namely 1,3,5-trisubstituted and 1,3,4,5-tetrasubstituted ones, were synthesized through different strategies including the cyclocondensation of chalcone derivatives with phenylhydrazine in acetic acid, followed by iodine-catalyzed oxidative cyclization, and copper iodide-catalyzed reactions of hydrazones with diethyl acetylenecarboxylate. Afterwards, radioligand binding assays as well as the pharmacological characterization of the synthesized pyrazoles, were performed to evaluate both the affinity for cannabinoid type 1 (CB1) receptor and to assess the functional activity, respectively.

Among the tested compounds, ten derivatives displayed moderate affinity (pK_i > 6) over CB1 receptors against [^{3}H]SR141716A. Two examples are shown in **Fig. 1**. *In vitro* functional [^{35}S]GTPgS binding assays performed using human prefrontal cortex membranes homogenates, allowed to determine their activity as agonists, antagonists or inverse agonists of CB1 receptors. Two compounds displayed an antagonistic effect, one behaved as an agonist, and the remaining compounds demonstrated an inverse agonistic activity.

In this communication are presented and discussed the synthesis and pharmacological characterization details and results.

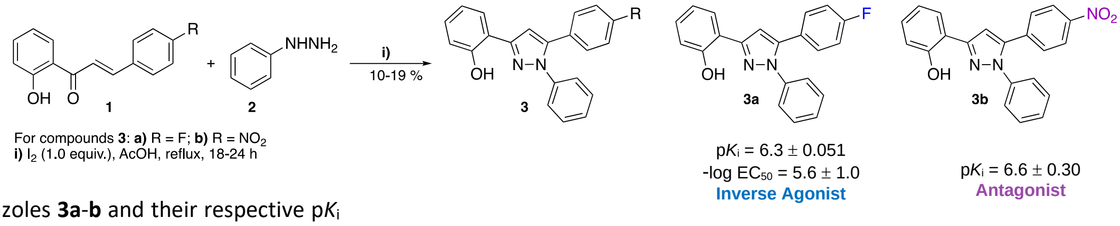

Fig.1. Synthesis of pyrazoles **3a**-**b** and their respective pK_i values and functional activities.

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Development of Diarylpyridines and Styrylisoxazoles: Novel Cholinesterase Inhibitors Targeting Neurological Diseases

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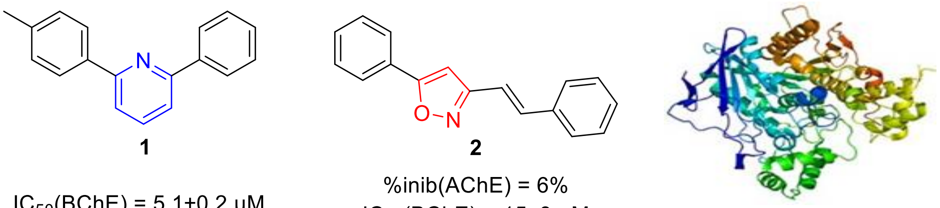
Neurological disorders have a profound and wide-reaching impact on society and healthcare systems worldwide. In particular, Alzheimer's disease (AD) is the most common neurological disease and the major cause of dementia, associated with loss of cognitive function and dependence in the elderly [1]. One cause of cognitive loss is the decrease of brain's cholinergic activity, which can be counteracted by anticholinergic drugs. These drugs inhibit the action of cholinesterase enzymes, decrease the cleavage of acetylcholine, and indirectly increase cholinergic transmission.

In this communication are presented the results of a study focused on the development and evaluation of novel compounds as potential cholinesterase inhibitors, targeting acetylcholinesterase (AChE) and butyrylcholinesterase (BChE), enzymes implicated in AD [2]. This study involved the synthesis of diarylpyridines **1** and styrylisoxazoles **2** (Figure 1)**,** including some reduced derivatives, through condensation reactions of (2*E*,4*E*)-1,5-diarylpenta-2,4-dien-1-ones and 1,5-diarylpenta-1,4-dien-3-ones with hydroxylamine hydrochloride followed by cyclization processes, generating a series of structurally diverse molecules which were characterized by NMR spectroscopy, X-ray diffraction, and mass spectrometry. In vitro enzyme inhibition assays were conducted to assess their activity against AChE and BChE. Structure-activity relationship (SAR) analysis was performed to identify key structural features responsible for enzyme inhibition. Two compounds, a diarylpyridine **1** and a styrylisoxazole **2**, showed promising inhibitory activity, particularly selective inhibition of BChE. One compound exhibited superior potency against BChE compared to the reference drug donepezil. These findings demonstrate the potential of isoxazole derivatives as promising leads for cholinesterase inhibition and highlight their potential as therapeutic candidates for the treatment of cholinesterase-related neurological disorders. Further optimization based on SAR and *in silico* ADMET studies insights could lead to improved pharmacological profiles for these inhibitors.



1

IC_{50}(BChE) = 5.1±0.2 μM

2

%inib(AChE) = 6%
IC_{50}(BChE) = 15±3 μM

BChE

Fig.1. Examples of a diarylpyridine **1** and a styrylisoxazole **2** active against BChE enzyme.

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Targeting HER2-Overexpressing Cancer Cells with Milk Extracellular Vesicles in Just a Click

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Milk-derived extracellular vesicles (EVs) have received considerable interest as nanocarriers for targeted delivery applications. Surface functionalization with antibodies have been studied to enhance the tissue selectivity of EVs [1]. However, directly conjugating antibodies to EVs has not proven to be as effective as expected, since it can increase hydrodynamic size and may lead to enhanced recognition by the immune system [1]. In this study, we propose a pretargeted delivery system using bio-orthogonal Syd-derivative/DBCO-based click chemistry to selectively deliver EVs to Human Epidermal Growth Factor Receptor 2 (HER2) in cancer cells, using Trastuzumab (Tmab). This pretargeting approach involves separating the targeting moiety (Tmab) from the drug-delivering vector (EVs), allowing them to react in biological conditions following separate incubations. Tmab was functionalized with clickable DBCO groups, while the EVs were modified with the Syd derivative and a fluorescent reporter (SCy5) to enable tracking of the EVs. Neither size nor morphology of the EVs suffered significant changes, as assessed by NTA and TEM. For the in vitro click chemistry efficacy experiments, three cancer cell lines with different HER2 expression levels were used: SK-BR-3 (HER2++), Caco-2 (HER2+), and MDA-MB-231 (HER2-). Following a 30-min incubation with Tmab-DBCO, another 30-min incubation with EVs-SCy5-Syd was conducted, simulating the two sequential administrations. Confocal microscopy and flow cytometry revealed that the EVs-SCy5 signal was mostly detected in SK-BR-3 cells, and strongly reduced when the blocking of the HER2 was performed (Fig.1 (a)). Furthermore, a comparison of the pretargeting strategy using click chemistry with the bioconjugation using conventional EDC/NHS bioconjugation of Tmab with EVs showed enhanced accumulation of EVs in SK-BR-3 cells. In conclusion, this study highlights the potential of a pretargeted delivery system using click chemistry to enhance the efficacy of EVs in targeting HER2-overexpressing cancer cells.

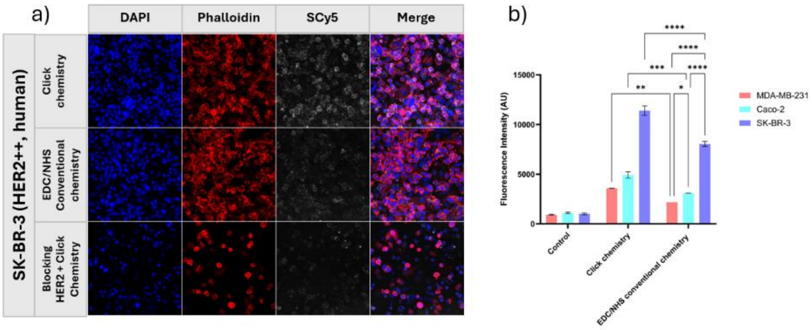

Fig.1. (a) Representative confocal microscopy images of SK-BR-3 cells with the pretargeting click approach, bioconjugation using EDC/NHS conventional chemistry and HER2 blocking before the click approach. (b) Flow cytometry results for the click and conventional approaches, for the three cell lines.

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Synthesis and Biological Evaluation of Novel Glypromate Conjugates with Application in Neurodegenerative Diseases

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Glypromate (glycyl-L-prolyl-L-glutamic acid, GPE) is an endogenous neuropeptide widespread in the brain that holds great potential to tackle neurodegenerative disorders, such as Parkinson's and Alzheimer's diseases.[1] However, the clinical application of this short neuropeptide is limited by its poor pharmacokinetic properties.[1] In this sense, a new series of GPE derivatives was designed by exploring the chemical conjugation of GPE, including a bioactive GPE analog bearing L-pipecolic acid as a proline surrogate, with important active pharmaceutical ingredients (API), such as amantadine, memantine, and (*R*)-1-aminoindane. A total of thirty-six conjugates were synthesized using a sustainable and chemoselective one-pot methodology,[2] and biologically evaluated to determine neuroprotection against 6-hydroxydopamine (6-OHDA) neurotoxicant and $A\beta_{25-35}$-induced protein aggregation.

Preliminary cytotoxic evaluation using non-differentiated and differentiated (dopaminergic phenotype) SH-SY5Y neuroblastoma cells (MTT reduction assay), demonstrated that the central amino acid residue is pivotal for the toxicological profiles of the conjugates, with pipecolyl-based conjugates exhibiting, in general, high cytotoxic effects in comparison with the prolyl counterparts.

Peptide-API conjugates with the most favorable toxicological profiles underwent protein aggregation studies evaluated in non-differentiated SH-SY5Y cells. In this assay, six conjugates were able to significantly reduce the protein aggregation induced by $A\beta_{25-35}$ up to 43%, showing a superior neuroprotective profile when compared to GPE (13%). Next, neuroprotection was assessed in dopaminergic differentiated SH-SY5Y cells against 6-OHDA. Among prolyl-based GPE conjugates, five of them were able to significantly counteract the cytotoxic elicited by 6-OHDA, with one conjugate demonstrating a 2.3-fold improvement in neuroprotective effect when compared to GPE.

In conclusion, the conjugation strategy of GPE with API herein described led to the discovery of bioactive conjugates with interesting biological responses and superior biological performance in comparison with the parent neuropeptide.

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New antimicrobial peptides derived from longibramide E: Synthesis and antibacterial activity

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In 2019, antimicrobial resistance (AMR) was directly responsible for over 1 million deaths worldwide, adding to almost 5 million related deaths [1]. As such, AMR poses one of the major threats to global health in the 21st century, and development of new strategies to fight bacterial infections is paramount.

Antimicrobial peptides (AMPs) have been widely investigated as an interesting alternative to the classic antibiotics due to their potent and broad-spectrum of action, including against both susceptible bacteria and multidrug-resistant (MDR) isolates, and to their low propensity to induce bacterial resistance mechanisms [2]. Peptaibols are nonribosomal linear AMPs (with 5–20 amino acids) produced by fungi, with the appealing feature of being intrinsically proteolysis-resistant due to a few specific structural traits; moreover, their antibacterial action does not involve specific bacterial targets, which reduces the likelihood of bacterial resistance development [3]. Recently, Zhang *et al*. isolated a series of 11-residue peptaibols from *Trichoderma longibrachiatum*, denominated longibramides [4]. Among them, longibramide E triggered us particular interest due to its activity against methicillin-resistant *Staphylococcus aureus* (MRSA), but like many peptaibols, this longibramide has poor water solubility.

In this study, we synthesized nine longibramide E analogs, aiming at improving water solubility, while ensuring antibacterial activity. The synthesis of the new longibramide E-inspired molecules was carried out by solid-phase peptide synthesis (SPPS) both manually and by automated synthesis on a Symphony® X system, to compare the efficiency of the two methods. The antibacterial activity of the synthetic analogs was determined against susceptible and MDR isolates of *S. aureus* (MRSA) and of *Escherichia coli*, through the assessment of the minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC).

Several of the nine longibramide E analogs synthesized showed improved hydrophilicity, and three of them exhibited broad-spectrum antibacterial activity against both susceptible and MDR isolates. These three promising AMPs were obtained by different modifications as i) the removal of the acetylation in the *N*-terminus and the replacement of the *C*-terminal leucinol moiety by a leucine amide, ii) the introduction of Lys residues, and iii) replacement of acetyl by *n*-octanoyl in the *N*-terminus. Relevantly, none of these molecules were haemolytic at the MIC.

In conclusion, the new AMPs derived from longibramide E pave the way towards new promising alternatives to conventional antibiotics, produced by rational modifications onto peptaibols aimed at increasing both solubility and antimicrobial action.

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Development of a library of flavonoid-based derivatives as P-gp modulators on resistant cancer cells

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The efficacy of cancer treatment has been seriously hindered by the development of multidrug resistance (MDR). Among the most significant mechanisms of MDR is the overexpression of the ABC transporter proteins, being P-glycoprotein (P-gp) the most important. As such, the development of P-gp modulators able to restore the cytotoxicity of anticancer agents is still considered one of the most promising strategies for overcoming MDR.

Natural products have long been recognized as valuable sources of anticancer drugs. Tangeretin, a natural polymethoxyflavonoid found in citrus peels, possess multiple biological activities, including anticancer activity. Based on these considerations, this scaffold was selected for further studies aiming at obtaining new derivatives for overcoming multidrug resistance in cancer.

In this way, after obtaining the corresponding oxime, a set of twenty-six new oxime carbamates was prepared, namely by carbonyldiimidazole-mediated reaction with primary or secondary amines, or reaction with different aromatic and aliphatic isocyanates. Their structures were assigned mainly by 1D (^{1}H and ^{13}C NMR) and 2D (HMQC and HMBC) NMR experiments.

The compounds were tested for their ability as MDR reversers, through the rhodamine-123 accumulation assay, by flow cytometry, and chemosensitivity assays, in a human *ABCB1*-transfected mouse T-lymphoma cell model, overexpressing P-glycoprotein. A significant increase of P-gp inhibitory activity was observed for most derivatives at non-cytotoxic concentrations. Several compounds exhibited strong P-gp inhibition at 2 µM, being more active than verapamil at 10-fold higher concentration. In drug combination assays, most all the compounds were able to synergize doxorubicin. Future studies will involve evaluating the underlying mechanisms of the most promising compounds through the ATPase assay.

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Heteroaromatic Scaffolds as Proline Surrogates in Melanostatin Neuropeptide for Application in Parkinson's Disease

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Melanostatin (MIF-1, Fig. 1) is an endogenous neuropeptide that acts as a selective positive allosteric modulator (PAM) of the dopamine D_2 receptors (D_2R). Given its PAM activity and D_2R selectivity, MIF-1 presents therapeutic potential for dopamine-related disorders, such as Parkinson's disease (PD). Nevertheless, its peptide nature poses significant challenges, including low gastrointestinal absorption and susceptibility to degradation by proteases found in the central nervous system, thereby limiting its oral availability.[1,2] It's known that L-Proline (Pro) is a suitable residue for chemical derivatization, since its replacement results in several active PAM molecules.[1,2] In previous studies, our research group developed MIF-1 derivatives by bioisosteric substitution of Pro with 2-furoic acid (2-Fu, Fig. 1) which promoted a specific increase of tritiated NPA ([^{3}H]-NPA) to D_2R in binding assays, underlying a PAM behavior.[1]

Motivated by these results, this work studied the influence of the position of the oxygen atom in the furanyl motif on PAM activity. For that, 3-furoic acid (**3-Fu**) was used as a Pro surrogate, and eight peptidomimetics were synthesized using a previously established protocol within our research group.[2] All the tripeptides were subjected to pharmacological evaluation through functional assays using CHO cells transfected with human D_2R to assess cyclic adenosine monophosphate (cAMP) mobilization. In these assays, two peptidomimetics promoted an increase of dopamine potency, at 0.01 nM.[2] Overall, the remarkable pharmacological profiles of these peptidomimetics validate 3-Fu as a promising Pro bioisostere, paving the way for the rational development of novel PAMs for application in PD.

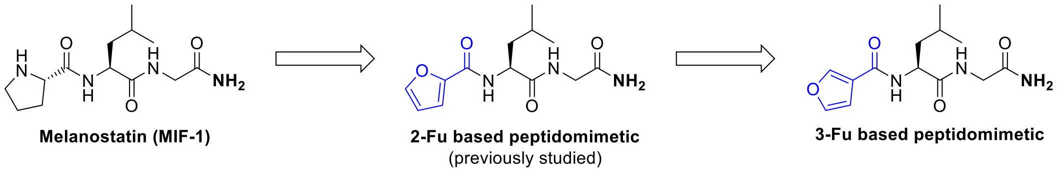

Fig.1. Chemical structures of MIF-1 neuropeptide and its furoyl-based peptidomimetics.

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The impact of metal on the antimicrobial Photodynamic Efficiency of Metalloporphyrins with Triphenylphosphonium Units: A Comparative Study

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Antimicrobial Photodynamic Therapy (aPDT) is a promising non-invasive technique for combating bacterial infections. This approach involves the use of a photosensitizer (PS) that, when exposed to visible light in the presence of dioxygen, generates reactive oxygen species (ROS), including singlet oxygen ($^1O_2$) [1]. These ROS cause oxidative damage to vital bacterial structures, such cytoplasmatic membrane and cell wall, ultimately leading to cell death. Unlike traditional antibiotics, that target specific molecular pathways, aPDT employs a broader, multi-target strategy. This versatility makes it particularly effective against a wide range of bacterial strains, including those that developed resistance to standard antibiotics, offering a novel treatment solution [2, 3].

The main goal of this work was to prepare a new series of PS that combines the antibacterial ability of triphenylphosphonium derivatives with the inherent ability of metal-coordinated porphyrins to produce $^1O_2$ (**Fig. 1**). In this communication, the synthetic methodologies envisaged to prepare the new cationic porphyrin-triphenylphosphonium complexes (zinc, palladium and cobalt) will be discussed. Furthermore, the photophysical/photochemical characterization of the new conjugates and their potential to photoinactivate Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacterial strains will also receive special attention.

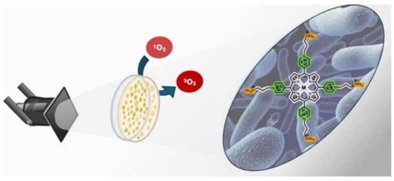

Fig 1. Schematic process of aPDT by using metalloporphyrins-based PS.

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In vivo activity of peptide-ionic liquid conjugates against diabetic wounds

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Due to widespread multidrug-resistant (MDR) microbes, efficient treatments for infected wounds are being exhausted, which means that there is an alarming lack of effective antibiotics to treat diabetic foot ulcers (DFU). The increasing life expectancy of the population and the growing incidence of unhealthy lifestyles is leading to a concerning rise in the number of people affected with diabetes and related complications, being DFU amongst the most troublesome. In 2014, already about 11% of the Portuguese population had diabetes and this number is continuously growing every year. [1] Like other chronic wounds, DFU are difficult to heal, but their association with other diabetes complications, such as peripheral neuropathy and ischemia, underpin an exceedingly low healing rate and high propensity for persistent infections.

In connection with the above, we have recently advanced peptide-ionic liquid conjugates (PILC) as potential active pharmaceutical ingredients for topical formulations to tackle DFU. PILC combine a short cosmeceutical peptide with collagen-boosting action, with an ionic liquid that has intrinsic antimicrobial action, linked together through the "click" copper-catalyzed azide-alkyne cycloaddition reaction. This revealed one conjugate with an outstanding performance *in vitro*, namely, potent collagen-inducing effect, alongside microbicidal (bactericidal and fungicidal) action.[2] This conjugate was now tested for its wound healing ability in a mouse model of streptozotocin (STZ)-induced type 1 diabetes. The promising results obtained thus far in this animal model, alongside biophysical investigations on the potential antimicrobial mechanism of action of PILC, will be presented in this communication.

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Stalling tumour cell growth with porphyrin-triphenylphosphonium conjugates

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Interest in telomeres and telomerase within the scientific community significantly increased after their role in chromosome protection and tumour cell growth was revealed. Due to their strong correlation with the initiation and progression of tumours, oncogenes and tumour suppressor genes have also gained significance [1]. The discovery that specific ligands can stabilise G-quadruplexes (G4), non canonic structures formed in telomeres and oncogene promoters, thereby inhibiting telomerase activity and/or regulating oncogene expression indirectly, has opened new avenues for cancer therapy. Consequently, several research groups are making considerable efforts to develop ligands that can effectively and selectively stabilize G4 DNA structures [2].

In accordance with the afore mentioned, we conducted an investigation into the ability of novel, highly charged porphyrins conjugated with triphenylphosphonium units to stabilise sequences capable of forming G4 structures, particularly the *c-myc* oncogene. In this study, diverse biophysical and biochemical methods, along with *in vitro* assays using two melanoma cell lines were employed [3]. The results obtained, concerning the affinity and selectivity of the porphyrin-triphenylphosphonium conjugates for G4 structures and their potential to interfere with tumour cell growth, will be presented and discussed.

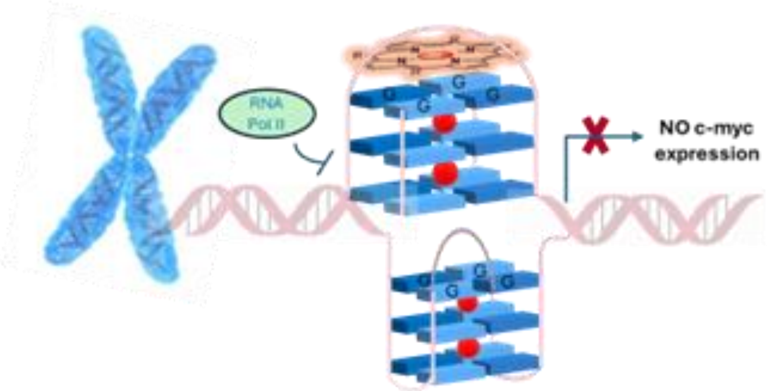

Fig.1. Indirect transcription suppression by *c-myc* inhibition

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Targeting G-quadruplexes with new acridone derivatives - an anticancer approach

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Due to the complexity of cancer disease, traditional therapies, such as conventional chemotherapy, might induce damage in human healthy tissues, as a result of the non-specificity of this therapy [1]. The discovery that telomeres and oncogene promoter DNA sequences can fold into G-quadruplex (G4) structures, that when stabilized by ligands can interfere with cancer cell replication, transcription and translation processes, prompted researchers to search for efficient G4 stabilizing ligands that can inhibit telomerase function and/or to regulate oncogene expression [2].

In this context, we report herein the ability of two novel acridone derivatives, the neutral **Acrid** and the cationic counterpart **Acrid+**, to stabilize telomeric and *c-myc* oncogene DNA sequences able to form G4 structures. In line with our interest in developing new heterocyclic compounds with the ability to stabilize G4 structures [3,4], the affinity and selectivity of acridones for G4 structures and their anticancer properties, will be presented and discussed based on the data obtained using different biophysical, biochemical methodologies and *in vitro* assays.

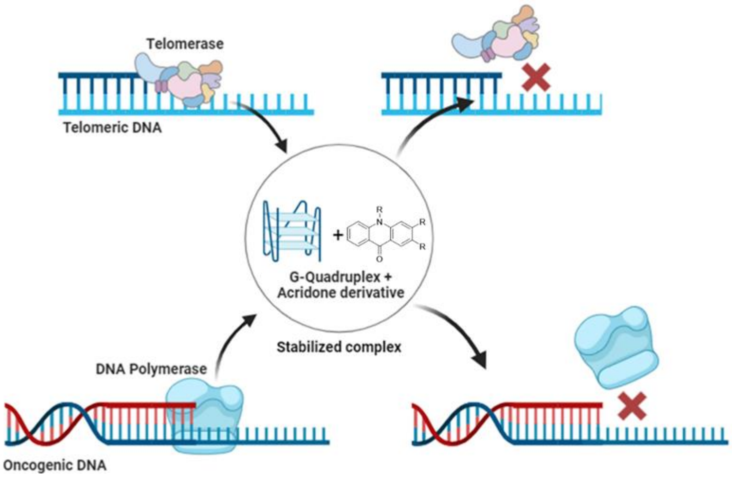

Fig. 1. Targeting telomeric and oncogenic processes with G4 stabilizing ligands.

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Caracterização química e propriedades antioxidantes das folhas de *S. oleraceus* cultivadas com diferentes soluções nutritivas

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Sonchus oleraceus L., popularmente conhecida como serralha, é um exemplo de Planta Silvestre Comestível (PSC) que têm ganho destaque para inclusão numa dieta devido ao seu alto valor nutricional e potencial terapêutico [1]. A serralha é rica em nutrientes e compostos antioxidantes que podem ajudar na prevenção de doenças relacionadas ao estresse oxidativo [2]. A utilização de diferentes soluções nutritivas através da hidroponia pode alterar a concentração de nutrientes e, consequentemente, a acumulação de compostos bioativos nas plantas [3], sendo isto essencial para otimizar as práticas agrícolas e maximizar o valor funcional, e comercial, das plantas cultivadas.

Este trabalho teve como objetivo caracterizar o perfil químico das folhas de *S. oleraceus* cultivadas com sob seis difererentes combinações de nitrogénio(N), fosforo (P) e potássio(K) que foram: 100-70-350 (N:P:K, Z1), 200-70-350 (Z2), 100-47-250 (Z3), 200-47-250 (Z4), 100-105-525 (Z5) e 200-105-525 ppm (Z6). Para isso, utilizaram técnicas cromatográficas para analisar os ácidos orgânicos (UPLC-PDA), tocoferóis (HPLC-FL), açúcares livres (HPLC-RI) e compostos fenólicos (HPLC-PDA/ESI-MS). Além disso, avaliou-se a capacidade antioxidante dos extratos hidroetanólicos das folhas através de dois ensaios *in vitro*: TBARS e OxHLIA.

Os ácidos orgânicos, oxálico, quinico, málico e cítrico foram identificados e quantificados em todas as amostras de *S. oleraceus*, sendo o ácido oxálico o composto maioritário presente, de 31.68±0.01 (Z2) a 45.9±0.3 mg/100 g de peso seco (Z6). As folhas de Z2 demonstraram o maior teor de ácido quinico. As isoformas α- e γ- tocoferóis foram identificadas em todas as folhas, verificando-se que um menor rácio de N favoreceu a concentração da isoforma α-tocoferol. Os açúcares, frutose, glucose e sacarose, apresentaram teores entre 9 a 13 g/100 g de peso seco das folhas, sendo a glucose o açúcar maioritário. Foram identificados e quantificados 4 ácidos fenólicos (derivados do ácido chicórico) e 3 flavonoides *O*-glicosilados, nomeadamente apigenina, luteolina e quercetina. Os maiores teores de ácidos fenólicos e flavonoides foram observados nas folhas originadas com concentrações baixas e intermediárias de P e K, tendo a solução nutritiva de Z1 demonstrado o maior conteúdo total de fenólicos, seguido de Z4. O extrato das amostras de folhas de Z6 revelaram maior atividade antioxidante no ensaio TBARS enquanto o extrato de Z2 destacou-se no ensaio OxHLIA. Este trabalho destaca a influência significativa e a importância da nutrição hidropónica com diferentes teores de N:P:K para a maximização do conteúdo em compostos de alto valor agregado e funcional, potencializando assim as aplicações das folhas de serralha.

Agradecimentos

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Impact of Solvents in Modulating Phytochemical Composition and Antioxidant Activity of *Cannabis sativa* Inflorescence Extracts

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The *Cannabis sativa* plant has been used for therapeutic purposes and has a rich history. Its complex chemical composition contains flavonoids, terpenes, cannabinoids, and other phytochemicals [1]. Among them, the medicinal properties of cannabinoids—such as their analgesic, anti-inflammatory, antioxidant, and neuroprotective qualities—have been the subject of much investigation [2]. Despite existing research, many questions remain unanswered regarding cannabis's ability to treat medical conditions. The goal of the current work is to explore the impact of different extraction solvents on the phytochemical composition and antioxidant activity of the resulting extracts, using both non-decarboxylated and decarboxylated plant material.

The extracts were obtained from *C. sativa* dried inflorescences by solvent extraction, using ethanol (EtOH), methanol (MeOH), hexane (Hex), and dichloromethane (DCM) applied to non-decarboxylated and decarboxylated plant material. Decarboxylation was performed at 120 ºC for 1 h before extraction. The phytochemical profile of the resulting extracts was determined by GC/MS after trimethylsilylation [3], and their antioxidant capacity was evaluated through the radical DPPH$^\bullet$ scavenging assay.

All extracts had high concentrations of cannabinoids, as would be expected. Within this family, tetrahydrocannabinolic acid (THCA) and Δ^9-tetrahydrocannabinol (Δ^9-THC) were the main compounds detected. Regarding minor components, some differences could be found among the extracts: MeOH extracts from both decarboxylated and non-decarboxylated samples contained a variety of compounds from different chemical classes, including amino acids, alcohols, carboxylic acids, sugars, and terpenes, Hex extracts mostly contained terpenes, while DCM extracts displayed a higher fatty acid predominance. Among terpenes, the GC/MS data allowed concluding that Hex mainly extracted sesquiterpenes, with *trans*-caryophyllene being the most abundant. Among monoterpenes, α-pinene and β-myrcene were the major compounds detected. As for amino acids, asparagine was identified as the most abundant, while α-linolenic acid was the dominant fatty acid extracted. Overall, decarboxylation primarily resulted in a reduction in terpene concentration, followed by a substantial reduction in the quantities of alcohol, sugars, and carboxylic acids. In terms of antioxidant potential, the MeOH extract revealed the highest activity, like that of the EtOH extract, while the DCM extract exhibited the lowest antioxidant activity. Notably, all extracts showed enhanced antioxidant activity after decarboxylation, suggesting that Δ^9-THC, the main product of this process, may be a key contributor to this bioactivity.

In summary, this work is essential as it improves extraction processes to increase the yield and bioactivity of extracts from *C. sativa*. It also offers important insights into how different solvents and decarboxylation affect the chemical composition and antioxidant qualities of the plant.

Fundings

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Exploring Alkylaminophenols for Anti-Inflammatory Activity via COX-2 Inhibition

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Alkylaminophenols are a family of synthetic phenolic Mannich bases that leverage the bioactivity of both phenols and amines. One of the main synthetic routes for these molecules is the Petasis borono-Mannich (PbM) reaction, a robust multicomponent reaction involving salicylaldehyde, an amine, and a boronic acid. This reaction is very robust and accepts a wide range of commercially available substrates, being excellent for chemical space diversification.[1] The bioactivity of alkylaminophenols is still a research topic lacking in understanding. In particular, while their anticancer and antimicrobial activities are well documented and reported in the literature,[2][3] their anti-inflammatory activity is largely unexplored. This study will explore the anti-inflammatory potential of these compounds by means of a multi-faceted approach based on computational, chemometric methodologies and experimental methodologies.

Building on our previous experimental and computational analysis of a library of 100 alkylaminophenols, we identified several compounds with COX-2 inhibitory potential for further derivatization and testing. Positional analog scanning (PAS), a computer-assisted molecular design technique, was employed to identify key single substitutions that could significantly enhance activity.[4] Following molecular docking studies, top performing derivatized scaffolds were selected and synthesized via the PbM reaction using a green protocol.[5] COX-2 inhibitor activity, and cell viability of the compounds in a human monocyte cell line (THP-1) were determined to provide insights into how these derivatizations affect the inhibition and toxicity of these compounds. Two alkylaminophenols with moderate inhibitor activity (33% and 47% at 100 µM) were selected for derivatization and seven new derivatives were synthesized (**Fig 1**). The new derivatizations produced an overall positive effect on inhibitory activity, increasing it by 10% in some cases, however solubility of the compounds in aqueous media seems to be reduced.

The synergy between computational methodologies, chemical design, and experimental testing has allowed us to unveil new properties of this alkylaminophenol family and potentially unlock a new family of COX-2 inhibitors.

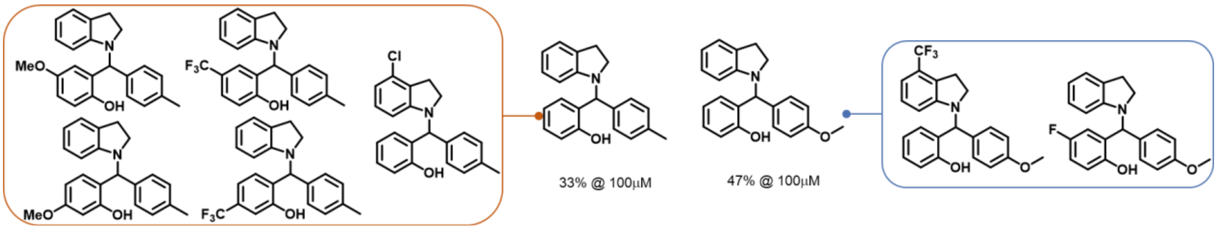

Fig.1. Chosen alkylaminophenols and their corresponding newly synthesized derivatives.

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Antioxidant and Neuroprotective Potential of Extracts from the Invasive Macroalga *Undaria pinnatifida* on the Coast of Portugal: A Comparative Study Using Sustainable Extraction Techniques

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This study aimed to evaluate the antioxidant and neuroprotective capacities of extracts of the brown macroalga *Undaria pinnatifida* (Harvey) Suringar, an invasive species on the coast of Portugal. Twenty-two extracts were obtained using efficient and sustainable methodologies, such as subcritical water extraction (SWE) and ultrasound-assisted extraction (UAE), using recovered acetone, ethanol and water as solvents. The best extraction yields were achieved with SWE at 120°C/20 bar and 150°C/30 bar, followed by the aqueous UAE extract. In terms of total carotenoid content (TCC) and total phenolic content (TPC), acetonic UAE and SWE-150°C/30 bar provided the best results, respectively. Based on these three parameters - yield, TCC and TPC - the extracts selected for antioxidant capacity evaluation included SWE-120°C/20 bar, SWE-150°C/30 bar, acetonic-UAE and aqueous-UAE extracts. The SWE-150°C/30 bar extract exhibited the strongest antioxidant activity, showing 73.58 ± 2.62 μg trolox equivalents/mg and 26.05 ± 1.29 μg ascorbic acid equivalents/mg using the ABTS and FRAP methods, respectively. The acetonic-UAE extract also demonstrated the highest phlorotannin content.

Subsequently, two extracts (acetonic-UAE and SWE-150°C/30 bar) were selected to be evaluated for their effectiveness against physiologically relevant radicals and enzymes associated with Alzheimer's disease. The SWE-150°C/30 bar extract demonstrated the highest nitric oxide (•NO) scavenging capacity, while the acetonic-UAE extract was the strongest against hydroxyl radical (•OH). Only the acetonic-UAE extract was able to inhibit both acetylcholinesterase (AChE) and butyrylcholinesterase (BuChE), with inhibitions of 81.61% and 47.92% at a concentration of 0.25 mg/mL, respectively. These results highlight these two extracts as the most promising candidates for further research, due to their potent antioxidant and neuroprotective properties.

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Nanoconstructed MMP9-targeted probes for therapy and medical imaging of airway inflammation in COPD

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Inflammatory airway and lung diseases, such as chronic obstructive pulmonary disease (COPD), arise from an imbalance between oxidants and antioxidants, leading to persistent airway inflammation. The increasing prevalence and significant burden of these conditions pose major global health challenges. In COPD, there is an elevated expression of various matrix metalloproteinases, particularly MMP9, which acts both as a downstream effector and an upstream mediator in growth and inflammatory pathways. This dual role makes MMP9 a compelling therapeutic target and prognostic biomarker [1,2].

Fluorescence-based optical imaging is extensively used in biochemical assays due to its high sensitivity and rapid response times [3]. Activatable fluorescent probes enhance the signal-to-background ratio, providing reliable tools for monitoring protease activity [4]. A promising design strategy for these probes involves energy transfer between a donor (fluorescent dye) and an acceptor (fluorophore or chromophore) positioned at opposite ends of a peptide. Upon cleavage of the peptide sequence by a specific enzyme, these activatable probes transition from a non-fluorescent (“off”) state to a fluorescent (“on”) state, emitting a signal proportional to the enzyme's activity (Figure 1).

Herein, we present our work on developing specific substrates for MMP9, the selected inflammation biomarker in COPD. Target peptides were synthesized using microwave-assisted solid-phase peptide synthesis (MW-SPPS) and labelled with a near-infrared FRET pair (Cy5/BHQ3). These probes were evaluated as fluorescent reporters for monitoring MMP9 activity within a nanoconstructed system designed for the targeted administration of an immunosuppressive drug.

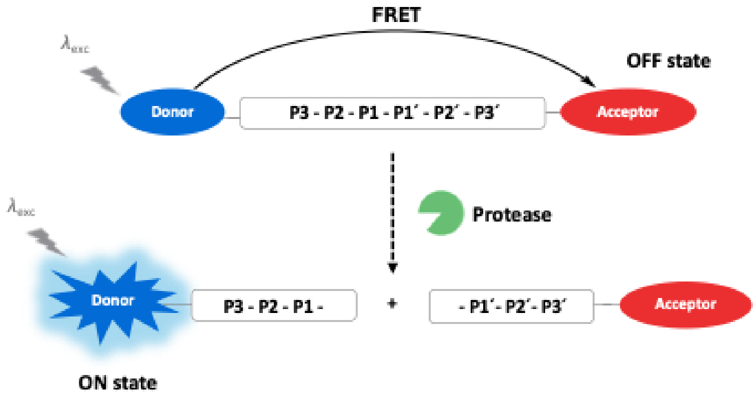

Fig.1. FRET process between donor and acceptor, and the action of a protease.

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C-Glycosylquinolones: Synthesis and Assessment of Anticancer Properties

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Quinolin-4(1*H*)-ones (or 4-quinolones), recognized for their antibiotic properties, are gaining attention as promising anticancer agents due to their ability to target type IIA topoisomerases like DNA gyrase and topoisomerase IV [1]. Recent *in vitro* and *in vivo* studies showed that glycosylated quinolines, designed to enhance solubility and bioavailability, exhibit improved selectivity for cancer cells while sparing normal healthy cells to some degree [2].

In this study, we synthesized novel *C*-glycosylquinolones through an ohmic heating-assisted Heck reaction, combining (*E*)-3-iodo-1-methyl-2-styrylquinolones with a vinylated sugar in a water/polyethylene glycol mixture as solvent. This heating method significantly reduced reaction time compared to traditional heating techniques. We then screened the resulting compounds' library in different human cancer cell lines - A549 (adenocarcinoma human alveolar) and SH-SY5Y (neuroblastoma) - to evaluate their toxicity and influence on enzymatic activity to identify potential anticancer agents.

After 24 hours of incubation, the synthesized *C*-glycosylquinolones exhibited low toxicity across both cell lines. However, extending the incubation time to 48 hours resulted in a marked increase in toxicity, with IC_{50} values decreasing significantly, at least 60% (Figure 1). The presence of a methyl group in the styryl moiety seems to enhance the cytotoxic activity of the compound when compared to the methoxy, chlorine and non-substituted derivatives, in both cell lines. This compound also leads to the disruption of mitochondrial membrane potential at 25 μM. Also, all compounds promoted a significant decrease in cellular ROS production, at least at 6.25 μM, being the methoxy derivative the most active. The activity of cytosolic antioxidant enzymes such as SOD and CAT, was assessed, showing that both methyl and methoxy derivatives significantly increase SOD´s activity. On the other hand, the non-substituted derivative shows an enhance of CAT's activity when compared to the control.

We are currently investigating the effect of these compounds in the activity of some other antioxidant and mitochondrial enzymes. Further details of this study, including a structure-activity relationship analysis toward the identification of a lead compound, will also be presented.

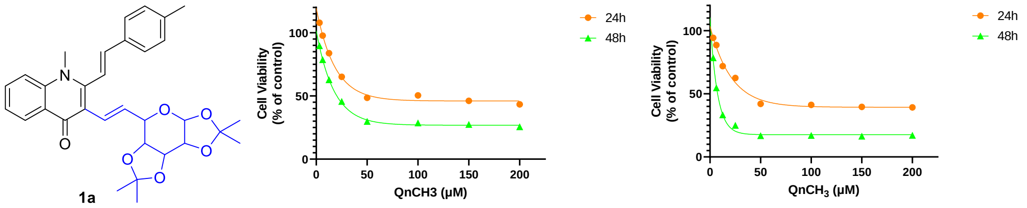

Fig.1. Results of incubation of A549 and SH-SY5Y cells with *C*-glycosyl quinolone **1a** at 24h and 48h.

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Molecular docking studies on agonist binding to somatostatin subtype-4 receptor

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The G-protein coupled receptors are pivotal in drug discovery, acting as therapeutic targets for a wide array of drugs due to their central role in cellular signaling processes [1]. The somatostatin receptor-4 (SSTR4) is a G-protein coupled receptor primarily located in the CNS and lungs, where it modulates inflammation and pain perception. Developing SSTR4-targeting drugs could lead to new treatments for inflammatory diseases and chronic pain [2]. Despite the limited exploration, SSTR4 agonists, like J-2156, have shown promise in preclinical studies [3]. Molecular docking studies can help address the relatively underexplored area of SSTR4-targeting drugs by providing detailed insights into its binding sites, enabling the rational design of molecules that can effectively target and modulate its activity. With the advent of machine learning, novel deep learning techniques that can learn complex patterns from GPCRs-ligands datasets can substantially improve classical docking and virtual screening studies [4].

This work aims to evaluate the plausibility of natural alkaloid and its analogues as SSTR4 agonists using molecular docking techniques. Classical molecular docking simulations were conducted using AutoDock Vina. Positional similarity among the top ten docking poses of the alkaloid was assessed using Maximum Common Substructure and root-mean-square deviation values and analyzed via hierarchical clustering.

The alkaloid displayed a binding site on SSTR4 distinct from the known ligand, J-2156. The binding affinities of two series of analogs were also studied. Series A analogs showed similar affinities to the natural product, while series B analogs demonstrated enhanced binding.

Additionally, we compared the scoring values from classical docking strategies with those from deep learning-based scoring functions to test the expected enhancement in accuracy provided by these methods.
In conclusion, the alkaloid and its analogs showed a high affinity for SSTR4, surpassing J-2156 in some cases, making them promising candidates for further investigation.

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Síntesis y estudio biológico de nuevos derivados de ácidos resínicos procedentes de biomasa como agentes antitumorales y antivirales

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En la búsqueda de fuentes renovables y sostenibles, la biomasa ha sido una opción prometedora que recibe cada vez mayor atención en la comunidad científica. En este contexto, la colofonia, un producto derivado de la resina de los pinos que tiene distintas aplicaciones industriales, es de interés debido a su riqueza en ácidos resínicos [1]. Numerosas publicaciones han resaltado la relevancia de estos compuestos y sus derivados, particularmente aquellos pertenecientes a la familia de los abietanos (Figura 1), por su potencial biológico como antitumorales y antivirales [2-7].

En este trabajo, presentamos la síntesis de nuevos derivados de ácidos resínicos obtenidos a partir de la colofonia, evaluando sus propiedades antitumorales y antivirales. Los ensayos biológicos preliminares indican que varios de estos derivados muestran una mejora significativa en la actividad antitumoral y antiviral en comparación con los compuestos de origen.

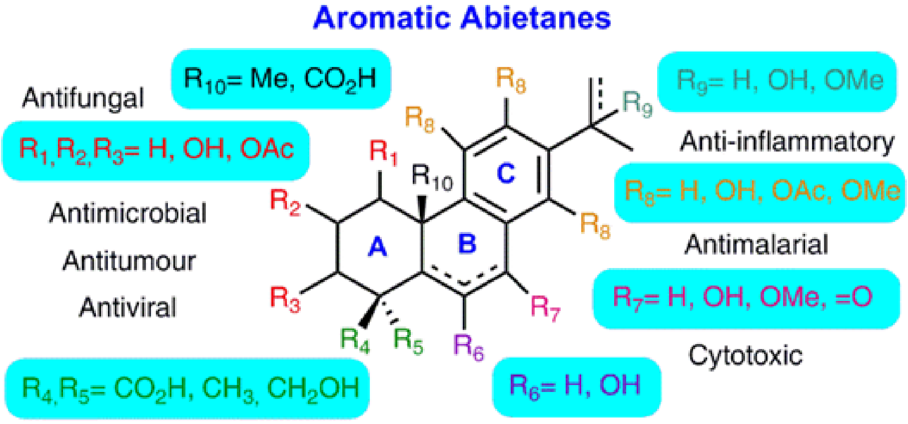

Figura 1. Estructura general de abietanos bioactivos

Agradecimientos
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QUÍMICA TEÓRICA

A computational strategy for the design of targeted nanomedicines in cardiovascular diseases

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Cardiovascular diseases (CVD) are responsible for 17.9 million deaths every year. Myocardial infarction kills up to 1 billion cardiac cells, which are replaced by fibrotic tissue, impairing heart function[1]. Current therapeutic options only manage the symptoms and produce side effects. To solve these issues, nanomedicine has emerged as a promising tool for the treatment of CVDs[2].

This work aims to development nanomedicines for targeted delivery to the cardiac tissue, through the rational functionalization of nanoparticles. For that, three membrane proteins expressed in the infarcted heart were selected: Atrial Natriuretic Peptide Receptor 1 and 3[3], and Angiotensin II Receptor type 1[4].

For each protein, multiple computational membrane models were built, and molecular dynamics simulations were performed for each model. Three replicas were performed for each model, all 300 ns in length. AMBER21 was used for the simulations[5]. Using MM/GBSA, the capability of each model to correctly represent the interaction between ligand and protein was assessed. The results indicated that all systems accurately modelled the interactions between the proteins and the ligands.

After analysing the results from the MD simulation, multiple structures of each protein were extracted from via cluster analysis. Across all proteins, a total of 109 structures were obtained, and then used for the optimization of a virtual screening protocol.

In this work, computational models for three membrane proteins were developed and a virtual screening protocol was optimized. In the future, the virtual screening will be performed, and the hits will be further studied with more advanced computational methods, culminating in experimental validation.

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Líquidos porosos y el comportamiento absortivo selectivo de CO_2 y SO_2 mediante Dinámica Molecular.

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En este estudio se analiza desde una perspectiva teórica utilizando Dinámica Molecular el encapsulamiento competitivo de SO_2 y CO_2 gaseoso en diferentes condiciones de temperatura y características de simulación en un líquido poroso de Tipo II [1-3], compuesto por una fase líquida de diclorometano y de un sólido poroso criptofano-111. El CO_2 gaseoso tiene a ocupar las cavidades con una mayor selectividad que se va viendo revertida conforme la temperatura aumenta en el sistema. Se observa la capacidad del CO_2 de ser empujado de la cavidad por otros gases. El SO_2 no es capaz de abandonar el poro, pero se observa cierta interacción con gases fuera del poro. La estabilidad de la molécula fue analizada mediante cálculos de Gaussian. Los resultados obtenidos muestran la selectividad de los líquidos porosos frente a la captación de diferentes gases de interés ambiental y como método de separación y almacenamiento de estos.

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Instituto de Química-Física Blas Cabrera, CSIC

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Unraveling the cellular battle: Antimicrobial peptides and membranes disrupted by COVID-19 using Molecular Dynamics

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In the current post-pandemic stage, an increasing number of people are being affected by persistent COVID (Post COVID condition, PCC). It is estimated that 10% to 20% of those who contracted the virus do not fully recover, experiencing persistent symptoms for months after overcoming the initial infection [1,2]. The lipid profile of patients has been shown to be altered due to infection [3,4], which could be a key biomarker in the search for therapies for patients with this condition.

Recently, we published an article exposing the possible relationship between AMPs and lipid alteration in these patients [5]. Antimicrobial peptides (AMPs) are able to detect and destroy pathogens by attacking their membrane. However, situations such as persistent COVID can lead to an uncontrolled inflammatory response by recognizing healthy host cells as their target, making them a "double-edged sword".

In this work, we employed Molecular Dynamics (MD) simulations to study the interaction of AMPs with a model cell membrane of a patient with persistent COVID. The results indicate that the modification of the composition increases the affinity of these peptides contributing to over inflammation, opening doors to future research on how AMPs may affect other chronic inflammatory diseases, as well as possible therapeutic.

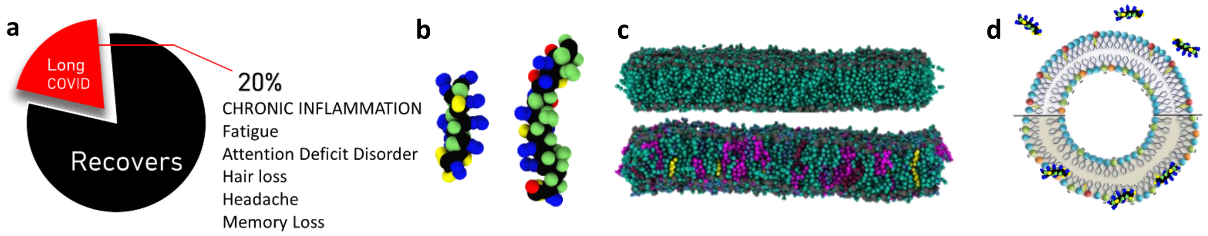

Fig.1. A. Pie chart representing the distribution of recovered patients versus those who maintain some symptoms of PCC. **B.** Parasin-I and LL37, the peptides used in this study at Coarse-Grained resolution. **C.** Membrane models in Coarse-Grained resolution: Healthy mammal in the upper part and PCC in the lower part. **D.** Representation of how the peptides interact with a healthy membrane, barely coming into contact, as opposed to the infected one. Lipids represented: POPC (Palmitoyl Oleoyl Phosphatidyl Choline, light green), POPI (Inositol, Curious Blue); POPE (Ethanolamine, Magenta); POPS (Serine, Violet); Cholesterol (Yellow) and Cardiolipin-II (Pompadour). Gray for polar heads (PO4).

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Exploring the Membrane Binding Interactions and Reaction Pathways of Snake Venom Phospholipase A_2 Toxin: A Computational Study

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Snake venom-secreted phospholipase A_2 (svPLA_2), a potent toxin found in almost all snake species, contributes significantly to the morbidity and mortality associated with snakebite envenomation. These enzymes disrupt the integrity of plasma membranes through the catalysis of phospholipid hydrolysis [1,2], leading to serious pathological manifestations such as muscle cell damage, paralysis, blistering, inflammation, and pain [1-3]. The critical role of svPLA_2s in the toxic process of envenomation is clear. However, our understanding of the precise reaction mechanism is limited, hindering the development of effective antivenoms. This study focuses on Myotoxin-I, a svPLA_2 enzyme isolated from the venom of the Terciopelo pit viper (*Bothrops asper*). This species, found throughout South and Central America, is known for its aggressive behavior and highly toxic venom [4], making it the leading cause of envenomation in its habitat [5-7].

Here, we investigate the interactions between svPLA_2 and a 1:1 POPC/POPS membrane and the impact of svPLA_2 binding on the structure and dynamics of the modeled membrane. Additionally, this study investigates the two most recognized reaction mechanisms for svPLA2s: the 'single-water mechanism' [8] and the 'assisted-water mechanism' [9]. Through umbrella sampling simulations at the PBE/MM level of theory, our findings suggest that while both mechanisms are feasible, the 'assisted-water mechanism' is more favorable, as it yielded a lower activation-free energy barrier (21.84 kcal/mol) for the cleavage of the substrate. The highly conserved active site structure in svPLA_2 enzymes across vipers likely indicates a shared catalytic mechanism.

Our study suggests that the only clinical-trial small molecule inhibitor for snakebite is an excellent model of a transition state analog, highlighting the need for research into svPLA_2 catalytic mechanisms to develop novel and effective inhibitors.

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Ensemble-weighted prediction of phtotophysical properties of BODIPY derivatives

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Fluorescence-based probes are a powerful tool to observe living systems in real time with spatiotemporal precision. 4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) derivatives are widely used as bioimaging probes due to their excellent photophysical properties, high quantum yields, and chemical stability[1]. Indeed, the spectral signature of a large number of BODIPY-derivatives is sensitive to its chemical environment, allowing interesting applications such as tracking intracellular pH variations within living cells[2]. Unfortunately, many of these properties are difficult to predict using traditional TDDFT due to the multiple solvent-BODIPY-derivative configurations that are thermally available. This has long prevented the rational design of novel BODIPY-derivatives for bespoke applications in analytical and bioanalytical chemistry.

In this work we report a simple protocol for predicting the UV/Vis absorption spectra of BODIPY-derivatives in different chemical environments using Molecular Dynamics (MD) simulations of a nanodroplet (approx. 3 nm in diameter). The UV/Vis spectra of randomly selected frames from the trajectory of the MD simulation are evaluated using the fast xTB-STDA approach by Grimme and co-workers[3] and weighted against a Maxwell-Boltzmann distribution function[4]. The resulting UV/Vis spectra closely resembles the experimental ones (specially around the signature signal at 500 nm), outperforming both the traditional TDDFT approach using continuum solvent methods (CPCM) as well as weighted TDDFT predictions on the sampled trajectory, as depicted in Figure 1.

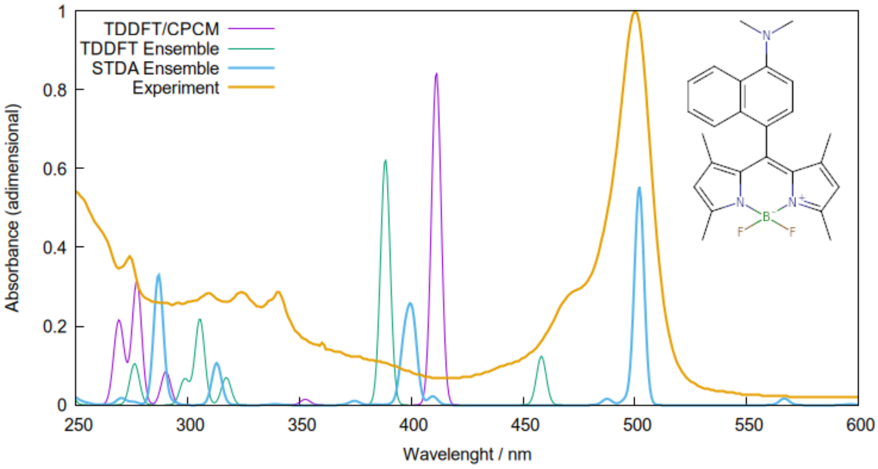

Fig.1. Experimental UV/Vis spectrum of *meso*-(*N,N*-dimethylaminonaphthyl)-BODIPY (yellow) and three different computational approaches: TDDFT/CPCM at the equilibrium geometry (violet), TDDFT of explicitly solvated molecule (green) and the method proposed in this work (blue).

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Molecular basis of a photoswitchable histone deacetylase inhibitor: N-(2-Aminophenyl)-3-(4-((methoxyphenyl)diazenyl)phenyl)propanamide.

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Cancer is one of the most prevalent diseases in the modern era. There are numerous therapeutic approaches to combat it, including anticancer drugs (chemotherapy). However, in the majority of cases, these drugs affect cancer cells and healthy cells indiscriminately, leading to the development of significant adverse effects in patients. Targeted therapies were developed to minimise the side effects, but selectivity remains a significant challenge. Nevertheless, in many cases, the tumour is localized to a specific part of the body. This presents an opportunity to develop a solution that reduces side effects and increases the efficiency of oncology treatment. One potential solution is the external and localized activation of drugs.

The present study examines the isomerisation of the cis and trans isomers of a photoswitchable histone deacetylase inhibitor (HDACi) that Josa-Culleré et al. developed as a potential anticancer drug[1], as well as the interactions between the isomers and the protein. For this purpose, quantum mechanics (QM), molecular dynamics (MD) and quantum mechanics/molecular mechanics (QM/MM) calculations were performed. The isomerisation of this molecule can be controlled by external visible light allowing the activation/deactivation of its properties as an inhibitor. This light-activatable anticancer drug can be activated locally in the tumour zone, increasing its efficacy and reducing the side effects.

The results demonstrate that the cis isomer is introduced into the active pocket of the HDAC, preventing lysine residues of histones from interacting with it and, as a consequence, inducing apoptosis in the cell. Conversely, the interactions of the trans isomer are not stable enough to produce this effect, allowing the interactions between lysine residues and the protein active site to produce the deacetylation. Therefore, healthy cells far from the tumour zone will not be affected by the inhibitor, as it is in the trans form. In contrast, the tumour zone will be affected, as it will be irradiated with light to activate the inhibitor.

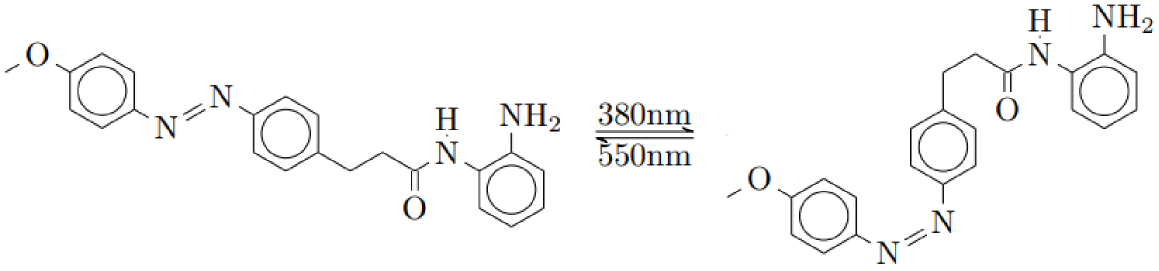

Fig.1. Chemical structures of photoisomers that will be studied.

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SEGURIDAD QUÍMICA

Exploring the effects of parabens on neutrophil activation: a study of oxidative burst in hyperglycemic conditions

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Parabens, a group of alkyl esters of 4-hydroxybenzoic acid, are widely used as antimicrobial agents in various industries, including cosmetics, pharmaceuticals, and food [1]. However, growing evidence suggests that parabens can act as endocrine-disrupting chemicals with the potential to induce inflammation. In the inflammatory process, neutrophils play a key role by generating reactive species as a defense mechanism against invading pathogens, a process known as oxidative burst. When overproduced, these species contribute to diseases such as Diabetes mellitus (DM) [2]. Therefore, this study aims to explore the impact of common parabens - namely methylparaben, ethylparaben, propylparaben, and butylparaben - and their metabolite, 4-hydroxybenzoic acid (4-HB), on human neutrophils' oxidative burst under physiological and hyperglycemic conditions, a hallmark of DM.

In this study, isolated human neutrophils were exposed to parabens and 4-HB. The oxidative burst in neutrophils was detected using the fluorescent probe dihydrorhodamine 123. Cell viability and the mechanisms involved in reactive species production were also assessed. The obtained results demonstrated that parabens stimulate neutrophils' oxidative burst under both physiological and hyperglycemic conditions via the activation of phospholipase C and protein kinase C, leading to the subsequent activation of nicotinamide adenine dinucleotide phosphate (NADPH) oxidase and myeloperoxidase. Methylparaben induced the highest production of reactive species under physiological conditions, while propylparaben triggered the greatest increase under hyperglycemic conditions. No significant effects were observed with exposure to 4-HB.

These findings suggest that paraben exposure induces oxidative stress in neutrophils, with heightened effects under hyperglycemic conditions, potentially contributing to the exacerbation of inflammation in DM. This underscores the need for further investigation into their broader health implications.

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COMUNICACIONES PÓSTER

QUÍMICA ALIMENTARIA

Vertical farming of micro- and baby greens: Influence on organic acid, free sugar, betalain, and phenolic compound contents

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Consumers are increasingly cautious about their dietary choices, searching for fresh foods, such as vegetables, for their functional and potential health-promoting effects [1]. Microgreens are small tender vegetables harvested when the cotyledon leaves are formed alongside one set of true leaves, typically between 7 and 14 days. In contrast, baby greens are also small vegetables but are harvested when true leaves have formed, generally containing between two and eight true leaves, with a growing cycle of 20 to 40 days [2]. Swiss chard (*Beta vulgaris* var. *cicla*), a member of the Amaranthaceae family, is rich in phenolic compounds, betalains, chlorophylls, and carotenoids, making it a suitable candidate for microgreen production [3,4]. This study aimed to produce Swiss chard micro- and baby greens from white, yellow, pink, and orange varieties under soilless conditions and to characterize their profiles of phenolic compounds, betalains, free sugars, and organic acids.

The microgreens were grown in a walk-in growth chamber equipped with LED lamps under controlled conditions and irrigated with a TriPart® Grow NPK 3-1-6 nutrient solution as necessary. Microgreens were produced in polystyrene trays filled with vermiculite, while baby greens were cultivated in individual phenolic foams. Microgreens and baby greens were harvested 14 and 34 days after sowing, respectively. A solid-liquid extraction using 80% ethanol was then performed to characterize the phytochemical composition of the plant material using different chromatographic techniques.

Although the samples did not present free sugars, one organic acid (oxalic acid) was identified, with the orange and white microgreens exhibiting the highest and lowest concentrations, respectively. For baby greens, the yellow and orange varieties presented the highest and lowest concentrations, respectively. Seven phenolic compounds were identified in the microgreen and six in the baby greens. Among baby greens, only the white variety contained betalains (one betacyanin and three betaxanthins). The white microgreens presented seven betalains (two betacyanins and five betaxanthins), while only one betacyanin was identified in the orange, white, and pink microgreens. This study highlighted the potential of environmentally sustainable agriculture practices to produce Swiss chard microgreens and baby greens. Nevertheless, further studies on optimized production conditions and compound extraction techniques are required.

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Comprehensive Analysis of Emerging and Persistent Contaminants in Widely Consumed Fish Species from the Portuguese Coast

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Portugal's extensive coastline has supported a longstanding and vital fisheries industry, with important socio-economic impact and making seafood (fish and shellfish) a key component of the Portuguese diet. In fact, Portugal's fish consumption is 2.5 times higher than the European Union average [1,2]. Fish is rich in several essential nutrients: vitamins (such as A, D, B2, and B12), long chain polyunsaturated omega-3 fatty acids (ω-3 PUFA), proteins and minerals (including magnesium, calcium, selenium, zinc, phosphorus, and iodine). Therefore, its consumption is encouraged [3] as part of a healthy diet. However, fish may also accumulate environmental contaminants, raising food safety concerns [4].

This work focused on two widely consumed and cost-effective fish species from the northern Portuguese coast: Atlantic horse mackerel (*Trachurus trachurus*) and blue whiting (*Micromesistius poutassou*). A validated analytical method involving QuEChERS extraction and dispersive solid-phase extraction (SPE) clean-up was applied to assess 40 environmental contaminants, including emergent and persistent contaminants. These are categorized into six chemical groups: 14 organochlorine pesticides (OCPs), 5 polychlorinated biphenyls (PCBs), 6 brominated flame retardants (BFRs), 6 organophosphorus pesticides (OPPs), 8 organophosphate esters (OPEs) and a dioxin. Quantification was performed either by gas chromatography (GC) flame photometric detection (FPD) or electron capture detection (ECD). Following the European Commission's SANTE guidelines [5,6], the method was validated for linearity, detection and quantification limits, precision (intra- and inter-day), recovery, matrix effect, and relative combined measurement uncertainty.

Trace levels of contaminants were detected in both fish species, although these levels were lower compared to those reported in other widely consumed species, such as salmon and tuna [7,8]. Atlantic horse mackerel and blue whiting, often overlooked in favour of more expensive fatty fish like salmon or tuna, offer a nutritious and affordable alternative. This study supports the increased consumption and recognition of these undervalued species. Despite deeming the fish samples analysed safe for consumption, this study emphasizes the need for continued surveillance of environmental pollutants, using greener, multi-analyte analytical methods, in line with *OneHealth* principles.

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Aromatic changes in Albariño wine processed by High Pressure Processing (HPP)

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Aroma is due to numerous compounds that provide flavor and taste to the wines, and are mainly responsible for the quality of the white wines. Galician wines elaborated with the autochthonous white variety Albariño have a typical aromatic profile and reported in several works [1-3].

High Pressure Processing (HPP) is a technology implemented in food industry since the end of nineties applied to preserve food products inactivating microorganism and enzymes while providing minimum changes in nutritive and sensory properties [4]. The first work applying HPP in enology was published 30 years ago, in order to reduce yeast counts in a sweet white wine [5]. In this work we have studied the effect that HPP can have on the aromatic profile of Albariño wine when used as a substitute for filtration prior to wine bottling, thus preventing oxidation, reduction, polymerization, esterification and hydrolysis processes, among others.

Two different HPP conditions (500 MPa during 6 min and 300 MPa during 3 min) were applied in Albariño monovarietal wines without filtering, provided by a warehouse from Rías Baixas Denomination of Origin (2022 vintage). Filtered wine using cellulose were also provided to be used as control sample. No filtered wines were placed in 100 mL polyethylene bags and processed at room temperature in a Stansted Fluid Power equipment. Volatile compounds were extracted by liquid-liquid extraction with dichloromethane and subsequent injection and quantification by gas chromatography-mass spectrometry (GC-MS).

In total 49 volatile compounds were found and identified, their variation in percentages considering samples processed by HPP *versus* control samples (no filtered wine) are shown in **Figure 1**.

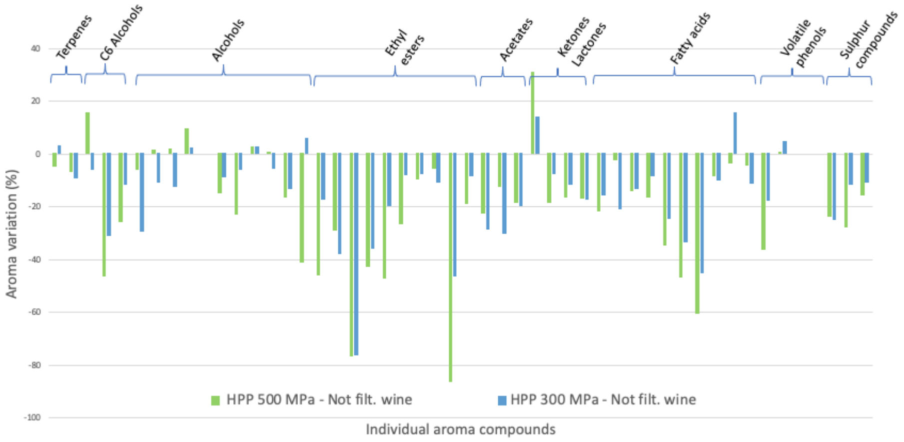

Fig.1. Aroma variation (%) in wine processed at 500 and 300 MPa compared to no filtered wine

Most of the aromas have less concentration in samples processed by HPP. It means that chemical reactions involved in aromas production are less favored by HPP. In fact, HPP promote reactions where the final products occupy less volume [6] and most of these volatile compounds are gases, so pressurization encourage those reactions that formed less aromas in not filtered wine.

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Comprehensive Profiling of Phenolic Compounds in Olive Pomace using HPLC-DAD-MS-ESI⁺

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Olive pomace, a by-product of olive oil production, has demonstrated phytotoxic properties that may hinder agricultural practices. However, the phenolic compounds responsible for this phytotoxicity could have further food applications and convey health benefits if extracted from olive pomace [1]. This study aimed to identify and quantify the phenolic compounds present in olive pomace collected in Alfândega da Fé, Portugal, through High-Performance Liquid Chromatography-Diode Array Detection-Mass Spectrometry with Electrospray Ionization in positive mode (HPLC-DAD-MS-ESI⁺) [2].

Fourteen compounds were identified, including several tyrosols, flavones, a cyclitol, and a hydroxycinnamic acid. The major phenolics present were oleacein (around 31.1 mg/g), ligstroside-aglycone (about 11.3 mg/g), and hydroxytyrosol (approximately 10.9 mg/g). The total phenolics content was 93.2 mg/g. The main antioxidants identified in olive pomace have a variety of beneficial effects. Oleacein, ligstroside-aglycone, and hydroxytyrosol are recognized for their powerful antioxidant properties, helping to neutralize free radicals and reduce oxidative stress. This contributes to the protection of cells from oxidative damage, potentially lowering the risk of developing chronic diseases such as cardiovascular disorders and certain types of cancer [3]. Additionally, these compounds have been shown to exhibit anti-inflammatory effects, further enhancing its role in promoting heart health and reducing inflammation-related diseases. Oleacein's potential neuroprotective properties also suggest a role in supporting cognitive function and reducing the risk of neurodegenerative diseases. Ligstroside-aglycone may also enhance metabolic health by promoting better blood sugar regulation and supporting weight management [3].

In sum, the comprehensive profiling of olive pomace revealed a rich composition of phenolic compounds, with tyrosols being predominant. While these compounds are partially responsible for olive pomace's phytotoxicity, their extraction can facilitate their use in the formulation of food products or dietary supplements with health-promoting properties, thereby enhancing the economic value of olive pomace and reducing waste. Future research should focus on the extraction methods and bioavailability of these compounds to explore their potential uses in food formulations.

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Evaluation of *Bacillus cereus* growth in different nutritional food matrices containing a biosurfactant extract from corn steep liquor produced at pilot scale

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Bacillus cereus is a common contaminant of plant-based food, such as cereals or fruits, due to infections through contaminated soils, being widespread in the environment [1]. Nowadays, formulation of biopesticides requires the introduction of novel compounds that are more environmentally friendly. Therefore, surfactants of microbial origin, called biosurfactants, obtained from agro-industrial residues represent an important new ingredient to be introduced in these formulations due to their antimicrobial, solubilizing and biodegradable features. Among the sources of production of biosurfactants, corn steep liquor (CSL), an aqueous stream derived from the production of corn, takes position as a significant resource for the extraction of low-cost biosurfactants extracts, being these metabolites produced by spontaneous fermentation by *Bacillus* species like *Aneurinibacillus aneurinilyticus* [2].

In this work, a biosurfactant extract obtained at pilot scale from CSL according to the methodology described in the patent WO2014/044876 [3], was subjected to antimicrobial tests on different nutritional food matrices to study its introduction as an ingredient in formulations of novel biopesticides. Factorial designs were carried out to evaluate the effect of a range of concentrations of the biosurfactant extract at different temperatures and times of incubation.

Results showed that in the antimicrobial tests performed in food matrices of oats and fruit purée, *B. cereus* was not detected, corroborating that the extracts produced by *A. aneurinilyticus* did not help in the development of the contaminant strain.

In conclusion, it can be determined that the biosurfactant extract under evaluation obtained from CSL at pilot scale, which is produced by strains of *A. aneurinilyticus* did not enhance the proliferation of *B. cereus* in food matrices of cereal and fruits. Therefore, the biosurfactant extract could be considered for its introduction as a novel ingredient in further biopesticide formulations contributing to give an added value to an agri-food residue as a source of new compounds.

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Amêndoas consorciadas com outras culturas cultivadas em Selca (Croácia): estudo das propriedades nutricionais e bioatividades

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Nos últimos anos, a diversificação de culturas em sistemas agroflorestais tem sido reconhecida como uma estratégia sustentável para melhorar a eficiência do uso da terra, restaurar o equilíbrio ambiental, atenuar as alterações climáticas, proporcionar benefícios económicos e garantir a segurança alimentar [1]. A investigação tem demonstrado que práticas como o cultivo intercalar podem melhorar significativamente a qualidade do solo, o que, por sua vez, aumenta a qualidade das amêndoas. Este estudo teve como objetivo avaliar os aspectos nutricionais e bioativos das amêndoas para investigar os benefícios resultantes das interações entre culturas, utilizando diferentes cultivares de amêndoa. A composição centesimal das amostras de amêndoa, incluindo proteínas, gorduras, hidratos de carbono, cinzas e humidade, foi determinada utilizando as Metodologias Oficiais de Análise e o seu valor energético total foi calculado. A cultivar Ferraduel apresentou o teor mais elevado de humidade e de hidratos de carbono. A cultivar Texas apresentou o maior teor de gordura bruta, enquanto a cultivar AI apresentou o maior teor de proteínas. Não houve diferença significativa no teor de cinzas entre as cultivares. Relativamente à composição bioativa, foram realizados vários testes para avaliar a atividade antioxidante, antiproliferativa e antimicrobiana. Para a atividade antioxidante, os extratos foram testados utilizando a atividade de eliminação do radical 2,2-difenil-1-picrilhidrazil (DPPH) e o ensaio de inibição da peroxidação lipídica (TBARS). A cultivar Ferraduel apresentou a maior atividade antioxidante. A citotoxicidade foi testada em cinco linhas de células tumorais humanas e numa linha de células não tumorais. A atividade antibacteriana foi testada contra oito bactérias, sendo *Bacillus cereus* a mais sensível ao cultivar Texas. Em termos de atividade antifúngica, a cultivar Ferragnès apresentou a Concentração Inibitória Mínima (CIM) mais baixa para *Aspergillus brasiliensis*. De modo geral, o estudo mostra que a interação com outras culturas não altera o perfil nutricional, trazendo benefícios para a saúde das amêndoas, sublinhando a importância de práticas agrícolas sustentáveis.

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Unveiling the Geographical Influence on Honey's Physicochemical Profile: A Case Study from Montesinho Natural Park

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In recent years, global honey consumption has significantly increased due to the rising demand for natural products with health benefits. Consumers are particularly drawn to honey recognized for its superior quality, such as Protected Designation of Origin (PDO) honey or honey produced in protected areas, which is associated with distinctive characteristics [1,2]. Portugal stands among the top producers of PDO honey, with Montesinho Natural Park (MNP) being a notable example of high-quality Portuguese honey. Despite its reputation, environmental challenges threaten both honey production and quality in this region [1].

This study aims to evaluate the physicochemical parameters and nutritional characteristics of honey from MNP and investigate the correlation between these properties and the geographical location of the apiaries. Honey samples (n=13) were collected from local producers and supermarkets. Standard physicochemical parameters, including 5-hydroxymethylfurfural (HMF), diastase activity, moisture and ash content, free acidity, electrical conductivity, and pH, were analysed following honey legislation guidelines. Additional parameters, such as colour, protein content, low-molecular-weight carbohydrates, and mineral composition, were also assessed [1].

The findings indicate that all honey samples complied with legal standards and align with previously published data, showing a high degree of homogeneity across the physicochemical properties analysed. Principal Component Analysis (PCA) revealed that parameters such as colour, HMF, and specific minerals (Mg, Ca, K, Mn, Sr, Cu, Ba) contributed to the clustering of honey samples, suggesting that geographical variations among apiary locations might influence these properties. However, these differences do not affect the overall quality of the PDO honey produced in MNP.

This study represents the first comprehensive characterization of honey from different apiaries within MNP. While the results demonstrate the consistency and quality of MNP honey, further research is necessary to explore the relationship between geographic origin and quality under varying environmental conditions. These insights could be valuable for maintaining sustainable beekeeping practices in the region and preserving the unique attributes of MNP honey.

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Valorização de compostos bioativos em excedentes da produção de *Lactuca sativa* L.

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A alface (*Lactuca sativa* L.), é uma hortense mundialmente cultivada para o consumo em saladas, com inúmeras variedades de folhas, cores, formatos, tamanhos e texturas. Contém água, fibras, minerais, vitaminas, entre outros compostos. Com a intensificação da agricultura, são geradas quantidades significativas de excedentes resultantes de práticas inadequadas de manuseio, transporte e armazenamento [1, 2, 3]. Este trabalho tem como objetivo determinar os compostos fenólicos e avaliar as propriedades bioativas dos excedentes da produção de diferentes variedades de *L. sativa*, com o intuito valorizar e promover o reaproveitamento dessa matriz. Amostras de diferentes variedades, nomeadamente, alface Lollo Rossa, Chicória e Frisada (var. Crispa), Iceberg (var. Capitata), e Little Gems e Romana (var. Longifolia), foram liofilizadas e procedeu-se à extração por decocção e maceração 80% em etanol/água (*v/v*). Os compostos fenólicos foram identificados por HPLC-DAD-ESI/MS_n; a atividade antioxidante foi avaliada através dos ensaios de DPPH (captação de radicais livres), Poder Redutor, TBARS (Inibição da peroxidação lipídica), e a atividade antibacteriana foi avaliada contra estirpes bacterianas de origem alimentar. O extrato hidroetanólico da variedade Lollo Rossa apresentou maior quantidade em compostos fenólicos (29,77 mg/g de extrato), a quercetina malonil-hexosídeo foi o principal composto fenólico identificado e quantificado (15,3 mg/g de extrato), enquanto as antocianinas totalizaram 1,20 mg/g de extrato com a cianidina-*O*-hexosídeo (0,497 mg/g de extrato) e cianidina-3-*O*-(6"-malonil)glucosídeo (0,706 mg/g de extrato) a destacarem-se. O extrato de decocção desta variedade apresentou também os melhores resultados em termos de atividade antioxidante nos ensaios de TBARS (valor EC_{50} de 0,08 mg/mL), DPPH (valor EC_{50} de 0,104 mg/mL) e Poder Redutor (valor EC_{50} de 0,2 mg/mL). Os extratos hidroetanólicos das variedades de folha Crispa, Iceberg, Little Gems e Romana apresentaram notável atividade antibacteriana contra a estirpe *Yersinia enterocolitica* (valor de concentração mínima inibitória (CMI) de 0,007 mg/mL). A caracterização bioquímica dos excedentes da produção de *L. sativa* evidencia o seu potencial como fonte de compostos bioativos. Além disso, o reaproveitamento de excedentes agrícolas contribui para a redução do desperdício de alimentos e diminui o impacto ambiental gerado pela produção em larga escala. Ao incorporar esses excedentes de produção em novos produtos ou processos, promove-se uma economia circular, que maximiza o uso de recursos naturais e minimiza os danos ao meio ambiente.

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Development of hydroelectrolytic beverages using subcritical water extract from kiwano (*Cucumis Metuliferus*) peel

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Kiwano peel, an often-overlooked agroindustrial byproduct, is rich in bioactive compounds with health benefits [1,2]. This study aimed to investigate the phytochemicals in kiwano peels, specifically phenolics and carotenoids, extracted using subcritical water extraction (SWE), an environmentally friendly technique, for use in hydroelectrolytic beverages.

SWE was conducted at varying temperatures (110, 130, 150, 180, and 210 ºC), under 15 bar pressure, 3 Hz, solid-to-solvent ratio of 1:30 g/mL (W/V), and a 30-minute reaction time. The extracts were chemically characterized in terms of antioxidant potential and phenolic composition. The two most promising extracts were further assessed for cytotoxicity (using MTT reduction and neutral red uptake assays) and their protective effects against oxidative stress in Caco-2 cells. The selected kiwano peel extract was incorporated into hydroelectrolytic drinks at two concentrations (0.5% and 1.0% W/V).Beverages with the highest overall acceptability were subsequently analyzed for color, physicochemical properties (total soluble solids, total titratable acidity), phytochemical content (total phenolic and carotenoid contents, and phenolic profile), and antioxidant activity. Additionally, a 7-day refrigerated storage study was conducted to evaluate the stability of total phenolic content (TPC) and total carotenoid content (TCC) in the beverages.

The kiwano peel extract obtained at 210 ºC had the highest phenolic content (123 mg GAE/g dw), antioxidant activity (ABTS-RSA of 123 mg AAE/g dw and FRAP value of 83 mg AAE/g dw), and protective effect against oxidative stress. When added to the beverages, sensory evaluations revealed high acceptability scores (≥6.25), indicating positive feedback from the taste panel. Both beverage formulations demonstrated significant antioxidant activity and a natural orange color due to the presence of phenolic compounds and carotenoids. A heatmap analysis confirmed strong correlations between TPC/TCC levels and antioxidant properties, suggesting that the favorable sensory attributes were linked to the high phenolic and carotenoid content. After 7 days of refrigerated storage, total phenolic content remained stable, although carotenoid levels decreased significantly, likely contributing to color changes.

This study highlights the potential of kiwano peel as a viable ingredient to produce sports drinks, serving as a natural colorant and offering health benefits through its bioactive compounds. The hydroelectrolytic beverages showed higher oxidative stability compared to the control beverage (which contained the artificial antioxidant Butylated hydroxyanisole, BHA) over the 7-day refrigerated storage period. These results suggest that kiwano peel extract prepared by SWE can be utilized to create functional beverages with enhanced shelf life and natural health-promoting properties.

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Estudo da aplicação do extrato de curcuma como ingrediente corante natural em queijadas de laranja

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Na indústria de panificação e pastelaria convencional, os aditivos artificiais como corantes, aromas e conservantes são comumente utilizados para melhorar a aparência, o sabor e a vida útil do produto. A tendência dos consumidores por produtos sem aditivos sintéticos está a impulsionar a indústria para o uso de ingredientes naturais e de produtos classificados como "*clean label*" [1]. Os corantes de origem vegetal, obtidos a partir de folhas, frutos e flores, surgem como alternativas promissoras na indústria alimentar. Os compostos de origem natural possuem propriedades antioxidantes e antimicrobianas, agregando valor funcional aos produtos [2]. O presente estudo teve como objetivo a substituição do corante artificial pelo extrato de curcuma (*Curcuma longa* L.) em queijadas de laranja. Para tal, foram preparadas quatro formulações de queijadas: i) com corante artificial, ii) sem corante, iii) com 50 mg de extrato de curcuma, e iv) com 100 mg de extrato de curcuma. Foram realizadas análises físicas de cor e de textura. Relativamente à cor, os resultados obtidos na análise instrumental foram expressos através do sistema CIE $L^*a^*b^*$ (L^* - Luminosidade, a^* - coordenada vermelho/verde, b^* - coordenada amarelo/azul). Internamente, os resultados dos parâmetros L^* e b^* para as queijadas enriquecidas com 50 mg de curcuma, assemelham-se à formulação com corante artificial (valores L^* de 52 e 53, e b^* de 41 e 44, respetivamente). Externamente, o resultado do parâmetro L^* para as queijadas com 50 mg de curcuma (57) aproxima-se da formulação com corante artificial (63). Para o parâmetro b^*, verifica-se que o valor da formulação com 100 mg de curcuma (43) é semelhante à formulação com o corante artificial (43). Nos resultados relativos à análise da textura verificou-se que as queijadas com 50 e 100 mg de curcuma apresentaram menor dureza (365,6 e 165,6, respetivamente), comparativamente com a formulação sem e com corante (679,9 e 483,2, respetivamente). A mesma tendência foi verificada para o parâmetro da adesividade, as queijadas com 50 e 100 mg de curcuma apresentaram menor adesividade (-220,0 e 359,8, respetivamente), comparativamente com as formulações sem e com corante artificial (-607,9 e -359,8, respetivamente). Estes resultados preliminares incentivam a substituição de corantes artificiais por alternativas naturais, demonstrando que a mudança pode ser realizada sem impactar de forma significativa as propriedades sensoriais (cor e textura) do produto. Este trabalho sugere que o uso de corantes naturais pode ser uma opção viável para a indústria alimentar que procura oferecer aos consumidores produtos mais saudáveis e sustentáveis, sem comprometer a qualidade.

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Optimization of fish by-products hydrolysis process using bromelain: a comparative study with alcalase

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Fish processing generates substantial by-products, representing a valuable source of proteins, peptides, and other bioactive compounds. The possibility of using these by-products is crucial for sustainable waste management and value-added product development. The main goal of this study was to investigate the potential of bromelain for the hydrolysis of fish by-products. Bromelain is a sulfhydryl protease obtained from pineapple by-products, also contributing to a circular economy approach as waste valorization.

The enzymatic hydrolysis process, using bromelain, was optimized. This was conducted in multifactorial assessment through the enzyme/substrate ratio (%E/S) from 0.1 to 1.5% and the incubation time from 1 to 4 h. The hydrolysis process was performed within the optimal conditions for bromelain activity, using an acetate buffer at a pH of 7 and 37 ºC for the incubation temperature.

The hydrolysis process was evaluated in terms of protein yield, degree of hydrolysis, and the antioxidant activity of the resulting peptides. The optimal operation conditions for the hydrolysis process of fish by-products using bromelain were 1.3% of %E/S for a 4 h incubation time. Additionally, these results were compared with the hydrolysis of fish by-products using alcalase, a commercial enzyme. For this enzyme, the optimal operation conditions for the hydrolysis process of fish by-products were 0.25% of %E/S for a 4 h incubation time.

This study highlights the promising advantages of using bromelain enzyme for fish by-product valorization, with implications for developing sustainable processes in the food industries.

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Mineral composition of Azorean coffee pulp

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The production of one of the world's most consumed beverage, coffee, generates a significant amount of waste/by-products, leading to disposal challenges. However, studies indicate that they could be a source of different valuable compounds, contributing to valorisation and sustainability in the coffee chain [1, 2]. Coffee pulp results from the wet post-harvest processing applied to the coffee cherries to obtain the green beans. The mineral composition of this by-product remains largely unexplored, and more studies must be done. The aim of this work was to analyse the mineral composition of dried coffee pulp provided by Quinta do Avô João, a coffee producer from S. Miguel, Azores, Portugal.

Elemental analysis of the digested samples was performed using an inductively coupled plasma mass spectrometer (ICP-MS), specifically the iCAP™ Q (Thermo Fisher Scientific, Bremen, Germany), equipped with a Meinhard® TQ+ quartz concentric nebulizer (Golden, CO), a high-purity quartz cyclonic nebulization chamber, and a detachable quartz torch with a 2.5 mm internal diameter injector [3]. Seven essential elements, fourteen non-essential and toxic trace elements, and five macro elements were identified. The major essential elements found were Fe (~27.2 ug/g), Cu (~13.4 ug/ g) and Zn (~9.3 ug/g). Among the macro elements, K (~42.5 mg/g) and Ca (~3.5 mg/g) were the most significant, while toxic elements such as Li, Ni, Cd, and Pb are present only in trace amounts. The results obtained in this study are in accordance with the results obtained in other studies [2, 4], although slight differences in values may be attributed to factors such as the location of coffee production, climatic conditions, harvest time, or variations in methodology.

In sum, coffee pulp is source of essential minerals required for numerous physiological functions and health maintenance. Major minerals such as Ca, P, and Mg, along with trace elements like Fe, Zn, and Se, also play a vital role in human health [5]. Repurposing coffee pulp as a mineral source adds value to the coffee chain, by offering opportunities for developing innovative products, reducing environmental pollution, and supporting circular economy.

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Advancing Clean-Label Meat Products: Enhancing Texture and Color with Plant-Based Bioactive Ingredients

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Consumers' growing interest in the origin and composition of their meals, particularly the preference for natural products has driven industries to find alternatives to synthetic ingredients [1]. Plants, vegetables, and agri-food co-products, highly rich in bioactive compounds, such as phenolic compounds associated with dietary fibers, may be used as alternative natural colorants, fat replacers, or texturizing agents in meat products. This association also affects polyphenols' potential health-related properties as polyphenols may transverse the small intestine intact tandem with dietary fibers and reach the colon, where they can be released, producing bioactive metabolites and an antioxidant environment [2]. This study focused on developing meat hams by replacing the nitrifying agent, which traditionally provides antimicrobial activity and the characteristic pinkish-red color. Several formulations were created to achieve this. The nitrifying agent was substituted with polyphenol-rich flour and vegetable-based concentrate in varying ratios. The formulations were characterized by Texture Profile Analysis (TPA) using a texturometer to measure hardness, cohesiveness, elasticity, and chewiness. Color attributes were evaluated with a colorimeter and compared to the control formulation containing the nitrifying agent. Replacing the nitrifying agent with fruit flour generally enhanced texture parameters, especially hardness, with cohesiveness, springiness, and chewiness values closer to the control. However, hams with higher amounts of fruit flour showed a more purplish hue, deviating from the typical pink of meat hams. In contrast, formulations with vegetable-based concentrate showed slight decreases in texture parameters, particularly hardness, though the results of cohesiveness and elasticity were still similar to the control. Higher concentrations of vegetable-based concentrate produced texture values closer to the control. Color differences with vegetable-based concentrate were less pronounced compared to fruit flour (Fig.1.).

Another objective was to reduce the salt content by 50% in the formulation, using yeast protein extract (YPE) in varying amounts as a flavor enhancer, due to its umami taste. The salt reduction primarily led to a decrease in hardness, and the addition of YPE did not fully compensate for this loss. There was no clear correlation between the amount of YPE and the texture, though higher levels resulted in lower hardness. Cohesiveness remained unchanged, while elasticity showed slight reductions in the formulations produced with higher amounts of YPE. Chewiness exhibited more noticeable differences compared to the control but without significant variation between YPE levels. Chromatic analysis (L, a*, and b*) showed notable differences from the control, particularly in the a* parameter, which shifted towards more positive values, indicating a redder hue, along with an increase in the b* parameter, reflecting a shift toward yellow.

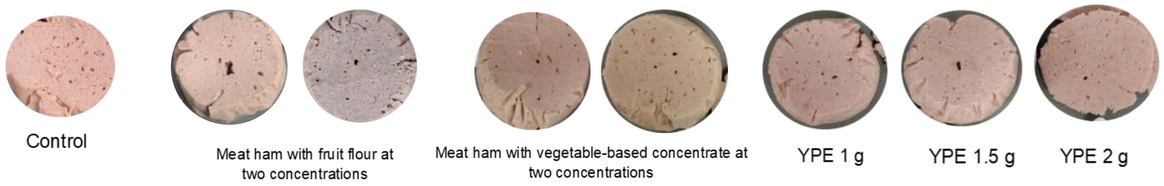

Fig.1. Examples of meat ham formulations with fruit flour, vegetable extract, and YPE.

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Metal-adsorbed polysaccharides: synthesis and structural characterization

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Polysaccharides (PSs) are vital macromolecules which exist in most life forms (e.g. algae, plants, animals, microorganisms), where they fulfill crucial biological functions. PSs have long stoked the attention of researchers for their excellent biological activities, biocompatibility, biodegradability or non-toxicity. More specifically, these materials have been found to have biological activities (e.g., antioxidant, antibacterial, antiradiation, or immune regulation), together with their relatively low-cost and the ability to be combined with a wide variety of chemical entities (from metal cations to organic acids and other biopolymers). This allows to the preparation of materials with enhanced qualities, making them highly valuable in fields such as food production, medicine, and cosmetics. [1]

Metal ions, particularly trace metal ions like zinc, copper, iron or magnesium, are essential to the life process of living organisms. Either as macro- or microelements, metal ions are protagonists in several structural and functional roles, participating in numerous biochemical reactions. [1,2] Although metal complexes have been known for a long time to have biological activity, research has long focused on the use of small organic ligands as complexing agents, which can, in some cases, lead to undesired effects (e.g., poor water solubility, high toxicity of metal ions). Recent studies, however, show that metal complexes with PSs exhibit enhanced biological activity, improved safety, and better solubility, [3, 4] making them promising candidates for developing new drugs or food supplements.

In this work, we report the preparation of novel metal-PS (PS = alginate, chitosan) complexes with Ca^{2+}, Cu^{2+}, and Fe^{3+}. These metal cations have been directly incorporated into PS films by adsorption, and the resulting materials have been fully characterized by infrared spectroscopy, thermogravimetric analysis, polarized optical microscopy, atomic force microscopy and static contact angle measurements.

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Economia circular na indústria alimentar: aproveitamento e valorização do subproduto de carambola

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Considerando a produção anual de resíduos agroalimentares e as metas Europeias de sustentabilidade que englobam o sistema alimentar desde a produção, ao consumo e ao desperdício, é importante estabelecer medidas estratégicas de redução dos mesmos, promovendo sua reintrodução na cadeia de valor. O uso de subprodutos de frutas e vegetais para a obtenção de compostos bioativos tem sido cada vez mais destacado, uma vez que são ricos em moléculas que podem ser aplicadas nas indústrias alimentar e farmacêutica, devido às suas características bioativas associadas [1]. No entanto, os processos de extração para obtenção desses compostos resultam numa grande quantidade de resíduos, que podem ser aproveitados como fonte de nutrientes [2]. Neste sentido, este estudo pretendeu promover a valorização dos resíduos de extração de um subproduto vegetal – fruta carambola (*Averrhoa carambola* L.) descartada por não corresponder aos padrões de comercialização. Os resíduos obtidos no processo de maceração foram separados, liofilizados e caracterizados em termos de conteúdo total, solúvel e insolúvel de fibras dietéticas; conteúdo de cinzas; gorduras; e proteínas brutas e totais, aplicando as metodologias oficiais de análise AOAC [3]. O perfil de açúcares e de aminoácidos foram determinados através de métodos cromatográficos, HPLC-RI (açúcares) e HPLC-MD-2015 (aminoácidos). Os resultados mostraram que o resíduo é composto maioritariamente por fibras, com um valor total de 69,8 ± 0,7%, sendo o conteúdo de fibras insolúveis predominante com 56,20 ± 0,25%. Seguiu-se o conteúdo de proteínas, com 15,0 ± 0,2% de proteína bruta e 14,62 ± 0,97% de proteína real. O conteúdo de cinzas, gorduras e açúcares surgiram como componentes minoritários não ultrapassando os 3%. De acordo com o pefil de aminoácidos, o resíduo de extração apresentou um valor total de 122,21 ± 7,57 mg/g de peso seco, sendo 46,72 ± 2,62 mg/ g correspondente a aminoácidos essenciais totais, destacando leucina e lisina como compostos predominantes. Com estes resultados obtidos foi possível constatar que o resíduo da extração de compostos bioativos da carambola apresentam potencial para utilização como ingredientes alimentares, devido ao seu elevado conteúdo de fibras e proteínas, moléculas de grande interesse, que estão no foco das tendências atuais dos consumidores e, consequentemente, do setor industrial. Assim, a exploração desses subprodutos da carambola não agrega apenas valor económico, mas também apoia o desenvolvimento de produtos sustentáveis, atendendo à demanda crescente por ingredientes naturais e funcionais no mercado.

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Color stability of a natural cyanidin-3,5-diglucoside and its derivative methylpyranocyanidin as potential food additives

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With consumers increasingly seeking clean label products, natural pigments are gaining significant attention as they are safe, healthy, and ecologic. Among these, anthocyanins (ACNs) are known for their coloring properties and have powerful antioxidant activity, making a diet rich in these compounds a great way to retard and prevent oxidative damage [1].

However, ACNs stability is influenced by factors like pH, temperature, light, solvents, and ascorbic acid, limiting their use in food. To address these challenges, ACNs can be converted into more stable compounds such as pyranoanthocyanins (PACNs). PACNs are formed by adding a reactive group at the C4 position of ACNs, followed by the creation of an additional pyran ring at the C5 position. This new ring is responsible for protecting PACNs from the nucleophilic attack of, for example, water or ascorbic acid. PACNs maintain their red/orange hues up to pH 7 and are known to exhibit greater heat stability. They also retain strong antioxidant and anti-inflammatory properties, similar to their ACN precursors [2-3].

In this study, natural cyanidin-3,5-diglucoside was extracted and isolated from petals of old red roses using a straightforward and cost-effective method. Its acid hydrolysis resulted in the respective aglycone cyanidin, which was chemically modified into methylpyranoanthocyanin through a treatment with acetone.

The stability of these three compounds (natural cyanidin-3,5-diglucoside, cyanidin and methylpyranocyanidin) in a solution was assessed in different conditions that mimic food media: pH, ionic strength, light exposure and thermal treatments, using spectroscopic measurements and CIELAB coordinates. As expected, the aglycone cyanidin was not stable in any of the tested conditions and quickly lost its color. On the other hand, natural C-3,5-D showed a quite good stability to some of the tested conditions since it has 2 sugar moieties that are known to confer some inner stabilization. Therefore, the color stability of the extracted natural C-3,5-D and the produced methylpyranoanthocyanin were compared, and some interesting results were obtained. Although the produced PACN showed higher thermal stability, as it was expected, the extracted natural anthocyanin revealed surprising stability in some of the other tested conditions.

The colorimetric properties of the natural cyanidin-3,5-diglucoside seemed to be promising and other stabilization strategies are being explored. Further studies will be performed considering its use as a colored antioxidant additive in foods.

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Mejoramiento de la calidad nutricional y de la tolerancia al estrés de microvegetales mediante el uso de bioestimulantes naturales

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Los microvegetales han surgido como una opción atractiva para enriquecer y diversificar la dieta humana, así como para combatir la malnutrición, debido a su alto contenido de nutrientes y compuestos bioactivos. Sin embargo, los estudios existentes se centran más en optimizar su rendimiento agronómico que en sus características de calidad bioactiva, especialmente en condiciones de estrés [1-3]. Por lo tanto, este trabajo pretende implementar una estrategia de investigación que comprenda técnicas de *priming* de semillas y transferencia interespecífica de metabolitos para mejorar el desarrollo y la tolerancia al estrés hídrico y salino de los microvegetales de soja y guisante. El objetivo es mejorar la calidad de los microvegetales explotando su potencial como alimentos funcionales con propiedades promotoras de salud. Para ello, se propone producir microvegetales mediante biofortificación con bioestimulantes en condiciones de estrés abiótico. Se implementará un enfoque de investigación que incluye técnicas de transferencia interespecífica de metabolitos y la preparación de semillas con bioestimulantes naturales que se desarrollarán a partir de subproductos agrícolas. El estudio incluirá la realización de perfiles bioquímicos y análisis de expresión génica para comprender los efectos de estos tratamientos sobre la composición de los microvegetales y los mecanismos de respuesta al estrés. Se evaluarán los potenciales efectos promotores de salud de los microvegetales biofortificados a través de ensayos biológicos *in vitro* y la simulación de la digestión gastrointestinal. Se espera que este trabajo contribuya al avance de los conocimientos relacionados con la optimización de los atributos de calidad nutricional y bioactiva de los microvegetales de soja y guisante, así como a su rendimiento en condiciones de estrés abiótico y sus beneficios potenciales para la salud de los consumidores. De este modo, se promoverá un sistema agroalimentario más sostenible, se fomentarán dietas más saludables y se aumentará la seguridad alimentaria.

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ALM39

Obtenção de estatinas e ergosterol de bio-resíduos de *Agaricus bisporus*: extração convencional vs emergente

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As estatinas são a terapéutica comum mais utilizada no tratamento do colesterol. No entanto possuem diversos efeitos secundários. Os cogumelos ricos em micosteróis, podem reduzir a absorção do colesterol e contêm ainda moléculas semelhantes às estatinas que inibem HMG-CoA reductase, enzima fundamental no metabolismo do colesterol [1][2]. O projeto Mush4Chol tem como objetivo explorar bio-resíduos da industria de cogumelos para a obtenção de um produto com capacidade para diminuir os níveis de colesterol. O projeto pretende desenvolver um produto estável que iniba quer a síntese que a absorção do colesterol. Para tal pretende-se valorizar os bio-resíduos de cogumelos (cogumelos partidos/irregulares ou com dimensões que não entrem nos padres de comercialização) numa formulação rica em compostos hipocolesterolémicos para varias aplicações. Para o efeito diversas técnicas de extração foram exploradas.

Neste contexto, este estudo pretendeu comparar a extração de compostos hipocolesterolémicos usando uma técnica de extração convencional e uma técnica de extração emergente. Para tal a exração assistida por calor e a extração assistida por ultrassons foram otimizadas. O desenho experimental combinou cinco níveis das variáveis independentes, utilizando a Metodologia de Superfície de Resposta (MSR). As variáveis independentes foram o tempo, a temperatura e a proporção de solvente, no caso da extração assistida por calor; e tempo, potencia do equipamento e proporção de solvente no caso da extração assistida por ultrassons. Já as variaveis dependentes, o rendimento e a concentração de ergosterol e de estatinas, tendo a combinação resultado em 25 pontos de extração. Relativamente à caracterização química, as amostras foram analisadas por Cromatografia Líquida de Alta Eficiência acoplada a um detector ultravioleta (HPLC-UV).

Independentemente das condições de extração ou da técnica de extração aplicada, moléculas de ergosterol e moléculas semelhantes à pravastatina foram identificadas. Como era de esperar, os pontos ótimos obtidos para cada um dos compostos-alvo foi diferente dependendo da técnica de extração empregue.

Os bio-resíduos de cogumelos comestíveis da especie *Agaricus bisporus* apresentam-se como uma fonte promissora de compostos hipocolesterolémicos, com potencial para inibir quer a absorção quanto a síntese do colesterol, oferecendo não só benefícios para a saúde como em questões de sustentabilidade.

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Opuntia ficus-indica (L.) Miller cladodes: a mineral-focused strategy for sustainable flour production

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Consumers are increasingly mindful of nutrition and food variety, opting for healthier choices that offer proven health benefits [1]. Simultaneously, there is a growing demand for sustainability, with consumers paying close attention to companies' sustainable practices. *Opuntia ficus-indica* (L.) Miller is a potential food alternative and has long been a part of the diet in countries like Mexico [2]. In Portugal, the rising production of prickly pear has created waste management challenges due to the discarded cladodes and the plant's invasive nature. Nonetheless, this underutilised by-product holds promise for valorisation thanks to its rich nutritional and chemical composition.

This study explores the potential use of cladodes for human consumption and/or in the food industry. An example is using cladode-derived flour in new food products, such as bread. The mineral profile of the cladodes (2 years old) of different varieties that produce white, orange and red pulp fruit was assessed. All the samples were grown in Torres Novas, Portugal, in organic production.

Methodologically, four macro-elements (Na, K, Ca, Mg) were measured using flame atomic absorption spectrometry, while 27 trace elements (^{7}Li, ^{9}Be, ^{11}B, ^{27}Al, ^{48}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{98}Mo, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{133}Cs, ^{137}Ba, ^{182}W, ^{208}Pb, and ^{209}Bi) were analysed using inductively coupled plasma-mass spectrometry [3]. In total, 31 mineral elements were analysed.

The results showed that all samples contained significant levels of calcium (30-110 g/kg) and high concentrations of potassium (10-50 g/kg). Noteworthy amounts of trace elements, such as manganese (15-330 µg/g), zinc (5-30 µg/g), and boron (10-20 µg/g), were also observed. All results were reported on a dry weight basis. Among the 27 trace elements analysed, essential elements such as iron, copper, zinc, manganese, molybdenum, cobalt, chromium, and selenium were identified in varying concentrations.

Based on these findings, and in line with circular economy principles, cladodes have the potential to be developed into nutritionally balanced, mineral-rich flours. This would not only enhance the value of this by-product but also contribute to greater sustainability in the food chain.

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A comprehensive analysis of the protein fraction of *Opuntia ficus-indica* (L.) Miller cladodes

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Nowadays, consumers are increasingly concerned about healthy lifestyles, with an increasing emphasis on foods with potential therapeutic properties [1]. *Opuntia* plant, including their cladodes, have been gaining prominence as promising alternatives due to their biofunctional characteristics [2].

The aim of this work was to assess the protein fraction of the white variety of cladodes (Torres Novas, Portugal) with two years of maturity, grown in organic production. The total protein and non-protein nitrogen content was determined, as well as the total and free amino acid profiles.

Total protein was measured using official methodologies, while the non-protein nitrogen was determined via protein fraction precipitation. Amino acid profiles were quantified using RP-HPLC with automated on-line derivatisation, and the results were reported as g /100 g of dry weight (dw).

Cladodes crude protein content was 7.6g/100g dw, with 90% of this being protein. A total of 18 amino acids were identified, including all essential amino acids. Glutamic and aspartic acids were the predominant non-essential amino acids (0.76g and 0.66g/100g, respectively), followed by arginine and proline (0.39g and 0.20g/100g, respectively). The total amino acid content was 5.3g/100g. Of the essential amino acids, approximately 45% were branched-chain amino acids (BCAAs), such as leucine, isoleucine, and valine. All essential amino acids were also found in their free forms.

Cladodes provide a complete profile of essential amino acids, particularly BCAAs, although their protein content is relatively low, which emphasises their potential as a nutraceutical. Cladodes can therefore be used in protein-restricted diets without compromising the intake of essential amino acids, particularly BCAAs.

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Biofortification of Swiss chard microgreens with selenium under indoor vertical farming

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Selenium (Se) is an essential micronutrient t for humans with critical biological functions [1]. Se deficiency affects millions of people, aggravating health problems, such as cancer and cardiovascular diseases [2,3]. This challenge can be overcome by indoor vertical farming conjugated to microgreen production and agronomic biofortification with Se. In this sense, this study aimed to assess the biofortification of white Swiss chard (*Beta vulgaris* subsp. *cicla*) microgreens with two inorganic forms of Se under indoor vertical farming and determine phenolic compound, betalain, organic acid, free sugar, and mineral element profiles through chromatographic and spectroscopic techniques.

Microgreens were grown in a walk-in growth chamber equipped with LED lamps under controlled conditions and irrigated with a TriPart® Grow NPK 3-1-6 nutrient solution supplemented with different concentrations (10, 20, 40, and a mix of 20 µM) of sodium selenate and sodium selenite. Seeds were sown in polystyrene trays filled with vermiculite. A photoperiod of 14/10 h (light/dark) was selected, and temperature and relative humidity were set between 20-25 ºC and 40-60%, respectively. Fourteen days after sowing, microgreens were harvested and the phytochemical analyses were performed using high-performance liquid chromatography and atomic absorption spectroscopy.

Microgreen samples showed no detectable free sugars. However, one organic acid (oxalic acid), up to eight phenolic compounds (including two phenolic acids and six flavonoids), and up to seven betalains were identified, with contents ranging between Se treatments. Se-enriched microgreens exhibited a robust mineral profile, with high concentrations of various essential minerals, in particular, significant levels of potassium (K), calcium (Ca), iron (Fe), and Se. Sodium selenate treatments, especially at a concentration of 40 µM, were most effective in boosting these minerals, with concentrations reaching 58.53 g/100 g fresh weight (fw) for K, 1.12 g/100 g fw for Ca, 1.43 g/100 g for Fe, and 36.89 mg/100 g for Se. This study suggests sodium selenate as the best inorganic form of Se to perform agronomic biofortification on Swiss chard microgreens. Further studies are required to assess how microgreens' nutrients can be bioavailable and bioaccessible for uptake by human gut cells.

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QUÍMICA AMBIENTAL Y SOSTENIBLE

Impact of Damming on Fluvial Nutrients and Trace Element Fluxes to the Ria of Ares-Betanzos (NW Iberian Peninsula)

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In comparison to the well-studied Galician upwelling, the chemical fluvial fluxes to rias have been poorly investigated. Even more, there is very limited information on the impact of dams on river-to-ria loads. To address this, we assess the role of damming by comparing between the fluxes of nutrients, organic matter, and dissolved trace elements from the Mandeo and Eume Rivers to the Ria of Ares-Betanzos (72 km^2). The Eume River is 92% dammed, while both rivers are neighboring temperate systems with similar average flows (15.5 and 13.2 $m^3 \cdot s^{-1}$) and basin areas (457 and 470 km^2).

River water samples were collected monthly near the river's mouths over two hydrological years (Oct. 2011 - Sept. 2013), one characterized as dry and the other as wet. Conductivity and temperature were measured, and the following parameters determined: (1) nitrate, nitrite, ammonium, phosphate, and silicate via autoanalytical techniques; (2) dissolved oxygen by Winkler method and chlorophyll-a by spectrofluorometry; (3) dissolved and particulate organic carbon and nitrogen using TOC-VCPH and CNH analyzers; and (4) dissolved and particulate trace elements (Al, Cd, Co, Cr, Cu, Fe, Ni and Pb), processed in a clean lab and analyzed by ICP-MS. River fluxes were calculated using a ratio estimator method based on concentration and river flow data.

Table 1 clearly shows the hydrochemical influence of damming on the Eume River, with concentrations more affected by damming than by annual flow variations. Consequently, the hydrochemical discharges from the Eume River to the Ria of Ares-Betanzos are predominantly controlled by damming, decreasing them for the most of the determined parameters. So, the Mandeo River is their main source of input to the ria. Damming has altered the fertilization pattern of the Eume River, with phosphate fluxes nearly depleted (66-78%) and nitrate fluxes decreasing from 6% in dry conditions to 56% in conditions, compared to those from the Mandeo River.

Table 1. Annual average concentrations (±SD) of nutrients, organic carbon, and dissolved (D) and particulate (P) trace metals in the outflowing water to the Ria of Ares-Betanzos.

Hydrological year:	Oct.11 – Sept.12 (dry)		Oct.12 – Sept.13 (rainy)	
River:	Eume	Mandeo	Eume	Mandeo
Nitrate (µM)	43 ± 5	87 ± 16	40 ± 5	104 ± 16
Phosphate (µM)	0.09 ± 0.06	0.27 ± 0.14	0.05 ± 0.03	0.20 ± 0.16
Dissolved silicate (µM)	81 ±4	141 ± 20	79 ± 4	136 ± 14
DOC (µM)	93 ± 25	188 ± 91	110 ± 29	165 ± 57
POC (µM)	17 ± 12	40 ± 48	27 ± 10	61 ± 76
D Cd	0.134 ± 0.056	0.043 ± 0.031	0.199 ± 0.063	0.051 ± 0.023
D Co	5.2 ± 4.6	1.1 ± 0.5	17.0 ± 7.7	1.3 ± 0.6
D Fe	203 ± 106	940 ± 490	209 ± 135	960 ± 480
P Cd	0.010 ± 0.010	0.019 ± 0.035	0.012 ± 0.008	0.036 ± 0.038
P Co	3.5 ± 3.5	1.2 ± 1.1	3.2 ± 2.1	1.5 ± 1.6
P Fe	1810 ± 1010	2980 ± 2950	1750 ± 640	3730 ± 4860

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La madera de *Robinia pseudoacacia* como fuente de compuestos de valor añadido: empleo de microondas como método de extracción sostenible

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Actualmente, existe una creciente tendencia hacia el consumo de productos más saludables elaborados con ingredientes funcionales de origen natural. La principal fuente natural de compuestos bioactivos (como polifenoles, polisacáridos o ácidos grasos) con comprobadas propiedades beneficiosas para la salud humana, es la biomasa vegetal.

Robinia pseudoacacia es un árbol de rápido crecimiento y elevado potencial de regeneración que es considerada una especie invasora en Europa. En este sentido, el uso de esta biomasa , puede promover un doble beneficio, ambiental y económico [1]. Sin embargo, para valorizar cada una de sus diferentes fracciones de interés, es necesario llevar a cabo un procesamiento que permita aislar los compuestos de valor añadido. En este contexto, la extracción asistida con microondas (MAE), constituye una alternativa sostenible y eficiente a los tratamientos convencionales. Entre sus ventajas se encuentran la reducción de los tiempos y temperaturas de reacción y el aumento del rendimiento de compuestos bioactivos [2].

Con este trabajo se persigue la evaluación de la idoneidad del tratamiento hidrotérmico con microondas para la producción de extractos ricos en oligosacáridos y polifenoles con potenciales actividades biológicas. Los extractos resultantes de la MAE fueron analizados por cromatografía líquida de alta eficacia para la cuantificación de oligosacáridos. Tras la selección de las condiciones óptimas de extracción de oligosacáridos, se analizó el contenido en fenoles y flavonoides totales (TPC y TFC), así como la actividad antioxidante mediante por los métodos de ABTS y FRAP. Además, se evaluó el perfil fenólico mediante HPLC-ESI-MS. En base a los resultados obtenidos se puede concluir que la MAE constituye una metodología apropiada y verde para la valorización de la madera de *Robinia pseudoacacia*.

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Versatilidad del Fe-MOF en diversos procesos de oxidación avanzada para la descontaminación y desinfección de aguas

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En las últimas décadas, la contaminación del agua ha sido una preocupación ambiental creciente, especialmente en áreas urbanas, debido a la presencia de patógenos y contaminantes emergentes como los compuestos farmacéuticos en las aguas residuales. Los residuos de hospitales, hogares y la industria farmacéutica introducen medicamentos y microorganismos peligrosos en los sistemas hídricos, lo que representa riesgos significativos para la salud y el ambiente, agravando la resistencia bacteriana y la toxicidad.

Aunque la eficacia de las plantas de tratamiento de aguas ha mejorado, los métodos convencionales no eliminan completamente estos contaminantes. Esto ha impulsado el desarrollo de procesos de oxidación avanzada, que generan especies reactivas para degradar compuestos orgánicos persistentes y eliminar microorganismos de forma más eficiente y respetuosa con el medio ambiente. La investigación actual se enfoca en el desarrollo y uso de catalizadores innovadores, como las redes metal-orgánicas (MOFs), que mejoran la eficiencia de estos procesos y evitan la liberación de metales al agua tratada.

Este estudio evalúa la capacidad del Fe-MOF (Basolite® F-300) para la desinfección y degradación de dos contaminantes: el fármaco antipirina y el patógeno *Escherichia coli (E. coli*). Se investigó la capacidad del Fe-MOF para activar el peroximonosulfato (PMS), generando radicales sulfatos, y su uso en el proceso electro-Fenton para la generación de radicales hidroxilos. En ambos enfoques, se optimizaron las condiciones operativas con el objetivo de maximizar la eficiencia en la eliminación de estos contaminantes.

En el caso del sistema de activación de PMS, se logró la desinfección completa en tan solo 5 minutos, trabajando con concentraciones de PMS de 153,7 mg/L y Fe-MOF de 65,8 mg/L. Además, también se evaluó la eficacia del sistema con una mezcla de agua contaminada con una alta concentración de *E. coli* y antipirina, obteniendo una eliminación completa de ambos contaminantes. En cuanto al proceso electro-Fenton, se optimizaron parámetros como el tipo de electrodos, la concentración de Fe-MOF, el pH, y la densidad de corriente, lo que permitió maximizar la eliminación de la antipirina y minimizar el consumo energético (94% eliminación de antipirina con un consumo de energía de 0,29 W·h por mg de antipirina eliminada. Además, se desarrollaron nuevos electrodos con Fe-MOF inmovilizado, creando un electrocatalizador mediante dos métodos: electrohilado en una lámina de espuma de níquel y un *composite*. Estos avances facilitaron la manipulación y recuperación del catalizador, además que permite mantener su capacidad catalítica. Un aspecto importante para destacar es que el Fe-MOF demostró ser reutilizable en ambos sistemas, con una pérdida de eficacia inferior al 10% tras varios ciclos de uso, lo que lo convierte en un catalizador estable y eficiente para la eliminación de diversos contaminantes.

En conclusión, los resultados resaltan el gran potencial del Fe-MOF para la eliminación de contaminantes como fármacos y patógenos, subrayando su versatilidad en la generación de radicales activos y su capacidad de ser reutilizado. Esto lo posiciona como una solución prometedora para procesos de descontaminación sostenibles en el tratamiento de aguas.

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Sustainable Synthesis of Gold Nanoparticles from *Osmundea pinnatifida*: A Green Approach for Antioxidant and Antitumoral Applications

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Nanomaterials have gained significant attention in the biomedical field due to their unique physicochemical, electrical, and optical properties, which lend themselves to applications in diagnosis, therapy, and theragnostic. However, concerns about the toxicity and safety of these materials, particularly when synthesized using traditional methods that employ hazardous reagents, have limited their clinical use. The toxicity of nanoparticles is influenced by their synthesis method, as conventional approaches often introduce harmful chemicals that compromise their biocompatibility. To overcome these issues, green synthesis, which uses natural extracts to reduce metal ions, is being explored as a safer alternative, eliminating the need for toxic reducing agents and offering a path towards more biocompatible nanomaterials for therapeutic use. Among the diverse array of alternatives for green synthesis of nanoparticles, algae emerge as a particularly noteworthy and promising avenue due to their abundant availability and rapid growth rate [1]. Here, *Osmundea pinnatifida* (OP) (Hudson) Stackhouse, 1809 has been selected. OP is a red alga found within the tidal zone of sheltered rocky shores and distributed in the Atlantic coasts of Europe, in the Mediterranean, South-West and East Asia,South Africa,and Australia. This alga species has high amounts of proteins and carbohydrates, mainly carrageenan and agar, and it's also rich in phenolic compounds. OP is not yet well studied, however recent investigations show that this is a very promising species with potential applications in the food industry, in the removal of toxic elements for environmental applications and in the medicine, with studies showing their potential antioxidant and antitumoral activity [2]. Here, we propose its use for the synthesis of gold nanoparticles, as follow:

First, aqueous extraction of OP was optimized. The obtained extracts were characterized using UV and FTIR spectroscopy and their reducing power, total phenolic content, and DPPH scavenging activity was evaluated. Then, the extract obtained under the best conditions was chosen for optimizing the syntheses of gold nanoparticle (Au@OP). The resulting nanoparticles were fully characterized, and their antioxidant activity was assessed.

A cell viability assay in a lung epithelial cell line was performed to test the potential antitumoral activity of Au@OP. The gold nanoparticles showed a relevant antiproliferative activity in the tumoral cells. Further studies will be conducted to confirm the mechanism associated to this potential antitumoral activity, as well as the cytocompatibility in human peripheral blood mononuclear cells and erythrocytes to test for biocompatibility and hemocompatibility of Au@OP.

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Dual Photocatalytic and Antibacterial Performance of Green-Synthesized Ag-TiO_2 Nanocomposites for Water Treatment

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The presence of pharmaceutical compounds in water bodies is a pressing issue with significant environmental and health implications. These emerging organic pollutants pose challenges due to their persistence, potential bioaccumulation, and adverse effects on aquatic ecosystems and human health [1]. Although no definitive solutions have been found to remove them, photocatalysis has emerged as a promising approach. TiO_2 is one of the most used catalysts; however, its limited activation under visible light poses a significant challenge. One strategy to overcome this is by incorporating plasmonic nanoparticles, such as silver, to enhance its ability to absorb visible light [2]. Traditional synthesis methods involve hazardous and costly reagents, but in this study, we propose an eco-friendlier method, using the natural flavonoid quercetin as a reducing agent for depositing AgNPs on the TiO_2 surface. The method was optimized, and different amounts of silver were tested. Full characterization of the nanocomposites showed increased absorption in the visible light spectrum, with values between 50-90% depending on the silver concentration. Additionally, the energy band gap was reduced from 3.05 to 2.76 eV. The photocatalytic activity of the nanocomposites was evaluated for the degradation of the antibiotic ciprofloxacin under UV and simulated sunlight, achieving degradation rates of 85% and 96%, respectively.

Further, the persistence of antibiotics in aquatic environment promotes the proliferation of antibiotic-resistant bacteria [1]. Functionalising the TiO_2 surface with silver can also contribute to its multifunctional application, enhancing the potential antimicrobial properties of the nanocomposite, targeting both gram-positive and gram-negative bacteria [2]. Antibacterial activity was evaluated by counting Colony-Forming Units (CFU) after exposure of the bacterial strains to the produced nanoparticles. The nanocomposite was observed to effectively inhibit both strains. The findings indicate that the nanocomposites, produced via green synthesis and activated by visible light can offer a sustainable solution for water decontamination and disinfection.

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O futuro sostible dos cosméticos con lúpulo

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A sustentabilidade provocou cambios significativos na industria cosmética. O crecente interese por reducir o impacto ambiental e promover prácticas máis responsables levou ao desenvolvemento de novos enfoques, como o uso de química verde e disolventes ecolóxicos [1]. Un exemplo de recurso natural usado é o lúpulo, unha planta empregada tradicionalmente na produción de cervexa, pero que tamén ten potencial para ser utilizada en produtos cosméticos naturais. O lúpulo, cuxo nome científico é *Humulus lupulus* L., é unha especie da familia das cannabáceas, con características trepadoras, perennes e dioicas, é de gran importancia polos seus compostos de interese, como os polifenois e os ácidos alfa e beta. Os compostos fitoquímicos da planta teñen propiedades beneficiosas como propiedades antiinflamatorias, antimicrobianas e antioxidantes [2].

Neste estudo empregáronse diferentes partes de *H. lupulus*, incluíndo os conos e a parte vexetativa do subproduto da variedade Nugget na industria cervexeira; estes subprodutos descártanse no proceso de recollida do lúpulo. O material vexetal foi sometido a diferentes métodos de extracción, como microondas, ultrasóns (duración de 30 minutos e 1 hora) e maceración, co obxectivo de determinar o método máis eficiente para a obtención de compostos bioactivos, para ser utilizado nunha formulación cosmética. Determinouse o número total de fenois e flavonoides e tamén se estimou a actividade antioxidante. Ademais, exploramos o uso de disolventes verdes como auga e etanol 80% (v/v), co obxectivo de minimizar o impacto ambiental do proceso de extracción.

Os resultados indicaron que a extracción realizada con solución hidroalcohólica ao 80% no microondas foi o máis rico en compostos fenólicos totais (TPC), seguido da extracción por maceración no caso dos flavonoides totais (TFC). Co disolvente de auga, o mellor método de extracción foi também o microondas, seguido do método de ultrasóns durante 30 minutos, para TPC e para TFC. En canto ao poder antioxidante, o método que deu os mellores resultados foi a maceración e o microondas, respectivamente, empregando o disolvente 80% etanol tanto no ensaio ABTS+ (ensaio de radicais 2,2'-azinobis(3-etilbenzotiazolina-6-sulfónico)) con 3723,1±933,0 mg TE (equivalente trolox)/g planta e 2.819,3±2,679 mg TE/g planta, e FRAP (Ferric Reduction Antioxidant Power) con 253,5±8,1 mg TE/g planta e 184,2±66,1 mg TE/ g planta, respectivamente. Co disolvente de auga, os mellores resultados foron polo método de ultrasóns durante 30 minutos e microondas con ABTS+ 2292,2±209,3 mg TE/g planta e en FRAP con 291,8±80,3mg TE/g planta, respectivamente.

Os resultados suxiren que os métodos de extracción empregados, xunto co uso de disolventes verdes, poden ser máis eficaces na obtención da extracción de compostos bioactivos, contribuíndo así ao avance de métodos sostibles que se poidan aplicar na industria cosmética.

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Assessing the Ecotoxicity Effects of Magnetic Nanoparticles applied for Microplastic Removal

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Countries worldwide struggle to manage the growing amount of plastic waste and persistent pollution. Millions of new tons of plastic waste are entering aquatic environments due to the overuse and mismanagement of plastics [1]. Despite efforts to reduce their use, it is estimated that 10% of plastic production ends up directly in the oceans, and around 95% of marine waste is primarily composed of plastics, where they persist, accumulate, and interact with other pollutants [2]. Due to environmental agents, such as UV radiation and physical abrasion, and biodegradation, plastics break down into smaller fragments (smaller than 5 mm), which are known as microplastics (MPs) [3].

Researchers are now exploring novel approaches, with the functionalization of magnetic particles emerging as a promising solution to remove MPs from wastewater, which investigate electrostatic interactions between magnetic particles and MPs.

Several reports have shown that aquatic animals easily ingest MPs. Although the full extent of their effects is still being explored, studies already indicate that MPs can cause oxidative stress, cytotoxicity, and translocation to other tissues (*e.g.* zebrafish, nematode, algae, snails) [4]. Their persistence in organisms has also been linked to chronic inflammation which increases the risk of cancer [2]. It is crucial to further explore the chronic ecotoxicological effects of MPs and assess the potential impact of new treatment processes under development.

In this study, the ecotoxicological impact of using treatments with different magnetic iron nanoparticles to remove three types of MPs (polyamide nylon 6, polymethylmethacrylate, polytetrafluoroethylene) was explored in water and wastewater samples. The algae *Paracercomonas sp.* was selected as test organism to evaluate growth/inhibition in wastewater samples before and after treatment, following the OCDE standard guidelines [5]. In water samples, no significant growth inhibition of algae was observed. However, a growth potentiation was shown in wastewater samples due to the presence of nutrients. Therefore, the tested treatment did not exhibit chronic toxicity to the microalga *Paracercomonas sp.*

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Water supply physico-chemical parameters in a Guinea-Bissau population district measured through the Water Quality Index (WQI)

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The world's fresh water is a finite resource of great importance to humans, since according to dietary recommendations we need to ingest about 2 liters per day [1]. Water supplies for human consumption, mainly for cooking and drinking, must meet minimum quality requirements to be safe. A safe water supply is more difficult to assess in underdeveloped areas of the African continent. Therefore, in 2022, we were awarded a cooperation project to implement a protocol for measuring the quality of the water for human consumption in an African population district of about 4000 people, placed in Guinea-Bissau.

One way of assessing this quality is the determination of the WQI (Water Quality Index), which consists of establishing a mathematical equation composed of several physico-chemical and microbiological parameters, which can be assigned different weights depending on their relevance [2]. WQI values range from 0 (poor quality) to 100 (excellent quality), according to the literature [3].

Five physico-chemical parameters were chosen in this work: dissolved oxygen, ammonium, conductivity, pH and temperature to propose a WQI equation. The measurements were performed using a YSI-ProQuatro multiparametric probe that allows to obtain values *in situ*. The sampling area chosen was Ponte Nova neighborhood of Bafatá town (Guinea-Bissau) and water was sampled in July 2023. In this area, the measurements were carried out by triplicate in 4 zones (well, storage tank, 8 fountains and 4 houses) in order to obtain measurements that would allow an overall assessment of water quality.

Water quality requirements are normally established by the legislation of each country, but in underdeveloped areas, such as Guinea-Bissau, there are practically no water quality standards. Therefore, in this study, both WHO recommendations and Spanish legislation have been considered to check the degree of compliance with the results obtained, with respect to the physicochemical parameters (Table 1). The WQI values obtained ranged from 69 (for the storage tank) to 80 (one fountain), so the water is of good quality, except in the tank, which would require conventional treatment to ensure its quality.

In addition, an analysis of variance (ANOVA) and Tukey's test were applied to see if there were significant differences in the 5 parameters evaluated, between the values obtained in the 4 types of sampling areas and between the points sampled. It was observed that both the well and the houses had slightly different values to the rest of the points.

Table 1. Physico-chemical parameters with Spanish legal limits and degree of compliance

Parameter	Limit RD 3/2023 [4]	Compliance with legislation
Temperature	ND	-
Conductivity	up to 4000 μS/cm	Yes
pH	4.5 – 10	Yes
Amonium	up to 1 mg/L	Yes
Dissolved oxygen	ND	-

ND: No data

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Sustainable food packaging solutions: Bioactive bacterial nanocellulose films loaded with Paulownia wood extract

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The increase in greenhouse gas emissions, global warming, and the depletion of fossil resources has prompted the development of strategies to utilize natural renewable resources, such as the rapidly growing tree Paulownia elongata x fortunei, in the pursuit of a biobased economy [1,2]. This species is known for its high biomass production and minimal growth requirements. Researchers have investigated its hydrothermal extract due to its significant content of phenolics and oligosaccharides, which could potentially serve as additives in functional films for food packaging [3].

The hydrothermal extract of Paulownia wood (PW), obtained at a non-isothermal temperature of 203 °C, was characterized and evaluated for its antibacterial properties against *S. aureus* and *E. coli*. This extract, rich in xylooligosaccharides and phenolics [3], was incorporated into bacterial nanocellulose (BNC) films, produced by *Gluconacetobacter sacchari* under static growth conditions for 15 days at 30 °C, at varying concentrations of 0-52.5 mg/mL/cm², with glycerol added as a plasticizer (25-30% w/w).

The films underwent thermal (TGA-DTG) characterization, besides evaluation of color parameters, antioxidant capacity, UV-vis spectra, tensile mechanical properties, and antibacterial activity. The hydrothermal extract of PW contained high levels of xylooligosaccharides and phenolics (45.3 and 6.3 g/100 g extract, respectively), showing over 87% DPPH inhibition at concentrations of 4.2 mg/mL or higher, and an inhibitory effect on bacterial growth at concentrations of 26.25 mg/mL or more.

When incorporated into BNC films, these extracts displayed excellent UV barrier properties (with transmittance below 0.5% at 200-400 nm) and DPPH inhibitions of 84% or greater. Furthermore, the films exhibited enhanced tensile properties (greater elongation to break, lower tensile strength, and Young's modulus), improved thermogravimetric properties, and antibacterial effectiveness (inhibiting bacterial growth after 48 h) compared to the unloaded BNC films. Overall, the extract from Paulownia wood demonstrated significant antioxidant and antibacterial properties, which were harnessed to create bioactive BNC films suitable for active food packaging applications.

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Valorization of *Himanthalia elongata* seaweed for the recovery of bioactive compounds by green processes

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In recent decades, rapid population growth and increasing resource demand have driven the search for renewable and sustainable sources for high-added value products. In this context, marine macroalgae like *Himanthalia elongata*, have emerged as a promising resource due to their high content in nutritional and bioactive compounds. This work focuses on the valorization of *Himanthalia elongate* algae for the extraction of bioactive compounds, specifically phenolic compounds and oligosaccharides, using a cascading biorefinery approach that combines conventional and emerging technologies for selective extraction of target compounds [1–3].

The methodology involved an initial stage of conventional extraction using three different solvents (water, ethanol 50% and 96% (v/v)). The effectiveness of each solvent in extracting phenolic compounds and polysaccharides, as well as the antioxidant capacity of the extracts, was evaluated. The selected solid residues from the conventional extractions (water or ethanol 50% v/v pretreated biomass) were subjected to a second extraction stage using of microwave-assisted autohydrolysis. A range of temperatures between 120 to 210 °C were tested to optimize the concomitant recovery of fucooligosaccharides and phenolic compounds.

The results obtained after conventional extraction showed that ethanol 96% v/v was not an effective solvent for extracting the target compounds. Water and ethanol 50% v/v allowed greater solubilization of polysaccharides and phenolic compounds with high antioxidant capacity. Microwave-assisted autohydrolysis at temperatures between 150-160 °C revealed maximum extraction of fucooligosaccharides, while temperatures between 190-210 °C maximized the recovery of phenolic compounds with antioxidant capacity.

This study showed that combining conventional methodologies with microwave-assisted autohydrolysis can be an effective and sustainable strategy for the comprehensive valorization of *Himanthalia elongata.* The obtained bioactive compounds have potential applications in food, cosmetics or pharmaceutical industries, contributing to the development of third-generation biorefineries.

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Estructuras metal-orgánicas de Fe-Cu como catalizadores para la degradación de pesticidas mediante procesos de oxidación avanzada

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Los contaminantes orgánicos persistentes (COPs) son una preocupación crítica debido a su alta estabilidad química, lo que les permite resistir la degradación en el medio ambiente y acumularse en los ecosistemas. Estos compuestos, como pesticidas y productos industriales, pueden propagarse por el aire, el agua y el suelo, afectando negativamente la salud humana y la biodiversidad. Su eliminación eficaz es esencial para mitigar sus efectos ecológicos y sanitarios [1]. Una de las soluciones más prometedoras para la eliminación de los COPs son los procesos de oxidación avanzada (AOP), métodos que se basan en la generación de radicales altamente reactivos, como el radical sulfato o hidroxilo, capaces de degradar una amplia gama de contaminantes que los tratamientos convencionales no logran eliminar eficazmente. Sin embargo, estas técnicas presentan desafíos en términos de eficiencia y sostenibilidad por la necesidad de la activación de los oxidantes primarios para la generación de los citados radicales. La investigación en nuevos catalizadores avanzados, como redes metal-orgánicas (MOF) ó nitruros de carbono grafíticos, es muy necesaria para mejorar la velocidad de reacción y reducir los costos energéticos, lo que permitirá una aplicación más amplia y económica [2].

Este estudio se centra en el desarrollo de un catalizador para procesos de oxidación avanzada, utilizando como soporte un hidrocarbón producido a partir de residuos agroindustriales. Sobre esta base se ha inmovilizado un MOF de Fe-Cu, lo que ha permitido una mayor eficiencia en la degradación de contaminantes. La capacidad del citado compuesto (composite) para actuar como catalizador en AOPs ha sido evaluado para diversos agentes oxidantes como el persultafo de sodio, peroxomosulfato de sodio y percarbonato de sodio. Los resultados más destacados se obtuvieron al emplear este catalizador en combinación con persulfato, logrando una eliminación de más del 95% del contaminante pesticida modelo, pimetrozina, en un tiempo de reacción muy corto, 15 minutos. Posteriormente se procedió a la optimización de variables que afectan al proceso como la concentración de oxidante y catalizador. Finalmente, para identificar el papel de los diferentes radicales (sulfato, hidroxilo, superóxido), así como el oxígeno singlete generados durante el proceso, se utilizaron *scavengers* específicos, permitiendo así la diferenciación y cuantificación de los radicales implicados. Los análisis demostraron que los radicales hidroxilo y sulfato son los principales responsables de la degradación del pesticida, indicando que estos radicales desempeñan un rol crucial en el mecanismo de oxidación promovido por el catalizador. Además, se identifican diversos intermedios de degradación generados lo que permite confirmar la mineralización del pesticida.

Este estudio proporciona una base para futuras investigaciones en la mejora de los AOPs, centrándose en la creación de catalizadores con mayor selectividad y eficiencia, esenciales para el tratamiento avanzado de aguas contaminadas. La identificación de los radicales predominantes permite optimizar los sistemas de tratamiento, lo que abre nuevas oportunidades para desarrollar catalizadores más eficientes y sostenibles.

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Evaluation and optimization of a multielectrode system for the treatment of effluents with high organic matter content

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Accumulation in aquatic ecosystems of recalcitrant pollutants to conventional processes involves a significant risk to the environment and human health, as these compounds are characterized by a high toxicity and persistence, as well as by the increase of chemical oxygen demand (COD) in effluents [1]. In addressing this issue, electro-advanced oxidation processes have been proposed as a promising alternative, since it is a cost-effective and sustainable technology aimed at the degradation of harmful compounds through the formation and later activity of reactive oxygen species [2].

This study proposes the application of an electrochemical process for treating effluents with elevated organic content by the use of a multielectrode configuration. Preliminary tests (0.75 L volume) were conducted using a single anode-cathode pair to evaluate the effectiveness of the system by monitoring COD in a model water, modifying the cathode material and performing tests both in the presence and absence of an adsorbent material. Subsequently, an assembled multielectrode (Fig. 1) with five anodes and six cathodes was assayed in order to establish the optimal working conditions. Once these conditions were defined, the system was evaluated for the treatment of a real industrial wastewater ($COD_{initial} \approx 1$ g/L), so that finally the process was implemented on a larger scale, reaching a final working volume of 6 L.

The favourable results obtained highlight the applicability of the system at different scales with a complex aqueous matrice, using an electrode configuration that is easily adaptable and which achieves high removal values of the organic content present in wastewater.

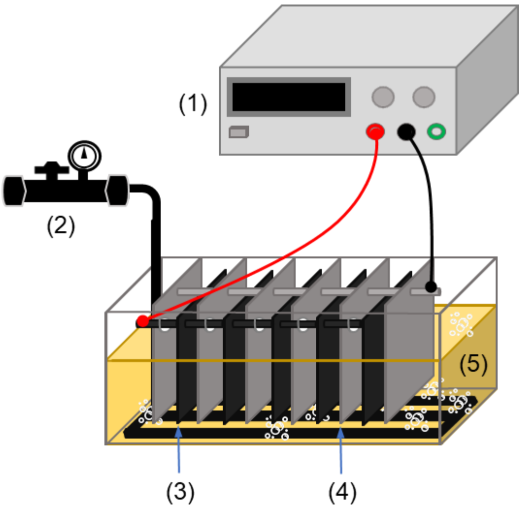

Fig.1. Schematic of the electrochemical system with multielectrode. (1) Power supply, (2) Air compressed, (3) Anode, (4) Cathode, (5) Waste effluent.

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Sustainable Synthesis of High Purity Biosilica from Rice Husk: Overcoming the Limitations of Mineral Acid Leaching

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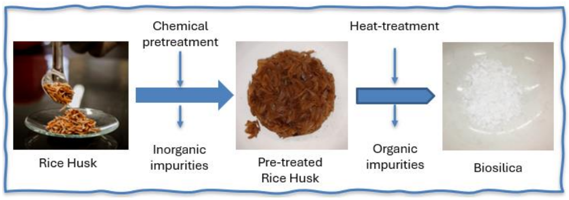
High purity silica nanoparticles have emerged as a promising material with unique physical and chemical properties, highlighting high stability, biocompatibility and tunable surface and porosity properties, making them desired in a wide range of industrial applications. Ongoing research is focused on improving those characteristics for construction and automotive industries, as reinforcing agents or fillers, and for biomedical applications, such as drug delivery [1].

The high industrial demand requires the replacement of the current energy-intensive processes used for the industrial synthesis of silica particles, such as the acidification of sodium silicate solution from melting quartz sand with sodium carbonate at high temperatures (1300 °C), with more sustainable approaches [2]. These novel approaches are based on the synthesis of biosilica from bio-wastes, such as rice husk (Fig. 1), which, depending on their origin, can contain up to 20% of silica content in their composition [3]. Biosilica is extracted from rice husk through three sequential steps: i) pretreatment, ii) thermal treatment and iii) post-treatment. Each step requires optimization to achieve high purity silica (>99.8%) while minimizing the overall environmental impact of the process. The first crucial step in obtaining high purity silica from rice husk is the efficient removal of inorganic impurities, which are entrapped within the rice husk's lignocellulosic structure. These impurities can be effectively removed using strong mineral acids as leaching agents, which are hazardous, limiting their use in the industry [1]. This limitation can be addressed by leaching with organic acids, which are widely accepted as a more sustainable option. These milder acids hydrolyze the lignocellulosic biomass from rice husk and form chelates with metallic impurities, increasing their aqueous solubility. The remaining organic material is removed by thermal treatment at temperatures <800 ºC to prevent biosilica crystallization.

This communication presents a systematic study on the use of new environmentally friendly and scalable pretreatment methods, including physical and milder chemical approaches, to obtain high purity biosilica from rice husk. A sustainability assessment of the process was conducted using a qualitative life cycle analysis for each organic acid, further complemented by the calculation of an Eco-Scale score [4].

Fig.1. Synthesis of biosilica from rice husk



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Removal of Zn(II), Cu(II) and Pb(II) from rainwater: white bean peel sorbent

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A recent work of the authors [1] assessed the use of the whole white bean (*Phaseolus vulgaris* L.) as sorbent for the removal of zinc from rainwater, having shown it is a promising viable solution for rainwater treatment. However, becomes important to evaluate the use only of bean peel for rainwater treatment, preserving the bean core for other purposes, namely for food consumption.
The aim of the present work was to evaluate the sorption efficiency of the peel of white bean (*Phaseolus vulgaris* L.) for the simultaneous removal of Zn(II), Cu(II), and Pb(II) from rainwater. The uniform experimental design was used to assess the effects of the initial concentration of the elements in water, the initial pH of the solution, and the contact time between sorbent and aqueous solution, as well as to optimize the removal process. The removal of the potential toxic elements was evaluated for model water solutions and real rainwater samples, and the variation of elements concentration was monitored by inductively coupled plasma mass spectrometry (ICP-MS). The chemical and structural characteristics of white bean peel during the sorption process were assessed by Fourier transform infrared (FTIR-ATR) spectroscopy and scanning electron microscopy (SEM).

The results of this work showed that the peel of white bean was able to reduce the concentrations of Zn(II), Cu(II), and Pb(II) in rainwater, which highlights its potential to be used as sorbent for rainwater treatment.

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STUDY OF THE ADSORPTION CAPACITY OF ACTIVATED CARBON DERIVED FROM KRAFT LIGNIN TOWARDS SULFAMETHOXAZOLE

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The occurrence and fate of antibiotics in the aquatic environment is a critical problem as they can potentially and permanently damage ecosystems and human health due to the promotion of antibacterial resistance. Antibiotics, such as sulfamethoxazole (SMX), a widely prescribed sulfonamide, are not fully removed by traditional wastewater treatments, highlighting the need for sustainable solutions to mitigate this growing threat [1]. Adsorption by activated carbon (AC) has been proven to be an effective methodology for the removal of antibiotics from water mainly due to the high surface area (S_{BET}) of AC. The use of industrial wastes as AC precursors, such as Kraft lignin (KL), contributes to the sustainability of these adsorbents, avoiding the use of non-renewable raw materials. In addition, such impact may be further reduced by the utilization of microwave instead of conventional pyrolysis in the production of AC, since it allows for a faster and more energy efficient process. For this purpose, AC-KL were produced following a procedure previously optimized (800 °C; 30 min and KOH:KL ratio 1:1 and 1:2) and characterized for N_2 adsorption-desorption resulting in materials with a specific surface area (S_{BET}) of 1262 and 963 $m^2\,g^{-1}$, respectively. After that, the optimized material was applied in adsorption studies in ultrapure water and buffered ultrapure water. The AC were tested for the removal of SMX, using capillary electrophoresis to determine the remaining concentration of antibiotic in the aqueous phase with the determination of the adsorbed amount onto the AC by mass balance. Kinetic and equilibrium adsorption experiments were run under batch operation conditions. Also, the effects of four pH levels (4, 6, 8 and, 10) on the adsorptive performance towards the SMX were evaluated. The obtained results revealed that adsorption kinetics were fast (equilibrium attained within ~120 min) and well fitted by the pseudo-second order kinetic model. Equilibrium isotherms were adequately described by Langmuir model with maximum adsorption capacities up to 100 and 64 mg g^{-1} for the materials obtained with KOH:KL ratios of 1:1 and 1:2, respectively. Considering that the S_{BET} is one of the key parameters of the adsorption process, these results must be associated with the difference between the S_{BET} of the two materials. As for the effect of pH, it was found that the pH of the matrix plays a crucial role in controlling the electrostatic interactions between SMX and the AC-KL adsorbents. These interactions are strongly influenced by the point of zero charge (PZC) of the adsorbents, which was determined to be 5 and 6, for KOH:KL_1:1 and KOH:KL_1:2, respectively. Below these PZC, the KOH:KL surface acquires a positive charge, favoring the adsorption of anionic species, such as the negatively charged forms of SMX. Above the PZC, the surface becomes negatively charged, which results in the absence of favorable electrostatic interactions with SMX, which are also negatively charged, thus reducing the adsorption capacity.

These results highlight that the pH of the matrix is a determining factor for adsorption efficiency, and that KL is a suitable precursor for producing AC that is efficient at removing SMX from water, especially at lower pH conditions than PZC, where electrostatic attraction forces are maximized. The results obtained demonstrate that KL is an adequate AC precursor for the efficient removal of SMX from water.

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Fixed-bed column adsorption studies for the removal of antibiotics from water using regenerable biochar obtained from brewery wastes

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Residual biomass from the brewery industry, particularly spent brewery grains (SBG), is generated in large amounts and constitutes a promising option as a precursor for carbon adsorbents for water treatment applications [1]. In fact, the use of agro-industrial wastes as precursors of adsorbent materials contributes to the environmental sustainability of this process, avoiding the use of non-renewable raw materials. Sustainable wastewater treatment, combined with advanced processes, is essential for meeting environmental standards and protecting water systems from harmful pollutants. In this regard, this work aims to assess the fixed-bed adsorption performance of biochar (BC) produced from SBG for the removal of three antibiotics, namely sulfamethoxazole (SMX), trimethoprim (TMP) and ciprofloxacin (CIP), from water. For this purpose, the impact of flow rate, aqueous matrix, and single/multi-component adsorption on the breakthrough adsorption curves was evaluated. Thermal regeneration of the exhausted BC was also considered to study its possible reutilization.

The BC used in this work was produced by microwave-assisted pyrolysis at 800 ºC during 20 min. For the fixed-bed adsorption experiments, a column (length of 13 cm and inner diameter of 1 cm) at controlled temperature (25 ± 1 °C) was packed with BC at a constant bed depth of 4.4 cm (approximately 2.0 g of BC). Fixed-bed studies on the removal of pharmaceuticals (SMX, TMP and CIP) by BC in continuous operation mode were carried out in three subsequent stages: i) study of the effect of flow rate (1, 2 and 4 L d^{-1}) using buffered distilled water (pH 8.0) as aqueous matrix; ii) study of the adsorption of the antibiotics under study from single or ternary solutions in buffered distilled water fed at the flow rate selected at the previous stage; iii) thermal regeneration of exhausted BC, performed by microwave pyrolysis (600 °C for 20 min) and packing of the regenerated material into the column for two additional adsorption cycles, using TMP as case study. Experimental data from the breakthrough curves were modeled using the Thomas, Yan, and Yoon–Nelson models. The flow of 2 L d^{-1} was selected at stage i) as operation condition for stages ii) and iii). The highest bed adsorption capacity, whether from single or ternary solutions, was observed for TMP, followed by CIP, and then SMX, likely due to unfavorable electrostatic interactions between SMX and BC at the working pH (pH 8). For the three target antibiotics, the bed adsorption capacity from the ternary solution was notoriously lower than that of their respective single solutions, decreasing in the order TMP>CIP>SMX, due to competitive effects between the three antibiotics. Regeneration studies showed that the BC adsorption capacity increased after each stage of thermal regeneration, aligned with the observed improvement in textural properties (S_{BET} increased after each regeneration cycle, from 281 $m^2 g^{-1}$ in cycle 1 to 462 $m^2 g^{-1}$ in cycle 3). The thermal regeneration process carried out with the exhausted BC provided good perspectives for the reusability of the material. It must be highlighted that few studies have explored the application of BC derived from residual biomass for the removal of pharmaceuticals from water in fixed-bed systems. Therefore, our research fills this critical gap and provides a novel approach to wastewater treatment.

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Enhancing nanocelluloses modified with succinic anhydride for efficient removal of heavy metals in aqueous medium

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The presence of metal ions in contaminated water from industrial processes has led to great concern regarding their harmful effects on human health and water resources. The removal of these elements in contaminated water is essential for cleaner production from a circular economy perspective. The sorption technique is considered an alternative technology with a high potential for removing these elements in low concentrations [1]. The use of modified nanostructures can induce a chelating effect on metallic contaminant, improving their removal. Furthermore, the functionalization of nanostructures with selective ligands also allows the separation through the coordination of the metal ions with the new functional groups added to the polymeric structures [2]. Thus, this work describes the preparation of two chelating materials: mercerized and non-mercerized nanocelluloses modified with succinic anhydride (NCT-MOD1 and NCT-MOD2, respectively) to remove metal ions from aqueous solution – Figure 1. The nanocellulose was successfully converted to nanocellulose succinate structures with degrees of substitution (DS) ranging from 1.876 to 5.322 mmol/g (NCT-MOD1) and 1.876 to 2.626 mmol/g (NCT-MOD2), depending on the reaction conditions. FTIR spectra revealed a new peak at 1704 cm^{-1}, attributed to the –C═O stretching vibrations of the introduced carboxyl moiety, while ^{13}C NMR showed methylene signals and new peaks on NCT-MOD2, which are characteristic of the ester and acid functionalities of the introduced succinates. The modifications also decreased the degradation temperatures compared to neat nanocellulose, as the increase in acid content via succinylation can induce the decrease in the degree of compaction of the polymeric chains. Furthermore, NCT-MOD1 was completely soluble in aqueous media, which makes its use in sorption processes impossible. On the other hand, the insoluble NCT-MOD2 showed sorption capacities of (0.326 ± 0.002), (0.112 ± 0.008), (0.056 ± 0.002), (0.053 ± 0.003) and (0.048 ± 0.009) mmol/g for $Pb^{2+,}$ Cu^{2+}, Cd^{2+}, Ni^{2+} and $HCrO_4^-$ removal, respectively, which were higher than those obtained for the pure nanocellulose. Thus, the use of modified cellulose nanostructures can be an alternative to increase the sorption capacity of metal ions from contaminated water.

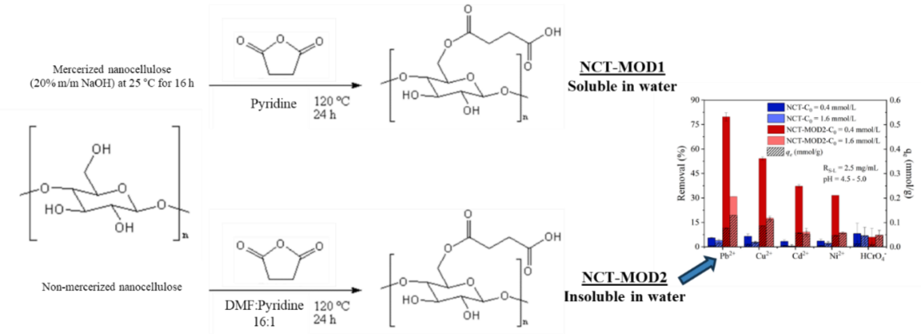

Fig.1. Modification of cellulose nanostructures by succinylation and metal ion removal potential.

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Evaluating the Cytotoxicity and Environmental Impact of Nanoparticles: Insights from Microtox® Bioassays

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Nanoparticles, characterized by their nanoscale dimensions, exhibit unique physical and chemical properties compared to their macroscopic counterparts due to their larger surface area and quantum effects. These distinctive traits make them highly valuable across diverse fields, including medicine, lubrication, and the food industry. In this sense, nanotechnology increased its global market value from approximately 14 billion euros in 2010 to 77 billion euros in 2021 and is expected to increase further in the future [1]. As their uses become increasingly diversified in recent years, it is vitally important to understand how nanoparticles relate to organisms and ecosystems. Understanding how they produce toxicity and what are the effect of their exposure is fundamental to making the use of this technology safe for everyone. However, the mechanisms underlying nanoparticle toxicity, and the consequences of long-term exposure remain only partially understood. This study bibliographically explores nanoparticle-induced cytotoxicity using a variety of assays, such as MTT, MTS, neutral red uptake, and lactate dehydrogenase tests, to examine their complex interactions with biological systems [2-4].

Additionally, the Microtox® toxicity test, assessing nanoparticle toxicity by measuring bioluminescence inhibition in the marine bacterium *Aliivibrio fischeri*, was employed to analyze nanoparticles' environmental and health impacts. Cellulose nanocrystals, graphene nanoplatelets and zirconium oxide nanoparticles were studied. This approach provides valuable insights into the potential hazards posed by nanoparticles in biological and ecological systems. Despite the tendency of nanoparticles to form aggregates in aqueous solution, which significantly complicates the application of the Microtox® test, low toxicity values were observed for the selected nanoparticles. A small phase of lethargy (lag phase) is observed at low concentrations, where it appears that the nanoparticle concentration does not influence the bioluminescence of the bacteria. However, starting from 5 g/L, the expected decrease in luminescent response becomes noticeable, and EC_{50} values for the different selected nanoparticles are obtained. Cellulose nanocrystals (CNC) can be categorized as practically harmless [5].

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Sustainable extraction techniques for bioactive compounds from marine biomass

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Sustainable extraction methods are critical for maximizing the recovery of bioactive compounds from marine resources like seaweeds and microalgae, with potential applications in food, pharmaceuticals, and biomaterials. This study overviews three green extraction techniques: Microwave-Assisted Extraction (MAE), Pressurized Water Extraction (PWE), and Ultrasound-Enzyme Assisted Extraction (US-EAE), to evaluate their efficiency in extracting valuable polysaccharides and pigments from *Spirulina* and *Ulva* spp.

MAE, employing green solvents and water, was tested on *Spirulina* to extract C-phycocyanin, a bioactive pigment with immune-boosting and antioxidant properties (1). A combination of microwave heating (80 °C for 5 minutes) and green solvents achieved moderate yields, though the freeze-thaw method with water resulted in higher C-phycocyanin concentrations (6.005 mg/mL). PWE, utilizing water under high pressure and temperature (T=121 °C, P=2 bar for 1.5-2.5 h), was applied to *Ulva* spp. to extract ulvans, sulfated polysaccharides with antioxidant and anti-inflammatory properties (2). This method provided extraction yields of 29.18 ± 2.21 % of crude ulvan. US-EAE (T=55 °C for 1-1.5 h), which combined ultrasound with the Cellic® CTEC3 enzyme cocktail, was also applied to *Ulva* spp. for ulvan extraction. This method significantly improved ulvan yield, with 32.18 ± 1.69 % crude ulvan. For further purification, crude ulvan fractions were ultrafiltered using a 10 kDa cut-off membrane and freeze-dried to obtain a homogeneous ulvan-enriched extract.

These sustainable extraction methods—MAE, PWE, and US-EAE—demonstrate effective, eco-friendly approaches for recovering high-value compounds from marine biomass, supporting advancements in green chemistry and bioactive compound production for various industries.

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Multiresidue analysis of 7 therapeutic classes of pharmaceuticals in sediments by US-SPE-LC-MS/MS

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Several studies have analysed antibiotics in sediments, but few pharmaceuticals from other therapeutic classes have been studied. These products primarily appear in this matrix mainly due to discharges from wastewater treatment plants (WWTPs), which lack specific technologies for their removal. Additionally, rainfall can transport pharmaceuticals excreted in the urine or faeces of farm animals or cause WWTP overflows [1]. The potential toxicity and the increasing occurrence of these compounds have led to their classification as contaminants of emerging concern (CEC) [2]. Some studies have reported pharmaceuticals detected in sediments that are not found in the water of the same river, attributed to their partition coefficients and the physicochemical characteristics of the sediments [3]. The aim of this study is to develop a multiresidue method for the determination of seven therapeutic classes of pharmaceuticals in sediments.

The best extraction solvent was tested, including solvent mixtures. The sonication conditions were studied: temperature, power, and frequency, and two different approaches for the clean-up were compared. In addition, a concentration step was tested under different pressure and temperature conditions; however, this was discarded due to analyte losses. The proposed method involves sonication extraction, solid phase extraction (HLB) clean-up, and LC-MS/MS (QqQ) determination.

The method allows the analysis of 48 pharmaceutical compounds, including antibiotics, NSAIDs, cardiovascular drugs, and psychiatric drugs, among others. Good accuracy (75-125%) and precision (<20%) were obtained with the method proposed, achieving method quantification limits (MQL) <0.1 ng/g for the majority of these compounds.

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Valorization of cork industry residues and its application for wastewater treatment

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The increase of the world population has made the access to clean and safe water to become progressively more challenging over the past decade. Occurring water pollutants range from organic contaminants, such as dyes, pesticides, and pharmaceuticals, to inorganic contaminants, such as heavy metals [1].

In recent years, scientists have been trying to identify and separate these pollutants to mitigate the damage, through what is known as environmental remediation [2]. There has also been a significant effort to promote the reuse of industrial residues, thus reducing the waste amount and creating cheaper alternatives for new materials [3].

In this work, we propose the use of cork powder (CP) residue, resultant from the cork stopper industry, and its valorization into magnetic adsorbents for water remediation. This has been achieved by impregnating the CP with adequate transition metals followed by its pyrolysis under inert atmosphere, leading to the formation of magnetic biochars with high porosity [4]. The prepared magnetic biochars were characterized by solid-state techniques and evaluated as adsorbents for the removal of water pollutants.

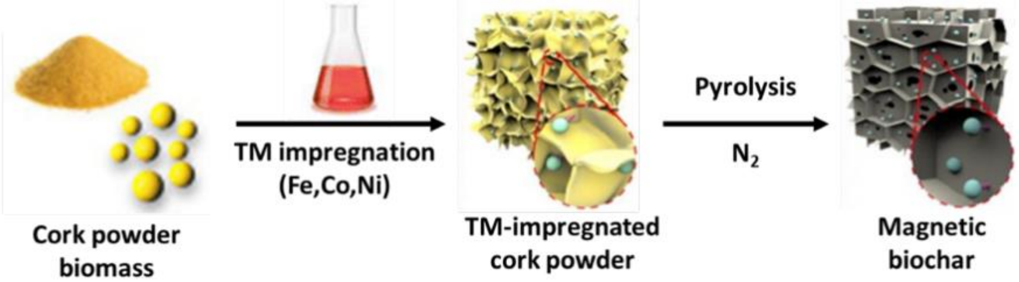

Fig.1. Preparation of porous magnetic materials derived from cork residues [5].

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Study of the adsorption of triazinic herbicides on microplastics

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The growing presence of microplastics in the marine environment is a current problem, because these pollutants have a negative impact on the ecosystems and, moreover, they act as vectors of other pollutants which adsorb on their surface [1]. Although many studies have been carried out about the adsorption of organic compounds by microplastics, few of them are focused on triazine herbicides.

Triazines are a group of herbicides widely used for pre- and post-emergence control of grasses, crops and weeds in cereals [2]. These compounds are highly resistant and are considered pollutants of priority concern. It has been estimated that a large proportion remains in the environment after application and, due to their widespread use, persistence and mobility, fluxes of these compounds can reach the marine environment [3].

In this work, a study of the adsorption of three triazine herbicides (atrazine, terbuthylazine and terbutryn) on different pristine and aged MPs (under dry and wet conditions) from surrounding waters was investigated. The target MPs included polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), poly (ethylene terephthalate) (PET) and polyamide (PA). The procedure is based on putting the microplastic in contact with the solution of the compounds under study for a certain time, using agitation. After the adsorption procedure, the compounds remaining in solution are analyzed by liquid chromatography with diode array detection.

Our results revealed that the most hydrophobic polymers exhibit higher adsorption capacity for the triazines of interest, being PE the polymer with the highest adsorption capacity followed by PS. On the other hand, terbutryn, which is the most hydrophobic compound, shows a higher adsorption than the other compounds in all cases, except for PS and for PVC wet-aged in which cases the adsorption is similar for the three studied compounds. Furthermore, in some cases, the triazines are not adsorbed or their adsorption is very low and lacks of reproducibility. This occurs for atrazine and terbuthylazine on pristine and dry-aged PA, all triazines on pristine PET and atrazine on dry-aged PET. Nevertheless, this latter showed a higher adsorption for terbuthylazine and terbutryn than PS and PVC under the same conditions. The study of the contact time shows that, in most cases, the adsorption increases with contact time up to 48 hours, for both pristine and aged microplastics.

The roughness and the specific surface area of the aged microplastics increase their adsorption capacity compared to the pristine ones, except for PA regarding the terbutryn adsorption and PVC, which shows a highly variable adsorption behaviour. On the other hand, the aging effect on the adsorption is different depending on the physicochemical characteristics of the polymer. So, while the adsorbent capacity of PE increases considerably with wet weathering, the behaviour is the opposite for microplastics with a higher percentage of crystallinity (PS and PET), as dry-aged microplastics show a greater adsorption than wet-aged ones.

Between the different polymers studied, the aged PE is the microplastic with the highest adsorption capacity for triazines and, looking to the future, it would be interesting to carry out more research on its adsorption and desorption properties.

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Adsorption behaviour and mechanisms of terbutryn on polyethylene microplastics in marine environment

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The presence of microplastics (MPs) in the marine environment has become a priority environmental problem, due to their impact on organisms and ecosystems. Their small size increases their bioavailability and they can be ingested by phytoplankton and microorganisms. MPs also act as vectors for various pollutants in the environment, as they can adsorb and transport pollutants present in water and subsequently release them into other environmental compartments and organisms [1].

This study is focused on the behaviour and adsorption mechanisms of terbutryn on pristine and aged polyethylene (PE) microplastics simulating both wet marine conditions and conditions on the dry part of beaches. Polyethylene, a polyolefin derived from the polymerisation of ethylene, is by far the most widely used plastic in the packaging industry [2]. Terbutryn is an herbicide with adverse effects on a wide range of organisms and considered a priority substance since 2013 [3]. The procedure employed involves contacting the microplastic with a terbutryn solution in seawater with agitation for a certain period of time. After the adsorption procedure, the terbutryn that has not been adsorbed, and therefore remains in the solution, is analysed by liquid chromatography with diode array detection.

The results show that the roughness and specific surface area of aged microplastics increase their adsorption capacity compared to pristine microplastics. Furthermore, adsorption capacity increases significantly with wet aging compared to dry aging, probably because the aging process under marine conditions is more energetic. Thus, the polymer showing the highest adsorption capacity for terbutryn is PE aged under wet conditions, followed by PE aged under dry conditions, with pristine PE being the microplastic presenting the lowest adsorption capacity.

The adsorption studies have shown that the process consists of three stages. A first stage of rapid adsorption (first 48 h), another of slow adsorption (next 24 h), and a final equilibrium until reaching the 144 h studied. However, for PE aged under dry conditions, it is not possible to specify that it has reached an adsorption equilibrium in this time, as its adsorption percentage continued to increase in greater proportion than for the other two microplastics studied.

The amount of terbutryn adsorbed by the MPs at equilibrium and the R^2 values obtained for the three kinetic models of adsorption studied to describe the adsorption behavior of terbutryrn have shown that both the wet-aged and pristine PE follow a second-order kinetics. However, dry-aged PE follows a first-order kinetics before reaching equilibrium. Moreover, it was also observed that intraparticle diffusion contributes significantly to the adsorption processes of the three MPs.

Regarding the study of terbutryn adsorption mechanisms, it has been observed that all three microplastics conform to the Henry model, a mechanism dominated by hydrophobic interactions. In the case of aged microplastics, it is noteworthy that, due to the high R^2 values and the parameter n values, they also conform to the Freudlich model, indicating that the surface of these microplastics presents a heterogeneous surface concerning terbutryn adsorption points.

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Potencial bioactivo de extractos ricos en compuestos fenólicos de *Arnica montana* L. obtenidos mediante métodos verdes optimizados

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Arnica montana L. ha sido identificada como una fuente considerable de compuestos bioactivos, en particular compuestos fenólicos, los cuales se asocian con sus propiedades antioxidantes y antiinflamatorias [1]. En la industria agroalimentaria, los extractos ricos en fenólicos han ganado relevancia por su potencial para el desarrollo de diversas aplicaciones, tales como ingredientes alimentarios, aditivos y conservantes [2]. La extracción eficiente de estos compuestos es crítica para su aplicación industrial y la evaluación de los factores que influyen en el desempeño de la extracción es altamente necesaria. Este estudio tuvo como objetivo optimizar las condiciones de extracción mediante extracción asistida por ultrasonidos (UAE) y líquidos presurizados (PLE) para maximizar la recuperación de fenólicos a partir de flores secas de *A. montana,* así como evaluar su actividad biológica. Para la optimización, se aplicó la metodología de superficie de respuesta (MSR) con un diseño central compuesto de cinco niveles, combinando tres variables experimentales para cada técnica: para UAE, se evaluaron tiempo (5-45 min), potencia (150-450 W) y proporción de etanol en agua (0-100%), mientras que para PLE se analizaron tiempo (1-21 min), temperatura (50-200 ºC) y la misma proporción de etanol. El rendimiento de extracción (mg de extracto/ 100 g de muestra seca) y el contenido fenólico total, evaluado mediante cromatografía líquida acoplada a espectrometría de masas con analizador triple cuadrupolo fueron las variables respuesta evaluadas. La última variable fue expresada en dos formatos: mg CFT/g de muestra y mg CFT/g de extracto. La función deseabilidad fue empleada para maximizar simultáneamente las variables respuesta. De acuerdo con el perfil fenólico, se extrajeron diferentes compuestos dependiendo de la técnica empleada, siendo los ácidos fenólicos los compuestos mayoritarios. Los modelos RSM mostraron un buen ajuste ($R_{2\ adj}$> 0,751) y la falta de ajuste no fue significativa ($p>0.05$). Las condiciones óptimas de UAE que maximizaron todas las variables de respuesta fueron 20 min, 400 W, 87% de etanol. Para PLE, las condiciones óptimas fueron 11 min, 125 °C y 76% de etanol. Comparando los valores predichos, PLE superó a UAE en términos de CFT/g de muestra, obteniendo 79 y 51 mg/g, respectivamente. Por otro lado, las condiciones UAE produjeron un extracto más purificado, alcanzando 500 mg CFT/g de extracto. La validación experimental confirmó la fiabilidad de los modelos predictivos. Posteriormente, se comprobó que el empleo de ciclos de extracción en condiciones óptimas mejoró la extracción de fenólicos, alcanzando 116 mg CFT/g de muestra para UAE y 140 mg CFT/g de muestra para PLE tras tres ciclos de extracción. Ambos procesos optimizados son eficientes para la extracción de fenólicos, destacando el óptimo de PLE por su corto tiempo de operación, 33 min para tres ciclos, frente a 1 h requerida para tres ciclos de UAE. Además, a pesar de que el proceso de PLE se realiza a temperaturas elevadas, su corta duración podría conllevar un bajo consumo energético. En cuanto a la evaluación biológica, el extracto optimizado de PLE mostró un mayor potencial antioxidante y antiinflamatorio que el extracto optimizado de UAE. En el ensayo antitumoral, el extracto de PLE fue más eficaz frente a la inhibición del crecimiento de células de cáncer de mama (7 mg ELI /g de muestra), mientras que el extracto de UAE exhibió mayor eficacia frente a células de cáncer de pulmón (2 mg ELI /g de muestra). En general, los protocolos optimizados UAE y PLE demostraron ser metodologías eficientes la obtención de extractos ricos en fenólicos con un gran potencial bioactivo, lo que contribuye significativamente a ampliar las aplicaciones industriales actuales de *A. montana*.

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IDENTIFICACIÓN DE MICROPLÁSTICOS MEDIANTE TÉCNICAS DE APRENDIZAJE AUTOMÁTICO MULTIMODELO

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Actualmente, los microplásticos (MPs) son uno de los contaminantes más relevantes a nivel mundial. Para evaluar su presencia es indispensable identificar su composición polimérica básica. Los métodos analíticos más utilizados se basan en técnicas de espectrometría en la zona infrarroja (IR). Cada partícula se identifica comparando su espectro IR con colecciones de espectros de referencia. Dos limitaciones habituales son: (i) el número de partículas por muestra es muy elevado (con frecuencia superior a 20000), lo que hace inviable la comparación manual; (ii) los equipos instrumentales de medida habituales disponen de algoritmos de comparación muy sencillos que no siempre conducen a resultados satisfactorios. Para paliar ambos problemas, en este trabajo se comparan varios algoritmos de clasificación multimodelo con los objetivos de (1) generar modelos de clasificación multi-clase a partir de conjuntos de espectros IR de polímeros conocidos; (2) clasificar automáticamente los espectros de todas las partículas desconocidas de una muestra según dichos modelos.

El desarrollo y validación interna de los modelos –empleando técnicas de validación cruzada- se realizó usando 1072 espectros IR de MPs conocidos. La validación externa utilizó 30 espectros IR de MPs desconocidos para los modelos. Cada espectro IR consta de 1651 variables numéricas predictoras (Absorbancias cada 0,5 cm^{-1}, entre 975 y 1800 cm^{-1}). Los algoritmos se implementaron en Matlab.

La metodología planteada consta de dos fases genéricas: (1) desarrollo de modelos basados en diferentes métodos de clasificación y (2) explotación de los tres mejores modelos obtenidos. Además, en la fase 1 se estudia el preprocesado de los datos. Los métodos de aprendizaje supervisado elegidos para generar los distintos modelos fueron el análisis discriminante (lineal, diagonal-lineal, pseudo-linear y diagonal-cuadrático), el algoritmo de los k vecinos más cercanos (KNN, donde k varió entre 4 y 6; y se utilizaron diferentes distancias: euclídea, euclídea estandarizada , coseno, correlación de Pearson, correlación de Spearman) y los árboles de decisión (donde el número máximo de divisiones fue 1071, el número mínimo observaciones de nodos hoja 1 y el número mínimo de observaciones de nodos rama 10).

En la Fase 1, para cada modelo desarrollado se evalúan diversos parámetros de rendimiento, de entre los cuales se elige el criterio F1-Score como estadístico general que permite comparar los modelos entre sí. Los mejores modelos de cada tipo clasificador fueron el discriminante lineal, el modelo 5-KNN con distancia de correlación de Pearson, y el árbol de decisión con los parámetros anteriores. Sus valores de F1-Score fueron 0.9730, 0.9913 y 0.9354 respectivamente. En la Fase 2 tiene lugar la explotación de estos tres modelos (validación externa). El modelo discriminante lineal consigue clasificar correctamente el 100 % de los espectros, mientras que 5-KNN+Correlación de Pearson y el árbol de decisión sólo alcanzan el 93.3 % y 86.7 %; con valores de F1-Score de 1, 0.9352 y 0.8625 respectivamente.

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EVALUACIÓN DE TRES TÉCNICAS DE FLOTACIÓN PARA LA SEPARACIÓN EFICIENTE DE MICROPLÁSTICOS EN SEDIMENTOS

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Hasta hace relativamente poco tiempo no se conocían los riesgos que los microplásticos (MPs) suponían para nuestro planeta, pero actualmente es uno de los contaminantes más preocupantes y su estudio se ha incrementado. Hasta ahora no se han desarrollado métodos estandarizados para realizar las etapas de muestreo, tratamiento de la muestra ni la identificación de los MPs.

Para poder llevar a cabo la caracterización de los MPs en sedimentos es imprescindible realizar una primera fase de separación entre las partículas plásticas y la matriz sedimentaria (tanto orgánica como inorgánica). Esta es una tarea muy complicada debido a la complejidad de la matriz. La técnica más comúnmente aplicada consiste en separar las partículas inorgánicas y plásticas mediante flotación diferencial en una disolución de alta densidad. Dicho medio de flotación se obtiene habitualmente a partir de una disolución (sobre)saturada de una sal. De entre las diversas posibilidades, que incluyen el uso de wolframatos, las sales más utilizadas son el cloruro de sodio (NaCl), el yoduro de sodio (NaI) y el cloruro de calcio ($CaCl_2$).

En este trabajo se comparan estas tres opciones y, además, se propone un nuevo protocolo de trabajo que ayuda a minimizar la flotación de las partículas inorgánicas más finas, problemática habitual en este tipo de matriz.

El NaCl es una sal muy utilizada debido a su bajo coste y baja toxicidad. Sin embargo, la densidad de su disolución saturada sólo alcanza 1.2 g/cm^3, lo que no permite flotar los plásticos más densos como el PET y el PVC (1.38 – 1.41 g/cm^3) . Por el contrario, la disolución saturada de NaI sí permite flotar los plásticos más pesados ya que alcanza 1.6 g/cm^3; pero tiene tres grandes inconvenientes: su elevado coste; su toxicidad aguda (desprende vapores durante su manejo, que incluso llegan a teñir la zona de trabajo y la ropa de color amarillo), y una flotabilidad relativamente elevada de partículas finas de sedimentos. Por ello, se propone como alternativa más adecuada el uso de disoluciones saturadas de $CaCl_2$, que también consiguen flotar los plásticos más densos puesto que su disolución saturada puede alcanzar 1.52 g/cm^3, sin llegar a flotar tanto sedimento fino como el NaI. Además, esta sal presenta baja toxicidad y coste relativamente moderado.

Para reducir la cantidad de material particulado inorgánico que flota durante la separación por densidad es frecuente el uso de tamices. Sin embargo, se ha comprobado que esto perjudica las recuperaciones analíticas y limitan el estudio de los MPs al tamaño de luz de malla del tamiz.

Por ello, se propone un nuevo método basado en trabajar en modo “estático” y por rebose. Es decir, en lugar de filtrar los sobrenadantes sobre un tamiz, la separación por densidad se realiza en un kitasato provisto de un tapón en la oliva lateral, a través de la cual se elimina el sobrenadante sin tener que mover el matraz evitando que se el material decantado se resuspenda.

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Metal(oid)s oral and inhalation bioavailability estimation in recycled tire rubber and related materials

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Recycled rubber (RR) materials, particularly from waste tire crumb, are widely utilized in constructing synthetic surfaces for playgrounds, sports fields, and as infill for artificial turf [1]. The RR market, valued at USD 100 billion in 2023, is projected to reach USD 200 billion by 2030, driven by demand for synthetic surfaces [2]. RR offers advantages such as enhanced safety, durability, cost-effectiveness, accessibility, design versatility, and environmental sustainability. However, concerns arise regarding the potential release of toxic compounds, including metals and organic pollutants, which can contaminate the environment and pose health risks, especially for children. Research has highlighted the presence of harmful substances in RR used in various applications, but assessing the real health risks requires understanding the bioaccessibility and bioavailability of these contaminants.

Considering this, the present study reports for the first time on the estimation of metal(loid)s oral and inhalation bioavailability found in RR and related materials used in various manufactured products and applications. The novel *in-vitro* oral/inhalation bioavailability approach used for this purpose employed synthetic gastrointestinal and lung fluids, human physiological conditions, and a dialysis membrane (to simulate the blood barrier).

A validated analytical methodology based on closed-vessel microwave-assisted digestion and inductively coupled plasma mass spectrometry (ICP-MS) was used to analyse the total concentrations of toxic trace elements. Also, ICP-MS was used for metal(loid)s quantification in bioavailable fractions.

Additionally, a health risk assessment will be conducted on the metal(loid)s bound to the RR and related materials, based on the bioavailable concentrations, for both oral and inhalation exposures. This approach may help to provide more accurate health risk assessments of these materials, as it considers the processes that occur within the human body, in contrast to the potential overestimation derived from models that solely account for total concentrations.

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AMB67

Oxidative stress associated with recycled tire samples and related materials through an in-vitro assay

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The use of recycled tire rubber (RR) and related materials is very extensive around the world. These materials are employed in playground flooring, as infill for artificial turf pitches, synthetic running tracks, and additives manufacturing (3D printing) [1]. However, the harmful substances within these materials could affect human health, mainly through oral, inhalation, and dermal absorption, due to people's direct interaction with these materials [2].

Considering this, the present study addresses for the first time the estimation of the oxidative potential (OP) caused by the solubilized components (inhalation bioaccessible fraction) of RR and related materials in a synthetic lung fluid. To obtain the inhalation bioaccessible fraction, conditions as close as possible to physiological ones are used, employing Gamble's solution at pH 7.4 as the extraction medium, incubation at a constant temperature of 37°C with gentle agitation for a period of 24 hours.

The OP, defined as the ability of the components of a sample to oxidize the antioxidant species present in lung fluids and generate reactive oxygen species (ROS) [3], can be a good indicator of the impact, via inhalation, of the components of recycled rubber and related materials on health. The presence of these reactive oxygen species can lead to various problems, including respiratory ones, due to the oxidative stress they generate in the organism.

In this work, the OP of the inhalation bioaccessible fraction of various samples made from RR (playground and gym surfaces, sports tracks, and artificial turf infill) and other related materials (artificial turf) is measured using two different in-vitro assays, the dithiothreitol (DTT) and the ascorbic acid (AA) assays, which indirectly evaluate the presence of ROS in the lung environment.

This approach can help provide more accurate health risk assessments of these materials, as it considers the processes that occur within the human body, in contrast to the potential overestimation derived from models that solely account for total concentrations.

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A FIRST INVENTORY OF PLASTIC LITTER AT THE COASTLINE OF BAY OF ASUNCIÓN AND ASSOCIATED TOTAL METALS CONTENTS

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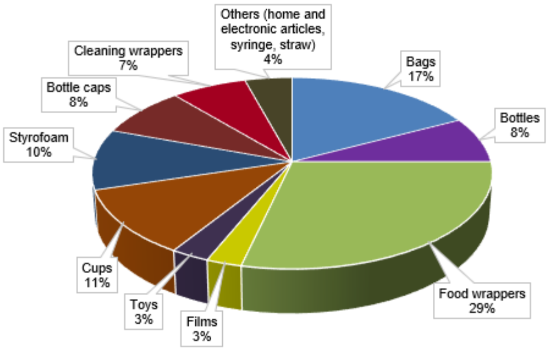
Global plastic production increased significantly in recent years and is expected to continue growing [1,2]. Many tons of plastics are disposed unduly in the environment due to bad habits and inefficient solid waste collection systems, as observed in the city of Asunción [3], Paraguay. The exposure of plastics to environmental conditions, particularly in surface water, causes their aging and also the adsorption of other contaminants present there, as it is the case for heavy metals [4].

The aim of this study was to evaluate the presence of total metals in plastic litter suspended along the coastline of Bay of Asunción in Paraguay. Four areas were selected. There total litter was counted and sorted as plastics, metals, rubber, ceramics/glass, natural materials, and miscellaneous. Plastics were classified further according to its size, original use, and type of polymer (PE, PP, PS, PET, PVC, PMMA). Identification of the polymers was done by infrared spectrometry. Microwave-assisted extraction with HNO_3 (65 %) and flame atomic absorption spectrometry was applied to quantify Fe, Mn, Zn, Cu and Cd.

The highest percentage of litter (60 – 82 %) at all points corresponds to plastics: PP, 42 % > PE, 31 % > PET, 12 % > PS, 10 % > PVC, 3 % > PMMA, 2 %, mainly food wrappers (**Figure 1**). The highest total metal concentrations were for Fe (3,224.2 ± 426.4 $\mu g \cdot g^{-1}$) and Mn (1,133.1 ± 41.9 $\mu g \cdot g^{-1}$). The concentrations of other metals decreased in the order Zn (307.8 ± 31.6 $\mu g \cdot g^{-1}$) > Cu (92.2 ± 3.8 $\mu g \cdot g^{-1}$) > Cd (16.8 ± 2.8 $\mu g \cdot g^{-1}$). The study provides first time information on the concentrations of typical metals in plastic litter in Paraguay, and is one of the very few available for South America.

Fig.1. Classification of plastic litter according to the original use of each plastic piece.



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Evaluation of Carbon and Nitrogen content of residual biomass from corn steep liquor after biosurfactant and gramicidin extraction for nutritional fermentation media

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Corn steep liquor (CSL), an aqueous stream from the corn industry, is used as nutritional supplementary media for animal feed and biotechnological processes including the production of Penicillin [1]. However, CSL was proved to be a source for the extraction of biosurfactant extracts and antibiotics, such as, Gramicidin S [2]. Thus, in the patent WO 2020/234501 [3] the protocol for the extraction of cell-bound biosurfactants from CSL is included. In addition, it was also demonstrated that *Aneurinibacillus aneurinilyticus* was responsible for the production of Gramicidin S [2]. Based on this, it should be interesting to evaluate the effect of the extractive process used for the biosurfactant and Gramicidin S extraction from microbial biomass contained in CSL to detect changes in the nutritional properties of the corn residue.

In this work, a preliminary study was developed where CSL was subjected to a cell-bound biosurfactant process with PBS following the methodology of the patent WO 2020/234501 [3], in addition to a Gramicidin S extraction of the antibiotic released from cell using acidic ethanol [4]. Moreover, this work includes also CSL subjected or not to a fermentation process with *A. aneurinilyticus*. The dependent variable studied was the Carbon and Nitrogen percentage of different treated CSL, in comparison with a control without any treatment.

The results show that CSL subjected to extraction processes with PBS or ethanol to obtain the biosurfactant extract or Gramicidin S respectively, in general maintained the Carbon/Nitrogen ratio, suggesting that the subproducts produced during the extraction processes can be used as nutritional supplement in fermentative operations.

In future works, the remain CSL from the biosurfactant and Gramicidin S extraction process would be evaluated for the growth of *Lactobacillus* strains since these bacteria have high nutritional requirements.

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Preliminary stability of cell-bound biosurfactant extract produced in corn steep liquor

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Environmental, social, and governance (ESG) aims involve the industrial production of more sustainable and environmentally friendly compounds. Therefore, biosurfactants, secondary metabolites of microbial origin, fit in this pool of substances. These compounds have demonstrated that are more biocompatible and biodegradable than their chemical homologous, synthetic surfactants, though one of their main drawbacks could be represented by their stability when they are storage at room temperature.

In this work, a cell-bound biosurfactant extract obtained from corn steep liquor (CSL); a residual stream from the corn-milling industry; following the patent WO 2020/234501 [1] was subjected to a stability study during 20 days at room temperature in an aqueous formulation at a concentration of 1 g/L. Previously to the experiment, surface tension (ST) of water, containing different concentration of biosurfactant extract, was measured with an Easy Dyne Tensiometer and the critical micellar concentration (CMC) for the biosurfactant extract was obtained. The dependent variable of the study was ST stability of the aqueous formulation containing the biosurfactant. It is important to remark that to notice changes in ST samples were diluted below CMC (8 and 16 times) and compare with the control.

The results showed that after 17 days (see **Figure 1**) at room temperature, the ST of the aqueous formulation containing the cell-bound biosurfactant extract started to increase, what it is indicative that the biosurfactant extract starts to be degraded. Notably, despite its high peptide content, this biosurfactant maintained stability at room temperature regarding its surface tension properties. Although in future works, more studies should be carried out, concerning the evaluation of microbial stability.

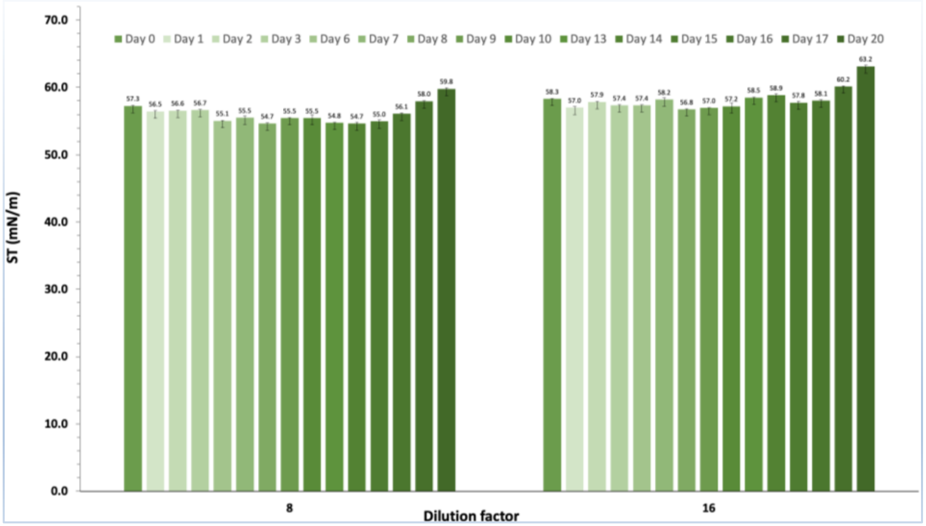

Fig. 1. Surface Tension evolution of cell-bound biosurfactant extract at different times

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Mechanical performance of fly ash-based geopolymer concrete as a sustainable alternative to ordinary Portland cement

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Increasing urbanization presents environmental, economic, and social concerns, mainly derived from the impact of carbon dioxide emissions and rapid waste generation. Geopolymer concrete (GPC) is an innovative construction material with the potential to minimize the environmental threat due to fly ash (FA) waste disposal and to reduce cement consumption[1,2]. In this study, cement-free GPC mixes are prepared using FA as a source of aluminosilicate material. Sodium silicate (SS) and sodium hydroxide (SH) solutions were used as alkaline activators with varying SH concentrations of 4, 10, and 16 M; sodium silicate to sodium hydroxide (SS/SH) ratios of 1.5, 2.0, and 2.5; and alkaline liquids to fly ash (AL/FA) ratios of 0.35, 0.525, and 0.70. The influence of the alkaline liquids on the mechanical properties of fly ash-based geopolymer concrete (FA-BGPC) was investigated through flexural strength and compressive strength tests in preliminary tests using prismatic molds. Additionally, water absorption tests through capillarity and immersion, as well as another trial of compressive strength tests, were done in the final tests using cubic molds. A reference composition using ordinary Portland cement (OPC) was produced to compare the results. All samples were cured at a controlled temperature of 25°C. The optimum flexural strength (6 MPa) and compressive strength (29.4 MPa) were attained with a GPC mix using 10 M, 1.5 SS/SH ratio, and 0.70 AL/FA ratio. It was found that the mechanical behavior of GPC is similar to that of OPC concrete.

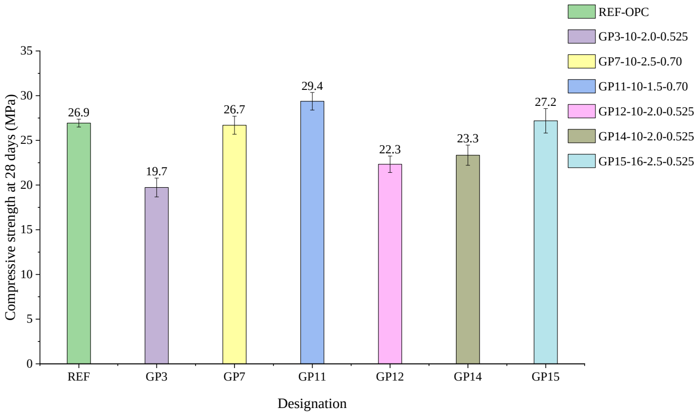

Fig.1. Analysis of geopolymers compressive strength.

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Novel Biodegradable Depigmenting Agents: Safe and Sustainable by Design to Address Environmental Concerns in Cosmetic Formulations

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The development of safe and sustainable by design (SSbD) criteria for chemicals was a key action defined in the Chemicals Strategy for Sustainability within the European Green Deal. The SSbD concept promotes a holistic approach that integrates safety, circularity and functionality of chemicals, materials, products and processes throughout their entire life cycle, minimizing their environmental footprint [1]. In our previous studies, we have identified 4-butylresorcinol as a widely used depigmenting agent in anti-aging cosmetic products, considered hazardous due to its environmental toxicity [2]. Herein, SSbD criteria were set to obtain a new library of resorcinol derivatives with potential tyrosinase inhibitory activity. Resorcinol derivatives were designed and an *in silico* screening study was carried out to evaluate their depigmenting activity through docking studies with tyrosinase, alongside assessments of biodegradability, aquatic toxicity, and ADMET properties (including molecular weight, logP, skin permeability, and skin toxicity). The synthetic feasibility of these derivatives was also examined in accordance with Green Chemistry principles, emphasizing the use of greener solvents and building blocks. Over 40 resorcinol designed derivatives achieved docking scores similar to 4-butylresorcinol and with favorable properties for topical application. Among these, derivatives obtained via hybridization and reductive amination approaches were the most promising regarding aquatic toxicity. Therefore, an initial library of aminated derivatives of resorcinol was planned to be synthetized. The selected one-pot reductive amination reaction conditions use green solvents and are depicted in figure 1 [3]. Further research is required to characterize their structure and evaluate the *in vitro* biodegradability, aquatic toxicity, and skin depigmenting activity of the synthesized resorcinol derivatives.

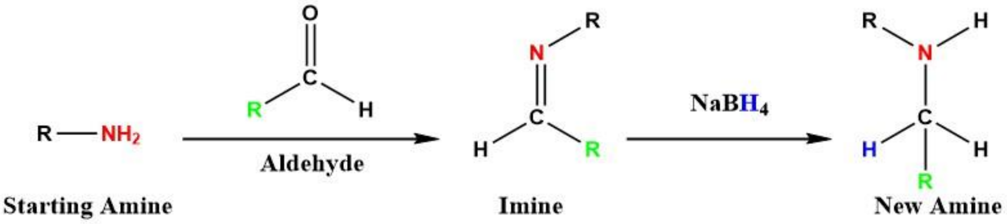

Fig. 1. Reductive amination reaction.

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Energy and Sustainability: Shaping Our Energy Future

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Abstract

Fossil fuels, including oil, natural gas, and coal, provide 70% of the global energy supply in 2022 [1]. These energy sources are responsible for over 75% of greenhouse gas emissions, contributing to climate change and posing risks to both energy security and resource depletion [2]. As the world seeks sustainable alternatives and diversification of energy sources, renewable energy sources like wind, hydroelectric, and solar power must be considered especially in countries like Spain, where these energy sources are the dominant [3, 4].

This work explores the future of energy, by analyzing the background and state of the art in terms of energy consumption and sources. Taking into account the real needs, and the current policies, short, medium and large terms of this future is clarified. The findings are analyzed from a critical viewpoint, to detect corrections in this way towards clean energy a net zero emissions. This study method employed the following steps: a global quantitative analysis of energy production from energy sources, a qualitative analysis of the current policies to be applied in the next years, and a detection of the erroneous advances in the energy transition.

The future of energy is practically written and marked by short, medium and long-term policies. In this future, fossil sources play a fundamental role. The effectiveness of the energy transition in relation to measures related to the increase in the use of renewable energy sources is not clear in all cases. And the role of energy efficiency is fundamental. As time passes, and the long term becomes medium and short, there is a need to adapt policies to reality and evidence of the effectiveness of technologies, a fundamental role of governance, with qualified advice that draws on critical studies in the field of energy.

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Detection and quantification of carbamazepine in water matrices using a simple MIP-based electrochemical sensor

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Pharmaceuticals, such as carbamazepine (CBZ, a widely prescribed anticonvulsant drug) are unfortunately detected in water environments worldwide, causing critical effects on aquatic species even at low concentrations [1]. Therefore, monitoring their presence in water bodies has become a pressing issue. In this context, electrochemical methods are gaining traction, since they overcome the drawbacks of chromatographic techniques (i.e. time-consuming sample preparation, long analysis time, expensive equipment) [2]. Among different strategies, the development of electrochemical sensors based on molecularly imprinted polymers (MIP) has demonstrated to be a promising technique, where cavities that are complementary to the analyte in shape, size and functional groups are created on the electrode surface, thus allowing the specific recognition of the desired molecule [3].

In this study, a novel MIP-based sensor using disposable screen-printed carbon electrodes (SPCEs) was developed in 4 simple steps (Fig. 1) applying cyclic and differential pulse voltammetry techniques. Surface imprinting was carried out by electropolymerization, using 3,4-Ethylenedioxythiophene (EDOT) as the functional monomer in the presence of CBZ as the template. The sensor was evaluated for the detection and quantification of CBZ, and the key process parameters (*i.e.* activation solution, concentration of template and monomer, number of electropolymerization cycles, extraction solution, or incubation time) were optimized to obtain a sensitive and selective response. Under optimal conditions, the sensor showed a good analytical performance for the quantification of CBZ in the range of 1-50 µM ($R^2 = 0.993$, limit of detection 0.58 µM and limit of quantification 1.93 µM). Additionally, it showed outstanding selectivity towards CBZ among other similar molecules tested (e.g. CBZ 10,11-epoxide, diclofenac and diltiazem, with a response of <5% of that for CBZ). Finally, the applicability of the developed sensor was assessed in three different real water samples: tap, river and sea water. Without any pretreatment procedure, the sensor showed great accuracy for the detection of CBZ in those matrices, with recoveries between 82-116%. All the obtained results proved the suitability of the novel developed sensor for the rapid and easy detection and quantification of CBZ.

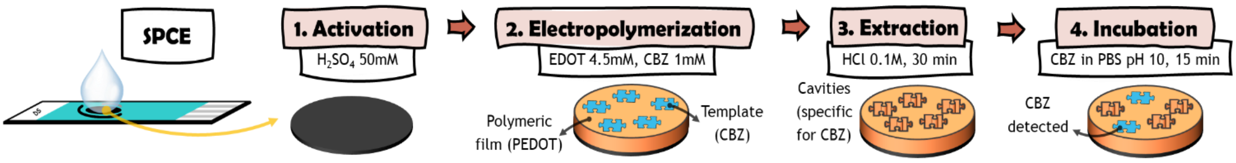

Fig.1. Fabrication of MIP sensor for detection and quantification of CBZ.

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A Sustainable Strategy in Peptide Synthesis for the Preparation of *cis*-4-Hydroxy-L-Prolyl Amides

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cis-4-Hydroxy-L-proline (*cis*-Hyp) is one of the four possible isomeric forms of 4-hydroxyproline that can be found in several natural products such as phallotoxins produced by mushrooms of the genus Amanita, being also a valuable scaffold to produce bioactive compounds with industrial and cosmetic interest.[1] However, contrary to its most abundant 4-hydroxyproline isomer found in nature, *trans*-4-hydroxy-L-proline (Hyp), which is readily available and cheap, *cis*-Hyp is considered an advanced starting material, thereby jeopardizing the development of *cis*-Hyp-based compounds.[2]

Over the past decades, many synthetic strategies have been described for obtaining *cis*-Hyp,[3] however, most of them rely on multi-step synthesis routes and inefficient protocols for its incorporation into peptide motifs.

In this work, an unprecedented one-pot methodology is described for the preparation of *cis*-Hyp amides from commercially available *trans*-4-hydroxy-L-proline without the need for peptide coupling reagents or capping strategies. Following this methodology, a total of 25 *cis*-Hyp amides were synthesized in good to excellent yields (76-97%) with full diastereoselectivity as determined by variable temperature NMR and HPLC experiments. Additionally, this protocol can be easily performed at a multi-gram scale (up to 91% yield) and upgraded to include an additional *O*-silylation step of the hydroxyl group in the same pot (three-step one-pot synthesis, 83% overall yield).

Compared to multi-step synthesis processes, the one-pot methodology displays a superior atom economy while exhibiting a substantial reduction of waste production. Moreover, it does not require chromatographic purification of intermediates and is compatible with greener solvents.

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Protic Organic Salts as additives in Vanadium Redox Flow Batteries

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As the climate change concern grows, investment from countries has been increasing directed at clean and renewable energy options. An important part of this investment focuses on more efficient energy storage capable of intermittent energy supply and demand [1,2]. Vanadium Redox Flow Batteries (VRFBs) are one of such batteries that use vanadium as mediator through two redox pairs (V^{2+}/V^{3+} and V^{4+}/V^{5+}). The standard electrolyte is composed of an aqueous solution with high concentrations of sulfuric acid that provides the necessary conductivity [3,4]. Currently, VRFBs are the only redox flow batteries commercially available.

In this work, several protic organic salts with hydrogen sulphate and mesylate as anions were prepared and characterized. These compounds were tested as additives for electrolyte formulations to avoid high concentrations of sulfuric acid. The alternative electrolytes, while maintaining conductivity and the battery's efficiency, would improve the half-life of the VRFB. These electrolytes were characterized through cyclic voltammetry, electrochemical impedance, polarization and cycling assays.

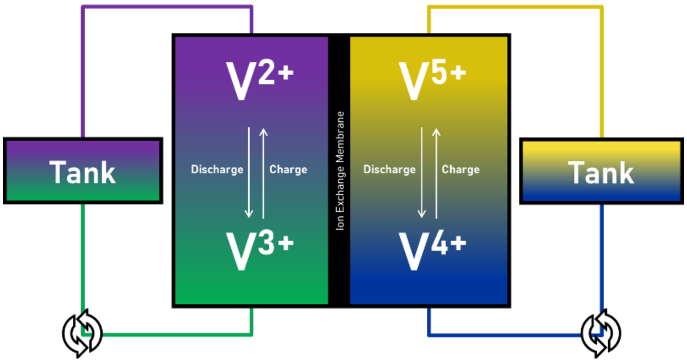

Fig.1. Diagram of a vanadium redox flow battery.

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The Impact of Grid-Connected Battery Storage Systems on Electrical Grid Variables

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Abstract

Integration of Renewable Energy Sources (RES) with Battery Storage Systems (BSS) in electrical transition contributes for advancing toward a cleaner and more sustainable energy future [1, 2]. This integration offers several environmental and electrical advantages, including greenhouse gas emission reduction by displacing fossil fuel-based generation, ensuring grid stability, minimizing energy losses, and improving integration of renewable energy [1-3].

RES such as solar and wind show inherent variability due to weather fluctuations [4]. Battery storage systems can be used to integrate these energy sources into the grid by storing surplus energy and releasing it as needed. This integration ensures a stable and reliable electricity supply, contributing to grid frequency and voltage balance [1,2]. Moreover, for overall energy efficiency, RES can be locally stored and used, reducing the reliance on long-distance transmission and associated energy losses.

The aim of this work is to investigate the impact of integrating battery storage systems with renewable energy sources on electrical variables. The selected variables are voltage, current, and power. MATLAB/Simulink was used to create a hybrid electrical system with solar and battery storage. After that, the solar system was exposed to different radiation to study the effect on the system's outputs.

The results demonstrate that the use of BSS in conjunction with RES leads to smoother output grid variables compared to relying solely on RES. It provides more stability at the grid level. Li-ion battery is shown to be fast-acting, thereby offering the possibility of voltage and current regulation. The effect of using a Li-ion battery on the generated voltage, current, and power under the change of radiation is demonstrated.

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Quality of biofertilizer produced in home composting

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The generation of Urban Solid Waste (USW) in Brazil has increased in recent years, and will be approximately 77.1 million tonnes in 2022, according to the Brazilian Association of Public Cleaning and Special Waste Companies (ABRELPE). Organic waste makes up around 43% of USW, which corresponds to a generation of around 35 million tonnes per year. Of this total, only 2% - 700,000 tonnes - is properly reused to produce energy and compost [1].

An environmentally suitable alternative for recycling organic waste is the composting technique, which is considered to be an aerobic biological process for decomposing and stabilising organic matter, producing a fertiliser that can be applied to soil and plants, improving their nutritional conditions. This technique can be carried out in homes through the use of home compost, which are easy to use, take up little space and are carried out by the user themselves. As a result of this practice, the disposal of this material in rubbish bins is avoided, contributing to an increase in the useful life of landfill sites and also producing a quality biofertilizer. Thus, environmental education is an important tool in disseminating knowledge of these sustainable practices that favour the environment, as we are increasingly seeking a better quality of life linked to a quality environment [2][3].

This work was carried out to evaluate the adoption of home composting as a way of reducing USW generation and assessing the quality of the fertilizer they produce. Firstly, the profile of volunteer users who were adept at home composting was identified, and each volunteer was instructed and monitored.

Fourteen volunteers were selected, with different levels of education, from high school to doctorate. All the guidance and monitoring took place over sixty days and a sample of the biofertilizer produced was collected for laboratory analysis of pH and conductivity. The pH ranged from 7.2 to 8.6, where pHs higher than 7.0, which may indicate more advanced composting or the addition of food with more basic acidity levels. Only two samples had higher conductivities, which could be due to a high concentration of salts due to the release of minerals in the decomposition process, while three samples had lower conductivities. Thus, the pH and conductivity results give an indication of the stage of decomposition of the materials in each compost, with one promptly having a pH of over 6.0. In this case, they all had the correct pH, which indicates correct maturation and stabilisation of the organic compost. As for the volunteer's perceptions, there were reports of a reduction in the amount of rubbish taken out of the house, the high quality of the biofertilizer, which was used in the gardens, and praise for the initiative of the work, as there was a great impact on raising awareness about the generation of household waste.

Acknowledgements
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AMB79

Rugulopteryx okamurae's Surprising Potential for Metal Nanoparticles Synthesis

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The brown macroalga Rugulopteryx okamurae *(E.Y. Dawson) I.K. Hwang, W.J. Lee, and H.S. Kim, 2009 (Dictyotales, Ochrophyta) is the first and only species to be included in the list of invasive alien species of notable importance to the European Union, whose negative effects on the environment and biodiversity in Europe are so serious as to require intervention concerted effort of the Member States of the Union. R. okamurae* originates from the northwestern Pacific. Known for its ability to colonize rocky substrates from the subtidal and intertidal zones, it has recently expanded beyond its native range [1], becoming a dominant invasive species with overwhelming competitive capacity and growth through the Strait of Gibraltar, the Atlantic coast of southern and northern Spain, the Canary Islands, and Madeira. Given the unsuccessful and costly eradication efforts, current research is exploring the potential uses of *R. okamurae*. This macroalga contains bioactive compounds with antimicrobial and anti-inflammatory properties, opening possibilities for applications in composting, biogas, bioplastics, biofertilizers, and the pharmaceutical and food industries [2]. Building on these diverse potential uses, we explored a novel application by investigating the ability of *R. okamurae* to synthesize gold (Au@RO) and silver (Ag@RO) nanoparticles.

First, an aqueous extract of *R. okamurae* was obtained and characterized using UV-Vis spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. The reducing power, total phenolic content, and DPPH scavenging activity of the extract were also evaluated. Subsequently, the optimal reaction conditions for the synthesis of Au@RO and Ag@RO nanoparticles were determined. Transmission Electron Microscopy (TEM) analysis confirmed the formation of spherical nanoparticles, with mean diameters of 6.7 ± 1.8 nm for Au@RO and 15.2 ± 4.4 nm for Ag@RO (Figure 1). The nanoparticles were further characterized by measuring their zeta potential (-25.4 ± 2.2 mV for Au@RO and -10.9 ± 0.3 mV for Ag@RO) and by using X-Ray Diffraction (XRD) to analyze their crystal structure. Finally, the antioxidant activity of the samples was analyzed by the assays previously indicated.

These findings suggest that *R. okamurae* has great potential in the field of the green nanotechnology, offering an environmentally friendly approach to the synthesis of nanoparticles with promising antioxidant properties.

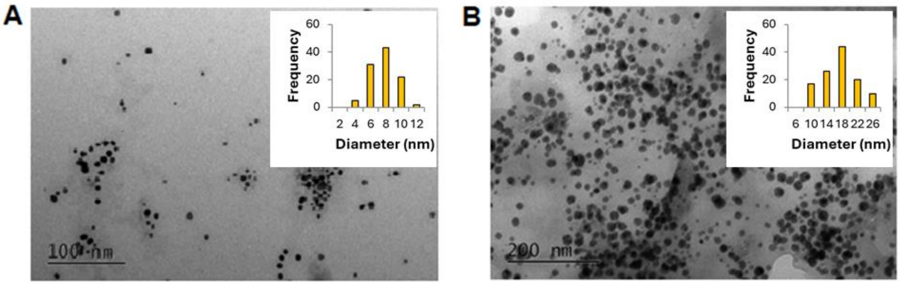

Fig.1. TEM images and size distribution histograms of A) Au@RO and B) Ag@RO

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Ulvan-Functionalized Gold Nanoparticles: Advancing Green Nanotechnology from Algae

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Ulvans are sulfated polysaccharides located in the cell walls of various macroalgae, predominantly in species of the green algae genus *Ulva*, which is native to temperate and tropical regions. Ulvans are attracting considerable attention in the medical and cosmetic industries due to their bioactive properties, as well as their usefulness in aquaculture, agriculture, and water treatment systems. The biological actions of ulvans encompass, among others, immunomodulation, antioxidant, antitumoral and antibacterial activity [1]. Previously, it has been demonstrated that the presence of gold nanoparticles can enhance the pharmaceutical effects of algae extracts [2]. With this aim, this research focused on using an aqueous solution from powdered ulvan derived from hydrothermally extracted *Ulva* spp. at 160ºC (AH160) [3], to produce gold nanoparticles (Au@AH160).

Initially, AH160 were characterized by UV-Vis and FTIR spectroscopy. The antioxidant potential was also determined by assessing their reducing capacity, total phenolic content, and DPPH scavenging activity. Subsequently, various assays were conducted to optimize the reaction conditions for the synthesis of gold nanoparticles, including adjustments to ulvan and gold concentration, temperature, and reaction time. These efforts successfully led to the synthesis of Au@AH160. Transmission Electron Microscopy (TEM) analysis confirmed the formation of spherical nanoparticles with an average diameter of 7.9±1.8 nm. Zeta potential analysis indicated that the nanoparticles were stable, with a value of -15.7±0.8 mV, carrying a negatively charged surface. The crystalline nature of the nanoparticles was further confirmed by High-Resolution TEM (HRTEM) (Fig. 1) and X-ray Diffraction (XRD), which revealed the face-centered cubic structure of gold. FTIR analysis was also performed after the formation of the nanoparticles to identify the functional groups of ulvan that may be involved in the formation and stabilization of the gold nanoparticles. Finally, the antioxidant activity of Au@AH160 was evaluated and compared to that of AH160.

These findings demonstrate the successful synthesis of stable gold nanoparticles using ulvan, highlighting their potential for future applications in nanotechnology and biomedical fields.

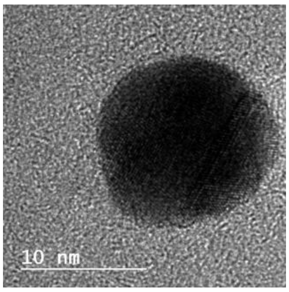

Fig.1. HRTEM image of Au@AH160

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INNOAQUA: Innovative Approaches for an Integrated use of Algae in Sustainable Aquaculture Practices and High-Value Food Applications

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Global food systems are facing significant challenges due to expected population growth, resource depletion, and other environmental constraints. Namely, humans' heavy seafood consumption has been depleting the aquatic ecosystems, which has leveraged the aquaculture practice. However, the intensified near-shore aquaculture gives rise to environmental and resource-related issues, mainly caused by waste streams, dependence on wild fisheries for aquafeed, disease outbreaks, and the potential introduction of invasive species into an environment where these do not belong.

The INNOAQUA project is an R&I plan developed to pave the way towards the upcoming EU in-land aquaculture industry, with a specific focus on the usage of algae. Showing the socio-economic and environmental benefits of the integration of fish and algae cultivation by recovering nutrients, such as N and P, from RAS (Recirculating Aquaculture Systems) sludge to produce a culture medium for algae cultivation without the need for commercial substrates [1].

In this project, the role of INESC TEC is to design and install optical sensors to collect and process data to monitor and optimize the macroalgae production processes. The developed optical sensors are conceived to track the dissolved CO_2 concentration in water, nitrite/nitrate levels, and the multispectral turbidity.

The CO_2 sensor relies on the reaction of a colorimetric membrane that reacts with dissolved CO_2, changing its color, which allows to detect a change in absorption and the concentration of this analyte [2]. The nitrates sensor is based on light absorption by dissolved nitrogen in the UV spectrum range, using LEDs and photodetectors to obtain its concentration through the values of absorbance detected. On the other hand, the turbidimeter uses spectrometer and photodetectors to analyze different color absorption and light scattering. These sensors will be able to communicate with a central computer, transmitting all the information to the production systems.

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Advancing Sustainability with Lithium-Ion Batteries: Economic and Environmental Impacts in Residential Energy Systems

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The European Commission launched several measures to promote sustainability and enhance energy transition [1]. Chemistry contributes to sustainability by developing advanced materials and processes for efficient and long-lasting Energy Storage Systems (ESSs) [2]. Lithium-ion batteries are widely used in many applications, such as Electrical Vehicles (EVs) and energy storage devices in independent systems such as at home [3]. In this context, the role of energy management in the residential sector should be reassessed including controlling the ESSs charging/discharging process to maintain the ESSs lifecycle while reducing the energy cost and CO_2 emissions [4]. This work discusses the benefits of energy management for energy consumers, the environment, and the overall energy system, taking a home profile in Spain and the Spanish electricity tariff scheme as a case study. The discussion includes the economic benefits, CO_2 emissions reduction, the lifecycle of the Lithium-ion battery, and self-energy consumption utilizing ESSs. The discussion underscores the transformative role of using ESSs within energy management in promoting the advancement towards a more sustainable and resilient energy future, emphasizing the significance of behavior changes of energy consumers in achieving sustainability goals. Additionally, it demonstrates the influence of sustainable utilization of ESSs according to the lifecycle and energy losses.

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Perspectivas Futuras y Desafíos en la Transformación Energética Global

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La transición energética hacia fuentes sostenibles es un desafío crítico en el contexto del cambio climático y la creciente demanda de energía. A medida que el mundo se enfrenta a la necesidad de reducir las emisiones de gases de efecto invernadero, se destacan las energías renovables como la clave para una matriz energética más sostenible. Sin embargo, la implementación efectiva de estas tecnologías presenta varios retos, desde la infraestructura hasta la aceptación social [1-5].

Este trabajo explora la situación energética actual, analizando las diferentes causas de tensión en el mercado energético y sus implicaciones globales. Además, se exploran las tendencias globales en materia de producción y consumo de energía, así como el impacto de políticas y tecnologías emergentes.

Finalmente, el estudio plantea perspectivas futuras en la evolución del sector energético, identificando oportunidades para la innovación y el desarrollo. A través de un enfoque multidimensional, se busca contribuir al debate sobre cómo lograr un equilibrio entre el crecimiento económico y la sostenibilidad ambiental.

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The Impact of Battery Size and Depth of Discharge in Battery´s Sustainable Use and Carbon Emission: Energy Management According to Spanish Electricity Tariff

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Clean energy transitions entail large increases in the widespread rollout of Renewable Energy Sources (RES), placing greater demands on power grids. Smart grid technologies can help to manage this transition to make grids more resilient and reliable [1]. Energy Storage Systems (ESS) allow for maintaining grid stability and balancing supply and demand in the presence of RES [2]. They also benefit energy consumers by reducing electricity costs and contribute to environmental sustainability by storing excess RES power for later use, thereby reducing carbon emissions (CO2) [3,4]. However, the inefficient operation of ESS such as batteries related to their installation cost and electricity tariff, improper setting of the Depth of Discharge (DOD), and inappropriate battery size might lead to limit the utilization of the benefits. This work aims to investigate the impact of battery size and DOD and determine the optimal battery parameters considering its lifespan, CO2 emissions, energy savings, and energy cost. A photovoltaic-battery integrated system is considered for two real homes in the northern and south of Spain. A sensitivity analysis is done including several scenarios carried out in summer and winter conditions. MATLAB is used to simulate the proposed system and obtain the results. The results show that battery size and DOD have a significant impact on key factors such as the cost of electricity, system payback period, CO2 emissions, and energy savings in residential energy systems. The findings indicate optimal battery parameters vary depending on weather conditions and energy consumption patterns. This work underscores the significance of precision and decision-making in the field of residential energy systems for maximizing the benefits of battery technology.

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BIOQUÍMICA Y BIOTECNOLOGÍA

Herramientas moleculares para la detección de *Mycobacterium bovis,* genes de resistencia antibiótica y la microbiota de leche y queso de bovinos de la región de Sumapaz, Colombia

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La tuberculosis bovina (TBB), producida por *Mycobacterium bovis*, es una zoonosis de alta prevalencia, que produce riesgos significativos para los animales, los ganaderos y los consumidores, así como pérdidas económicas significativas [1]. Este tipo de enfermedad puede generar altas pérdidas a nivel del sector ganadero, tanto a nivel de la producción cárnica y lechera. La industria láctea es una de las principales actividades económicas de Colombia; sin embargo, las malas prácticas higiénicas provocan la contaminación de los productos, junto con el uso indiscriminado de antibióticos con fines económicos [2, 3].

En este trabajo se evaluo la microbiota asociada a muestras de leche cruda o derivados, obtenidas de pequeños centros de producción ganadera con casos sospechosos de TBB y otros patógenos potenciales, en pequeños centros de producción de la Región Sumapaz (Fusagasuga, Colombia). Inicialmente se estandarizó un protocolo para aisalmiento de ADN total de leche y queso basado en extracción con fenol-cloroformo y columnas de sílice, que produjo ADN con la calidad suficiente para análisis metagenómico. Este ADN se utilizó inicialmente para la amplificación específica de *M. bovis* por PCR, observando ausencia de este patógeno en las muestras procesadas. Estos resultados se confirmaron utilizando una LAMP-PCR (*Loop-mediated isothermal amplification*) diseñada por nuestro grupo de investigación sobre la región de diferencia 12 (RD12) del complejo *M. tuberculosis* [4].

Por otra parte, un analisis metagenómico del ADN total de las muestas procesadas mostró la presencia de otras especies patógenas como *M. tuberculosis*, *A. baumannii, S. aureus, P. putida, E. coli y K. pneumoniae* en abundancias relativas bajas. La anotación funcional reveló 49 ARGs, 33 asociados con resistencia a fármacos y biocidas relacionados con bombas de eflujo de resistencia-nodulación-división (RND). Se destacaron los genes TETA, TETC y TETK asociados con la resistencia a tetraciclina y se encontraron genes CTX y OXA asociados a la producción de betalactamasas y carbapenémicos en todas las muestras con valores medios de cobertura/identidad del 99,9% y 97%, respectivamente. Los resultados obtenidos sugieren problemas en las prácticas higiénicas que afectan la inocuidad de la leche y sus derivados en pequeños centros de producción de la región de Sumapaz, Colombia.

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Efecto de Análogos de Brasinoesteroides (BRs) del tipo 24-norcolanos para la inducción de callo de *Aristotelia chilensis* (Mol.) Stuntz y ultraestructura del callo productor de antocianinas.

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Los reguladores de crecimiento vegetal pueden ser utilizados en biofactorias para la producción de compuestos bioactivos. Por ello, en este estudio, el objetivo es aumentar la inducción de callos y producción de antocianinas en los callos e investigar la ultraestructura de las células en desarrollo de callos de explantes de hoja de *A. chilensis* producto de la elicitación de distintos análogos de BRs [1,2]. Para la generación de callos, se sembraron explantes de hojas esterilizados en medio de cultivo de inducción estándar [3] que contenía diferentes concentraciones (0,01, 0,1 y 1µM) de distintos análogos de BRs de tipo 24-norcolanos y brasinólida comercial (Fig.1).

La mejor inducción y biomasa de callos se obtuvo con explantes de hojas cultivados en un medio que contenía 1 µM de **1** y **4**, obteniendo un 54,5 % mayor en biomasa al control negativo y un 19,5% superior a la brasinólida (**5**), tras 15 días de cultivo. Se observó como resultado un callo de color rosa y morado, se examinó bajo un microscopio de fluorescencia con longitudes de onda de 525-nm verde y 610-nm rojo para observar su fluorescencia. Las ultraestructuras celulares de los callos de morado fueron examinadas con un microscopio electrónico de transmisión (TEM), observándose que las células desarrolladas a partir del callo de color morado tenían una forma elíptica, con vacuolas grandes, con reducido espacio intercelular y las células productoras de antocianina presentan inclusión vacuolar antocianica. Este es el primer estudio respecto del efecto elicitor de este tipo de análogos de BRs, por lo que es extremadamente importante como fuente para futuros estudios, para la producción de antocianinas.

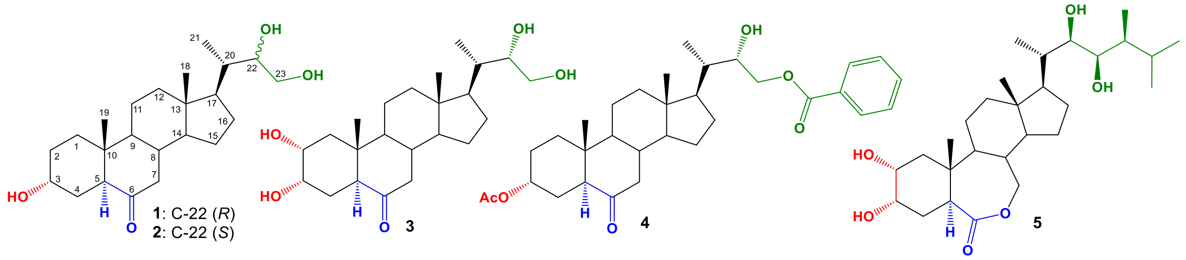

Fig. 1. Estructuras de Análogos de BRs del tipo 24-norcolanos (**1-4**), y Brasinólida comercial (**5**) aplicados al medio de cultivo estándar para la inducción de callos de *A. chilensis.*

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Extracción de xilano β-1,3 a partir de algas marinas

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Las algas marinas son un recurso de gran interés para la industria biotecnológica debido a la presencia de compuestos con propiedades diferentes a las de los vegetales terrestres. Recientemente se ha detectado actividad prebiótica asociada a ciertos polisacáridos y carbohidratos complejos de las algas [1]. El género *Porphyra* sp., ampliamente distribuida en la costa atlántica, contiene en sus paredes celulares xilanos característicos constituidos por unidades de D-xilosa unidas mediante enlaces glicosídicos β-1,3, diferentes a los enlaces β-1,4 de los xilanos de las plantas terrestres. Esto convierte a *Porphyra* sp. en una excelente materia prima para la generación de nuevos xilooligosacáridos (XOS) con propiedades biológicas distintas a las de los XOS β-1,4 de origen terrestre, considerados los prebióticos con mayor actividad biológica [2,3].

Este trabajo se desarrolla dentro de un proyecto de investigación dirigido a la generación enzimática de nuevos XOS a partir de *Porphyra* sp. mediante el empleo de xilanasas específicas para los enlaces β-1,3 (proyecto BLUE-XOS). Puesto que en la actualidad apenas se ha descrito un número muy limitado de estas enzimas, el primer reto que afronta el proyecto es la búsqueda de nuevas xilanasas β-1,3. La estrategia propuesta fue el aislamiento de microorganismos que se desarrollan espontáneamente durante los procesos de deterioro natural del alga *Porphyra* sp. capaces de crecer sobre xilano β-1,3 como única fuente de carbono. Una dificultad añadida a esta estrategia fue que como este xilano no se comercializa, fue necesario extraerlo a partir de algas.

La presencia mayoritaria en *Porphyra* sp. de galactano y manano, con propiedades químicas muy próximas a las del polisacárido de interés, dificulta en gran medida esta tarea, por lo que este trabajo describe las estrategias empleadas para lograr este fin. A partir del trabajo de Lahaye et al. (2003) [4] se ha diseñado un nuevo protocolo de extracción y purificación modificando las condiciones de tres etapas consecutivas de extracción sólido-líquido sobre el alga seca y triturada: T1, NaOH 0,3 M (100ºC, 30 min); T2, H_2SO_4 0,25 M (100ºC, 30 min) y T3, NaOH 2,5 M (4ºC, 1 hora). En los dos primeros tratamientos se recupera el sólido, mientras que en el tercero se recoge el extracto para, a continuación, realizar una precipitación ácida del xilano como alternativa a la precipitación con etanol al 95% para reducir el coste del proceso en caso de escalarlo. A su vez se ha evaluado la influencia del grado de trituración de la muestra, la relación líquido-sólido y el empleo de ultrasonidos como pretratamiento. Como resultado final, el método consigue eliminar la práctica totalidad del galactano y parte del manano, y obtener un xilano parcialmente purificado con presencia de manano en una relación 1:1 respecto al polisacárido de interés.

Para aumentar el rendimiento se ha aplicado el mismo procedimiento a un alga verde de aguas templadas (*Caulerpa lentillifera*) con mayor contenido en xilano β-1,3. En este caso se ha mejorado sensiblemente el proceso aumentando el rendimiento de extracción al 70% y la pureza del xilano al 76% mediante el incremento del tiempo de incubación de la etapa T3 de extracción alcalina a 4ºC de 1 a 2 horas. El proceso completo optimizado ha permitido mejorar los resultados de pureza del xilano extraído de *Caulerpa lentillifera* obtenidos previamente por Liu et al. (2024) [5], y ha permitido disponer de cantidad suficiente de xilano, que ha probado ser adecuado para el crecimiento selectivo de microorganismos aislados a partir de *Porphyra* sp. recolectada en la costa gallega.

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Antimicrobial Activity Evaluation of the Biosurfactant Extract Obtained by Membrane Technology Against Different Pathogenic Bacterial Strains

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Growing concern for the environment has highlighted interest in biosurfactants, natural surface-active compounds produced by microorganisms, that have potential applications for replacing synthetic surfactants in many industrial sectors [1]. Particularly in the food industry, biosurfactants have emerged as a new alternative to control the growth of food pathogens, as their antimicrobial capacity against some bacterial pathogens involved in foodborne diseases has been demonstrated [2]. Therefore, the goal of this work is to evaluate the antimicrobial capacity of the biosurfactant extract obtained from agroindustrial stream, corn steep water (CSW), by membrane tecnology against different pathogenic bacterial strains. CSW was provided by FeedStimulants company (Lot No. CSL-0003-1217), diluted to 50 g/L and centrifuged to remove solids (5000 rpm, 30 min, 4ºC). Then, the liquid phase was subjected to a laboratory dialysis process using 6-8 kDa cellulose dialysis membranes at 4 ºC for 48 hours, following the patent ES 2 931 088 B2 [3]. After the dialysis process, samples were freeze-dried and an aqueous solution at 5% concentration (w/v) was prepared and sterilized by 0.22 μm filtration for the next assay. The antimicrobial activity was determined by using the disk diffusion method, testing the susceptibility of *Staphylococcus aureus*, *Escherichia coli*, *Bacillus cereus*, *Bacillus subtilis*, *Listeria monocytogenes*, *Enterobacter sakazakii*, *Salmonella enterica* and three different strains of *Pseudomonas aeruginosa* towards the biosurfactant extract. A growth from an isolated colony of the bacteria was added to 5 mL of sterile normal saline to obtain a cell density of $1x10^8$ UFC/mL, which usually corresponds to an absorbance value of 0.11-0.13 at 610 nm. After that, the solution was streaked on Tryptone Soy Yeast Extract Agar media (TSYEA) using a sterilized cotton swab, and a disk with the biosurfactant extract solution was added to the plate in triplicate. A positive control of the bacteria growth without sample disk was also performed and finally, plates were incubated at 37 ^{o}C for 24h. Results showed the appearance of a white precipitate around the disk with a small halo of inhibition for *P. aeruginosa* strains and only a precipitation zone was observed around the sample for *S. enterica* and *E. coli*, which could likely be due to the interaction of the biosurfactant extract with the bacteria. Although it cannot be confirmed that there is growth inhibition and it would be advisable to conduct other types of assays to continue investigating this matter, the findings of this preliminary study could indicate the possible potential for using this biosurfactant extract from CSW, obtained by membrane tecnology, to control the growth of pathogens in the food industry.

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Improving Hybrid Carrageenan Gel Properties and Extraction Efficiency from *Mastocarpus stellatus* and *Chondrus crispus* with Subcritical Water

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This study aimed to optimize the extraction of carrageenan from two species of red macroalgae, false Irish moss (*Mastocarpus stellatus* Stackhouse Guiry) and Irish moss (*Chondrus crispus* Stackhouse) using subcritical water extraction (SWE).

A central composite factorial design was applied to evaluate the influence of temperature (90- 160 ºC) and pressure (40-90 bar), keeping extraction time and solid-to-liquid ratio constant, i.e., 30 min and 1:30 g/mL (w/v), on two responses: carrageenan yield (%) and gel capacity. For each species, 13 different SWE conditions were performed. These extracts were then compared to those obtained through conventional extraction performed with water (3h at 80 ºC + 1h at 90 ºC). All extracts were characterized based on their yield, gelling capacity, and gels rheological characteristics

The carrageenan yields from *M. stellatus* ranged from 51% (125 ºC, 65 bar) to 74% (100 ºC, 90 bar); for *C. crispus*, values ranged between 26% (100 ºC, 90 bar) and 68% (140 ºC, 40 bar). Concerning *C. crispus*, gelling capacity in 0.1 M KCl was verified for all extracts except those obtained at 150 ºC, while for *M. stellatus*, gel was only formed with the extract obtained at 90 ºC and 65 bar. Thus, *M. stellatus* is more sensitive to high pressure and high temperature treatments than *C. crispus*. Gels from *C. crispus* are formed at higher temperature and are up to 30 times stronger than gels from *M. stellatus*, but are more brittle, in contrast to the strain hardening of *M. stellatus* gels.

Overall, SWE gives hybrid carrageenan with better gel properties.

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Tratamento hidrotérmico da macroalga invasora *Sargassum muticum* para a produción de oligosacáridos, bioetanol e ácido succínico

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A macroalga marrón *Sargassum muticum* é unha especie invasora orixinaria de Xapón e China, que se propagou por todo o mundo durante o século XIX, principalmente debido á importación da ostra rizada [1]. Na última década, esta especie gañou interese polo seu potencial aproveitamento na produción de diferentes compostos de alto valor engadido, como biofertilizantes [2], [3], cosméticos [4] e biocombustibles [5]. O obxectivo deste traballo é estudar a tecnoloxía de autohidrólise para producir un licor rico en oligosacáridos e compostos antioxidantes, así como unha fracción sólida con alta susceptibilidade enzimática, apta para ser empregada en procesos fermentativos.

Unha vez acondicionada e caracterizada a materia prima, esta someteuse a un tratamento hidrotérmico en réxime non isotérmico a diferentes temperaturas obxectivo (Tmáx = 160, 165, 170, 175 e 180 ºC), cunha relación líquido-sólido (RLS) de 15 g/g. A continuación, determinouse a concentración de oligosacáridos, os compostos fenólicos totais (TPC) e a capacidade antioxidante total (TAC) dos licores recuperados. Á severidade de 2.67 (Tmáx = 170 ºC), extraeuse o máximo de oligosacáridos (8.07 g/100 g de materia prima), sendo maioritaria a presenza de fucooligosacáridos (4.09 g/100 g). Baixo estas condicións, o TPC e o TAC acadaron valores de 14.46 mg GAE/g e 47.35 mg TE/g, respectivamente.

O sólido obtido a Tmáx = 170 ºC sometouse a unha hidrólise enzimática secuencial en catro etapas de 9 h cada unha, nas que se foi recuperando o licor para introducilo no seguinte ensaio. Co licor obtido na última etapa (22.11 g/L de glucosa), leváronse a cabo dous procesos fermentativos independentes que permitiron producir 18.64 g/L de etanol e 12.51 g/L de ácido succínico.

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Antimicrobial Susceptibility Pattern of Fecal Bacteria isolates from Wastewater: Impact of WWTP Effluents

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The global dissemination of antimicrobial resistance has been a current concern, mainly due to the emission of antibiotic-resistant bacteria and antibiotic-resistant genes into the environment. Wastewater Treatment Plant (WWTP) effluents are believed to be one of the point sources of this kind of dissemination [1]. Thus, this study aimed to perform an antimicrobial susceptibility pattern of bacterial isolates identified in wastewater samples from the Fervença River, downstream from the municipal WWTP, in Bragança, Portugal. The ENTEROSYSTEM 18R® system was used to identify Gram-negative bacteria (*Escherichia coli*, *Serratia liquefaciens*, *Klebsiella oxytoca*, *Citrobacter freundii*, *Enterobacter agglomerans*) and selective culture medium to detect *Enterococcus* (ISO 7899–2:2000) [2]. The Kirby-Bauer Disk diffusion method was used to determine the sensitivity or resistance of bacteria to six antibiotics, namely: Sulfamethoxazole (SMX, 100, 50 and 25 µg/disc), Ceftazidime (CAZ; 30 µg/disc), Netilmycin (NET, 30 µg/disc) and Nitrofurantoin (NF, 300 µg/disc). Four bacterial reference strains (ATCC - American type culture collection and NCTC – National collection of type cultures) were used as control (table 1). After the incubation period (37°C for 24 hours), the inhibition zone diameters were measured, interpreted, and categorized as susceptible, intermediate, or resistant according to the EUCAST clinical breakpoint tables [3]. The results can be observed in Table 1. Most bacteria presented resistance to SMX at 25 µg/disc, which may pose risks to the population with contact with the river water.

Table 1. Antimicrobial Susceptibility Testing

Microorganism	SMX 100µg	SMX 50µg	SMX 25µg	CAZ 30µg	NET 30µg	NF 300µg
E. coli	-	-	I	S	S	S
S. liquefaciens	S	S	S	R	S	-
K. oxytoca	-	-	R	S	S	-
C. freundii	-	-	R	S	S	-
E. agglomerans	-	-	R	S	S	-
*Enterococcus*1	R	R	R	-	-	S
Enterococcus 2	R	R	R	R	-	S
E. coli NCTC	-	-	R	I	S	S
S. aureus ATCC	-	-	R	R	-	-
Pseudomonas NCTC	R	R	R	I	S	R
Enterococcus NCTC	R	R	R	-	-	S

S = Susceptible; R = Resistant; I = Intermediate.

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Isolamento e estabelecimento de condições de crescimento *in vitro* do fungo *Terana caerulea* para potencial produção de pigmentos

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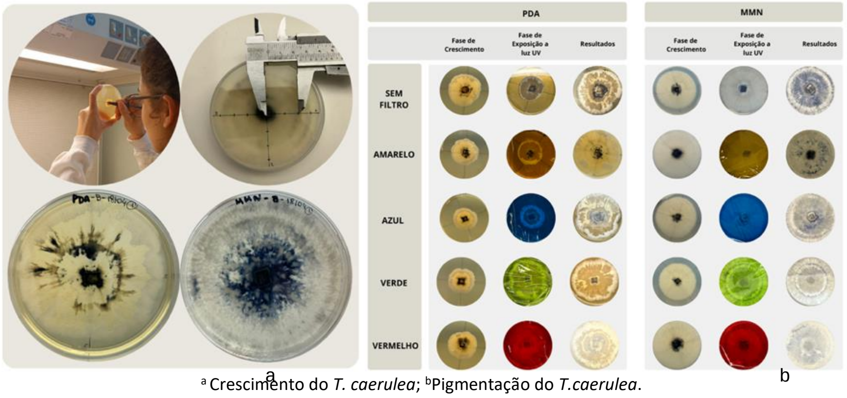
O fungo *Terana caerulea (Lam.) Kuntze* (Phanerochaetaceae) possui uma característica única, a sua capacidade de produção de pigmentos azul-cobalto. Encontra-se principalmente em florestas quentes e húmidas, crescendo na parte inferior de troncos caídos e ramos de árvores[1]. A cor azul característica deve-se a uma mistura de polímeros relacionados com o ácido telefórico[2] e tem vindo a despertar elevado interesse na indústria de corantes naturais. Este trabalho teve como objetivo o isolamento *in vitro* e a avaliação das condições de crescimento de *T. coerulea* para obtenção de pigmentos.

Esta avaliação iniciou-se com a monitorização da taxa de crescimento em dois meios de cultura sólidos Melin & Norkrans modificado (MMN) e o Ágar Batata Dextrose (PDA). Após o crescimento inicial, o fungo foi exposto à luz ultravioleta (UV) para avaliação do seu efeito na produção de pigmentos. Foi realizada uma análise da pigmentação sob diferentes filtros de luz com o objetivo de verificar como diferentes comprimentos de onda afetam o desenvolvimento e intensidade da coloração azul, recorrendo a filtros de luz de coloração amarela, vermelha, azul, verde e sem filtro.

De acordo com os resultados obtidos da pigmentação e da taxa exponencial de crescimento ($\mathbf{r_{médio}}$), foi possível o estabelecimento do *T. caerulea* nos dois meios de cultura, com intensidade de pigmentação e crescimento mais rápido no meio MMN (Figura 1.a, Tabela 1). Foi possível ainda verificar que os testes de pigmentação com filtros de luz mostraram que os fungos cultivados sem filtros de luz apresentaram uma pigmentação mais intensa, seguidos pelos fungos expostos aos filtros de luz azul, verde, vermelho e, por último, amarelo. Assim, a utilização de filtros de luz não se revelou eficaz para a estimulação da produção do pigmento. Estão em curso outras abordagens de cultivo, estabelecimento e estimulação da formação de pigmentos a partir do *T. caerulea*.

Fig.1. Isolamento e estabelecimento de *T. caerulea*



ᵃ Crescimento do *T. caerulea*; ᵇPigmentação do *T.caerulea*.

Tabela 1. Taxa de crescimento exponencial do *T. caerulea*

Meio de Cultivo	$r_{médio}$ (dia^{-1})	Variância
PDA	0,2548	4,02E-04
MMN	0,3163	2,49E-04

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Aislamiento e inoculación de especies de *Trametes versicolor* del Parque Natural de Montesinho

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La especie *Trametes versicolor* es una de las 168 especies de hongos comestibles que se han identificado en el Parque Natural de Montesinho (PNM). Entre estos hongos, algunas especies de macrohongos comestibles son de alto valor comercial por ser ampliamente apreciadas en la cocina tradicional, además de tener un alto potencial nutricional [1]. Además, esta especie en particular es de gran importancia medicinal y, como tal, su incorporación en matrices alimentarias podría contribuir en el desarrollo de alimentos funcionales con características únicas [2]. Sin embargo, su disponibilidad, junto con la de otros productos de montaña, está limitada por la estacionalidad y las condiciones climáticas, un problema intensificado por el cambio climático [3]. Por lo tanto, este estudio propone la producción de especies de *Trametes versicolor* del PNM en un ambiente *ex situ* controlado.

El micelio previamente producido en un ambiente estéril se utilizó para llevar a cabo la producción *ex situ*. Los troncos se procesaron y prepararon para la inoculación, eliminando toda la suciedad externa y perforando una serie de pequeños agujeros en cada tronco en un patrón de diamante para asegurar un rápido crecimiento del hongo en todo el tronco. Luego, cada orificio se rellenó con micelio y se selló con cera de parafina de grado alimenticio para reducir la contaminación por otras especies de hongos. Los troncos inoculados se colocaron en un ambiente adecuado para el desarrollo del micelio y la fructificación de los hongos, donde se mantuvieron las condiciones adecuadas de temperatura y humedad. El crecimiento del micelio en el sustrato se monitoreó para detectar cualquier signo de contaminación a lo largo del período de inoculación y la fructificación se produjo después de 12 meses. El rendimiento de producción fue bastante variable entre los diferentes troncos, oscilando entre 5,88 y 21,57 g de hongos por kg de tronco, lo que se espera dada la variabilidad de la composición del tronco y los diferentes parámetros que afectan el crecimiento del micelio y la fructificación más allá de la temperatura, la humedad relativa y la exposición a la luz. Posteriormente se realizará una amplia caracterización nutricional, química y biológica para garantizar la calidad de las especies producidas y la preservación de sus características originales, comparándolas con análogos silvestres recolectados en el PNM. Este enfoque permitirá la trazabilidad de toda la cadena de producción y aumentará la confianza del consumidor en estos productos.

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In Vitro Cell Models for Assessing Ingestion Exposure in Firefighters: New Insights into Occupational Risk

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Global warming and climate change have increased the frequency and intensity of fires worldwide [1]. Firefighters, key responders to wildfires, are at significant risk due to their exposure to carcinogenic compounds during firefighting activities [2]. Studies have shown that firefighting is linked to cancers such as mesothelioma and bladder cancer, emphasizing the need for biomonitoring this high-risk population [2]. This typically focused on blood and urine to assess occupational exposure to hazardous chemicals [3, 4], however, saliva represents a promising alternative [3]. Several technological advances have been made in terms of in vitro toxicity assessments to better understand the cellular impacts of exposure to firefighting, focusing mainly on respiratory models, leaving ingestion routes underexplored [5]. Therefore, this study aims to investigate the cellular effects of exposure during firefighting activities through ingestion route by exploring the links between the saliva content and firefighting activities. Saliva from 41 firefighters, professional and sappers, smokers and non-smokers, from different corporations located in Oporto district were voluntarily collected and used to quantify 18 polycyclic aromatic hydrocarbons (PAHs) and 16 metals and assess the in vitro toxicity of saliva on buccal (TR146 and HSC-3) and intestinal (Caco-2 and HT29-MTX) models. To the best of our knowledge, this is the first study that evaluated the in vitro toxicity of firefighters' saliva during real-life and controlled fires. Median total PAH levels ranged from 1.948 to 3.613 µg/L, with naphthalene and anthracene being prevalent, especially in those involved in forest and industrial fires. The concentrations of metals and metalloids ranged from 23.61 to 90.95 µg/L, with the highest levels seen in those engaged in active firefighting. Zinc, copper, strontium, selenium, and manganese were the most abundant elements, while cadmium, antimony, thallium, cobalt, and lead were less common. Industrial fire exposure significantly raised the metal levels, particularly lead, barium, antimony, and mercury, showing how although firefighters use protective gear, contamination remains a risk. In vitro testing on buccal and intestinal cell lines revealed no major cytotoxic effects (above 70%). Further testing using advanced in vitro buccal and intestinal 3D models confirmed that the saliva had minimal impact on the barrier integrity and cell viability after 4-hours exposure. Overall, the study highlights the variability of chemical exposure across firefighting scenarios and underscores the need for continued investigation into occupational hazards for firefighters.

Agradecimientos

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Impact of Subcritical Water Extraction on the polysaccharide characteristics of hybrid carrageenans from *Mastocarpus stellatus* and *Chondrus crispus*

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This study focused on optimizing the extraction of carrageenan from two species of red macroalgae, false Irish moss (*Mastocarpus stellatus* (Stackhouse) Guiry) and Irish moss (*Chondrus crispus* Stackhouse), using subcritical water extraction (SWE). A central composite factorial design was used to assess the impact of temperature (90-160 ºC) and pressure (40-90 bar) on carrageenan yield (%) and gelling capacity. The extraction time and solid-to-liquid ratio were kept constant at 30 minutes and 1:30 g/mL (w/v), respectively. Thirteen different SWE conditions were tested for each macroalgae species. The resulting extracts were compared to those obtained through conventional extraction, which involved treatment with water for 3 hours at 80 ºC followed by 1 hour at 90 ºC. All hybrid carrageenan extracts were analyzed for molecular mass distribution, chemical composition, and gelling capacity in 0.1 M KCl.

Carrageenan yields from *M. stellatus* varied between 51% (at 125 ºC/65 bar) and 74% (at 100 ºC/90 bar), while for *C. crispus*, yields ranged from 26% (at 100 ºC/90 bar) to 68% (at 140 ºC/40 bar). SWE had different impact on the characteristics of hybrid carrageenans isolated from *C. crispus* or *M. stellatus*. For the latter, both high pressure and temperature are detrimental to the content in iota-carrageenan in the hybrid, or even to the extraction of carrageenan. As a result, less *M. stellatus* extracts could actually gel in the presence of KCl.

Overall, high temperature is a more limiting parameter than pressure as it directly leads to the extraction of shorter carrageenans. Smaller chain, of the order of 100 kDa were achieved at highest temperatures, whereas both seaweeds gave hybrid carrageenans of the order of 700 to 500 kDa. In general, extraction parameters did not notably impact the distribution of molecular masses, and *C. crispus* is more resistant to SWE.

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STUDY OF THE COSMECEUTICAL PROPERTIES OF THE PLANT ANACYCLUS MONANTHOS SUBSP. MONANTHOS

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Abstract

Anacyclus monanthos subsp*. monanthos*is a plant species endemic to North Africa (specifically Algeria, Tunisia, and Morocco), highly valued in traditional medicine. Recently, it has raised significant interest regarding its potential cosmetic applications. The current study aims at explaining the biological and cosmeceutical functions of the plant, together with the mechanisms that contribute to its efficacy for the improvement of skin health and aesthetic appeal. Employing a multidisciplinary methodology, involving cosmeceutical analysis, *in vitro* and *in vivo* investigations, this research examines the cosmetic features of the plant, its phytochemical constituents, categorization into the cosmeceutical framework, and prospective advantages in skin care formulations.

The extraction of the essential oils yielded 0.4%, and its chemical constituents were identified using Gas chromatography showing 69.9% of the total volatile compounds such as Fragranyl 2-methyl butyrate (32.9%), cis-Chrysanthenyl acetate (24.6%) and trans- chrysanthenyl acetate (9.8%). The quantification of total phenolic and flavonoid content gave values of 27.47 ± 0.58 mg GAE/g for the total phenolic compounds and 8.40 ± 0.021 mg QE/g for flavonoids, which reflects very remarkable antioxidant activities. On the analysis of the fat content, a percentage of 0.081 ± 0.024 % was obtained, and the fatty acid profile showed major components to be Methyl butyrate 69.30% and Methyl palmitate 7.12%. Protein content determination indicated 13.69%, which adds weight to the nutritional value of this plant. Assays of minerals, including boron determinations, showed concentrations of 77.5 mg/L of boron, indicating the richness of minerals within the plant.

Bioactivity assays, which investigated the plant's potential advantages, gave notable antioxidant properties through the DPPH radical scavenging activity assay with an IC50 value of 0.57 ± 0.01 mg/mL. The reducing power assay further confirmed this result by showing considerable electron donation capabilities of 0.55 ± 0.076 mg/mL. Toxicity testing was carried out using the brine shrimp test and recorded LC50 value of 0.016 mg/mL for the essential oil and 0.038 mg/mL for the hydroalcoholic extract, thus confirming the satisfactory bioactive profile of the plant. The SPF of the plant was measured at an SPF value of 22.42 ± 1.42, hence making it suitable for use as an ingredient in sunscreen preparation.

A cosmetic cream was developed utilizing hydroalcoholic extracts and essential oil as preservatives, and the camel fat as emollient, which underwent a series of stability assessments. The texture of the cream exhibited a smooth and consistent quality, maintaining a pH of 5.16. Density evaluations indicated uniformity, and the light stability assessment revealed no considerable alterations when subjected to intense light exposure. Viscosity tests showed a very constant value, which assured the cream would be easy to spread and apply. Spectrophotometric analysis proved that the product contained compounds which absorbed UV radiation, thus supporting its viability as a sunscreen. Accelerated stability tests demonstrated that the cream was resistant to higher temperatures and humidity. Moreover, the HET-CAM ocular irritancy test indicated low irritation, proving the safety of the cream. This work, through thorough phytochemical investigation and empirical studies, positions *Anacyclus monanthos* subsp*. monanthos* as one of the important ingredients in cosmeceutical fields with much underlining of the bioactive compounds, thus enriching the accumulating database on plant-based cosmeceuticals and thereby paving the way for sprouting new skin care formulations inspired by natural materials. Notably, this study is the first to provide such comprehensive information about this plant, whereas previous studies have been limited. The applications outlined from such deep analysis of the plant to cosmetics, nutrition, and bioactive compounds were seen to have a strong foundational background for further research and development studies.

Keywords: *Cosmetic formulations, Biological activities, chemical analysis, Antioxidant properties, Stability tests, Sun protection factor (SPF), Camel fat*

CATÁLISIS Y FOTOCATÁLISIS

Surface response methodology to optimise orange peel biochar synthesis for water splitting applications

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Food waste continues to increase along with global population growth and human activity [1]. Consequently, tons on waste get accumulated, contributing to the climate change due to the need to eliminate these residues [1]. To reduce them, biomass-based catalysts have been proposed for hydrogen obtention as a greener method to obtain energy by water splitting reaction [2].

These biomass-based catalysts are obtained by the pyrolysis of the organic material. This process involves different factors that can affect the physicochemical properties of the synthesized product, known as biochar. To optimize the process, some authors have studied one factor at a time while others have proposed the use of Response Surface Methodology (RSM) as a solution, studying multiples variables, their interactions and responses by statistical methods [3] .

In our study, orange peel biochar obtained by pyrolysis have been studied by RSM to optimise synthesis conditions, considering treatment time (30-720 min) and the reaction temperature (300-900 ºC) which was reached at 10ºC/min. Our results showed that the optimal surface response has been achieved at the highest temperature with the lowest treatment time (900ºC during 30 min) (Fig.1). Under these conditions, only 374.8 mV have been needed for attaining 10 mA/cm^2 demonstrating a promising catalytic activity which could be further optimized in order to compete with benchmark catalyst. This study highlights the importance of biochar synthesis optimization for further catalytic applications.

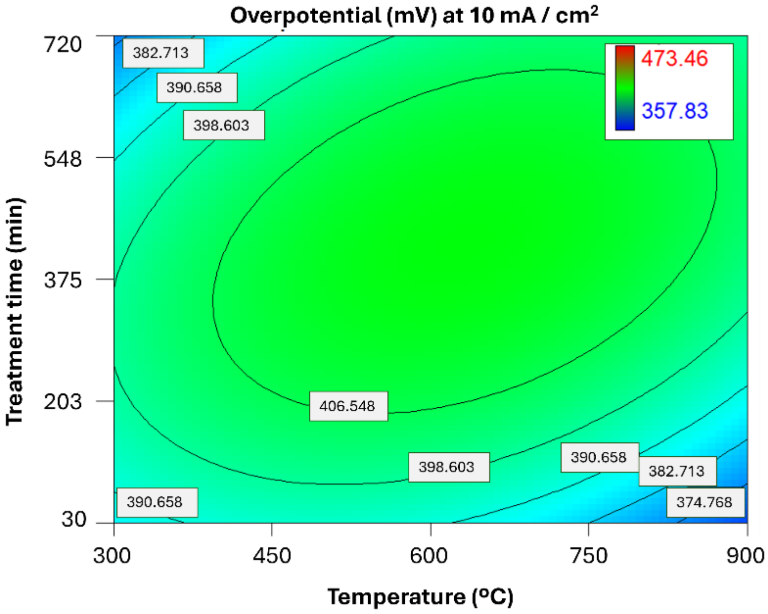

Fig.1. Contour surface response of orange peel biochar synthesis.

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Nitruros de carbono grafíticos modificados como fotocatalizadores verdes para la eliminación de contaminantes emergentes

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La presencia de contaminantes emergentes (CEs), como derivados farmacéuticos y pesticidas, en las masas de agua representa una amenaza considerable para el medio ambiente y la salud pública. Las plantas de tratamiento de aguas actuales (EDARs, ETAPs) no son completamente efectivas en la eliminación de este tipo de compuestos, lo que hace necesario desarrollar nuevas alternativas de tratamiento.[1] De entre esos nuevos procesos, los procesos de oxidación avanzada (POA) y más específicamente los procesos fotocatalíticos representan una opción con un elevado potencial. Este proceso se basa en la fotoactivación de un catalizador con radiación lumínica a longitudes de onda específicas, generando diversas especies reactivas oxidantes (ROS), o radicales, que poseen una alta capacidad para degradar una amplia variedad de compuestos orgánicos. La capacidad de generación de dichos radicales viene influenciada profundamente por el fotocatalizador empleado. Habitualmente se emplean compuestos basados en óxidos metálicos, como el óxido de titanio (TiO_2), pero estos catalizadores convencionales presentan limitaciones como baja absorción el espectro visible, rápida recombinación de cargas, liberación del metal etc. Por ello, el desarrollo de nuevos fotocatalizadores, más sostenibles en su preparación y libres de metales, se ha convertido en una necesidad.[2]

Este trabajo se centra en el diseño y optimización de fotocatalizadores libres de metales basados en nitruros de carbono grafíticos (gCN) como una solución sostenible para la eliminación de estos contaminantes. Para ello se realizó a la síntesis de diversos fotocatalizadores basados en gCN los cuales han sido modificados tanto superficial como funcionalmente. Dichos fotocatalizadores fueron caracterizados, seleccionando aquellos con un mayor potencial para su uso en procesos fotocatalíticos. Una vez confirmado este potencial, se ha evaluado el desempeño del catalizador en la degradación de un contaminante como la rodamina B (RhB), utilizando diversos tipos de radiación en el rango del ultravioleta y visible (365 - 417 nm). Durante dichas pruebas alcanzó la completa eliminación del tinte en menos de 25 minutos bajo luz visible. Para el fotocatalizador que presenta mejor desempeño se procedió a estudiar el efecto de variables como la intensidad de la radiación o concentración del catalizador. Como resultado se obtuvo que, presenta un rendimiento mejor que los fotocatalizadores convencionales bajo luz ultravioleta, como con fotocatalizadores basados en el gCN bajo luz visible, lo que hace que el proceso de degradación fotocatalítica sea más sostenible, barato y escalable. Posteriormente se procedió a identificar las distintas especies oxidantes que participaban en el proceso de degradación y su aplicación a la degradación de un compuesto modelo de medicamento, y pesticida.

Los resultados de este estudio prometen proporcionar una alternativa de fotocatalizadores avanzada y sostenible para la degradación de contaminantes emergentes, mejorando la eficiencia de los procesos fotocatalíticos actuales y contribuyendo al desarrollo de tecnologías limpias de descontaminación de aguas.

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Synthesis of Zn and Fe nanocomposites obtained by pyrolysis of ternary deep eutectic solvents for catalytic water treatment applications

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Recently, growing environmental concerns have increased the demand for sustainable and clean technologies. Researchers worldwide are actively working to create greener methods for catalysts synthesis. Their efforts focus on minimizing the use of hazardous solvents during synthesis and purification, avoiding toxic substances, reducing energy consumption and promoting synthesis under ambient conditions. In this context, Deep Eutectic Solvents (DES) stand out. DES are liquid systems formed by the interaction of two or more components, usually a hydrogen bond donor and a hydrogen bond acceptor, in specific molar ratios to form a eutectic mixture with unique solvent properties. DES represent a new class of low-cost, environmentally friendly solvents with great potential to replace traditional catalysts and solvents. A key advantage of DES is their compatibility with numerous metal salts, enhancing the incorporation of metal salts into the final product [1]. For this reason, DES have recently gained attention in the synthesis of catalytic materials, especially in combination with Advanced Oxidation Processes (AOPs) for water treatment, offering a sustainable alternative to conventional methods.

This research focuses on the synthesis of Zn and Fe nanocomposites obtained by pyrolysis of DES and evaluating their application as a catalyst for treating dyes and drugs contaminated water. The synthesis was performed in two stages (Fig. 1): first, the DES was prepared from a mixture of melamine, urea and $ZnCl_2$ or $FeCl_3$ followed by calcination to obtain Zn or Fe nanocomposites respectively. Catalyst yield and reusability were evaluated by the degradation of Rhodamine B by photocatalysis and electro-Fenton tests. The obtained results demonstrated that Zn nanocomposites achieved complete dye degradation within approximately one hour in both processes. In the case of Fe nanocomposites, they exhibited good catalytic performance in the electro-Fenton process, achieving total dye removal in less than 45 minutes. Moreover, both materials presented remarkable reusability.

To further this research, immobilizing the nanocomposites using different techniques was proposed, with the subsequent testing of efficacy of the retained material in the elimination of different drugs.

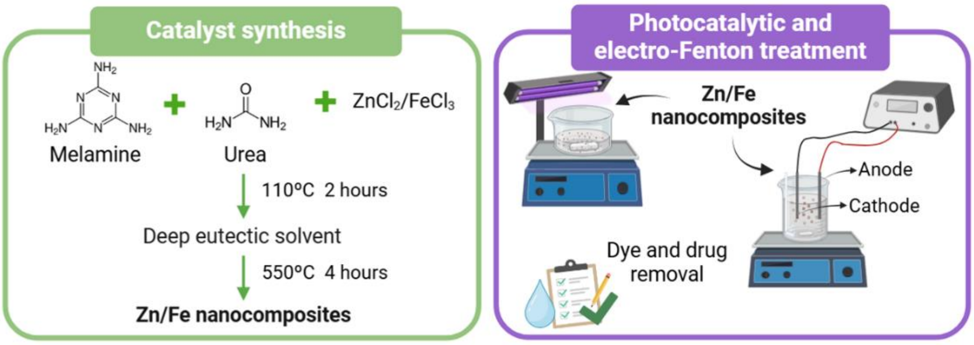

Fig.1. Graphic summary illustrating the synthesis pathway and experimental procedures

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Copper effect in catalytic performance of transition metal-doped ferrites involved in the synthesis of tacrine derivatives

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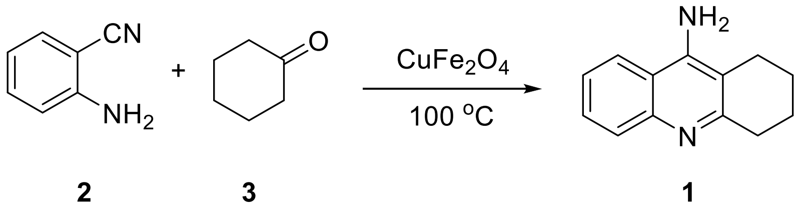
Ferrites are useful materials for a great variety of applications mainly due to their stability, excellent magnetic, electric and optical properties. This class of inorganic solids have been applied in batteries, sensors, solar cells, but also in biomedical fields, among others.

Recently, there is a growing interest on using ferrites as catalysts. In this context, transition metal-doped ferrites (TM-doped ferrites) have been reported as catalysts of different organic reactions including alkylation, dehydrogenation, oxidation, C–C coupling, but also multicomponent reactions [1, 2].

We report herein for the first time the catalytic performance of TM-doped ferrites (where TM is Cu, Zn or both) in the synthesis of tacrine **1**, a reversible inhibitor of acetylcholinesterase (AChE) for symptomatic Alzheimer treatment (Scheme 1).



Scheme 1. Synthesis of tacrine, **1** from 2-aminobenzonitrile **2** and cyclohexanone **3**, catalyzed by $CuFe_2O_4$, at 100 °C, under solvent-free conditions.

The investigated TM-doped ferrites resulted active in the reaction reaching conversions from 40 to 71% after 4h of reaction time. Cu-doped ferrites, $CuFe_2O_4$ or $CuZnFe_2O_4$, were found to be totally selective to tacrine **1,** whereas magnetite or Zn-doped ferrite, Fe_3O_4 or $ZnFe_2O_4$, selectively afforded the corresponding intermediate compound, consisting of an imine derivative as result of the condensation between **2** and **3**. Interestingly, when using Zn-doped ferrites, an acceleration of the reaction towards the formation of imine intermediate was observed. Cu-doped ferrite was recycled during at least two cycles without any activity loss, obtaining **1** in 57% of conversion in the third run. The scope of the reaction was checked by using substituted-2-aminobenzonitriles affording the corresponding tacrine derivatives with similar conversions. On the other hand, we also check the catalytic performance of a series of reduced graphene oxide (rGO) or Fe or Cu-doped rGO and others Zn-supported carbons selectively leading to the imine intermediate compound.

In summary, the obtained results indicate that the observed reactivity is a consequence of the inherent structure of Cu/Zn-doped ferrites. In accordance with the literature, the presence of TM doping ferrites modifies the electrophilicity of these compounds, which can act as Lewis acids; the presence of Zn strongly favors the condensation between reagents, while Cu is responsible of the final cyclisation to **1**.

Acknowledgements
This work was supported by Projects ref. PID2021-126579OB-C31 and PID2021-126579OB-C32 from MCIN/AEI/10.13039/501100011033.

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Nitrogen catalytic sites on carbon surface able to promote the Friedländer reaction: DFT calculations

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One of our main research lines is the development of new carbon-based catalysts for the Friedländer reaction, aimed at synthesizing quinolines using modified carbon materials with acidic or basic properties [1]. Currently, we are investigating the catalytic performance of *N*-doped carbons in the synthesis of poly-substituted quinolines, from 2-aminoaryl aldehydes and ethyl acetoacetate. To understand the role of *N*-containing catalytic sites on the carbon surface that contribute to the catalytic performance, we carried out a computational study by DFT calculations (RB3LYP 6-31+G(d,p)), selecting the most reduced models simulating the *N*-functional groups which can work by catalyzing the rate-limiting step of the process, i.e., the aldol condensation between reagents.

Based on the surface composition determined by XPS, the investigated *N*-doped carbons exhibit different nitrogenated species such as pyridine (N6), pyrrolic (N5), pyridones (N-pyridone) and quaternary nitrogen (QN) functional groups. We can establish the following reactivity order in terms of DG obtained for the corresponding optimized transitions structures (TS): N-pyridone > QN ≈ N6 > N5. In this context, the combination of experimental and theoretical results seems to indicate that the most efficient catalytic sites are composed by N-pyridone functions although the participation of N6 or QN cannot be neglected. However, the highest DG computed for TS involving N5 function strongly suggests that this N-containing function does not participate catalyzing the first step of the reaction. Note the differences in the interactions between reagents and catalytic sites for the investigated reduced models (Fig. 1). Although the $TS_{N\text{-pyridone}}$ is less advanced, the C-C bond formation is synchronized with the H-migrations (Fig.1a), whereas in the case of TS_{N6} firstly the acidic proton abstraction occurs, followed by C-C bond formation and proton transfer (Fig.1b). Finally, in the presence of QN functions, the interaction mode is totally different; the -NH_2 group of the substituted benzaldehyde interacts with adjacent carbons to quaternary nitrogen while C-C bond and proton transfer between reagents take place.

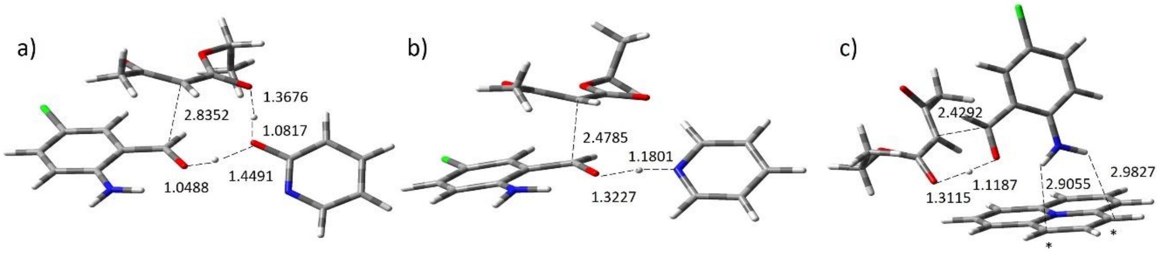

Fig.1. Optimized TS in the presence of a) N-pyridone, b) N6 and c) QN models. Relevant distances are expressed in Å.

Acknowledgements
This work has been supported by Projects ref. PID2021-126579OB-C31 and PID2021-126579OB-C32 from MCIN/AEI/10.13039/501100011033.

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Stable and cost-effective catalysts for the degradation of dyes in water

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Rhodamine B (RhB) is a water-soluble fluorescent dye belonging to the xanthene class, which is used widely in the printing, textile, and photographic industries and as a water tracer fluorescent [1]. Under anaerobic conditions, Rhodamine B undergoes natural reductive degradation, potentially generating carcinogenic aromatic amines. To mitigate the environmental impact of RhB, advanced oxidation processes (AOPs) have been proposed as an alternative to conventional biological wastewater treatments, which are not effective at removing the dye [2]. A variety of semiconductor photocatalysts have been used for this purpose, such as TiO_2, ZnO, CeO_2, WO_3, or SnO_2 as well as graphite carbon nitride (g-C_3N_4) based materials [1]: non-metal doped (P, S, B and O), halogens (F, Cl, Br, and I) or semiconductor heterojunction modification with $BiVO_4$, Ag_2CO_3, WO_3, Bi_2WO_6, Ag_3PO_4, and Fe_2O_3, among others. However, their cost and the luminous energy consumption are usually relatively high. In that point of view, the Fenton-like oxidation processes are more promising especially under visible light irradiation where the dye absorbs the light and becomes excited. The subsequent electron transfer from the excited dye molecules to the active species would enhance Fenton-like chain reactions.

In this work, the cost-effective, three-component composites were prepared and tested as photoFenton -like catalysts for the removal of RhB. The fly ash from coal combustion (CFA) after beneficiation by sieving and magnetic separation leading to silica rich fraction (Si-CFA) was used as support for the active sites. The composites contain (Si-CFA (support), biopolymer (chitosan, CS) linker and Mn_3O_4, Fe_3O_4 or $MnFe_2O_4$ (active center), were prepared using environmentally friendly approach. The composites, pristine semiconductor NPs (Mn_3O_4, Fe_3O_4 or $MnFe_2O_4$) as well as Si-CFA fraction were characterized by: SEM-EDS, XRD, XRF, Raman and FTIR. The results confirmed the presence of all components in the fabricated materials. The materials were tested as photocatalysts for oxidative degradation of RhB in water, under simulated solar light irradiation. The adsorption tests (in the dark) were also performed. The materials show similar activity in RhB removal (RhB removal 95% during 180 min).

Funding

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Removal of a micropollutant model using novel three-electrode cells with advanced oxidation treatments

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In this work, the degradation of carbamazepine (CBZ, a widely used anticonvulsant pharmaceutical) has been investigated as a model micropollutant through three-dimensional electrochemical advanced oxidation processes (EAOPs). The creation of a third (particulate) electrode that also acts as a catalyst was carried out from a combination of components, among which carbon black and perovskite stand out. Once the particulate electrode was obtained, its catalytic power was verified, as well as the improvement in the degradation of CBZ compared to the traditional two-dimensional configuration of anode and cathode.

From this atypical and novel three-dimensional configuration, different improvements were made. Initially, the most notable change was the study of different electrochemical reactors, with different formats and geometric shapes, such as the spherical shape with the third electrode between anode and cathode (Fig. 1). In addition, the operational arrangement of the third electrode-catalyst in the electrochemical cell was a key parameter, playing with its position and with the mass/volume ratio necessary to accelerate the process (an excess of particles caused the opposite effect). Afterwards, other parameters, no less important, were optimized, namely the aeration and the intensity applied in the cell. Taking advantage of the perovskite present in the composition of the third electrode-catalyst, light was added as a possible alternative for the generation of hydroxyl radicals (applying photo-Fenton, within the AOPs) for the removal of the model pollutant. Finally, the combination of light and electricity brought the best CBZ elimination rate, close to 100%, considerably reducing the test time, if compared with the first essays carried out with this novel electrode-catalyst material.

For all the above, this study brings together all the conditions for it to be extrapolated to larger scales. In this way, it could become one of the treatments (tertiary or quaternary) to treat wastewater contaminated with micropollutants such as pharmaceuticals, to comply with European legislations that are increasingly closer to becoming a reality.

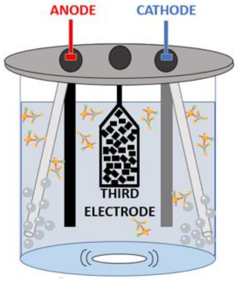

Fig.1. CBZ degradation in a spherical electrochemical cell with the novel third electrode-catalyst material suspended equidistant from the anode and cathode.

Acknowledgments
This work was supported by projects REQUIMTE/LAQV—UIDB/50006/2020, UIDP/50006/2020, LA/P/0008/2020 and EXPL/BII-BIO/0436/2021 and financed by FCT/Ministério da Ciência, Tecnologia e Ensino Superior (MCTES) through national funds. This work was also supported through the Biodiversa & Water JPI joint call for research proposals under the BiodivRestore ERA-Net COFUND program, BiodivRestore-406DivRestore/0002/2020, and cofunding by FCT, Portugal and Project PCI2022-132941 cofunding by MCIN/AEI/10.13039/501100011033. A. Puga acknowledges FCT for his grant (2021.08888.BD) and V. Poza-Nogueiras also acknowledges Xunta de Galicia (Consellería de Cultura, Educación y Universidad) for the postdoctoral fellowship financial support (ED481B-2022-077).

Eco-Friendly Catalysts Derived from Biowaste for Efficient Hydrogen Production

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The urgent global shift towards renewable energy sources, driven by the combined pressures of population growth and fossil fuel depletion, emphasises the critical need for efficient and sustainable alternatives. This fact drives the current research efforts focused on water splitting processes, a technology currently limited by the cost and environmental impact of conventional metallic catalysts like Pt/C and IrO_2 [1].

The present study explores the conversion of lignocellulosic biomass, an underutilized resource, into low-cost catalysts for water splitting. The obtained materials, referred to as chars, were characterized in detail to assess their electrochemical and physico-chemical properties. Thermal treatments such as pyrolysis (synthesizing biochar:BC at 400 ºC or 800 ºC) and hydrothermal processes (obtaining hydrochar:HC), are being used to develop biomass-derived chars as viable and environmentally friendly catalyst alternatives. Initial screenings after the thermal treatment of chestnut and potato peels (CP and PP, respectively/, spinach stem (SS), rice bran (RB) or banana peels (BP) are shown in Figure 1. Some materials, particularly potato peel-derived HC (PP-HC), exhibited catalytic efficiencies comparable to traditional catalysts, requiring low overpotentials (352, 409 and 431 mV for 10, 50 and 100 mA/cm^2, respectively) and higher electron transfer rates (low Tafel slopes). This performance was even improved (340, 400 and 410 mV required for 10, 50 and 100 mA/cm^2, respectively) when applying selective laser oxidation (LO) with 10 pulses of 193 nm wavelength with 371 mJ/cm^2 radiant exposure, resulting in Ox-PP-HC. The physico-chemical properties of these materials are explained by their catalytic behaviour based on the high content of nitrogen and oxygen groups (the latter increased by LO), its acid point of zero charge and their enhanced content of electroactive sites (increased by LO), as measured by Electrochemical Active Surface Area (ECSA) analysis.

This novel Ox-PP-HC catalyst also demonstrated high stability, with less than a 1.5% decrease in performance during both Accelerated Durability Tests (ADT) and chronopotentiometry studies, where 10, 50 and 100 mA/cm^2 were kept for 30 h each. This innovative approach not only contributes to the promotion of renewable energy, but also offers a solution for the disposal of biomass waste and its management, highlighting the potential for producing sustainable, cost-effective, and high-performance catalysts in the field of water splitting.

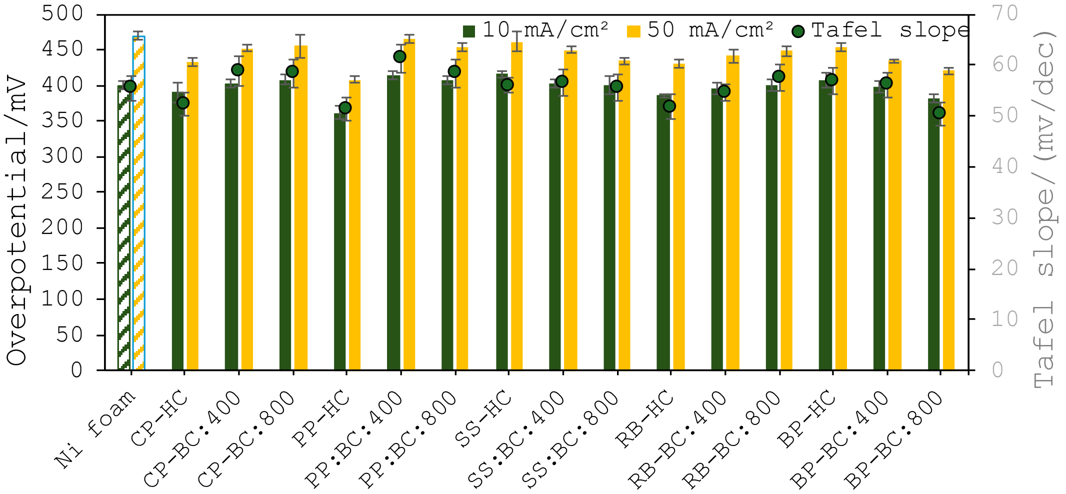

Figure 1. Comparison of the overpotential required for 10 and 50 mA/cm², as well as the Tafel slope values for the synthesized chars.

Acknowledgements

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g-C_3N_4-TiO_2-SiO_2 nanocomposites for producing multifunctional buildings with hydrophobic, self-cleaning and depolluting properties

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Nanotechnology research has enabled the development of innovative solutions for preparing advanced functional building materials. An example is the integration of photocatalytic nanoparticles into building materials, which allows to obtain buildings with self-cleaning, depolluting and self-sterilizing properties [1] that help maintain the aesthetical features of the buildings and can promote the citizen health by cleaning the polluted air. There is also great interest in protecting buildings by developing hydrophobic materials since the most common decay processes of buildings are directly related to the presence of water [2]. For this reason, there is a focus on developing multifunctional construction materials that combine several effects to create buildings with high-added value and outstanding durability.

In this work, a g-C_3N_4-TiO_2 hybrid photocatalyst has been synthesized to boost visible light activity and solve the main problem of TiO_2 for outdoor applications: its exclusive absorption in the UV range. The g-C_3N_4-TiO_2 photocatalyst has been integrated into an alkoxysilane/alkylalkoxysilane sol that was applied by brush on cement mortar samples where the sol spontaneously reacts, producing an organically modified silica (ormosil) that act as the binder of the photocatalyst and provide hydrophobic properties to the substrate.

The characterization of treated surfaces revealed the formation of a well-adhered homogeneous coating containing the partially exposed photocatalyst, producing a visible light photoactive surface that increases the degradation of methylene blue stains by 50% compared to the equivalent TiO_2 coating. The photoinduced superhydrophilicity effect of TiO_2 causes the samples to present water contact angles of less than 10 after UV-Vis irradiation, while the interior of the substrate is hydrophobic, reducing the capillary water absorption by more than 97%. This combination of wetting properties gives the material a tremendous self-cleaning capacity, allowing it to remove various types of stains with simple water action. Finally, it was confirmed that the photoactivity of the sample also generates a decontaminating effect, which was evaluated through NO photoelimination tests under UV-Vis radiation.

These preliminary results are promising because the treatment obtained can be easily applied to buildings *in-situ* to obtain multifunctional buildings with solar activity while protecting against water damage.

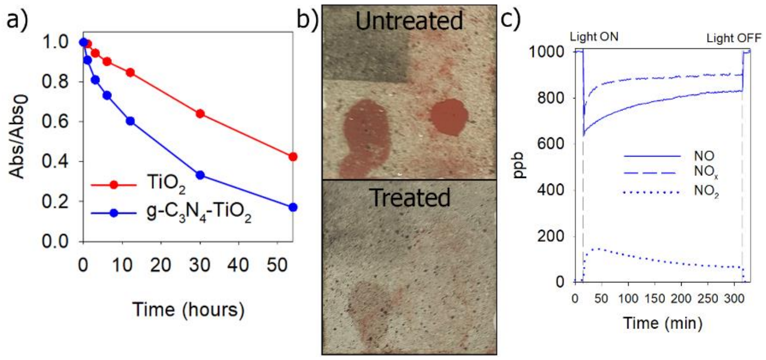

Fig.1. a) Methylene blue degradation, b) Self-cleaning effect and c) NO photoabatement.

Acknowledgements
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Immobilised $Cs_3Bi_2Br_9$ Perovskites for Photocatalytic Imines Synthesis

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Conventional imine synthesis processes involve dehydrating agents and homogeneous catalysts to promote the condensation of amines with aldehydes. This process frequently produces by-products and requires high temperatures and pure oxygen. Heterogeneous photocatalysis has demonstrated great promise in imine synthesis, though controlling selectivity remains challenging. Therefore, creating efficient photocatalysts and carefully managing reaction conditions are essential for practical applications. Bismuth-based perovskites have emerged as promising photocatalysts due to their narrow bandgap and high surface area. Combining continuous operation with immobilised photocatalysts improves productivity, reduces resource consumption, and enables seamless scale-up to industrial levels.

In this work, caesium bismuth bromide perovskites ($Cs_3Bi_2Br_9$, CBB) were synthesised by a one-step solution process and employed to produce N-benzylidenebenzylamine (BZI) under visible light radiation at room temperature. Immobilising CBB in a 3D-PET structure enables efficient BZI production without a final catalyst separation step. The photocatalytic evaluation demonstrated that supported CBB allowed the complete conversion of benzylamine (BZA) and benzyl alcohol (BA) after 1 h, yielding 70 % of BZI in a basic medium operating in batch mode.

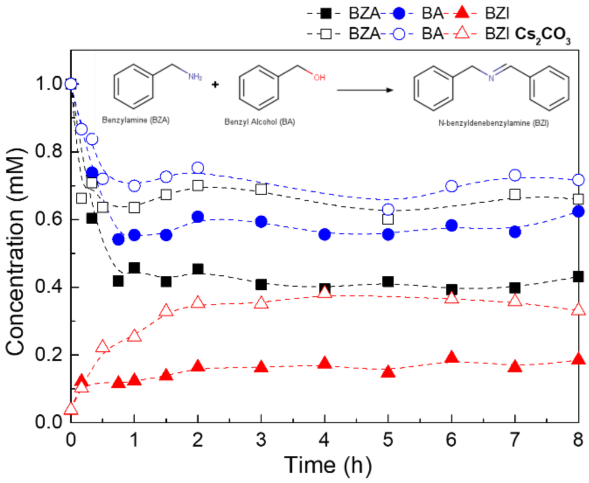

Fig.1. Concentration profiles of BZA, BA and BZI using immobilised CBB under a continuous flow without (filled symbols) and with the addition of Cs_2CO_3 (open symbols).

Continuous production of BZI was successfully achieved using immobilised CBB, with a maximum yield of 0.35 mM of BZI after 2 h reaction, and the supported CBB remained stable after more than 50 h reaction (Fig.1).

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ENSEÑANZA DE LA QUÍMICA

Cinética de las reacciones químicas

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Los planes de estudio de las titulaciones de Grado en Ingeniería Eléctrica y en Ingeniería Electrónica Industrial y Automática de la Escola Politécnica de Enxeñaría de Ferrol de la Universidade da Coruña, incluyen la Química como asignatura de formación básica, impartida en el primer cuatrimestre del curso primero de ambas titulaciones [1]. La unidad didáctica número 3 de la asignatura se compone del tema "Cinética química", en el que se introducen los aspectos de la velocidad de las reacciones químicas, los factores que la afectan, la catálisis y los mecanismos de dichas reacciones.

El tema incluye numerosos conceptos nuevos y algunos desarrollos matemáticos que hacen que su estudio pueda resultar árido y difícil para una parte del alumnado. Por ello se ha considerado conveniente impartir, dentro del programa de laboratorio, una práctica de cinética, con la finalidad de que contribuya a la comprensión y consolidación de los conocimientos expuestos [2]. La velocidad de una reacción química se mide por la variación de la concentración de un reactivo o de un producto en la unidad de tiempo. En la práctica que se presenta en esta comunicación se evalúa la influencia de los factores concentración y temperatura sobre la velocidad de la reacción que tiene lugar entre el tiosulfato de sodio y el ácido clorhídrico, para dar lugar a ácido sulfuroso, cloruro de sodio y azufre.

La práctica de laboratorio se compone de los siguientes apartados: a) Cuestiones previas que el alumnado, apoyándose en la bibliografía de la asignatura, deberá resolver antes de comenzar el desarrollo experimental. b) Objetivos de la práctica. c) Indicación del material necesario. d) Indicación de los reactivos necesarios. e) Procedimiento [3], en el que primeramente se guía al alumnado en la evaluación de la influencia ejercida por las concentraciones de tiosulfato de sodio y de ácido clorhídrico sobre la velocidad de la reacción. Para ello, se llevan a cabo los cálculos de las concentraciones de las disoluciones necesarias para cada uno de los experimentos a realizar [4], de los valores de los órdenes parciales de reacción con respecto a cada reactivo, y de la constante específica de velocidad de reacción [5].

A continuación, siguiendo con el procedimiento, se estudia la influencia de la temperatura sobre la velocidad de la reacción. Una vez finalizado el procedimiento experimental y los cálculos precisos, se pasa al apartado f) Cuestiones a resolver por el alumnado. Con la finalidad de verificar si han comprendido y asimilado los conocimientos expuestos, deberán resolver unas cuestiones sencillas relacionadas con el desarrollo de la práctica y con sus fundamentos teóricos.

El apartado g) y último, consiste en el informe final a presentar por el alumnado al terminar la práctica, en él se recogen los cálculos que permiten obtener las concentraciones de las disoluciones preparadas de los reactivos, los órdenes parciales de reacción, la constante específica de velocidad de reacción y la expresión de la ecuación de velocidad para la reacción.

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Práctica virtual de Laboratorio de Química: Determinación del calor específico del plomo

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La experiencia como docentes nos indica que, debido a la disminución de horas dedicadas al estudio de la Química en los actuales grados de Ingeniería, el tiempo que el profesorado dedica a las prácticas de laboratorio es mínimo, quedando reducida la presencia del alumnado en el laboratorio a un valor casi testimonial. En consecuencia, la presentación de videos de carácter descriptivo sobre prácticas virtuales en la clase, sin el condicionante de espacio del laboratorio, permite al profesorado explicar con detalle el tema correspondiente y promover el debate con el estudiantado lo que favorece la mejor compresión de los conceptos expuestos.

Las consideraciones anteriores nos han conducido a llevar a cabo un estudio sobre las prácticas virtuales de Química que puedan complementar a las efectuadas en el laboratorio, sin pretender que lleguen a sustituirlas, ya que se considera imprescindible que el alumnado adquiera destreza en el trabajo experimental a desarrollar en el laboratorio.

Para ello, se escogieron y realizaron prácticas, dentro de los campos de la Química General y Analítica, relativas a los apartados de: preparación de disoluciones [1,3], calor específico [2], calor de reacción [3,4], propiedades termodinámicas [5], valoraciones ácido-base [1], identificación de metales a la llama y de iones en disolución a partir de sus mezclas [6], Con esa finalidad se utilizó el programa Virtual ChemLab, General Chemistry Laboratories, v.2.5, citado en el texto de la referencia [7].

En la presente comunicación se lleva a cabo, de forma virtual, la obtención de los parámetros necesarios para la determinación de una propiedad básica en calorimetría: el calor específico [8], en este caso concreto del plomo, metal que presenta múltiples aplicaciones como material en ingeniería, solo o aleado con otros elementos. Una vez conocidos los parámetros, en una segunda fase, se realizan los cálculos mediante ordenador o una calculadora básica; el resultado obtenido se compara con el valor de referencia [8], encontrándose un error porcentual dentro de los límites permitidos en prácticas virtuales basadas en simulación y muy similar al obtenido en un trabajo previo [2].

Agradecimientos

Queremos expresar nuestro agradecimiento a la Universidade da Coruña por la concesión de una Beca del Programa de Formación Complementaria a la alumna del último curso del Grado en Ingeniería Naval y Oceánica, Dña. Andrea María Gómez Rodríguez y al Técnico del Laboratorio de Química, D. Juan Antonio Castro Amado.

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Caso Práctico: uso de herramientas Jupyter Notebooks para la resolución de problemas de gases reales

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El Proyecto Jupyter es un spin-off de IPython. Jupyter Notebook es un entorno web que ejecuta un conjunto de comandos del lenguaje de programación Python, el más utilizado en la actualidad.Jupyter notebook posee muchas características que lo hacen idóneo para un entorno universitario, como son que es un entorno de libre distribución y gratuito, usa formatos contrastados y fácilmente intercambiables a partir de un único código fuente (markdown) por lo que es fácilmente publicable en webs, blogs, etc. sin necesidad de cambiar casi nada del documento original, sólo el mecanismo de "deploying". También ofrece la posibilidad de crear simulaciones dinámicas e interactivasa que permiten la elaboración de practias y laboratorios virtuales. Desde su lanzamiento, en el año 2014, se pueden utilizar otros lenguajes, como MATLAB, R y Julia. Una de las principales ventajas es la alta interactividad del entorno Jupyter Notebook, a través del intercambio de contenido multimedia y la ejecución de un código escrito. No se necesitan conocimientos previos de programación informática para interactuar o visualizar el contenido de los cuadernos, lo que fortalece su capacidad de transmisión de conocimientos y su uso como herramienta de enseñanza. El proyecto Jupyter y sus subproyectos se centran en proporcionar herramientas (y estándares) para la computación interactiva con cuadernos de notas computacionales.

En el presente trabajo usamos esta herramienta Jupyter Notebook para resolver un problema de gases reales. En el se detalla todo el recorrido cognitivo, fundamentos teóricos y cálculos necesarios. EL problema trata sobre cartucho de CO_2 que contiene 12 g de gas, en un volumen interno de 17,6 cm^3. Se pide estimar la presión dentro del cartucho en condiciones, a 40 ºC, mediante varios métodos de cálculo o modelos teóricos; ecuación de los gases ideales, Ecuación de Van der Waals y Diagramas de compresibilidad. El uso del entorno Jupyter le permitirá al alumno responder a las siguientes cuestiones:
¿Cómo depende la presión del CO2 de la temperatura en el rango de 30 ºC a 50 ºC?.
¿Por qué tanto error en la ley de los gases ideales?
¿Por qué los diagramas de compresibilidad funcionan tan bien en este caso?
El uso de este tipo de herramientas posibilita una resolución sencilla y un aprendizaje más atractivo para el alumno, además de una ágil interacción Alumno-Profesor.

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Caso Práctico: uso de herramientas Jupyter Notebooks para la resolución de problemas de Cinética

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En este trabajo se plantea la resolución de un conjunto de problemas de cinética química usando herramientas Jupyter Notebook y programación en Python. Aunque se pueden usar como motor de cálculo otros kernels como MATLAB/OCTAVE R y Julia, es Python el motor de cálculo preferido para usar en los Notebooks de Jupyter. En este trabajo se presenta un entorno web que ejecuta un conjunto de comandos orientado a la solución y representación de resultados de cálculos cinéticos, a través del intercambio de contenido multimedia. Este cuaderno se centra en proporcionar un tipo de computación interactiva con cuadernos de notas computacionales y cálculos en el mismo documento exportable a diferentes formatos de presentación visual con el mismo archivo fuente.

Como ejemplo de uso se plantea en este caso una reacción química

Ecuación 1 $A + 2B \rightarrow C$

Cuya cinética es:

Ecuación 2 $r_1 = k_1 C_A C_B$

Se supone que la densidad del sistema reaccionante se mantiene constante, y que inicialmente k_1 es 0,1 L·mol^{-1}·min^{-1}, la concentración inicial de A es 10M y la de B es 12M, se resuelve el sistema de ecuaciones resultante de el equilibrio de materia para cada una de las especies A y B y representa la variación en la concentración de las dos especies durante los primeros 5 minutos de reacción.

Una vez planteados los scrips se obtiene la siguiete gráfica de manera sencilla e intutiva

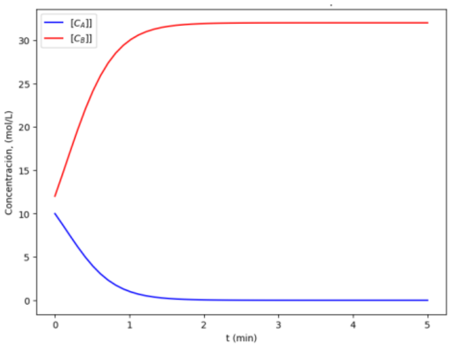

Fig.1. Variación de la concertación con el tiempo

Una vez resuelta una ecuación Jupyter Notebook nos permite repetir el proceso pueden repetir con distintas reacciones, de una manera sencilla.

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QUÍMICA INDUSTRIAL E INGENIERÍA QUÍMICA

Autothermal pyrolysis of a photopolymer demonstrated by TGA-DSC and simulated by ASPEN Plus software

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Polymer-derived activated carbons (PDAC), synthesized from photopolymers, present a promising avenue for generating carbon materials with fined-controlled properties and 3D structures for several applications [1,2]. Carbonization is typically conducted by pyrolysis, which takes without oxygen, but the process is globally endothermic, bringing a great challenge as the pyrolysis system scales up. However, partial oxidation in the first steps of the carbonization may increase carbonization yield and, in addition, generate enough heat to make pyrolysis as an autothermal process [3]. In this work, the photopolymerization of a tailored photoresin and the autothermicity in its carbonization were deeply studied at different operating conditions. Photopolymerization was performed from the photoresin reported in previous works [1,2]. Carbonization was studied through preoxidation ranging temperatures from 200 to 435ºC, followed by pyrolysis up to 900ºC with different heating rates (0.5-6.5ºC/min) using TGA-DSC (thermogravimetric analysis and differential scanning calorimetry) equipment. Ultimate and proximate analysis of carbon precursor and PDAC were evaluated by CNHS-elemental and TGA to define all compounds as non-conventional components in ASPEN Plus v12.1 software and simulate the autothermal pyrolysis. Thermal efficiency (η) was determined as the heat generated in pyrolysis reactor plus the heat recovered from gas effluent when cooled at 60ºC divided by the heat required to reach the reaction temperature (900ºC) when using an influent at 25ºC. Fig. 1(a) shows TGA-DSC of the photopolymer carbonized by preoxidation in air atmosphere up to 435ºC followed by pyrolysis up to 900ºC in a nitrogen atmosphere. As observed, the heat flow generated by combustion exceeds the heat required for pyrolysis, meaning pyrolysis may be conducted without additional heat sources. This fact was supported by simulation (Fig. 1(b)), since η reaches values higher than 115% for different air/PDAC flow rate ratios and preoxidation temperature. In conclusion, autothermal pyrolysis can be conducted at stationary state.

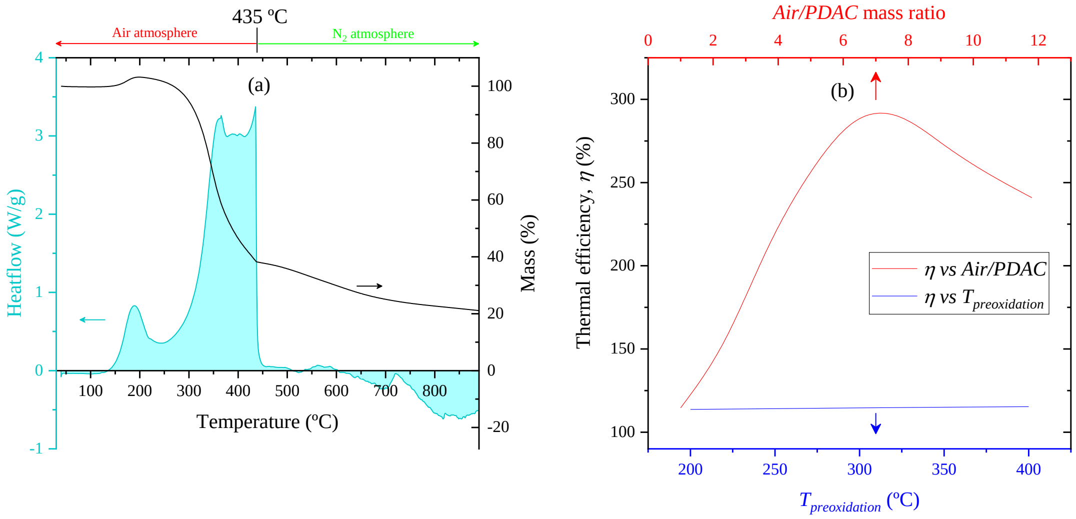

Fig.1. (a) TGA-DSC made of a photopolymer at oxidative and inert atmosphere up to 435 and 900 ºC, respectively; and (b) thermal efficiency as function of air/PDAC flow rate ratio and preoxidation temperature.

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Analysis of gorse flower extracts obtained by ultrasound assisted technology: determination of phenolic compounds and antioxidant activities

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Gorse (*Ulex europaeus*) is a perennial shrub belonging to the Fabaceae family. It is characterised by its thorny branches and bright yellow flowers that give off a strong, distinctive odour [1]. Although it is native to western and central Europe, it has spread to many other regions of the world. Its presence in Galicia stands out, where it is found in 74% of its forests and extends over 30% of its territory [2][3]. Due to its high reproductive capacity, long seed dormancy, long life cycle, rapid growth and lack of natural predators, gorse plays a crucial role in the spread of forest fires and is considered one of the 100 most dangerous invasive species in the world. Finding a cost-effective way to use gorse could generate environmental benefits and promote sustainable development in agriculture and forestry activities [3].

The flowers of gorse contain mainly terpenoids and glycosides, and their phenolic content is higher than that of other parts of the plant [1]. The aroma, antioxidant properties and colour of the flowers could make them useful in the cosmetic or perfume industry, either as whole flowers or as extractives. The compounds responsible for these characteristics have also been widely used as ingredients, additives or flavourings in foods, or in packaging materials.

Extracts of gorse flowers were produced by different techniques (i.e. microwave hydrodiffusion and gravity, distillation, etc.) and solvents (i.e. acetone, methanol, ethanol, hexane and others) [1]. Recently, the ultrasound-assisted extraction (UAE) was considered an efficient and economical technique for obtaining bioactive compounds from plants. Its advantages include less solvent use, lower temperatures and shorter extraction times [4].

This study proposes ultrasound-assisted extraction (UAE) using water and ethanol, with the aim of determining the most favourable conditions for the extraction of phenolic compounds, their phenolic content and the *in vitro* evaluation of the antioxidant activity.

The results indicated that the highest concentration of phenolic compounds was achieved in the sample using 50% EtOH as solvent. In vitro antioxidant activities reached the highest values under these same conditions. In the case of phenolic compounds, the maximum obtained was around 10.67 g gallic acid equivalents/100 g extract. The trend was the same for the antioxidant capacity evaluation methods where maximum values of 59.14 g Trolox/ 100 g extract and 5.39 g Ascorbic acid/ 100 g extract. 3,4-dihydroxybenzoic acid, naringenin, genistein, luteolin or p-coumaric acid were some identified phenolics and flavonoids.

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A biorefinery approach for the manufacture and characterization of oligosaccharides from gorse

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Gorse (*Ulex europaeus*, UE) is a woody and highly spiny shrub that is found practically over the world due to its invasive and colonizing character [1]. In Galicia, this species is native and highly prevalent, being present in 74 % of the forests and in about 30 % of the territory [2, 3]. Harvesting gorse is very important, as it can contribute to mitigating the serious threat of forest fires by being an important substrate for their spread. Therefore, a biorefinery strategy for the valorization of gorse would promote a sustainable forest management [2].

Between the various technologies for the fractionation of biomass into its main constituents, hydrothermal processing is a cost-effective and green option that utilizes hot compressed water as the sole reagent. Under optimal conditions, hydrothermal processing results in the solubilization of hemicelluloses, leading to the formation of oligosaccharides (OS) as the main products, while cellulose and lignin remain in the solid phase [4].

Hemicellulosic OS can be used in a variety of applications, with increasing interest from the cosmetic, pharmaceutical and food industries. To achieve the required purity levels for these commercial purposes (>75 %), it is essential to selectively remove unwanted components through an additional purification step. For this purpose, membrane processing offers a promising strategy for the industrial production of high-purity OS.

In this work, a biorefinery approach for the valorization of gorse is proposed. The biorefinery strategy includes a previous ultrasound-assisted extraction (to obtain extracts with antioxidant bioactivities) and the optimization of the hydrothermal processing to maximize de production of xylooligosaccharides (XOS) from hemicelluloses. Membrane processing was used as an environmentally friendly technology that assures the purification of XOS. Final product characterization was accomplished by HPLC, HPSEC, HPAEC and *in vitro* antioxidant activity.

The results indicated that hydrothermal processing is a suitable method for the manufacture of hemicellulose derived OS, reaching a concentration of 16 g/L at 30 minutes. XOS constituted around 60 % of hemicellulose derived saccharides, and were partially branched by acidic groups (acidic and uronic). Membrane processing allowed to increase OS purity up to 77 % achieving the requirements needed for commercial purposes. The molar ratio of XOS:AcG:UA in the retentate were 1:0.60:0.11.

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Obtención de 5-HMF a partir de bagazo de mazá usando disolventes verdes asistidos con microondas

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A biomasa lignocelulósica preséntase como alternativa renovable aos produtos obtidos de recursos fósiles [1]. Nun contexto de biorrefinería, o bagazo de mazá é un subproduto abundante derivado do proceso de produción da sidra, o cal destaca polo seu elevado contido en azucres solubles, frutosa e glicosa principalmente. Por outra banda, o 5-hidroximetilfurfural (5-HMF) é un composto multifuncional que pode ser obtido destes azucres. É considerado unha das moléculas plataforma máis versátiles, o que permite a súa transformación noutros produtos de alto valor como poden ser plásticos, produtos farmacéuticos, de cosmética e téxtiles [2]. Este composto obtense mediante a deshidratación das hexosas, unha vía sostible para esta reacción podería ser o uso de disolventes eutécticos profundos (DES) combinados con técnicas de quecemento non convencionais, as cales permiten un aforro enerxético [3].

O obxectivo deste traballo foi poñer en valor o bagazo de mazá como fonte de obtención de 5-HMF mediante tratamentos sostibles. Para a solubilización destes azucres, empregáronse dous métodos diferentes, por un lado unha extracción acuosa a temperatura ambiente, e por outra banda, unha esterilización en autoclave seguida de unha sacarificación encimática. A tecnoloxía empregada para a deshidratación de hexosas presentes nos licores obtidos foi o uso de DES, baseado en cloruro de colina e ácido láctico, asistido con microondas. As variables avaliadas para a obtención de 5-HMF foron: (i) tempo, (ii) temperatura, (iii) % de DES e (iv) proporción molar da mestura eutéctica.

Primeiramente analizouse os licores obtidos por extracción acuosa e por sacarificación encimática, comprobando que a hidrólise encimática permite unha maior recuperación de hexosas, 71.57% fronte 63.84% e tamén se puido comparar a resposta destes, a un tratamento coas mesma condicións (140 ºC, 30 min, 50% DES), comprobando que o licor obtido a partir sacarificación mostrou mellores resultados en canto a produción de 5-HMF. Unha vez elixido o licor da hidrólise encimática, estudouse a resposta ante a variación de condicións de tempo, % de DES e temperatura, nos tratamentos de microondas. Un aumento de 15 minutos no tempo de reacción de microondas (de 30 a 45 min), resultou nun aumento de 5-HMF de máis do 25%. Por outra banda, aumentando o % DES na reacción de deshidratación de hexosas, (de 50 a 70%), traduciuse nun aumento na conversión de frutosa a 5-HMF, case duplicando o rendemento molar deste. Tamén presentou resposta positiva da obtención de 5-HMF ante un incremento da temperatura (de 140 a 160 ºC), aumentando nun 57.8%. En canto á variación da proporción molar dos compoñentes do DES empregado, o que mellor resultado de conversión de frutosa en 5-HMF presentou foi o cloruro de colina: ácido láctico 1:5.

Este traballo pon en manifesto o bagazo de mazá como recurso prometedor para a obtención de bioprodutos de valor engadido como o que se procurou. Tamén confirma o tratamento de microondas asistido con solventes eutécticos como tecnoloxía favorable na transformación de frutosa en 5-HMF.

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Physical Properties of Cholinium L-Lysinate and its Mixtures with Different Solvents

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In recent years, there has been a great interest in the preservation of the environment and the proper use of natural resources, with the aim of achieving the objectives of sustainable development. In this regard, ways are being sought to create more environmentally friendly industrial production processes [1]. Ionic liquids can play a key role in this industrial transformation due to their interesting properties such as: thermal stability, low volatility and the ability to dissolve a wide range of compounds. So, they are ideal for generating more efficient and sustainable industrial processes. However, the term "green" has been used to describe many of these salts that, in terms of toxicity and biodegradability, are far from deserving that label. It is essential to pay special attention to the cations and anions chosen from the nearly infinite possibilities available.

Cholinium L-lysinate ([Ch][Lys]) is a bio-based ionic liquid, derived from an amino acid, with really green credentials. Due to its characteristics, it has been widely proposed for biomass pretreatment [2], but also for CO_2 capture [2], or in the pharmaceutical industry [3]. The correct design, optimization and operation of these processes require the knowledge of the physical properties involved. These drastically affect parameters such as equipment sizing and energy requirements.

This research aims to study two physical properties, namely viscosity and density, of mixtures of [Ch][Lys] with several conventional solvents: water, acetone, ethanol and methanol. The interest of these mixtures lies in the fact that these organic compounds are frequently used in chemical industry as co-solvents, or as anti-solvents to recover the ionic liquid after its utilization. The binary systems were studied in all the range of concentrations. Determinations were carried out at atmospheric pressure and temperatures ranging from 298.15 to 338.15 K. Both density, and mainly viscosity, drastically decreased with the content of the organic solvent in the mixture and with temperature. Moreover, excess properties were determined and adequately correlated using the Redlich-Kister polynomial. These changes of properties by mixing allow for the discussion of the interactions between components.

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Neutralization of Bauxite Waste (Red Mud) through CO_2 Absorption

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In a context of environmental concern, with trends in both legal regulations and social awareness, the bauxite residue, known as red mud, is a long-standing problem whose solutions have not proven effective. Although categorized by the European Waste Catalogue as a non-hazardous waste, the risks to the environment and human health are evident attending to the high alkalinity (pH> 12) of the red mud. They are usually deposited in reservoirs, in aqueous state, with the consequent environmental risk, so neutralization could not only significantly reduce the threat, but also allow their reuse for different purposes.

Due to their composition -they are rich in metallic oxides- have excellent properties as ion adsorbents or anti-corrosion additives, however its applicability is limited by their high alkalinity. The alkalinity of red mud is due to the presence of sodium, calcium and potassium oxides that, in aqueous media, are transformed into the corresponding hydroxides, which dissociate completely liberating OH^- ions. This fact confers to red muds a great potential as a CO_2 remover since, in aqueous suspension, the presence of compounds that would react rapidly with CO_2 favouring its elimination is assured, while the other components would remain unaltered giving a "neutralized mud" that maintains intact the corrosion-inhibiting properties of the initial mud.

In this work [1], CO_2 absorption in liquid red mud was analysed using a batch stirred tank absorber (Figure 1). The process was monitored by measuring, in real time, the pH and temperature inside the tank. Wet sludge from the ALCOA reservoir and dry sludge were used, and in both cases three mud:water ratios were tested. For dry slugde, three particle size fractions were used (0.08-0.16 mm, 0.16-0.5 mm and > 0.5 mm) and, to reach an identical initial pH, each blend was stirred mechanically and/or ultrasonically for several hours.

From experimental data it is concluded that after CO_2 absorption the mud pH is 6.4 – 6.5, both for dry and wet sludge. On the other hand, for a same *mud:water* ratio, the decrease in pH is higher for wet sludge, while for dry mud it also varies with particle size (Fig. 2). Finally, the neutralization time also varies with particle size, being smaller for particles < 0.16 mm (Fig. 2).

Fig.1. Experimental set-up

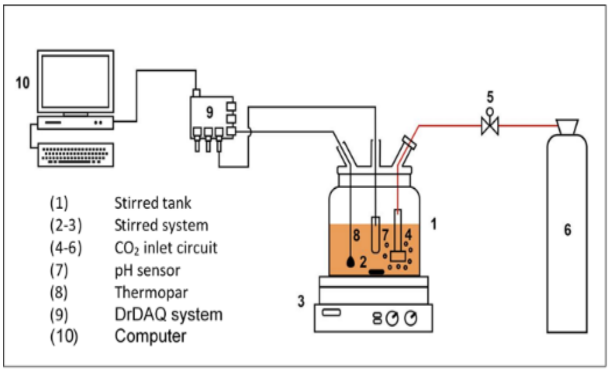
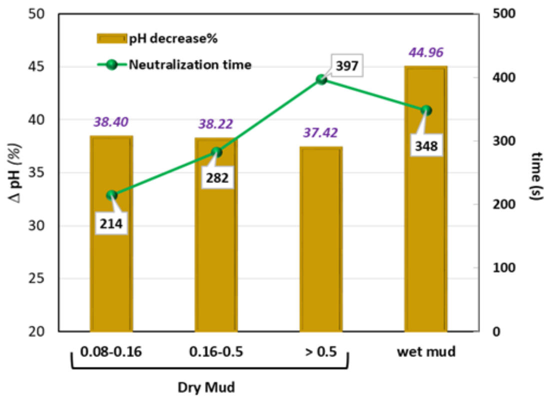


Fig. 2. Neutralization time and pH reduction for wet and dry mud: mud:water ratio of 1:10



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Evaluation of the effectiveness of impregnated activated carbon in monoethanolamine or diethanolamine for CO_2 capture

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In this work, an alternative is proposed that seeks to significantly reduce greenhouse gas emissions, specifically carbon dioxide (CO_2). In the industrial field, the capture of carbon dioxide is carried out mainly through two techniques: absorption and adsorption. The absorption technique involves the passage of CO_2 through an absorbent liquid, such as amines, at a specific pressure and temperature, with the aim of retaining the CO_2. On the other hand, adsorption is based on the capture of gases or liquids in the internal pores of a solid.

This project [1] proposes to improve the efficiency of CO_2 capture by combining both techniques. Activated carbon (CA) is used as adsorbent material, highlighting its highly porous and extensive surface area, which allows it to retain CO_2 molecules on its surface. Alkanolamines, in particular monoethanolamine and diethanolamine, are used as absorbent materials. It is intended to increase the efficiency of CO_2 capture by impregnating activated carbon with different proportions and concentrations of these alkanolamines.

Tests were carried out under a pressure of 1 atmosphere and at temperatures ranging between 293 and 295 K. **Figure 1** shows the experimental setup. Different samples were used, with impregnation ratios of 1:1, 1:3 and 1:5, and alkanolamine concentrations that varied from 10% to 30%. Notably, it was observed that samples impregnated with monoethanolamine presented a highest adsorption capacity, reaching maximum values at 20% amine concentration. Physisorption tests with nitrogen were carried out to evaluate the effect of alkanolamine inside the active carbon pore. Below, the results obtained are shown in **Table 1**.

Fig.1. Experimental Installation.

Table 1. CO_2 adsorbed by CA impregnated with [a]MEA or [b]DEA

Sample	Ratio	m_{sample} (g)	n_{ads} (mmol CO_2)	m_{ads} / m_{sample} (mg CO_2/g)	Increment CA (%)
CA		0.2569	0.1451	24.85	-
CA MEA 10/90	1:1	0.2534	0.1887	32.77	31.87
	1:3	0.2564	0.2846	48.84	96.53
	1:5	0.2549	0.3486	60.20	142.20
CA MEA 20/80	1:1	0.2545	0.2884	49.87	100.60
	1:3	0.2569	0.3933	67.38	171.10
	1:5	0.2567	0.4054	69.50	179.60
CA MEA 30/70	1:1	0.2685	0.3157	51.73	108.00
	1:3	0.2582	0.3269	55.72	124.20
	1:5	0.2549	0.3293	56.60	127.70
CA DEA 10/90	1:1	0.2535	0.1830	31.76	27.80
	1:3	0.2542	0.2643	45.66	83.74
	1:5	0.2580	0.3021	51.53	107.30
CA DEA 20/80	1:1	0.2554	0.3041	52.42	110.90
	1:3	0.2598	0.3404	57.66	132.00
	1:5	0.2532	0.3281	56.03	125.40
CA DEA 30/70	1:1	0.2566	0.2419	41.18	65.71
	1:3	0.2528	0.2342	40.77	64.06
	1:5	0.2553	-	-	-

[a]MEA, monoethanolamine; [b]DEA, diethanolamine

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Strategies for the integral valorisation of wine industry waste through sustainable processes

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The increase in food processing and production has a significant impact on the accumulation of agro-industrial waste. Portugal and Spain are two of the world's largest wine producers, and consequently, this vast production generates a substantial amount of wine waste. This encompasses both agricultural production, such as vine pruning cuttings, and industrial manufacture and processing, including grape marc and wine lees, among other by-products. Grape pomace constitutes the primary solid residue produced during the processes of pressing and fermentation employed in the production of wine. Most of its composition is comprised of skins, stalks, and seeds. This by-product constitutes approximately 10%–30% of the crushed grape mass and other value-added products, including unfermented sugars, polyphenols, pigments, alcohol, and tannins [1]. Considering the current environmental crisis, which is largely attributed to the depletion of fossil resources and their detrimental impact on the environment, the wine sector has been developing the concept of biorefining to attain a Circular Economy in line with the sustainable development goals (SDG). This entails the utilisation and exploitation of wine production waste to produce fuels, energy, chemicals and other products [2] .

Grape pomace, like other industrial by-products, is a rich source of polysaccharides and soluble sugars. The objective of this study is to fully valorise grape pomace to obtain value-added compounds (such as oligosaccharides, antioxidant compounds) and fermentable sugars. To this end, an autohydrolysis treatment was conducted at temperatures between 150 and 190°C at liquid to solid ratio of 4 g/g, resulting in an enrichment of 30–40% in glucan of solid residue. The the autohydrolysis treatments also allowed the solubilisation of antioxidant compounds, with values ranging from 17.99 to 23.49 mg GAE/g of grape pomace treated and 11.71 to 24.42 mg RE/g of grape pomace treated, determined by total phenolic content (TPC) and total flavonoid content (TFC) methods, respectively. In addition, the grape pomace hydrolysates showed antioxidant activity in the range of 2.25 to 7.51, 1.95 to 15.23 and 4.62 to 7.65 mg TE/g of grape pomace treated for DPPH, ABTS and FRAP methods, respectively. Furthermore, the grape pomace was subjected to an enzymatic hydrolysis process, resulting in a glucose concentration of between 6.62 and 27.02 g/L, with different strategies considered. As an alternative approach to the valorisation of another waste product from the wine industry, the solid residue resulting from the steam explosion treatment of vineyard pruning cuttings was mixed with grape pomace in order to increase the glucose content. As a final recovery strategy, the wastes under study were employed together to an enzymatic hydrolysis with the objective of developing a process for the integral recovery of various agro-industrial wastes generated by the wine production industry. This approach contributes to sustainability, as well as the reuse of waste materials and circular economic principles.

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MICROWAVE PYROLYSIS OF KRAFT LIGNIN FOR SUSTAINAGLE ACTIVATED CARBON PRODUCTION

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Biomass represents a renewable resource of abundant neutral carbon and its importance is increasing aiming at the development of a more sustainable industrial system. Among biomass, Kraft Lignin stands out because it is generated in increasingly larger quantities in pulp and paper companies, been considered as waste. Lignin is present in plant cell walls, is rich in carbon, and is a potential precursor in the production of activated carbon (AC) [1]. AC is considered an excellent adsorbent due to its high surface area, pore size distribution, and the presence of functional groups on its surface. AC can be prepared by physical activation, where the organic raw material is pyrolysed, followed by activation in the presence of activating agents such as CO_2 and steam; or by chemical activation, where the raw material is impregnated with activating agents such as $ZnCl_2$, H_3PO_4, KOH, and K_2CO_3, followed by thermal treatment in an inert atmosphere. Currently, thermal treatment using a tubular furnace is one of the most used methods in AC production. However, this method is characterized by high costs due to the long processing time and high energy consumption. In this context, the microwave pyrolysis has shown to be a promising option to convert lignin into AC, offering the advantages of lower energy consumption and reduced processing time, while achieving the same quality of AC as the ones produced by conventional thermal methods.

The objective of this work is to use Kraft lignin as a precursor material in AC production, using microwave pyrolysis combined with chemical activation. The influence of different parameters, such as effect of activating agent (H_3PO_4, KOH and K_2CO_3) and different precursor:activating agent ratios (1:1, 1:0.5, 1:0.2) on the surface area (S_{BET}) of the produced ACs were investigated. The N_2 adsorption/desorption analyses of AC show a combination of type I and type IV isotherms, according to the International Union of Pure and Applied Chemistry (IUPAC). This result indicates that the produced AC are both microporous and mesoporous. The AC samples showed S_{BET} values ranging from 85 to 1262 m^2g^{-1} and total pore volume from 0.04 to 0.58 $cm^3\,g^{-1}$. Fourier transformed infrared spectroscopy (FTIR) analysis revealed the presence of functional groups on the surface of AC, with main bands at 3400, 1700, 1600 and 1300-1000 cm^{-1}, referring to OH, C=O, C=C and C-O groups, respectively. Microscopic analyses show that AC exhibit a rough surface with diverse pore shapes and sizes, highlighting their heterogeneous pore structures. X-ray photoelectron spectroscopy showed that AC with lower activating agent ratio (1:2) has more functional groups. X-ray diffraction of the AC samples present two broad and diffuse peaks, centered at 23° and 43°, corresponding to reflections (002) and (100), characteristic of the turbostratic structure associated with graphitic microcrystallites. Overall, the obtained results show that the type of activant agent and precursor:activating agent ratio clearly influences the S_{BET} of the AC, and that microwave pyrolysis is a suitable and efficient process for AC production.

Acknowledgements

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Impact of organic acids during pilot-scale dialysis for biosurfactant recovery

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Biosurfactants, which are surface-active compounds produced by microorganisms, can be separated from larger molecules and contaminants through a semi-permeable membrane [1]. For that, ATEMBIO project purposes to scale-up the dialysis process for biosurfactant recovery from corn steep water (CSW) due to its simplicity, green, and ability to preserve the bioactivity of the biosurfactants. Thus, in this study was evaluated the impact of organic acids (lactic acid, phytic acid, and acetic acid) on the recovery of biosurfactants by means of both closed and open dialysis processes. Experiments were carried out with the Diffusion dialysis (DD) unit (Model AP-L05) from Mech-Chem (USA) with a membrane stack arranged in a plate and frame configuration (6-8 kDa regenerated cellulose membrane sheets (8)) with a total area of 929 cm^2. Centrifuged CSW was pumped to the DD unit and counter current Milli-Q water using different volume and fluxes rate. Also, the pH of the centrifuged CSW was evaluated at 4.0 (unchanged) and 6.5 (adjusted with 1 M NaOH) as indicated in **Table 1**. During the experiments, organic acids were measured by HPLC-DAD-RID using the experimental conditions described in a previous works [2]. In a closed system, the lowest elimination percentages were obtained with assay 1 and the highest with assay 4 (see **Table1**), being lactic acid (50-75%) the most effectively removed, followed by acetic acid (44-66%), and lastly, phytic acid (38-53%) after dialysis time around 72 h. In the open system, when the CSW flow rate was set to 0.56 L/h·m^2 (assay 6 and 7), a higher efficiency in the dialysis process was observed, enhanced by adjusting the CSW pH to 6.5. The removal sequence remains the same as in the closed system: lactic acid (64-78%), followed by acetic acid (60-71%), and finally phytic acid (46-55%). This improvement could be attributed to the fact that deprotonated organic acids might exhibit higher diffusion rates. Consequently, the effective removal of organic acids from the CSW results in a more purified biosurfactant extract after the dialysis process.

Table 1. Experimental conditions used in this study.

Configuration	Assay	V_{CSW} (L)	$^{a}F_{RCSW}$ (L/h·m^2)	Nº cycles$_{CSW}$	pH_{CSW}	V_{H2O} (L)	$^{a}F_{RH2O}$ (L/h·m^2)
Closed	1	1.5	0.56	26.1	4.0	1.5	0.56
	2	1.5	0.56	27.8	4.0	4.5	0.56
	3	1.5	0.56	26.9	4.0	4.5	1.12
	4	1.5	0.56	27.1	6.5	4.5	1.12
			$^{a}F_{RCSW}$ (L/h·m^2)		pH_{CSW}		$^{a}F_{RH2O}$ (L/h·m^2)
Open	5		0.56 – 3.20		4.0		0.56 – 3.20
	6		0.56		4.0		0.56 – 3.20
	7		0.56		6.5		0.56 – 3.20

^{a} F_R = flux rate

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Metals dynamics in pilot-scale dialysis for biosurfactant recovery

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Corn steep water (CSW) is a complex agro-food stream rich in carbohydrates, amino acids, polypeptides, fatty acids, biocompounds like biosurfactants, as well as hydrolytic enzymes, heavy metals, and inorganic ions [1]. In this sense, separation techniques are necessary to purify CSW to be employed as a direct source of biosurfactants. Thus, the ATEMBIO project aims to recover biosurfactants from CSW using the dialysis process, currently at a TRL of 4-6, while also assessing the presence of metals. Experiments were conducted using the Diffusion Dialysis (DD) unit (Model AP-L05) from Mech-Chem (USA), equipped with a membrane stack in a plate-and-frame configuration consisting of 6-8 kDa regenerated cellulose membrane sheets (8), with a total surface area of 929 cm². Centrifuged CSW was pumped into the DD unit alongside counter-current Milli-Q water, in closed and open configurations, under the operating conditions shown in **Table 1**. Metal concentration was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) for Fe, Mn, Na, S, Si, Zn, K, and by inductively coupled plasma mass spectrometry (ICP-MS) for ^{27}Al, ^{59}Co, ^{63}Cu, ^{88}Sr, ^{111}Cd, using the experimental conditions described in a previous works [2]. Results showed that in the closed system, Si, Zn and K were the metals with the highest tendency to diffuse through the dialysis membranes reaching around 50% removal of the initial CSW; followed by Na $>$ ^{63}Cu $>$ Mn $\approx$ ^{59}Co $>$ ^{27}Al $>$ ^{111}Cd $\approx$ S $>$ Fe $>$ ^{88}Sr. Otherwise, in the open system, a higher percentage of metal removal was observed when operating at low CSW flow rates. Under these conditions Si, K, Na, and ^{88}Sr were significantly (*t-test, p= 0.05*) more removed from CSW, being these differences more notable in the case of K, Na and Si, which achieved removal rates of over 67%; whereas S, ^{59}Co and ^{111}Cd were removed in a similar way from CSW in comparison with closed system. Finally, Zn, Mn, Fe, ^{63}Cu and ^{27}Al exhibited a decrease in their removal rates, in open system, when comparing with closed system. Consequently, dialysis process at pilot-scale allows the removal of impurities like metals without loss of biosurfactants from CSW.

Table 1. Experimental conditions used in this study.

Configuration	V_{CSW} (L)	$^{a}F_{RCSW}$ (L/h·m²)	pH_{CSW}	V_{H2O} (L)	$^{a}F_{RH2O}$ (L/h·m²)	Nº cycles
Closed	1.5	0.56	4.0	1.5	0.56	26.1
Open	-	0.56 – 2.24	4.0	-	0.56 – 2.24	-

^{a} F_R = flux rate

Agradecimientos

This study was supported by the Xunta de Galicia under the project ED431F 2023/17. Also, X. Vecino and A. Martínez acknowledge to the MICINN through the grant RYC2021-030966-I and the University of Vigo for her pre-doctoral fellowship (PREUVIGO-21), respectively.

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Microwave hydrodiffusion and gravity as pretreatment to enhance phenolic compounds and polysaccharides extraction from terrestrial and marine biomass

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The current environmental crisis leads us to rethink our use of raw materials, favoring natural compounds instead of synthetic ones. In that sense, sustainable techniques have been developed to enhance the extraction of natural bioactive compounds and polysaccharides. That is for example the case of microwave hydrodiffusion and gravity (MHG) [1]. This technique was developed to extract essential oil and resulted in being an interesting dehydration technique. It allows the internal water trapped in the cells to diffuse outside the biomass and also causes cell wall disruption [2].

In this work, the drying of chestnuts burs, Ulva sp. green algae and Camellia japonica flowers by MHG was studied as a pretreatment to enhance the extraction of bioactive compounds and polysaccharides. Specifically, conventional oven drying of chestnut burs was compared to MHG drying, and the influence of each technique on the ethanolic extraction of phenolic compounds was assessed using spectrophotometric protocols. The impact of (MHG) as a drying technique was investigated in relation to the extractability of sulfated polysaccharides from Ulva sp. using sequential microwave hydrothermal extraction. Polysaccharides were precipitated using ethanol and quantified gravimetrically. The findings were compared with those obtained from samples subjected to conventional drying, providing insights into how different drying techniques influence the efficiency of polysaccharide extraction and overall biomass processing. In the case of Camellia japonica flowers, MHG will be used as a pretreatment to enhance the release of phenolic compounds after an ethanolic extraction.

Regarding the chestnut burs, in addition to reducing the drying time from around 10 hours to 5 min, extracts from MHG drying showed a higher total phenolic content and similar Trolox Equivalent Antioxidant Capacity. No significant differences were observed for the extraction of proteins. The proposed (MHG) technique demonstrated a significant enhancement in ulvan extractability, yielding 26.83% compared to 17.24% obtained via traditional drying methods. MHG has proven to be an effective pretreatment strategy, facilitating the disruption of the cell wall matrix and enhancing the release of ulvan. The increased efficiency is likely due to the rapid heating and irradiation power during the MHG process, which effectively breaks down the algal cell wall, increasing matrix permeability and making ulvan more accessible for extraction, leading to improved yields. MHG drying also significantly enhanced the extractability of phenolic compounds of the flowers as well as the drying time, compared to the use of a conventional oven.

Table 1. Comparative of the extraction of phenolics and polysaccharides after oven or MHG drying

Material	Target compounds	Oven	MHG
***Castanea sativa* burs**	Folin (g/100 g extract)	20.01 ± 0.08	22.01 ± 0.31
***Camellia japonica* flowers**	Folin (mg/g dry flower)	0.10	0.28 ± 0.11
Ulva sp.	Ulvan yield (%)	17.24 ± 0.15	26.83 ± 2.3

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Extraction of pectin from inner orange peel with aqueous solutions of different biobased organic acids

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Pectin is a natural polysaccharide very valued in the food, pharmaceutical, and cosmetic sectors for its gelling, thickening, and stabilising properties [1]. An attractive source of pectin is the inner part of citrus fruit peels, which constitute a relevant fraction of the copious organic waste generated in the processing industries for production of juices, jams, etc. [2]. The benchmark technology uses strong mineral acids for the extraction of pectin from this resource, but potentially more sustainable alternatives are being explored through the utilisation of biobased organic acids in aqueous solution as extracting agents. The extraction yield and the molecular and functional characteristics of the obtained pectin can be significantly affected by the specific acid used [3,4]. From this perspective, this study has investigated the aqueous solutions of three biobased acids, namely malic, tartaric, and pyruvic acid, for the extraction of pectin from the inner peel of an archetypal citrus fruit: orange.

With an acid concentration of 15 g/L, a temperature of 100 °C, and a liquid-to-solid ratio of 40 (v/w) set for all the 60-min extraction experiments, two different particle size ranges of the raw solid material were explored, since this factor also has an important influence in the extraction process. The results showed that, as expected, the smaller particle size (0.125-0.250 mm) leads to a higher extraction yield, compared to the larger particle size (0.250-0.500 mm). Among the acids tested, pyruvic acid consistently produced the highest pectin yield. This performance may be attributed to the stronger chelating properties of pyruvic acid. Malic acid led to the lowest yields, while tartaric acid produced pectin with superior gelling and viscosity properties, as assessed by a rheological characterisation of aqueous solutions of the obtained pectin. This aspect can render tartaric acid solutions as promising candidates for the extraction of pectin destined to industrial applications requiring specific textural attributes.

To sum up, the judicious choice of acid and optimised particle size can significantly enhance the quality and/or quantity of pectin extracted from citrus waste, promoting a more sustainable and economically viable approach for the valorisation of this waste. The findings in the present work represent a contribution towards the design of tailored pectin products for diverse industrial applications and with improved sustainability credentials.

Acknowledgements
This work was supported by *Ministerio de Ciencia e Innovación, Proyectos Estratégicos Orientados a la Transición Ecológica y a la Transición Digital* (project TED2021-131784B-I00), co-funded by the European Regional Development Fund, NextGenerationEU.

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Sequential extraction of biosurfactants from corn steep water combining liquid-liquid extraction and dialysis process: A comparative study

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Corn steep water (CSW), a byproduct of the corn wet-milling industry, is a valuable source of economically viable biocompounds, including organic acids and biosurfactants (BS). These compounds are naturally produced by the bacteria present in CSW, avoiding the need of additional production costs. However, the extraction of many of these beneficial compounds remains a challenge for cost-effective and large-scale applications [1]. Previous studies have successfully developed extraction processes based on organic solvent extractions (OSE) and dialysis (D) to obtain different BS extracts from CSW [2,3]. Therefore, the aim of this work is to compare BS extracts obtained by closed dialysis system, at lab-scale (D_{lab}) and pilot-scale (D_{pilot}), with a new BS extract obtained from the sequential combination of organic solvent extraction and dialysis at lab-scale process (OSE+D_{lab}). CSW was provided by FeedStimulants company (Lot No. CSL-0003-1217), diluted up to 50 g/L and centrifuged for solids removal (5000 rpm, 30 min, 4ºC). Then, the first new BS extract was obtained by subjecting the centrifuged CSW aqueous phase to a liquid-liquid extraction with ethyl acetate following the patent ES 2 862 624 B1 [2]. Once this biosurfactant extraction was completed, the CSW aqueous phase was recovered and subjected to a lab-scale dialysis process with 6-8 kDa cellulose dialysis membranes at 4ºC for 48 hours, following the patent ES 2 931 088 B2 [3]. For comparative purposes, without previous liquid-liquid extraction step, the centrifuged CSW aqueous phase was subjected to a pilot-scale dialysis process using Diffusion Dialysis unit (Model AP-L05) equipped with 8 regenerated cellulose membrane sheets (6-8 kDa), with a total surface area of 929 cm². After both protocols, samples were freeze-dried and taken for surfactant analysis (see **Table 1**). Surface tension (ST) results showed the OSE process does not affected the surface tension activity of the BS extract, which maintained a minimum ST around 55 mN/m, slightly higher than D_{lab} value (53.3 mN/m). Moreover, the comparison of %N and %C content in the BS extract after D_{lab} with the new BS extract obtained after OSE+D_{lab} process, showed a slight decrease in %N and %C levels. Based on the results obtained in this study, it is concluded that the OSE and D_{pilot} processes scarcely affect the BS extract, as its properties were not significantly altered.

Table 1. Characteristics of biosurfactant extracts obtained after the different processes studied.

Process	D_{lab}	OSE+D_{lab}	D_{pilot}
Minimum ST (mN/m)	53.3	54.7	55.0
N (%)	8.3	7.4	6.8
C (%)	35.2	30.9	34.7

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This study was supported by the Xunta de Galicia under the project ED431F 2023/17. Also, X. Vecino and A. Martínez acknowledge the grant RYC2021-030966-I (MICINN) and the Uvigo pre-doctoral fellow, respectively.

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Renewable Energy Sources: Battery Storage Systems for a Sustainable Future

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Abstract

The increasing global demand for clean and sustainable energy has driven the widespread adoption of Renewable Energy Sources (RES) systems such as solar and wind power [1]. However, the intermittent nature of these energy sources presents challenges for maintaining grid stability and ensuring a reliable energy supply. To address these challenges, Battery Storage Systems (BSS) are being integrated with RES systems to store in the form of chemical energy generated during peak production periods and release it during low generation [2-4]. This study explores the critical role of BSS in complementing RES systems and improving grid resilience. The research investigates different types of BSS, including lithium-ion, lead-acid, and flow batteries, focusing on their energy density, efficiency, lifespan, and cost performance. It also assesses the environmental impact of each system, considering factors such as recyclability and greenhouse gas emissions. By comparing various BSS technologies, the study aims to identify their strengths and limitations in mitigating the intermittency of RES technologies.

The research highlights the broader environmental benefits of BSS integration, such as reducing reliance on fossil fuels and minimizing carbon emissions. The results demonstrate how BSS can smooth out fluctuations in energy supply, reduce energy noise, and ensure a more reliable and consistent power output. This contributes not only to grid stability but also to the long-term sustainability of energy systems. The integration of RES systems with advanced BSS technologies is necessary for achieving a reliable, efficient, and sustainable energy future. The study underscores the importance of adopting energy storage solutions to enhance the viability of renewable energy and reduce the environmental impact of electricity generation.

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Synthesis and purification of ethyl lactate (EL) using a sustainable process

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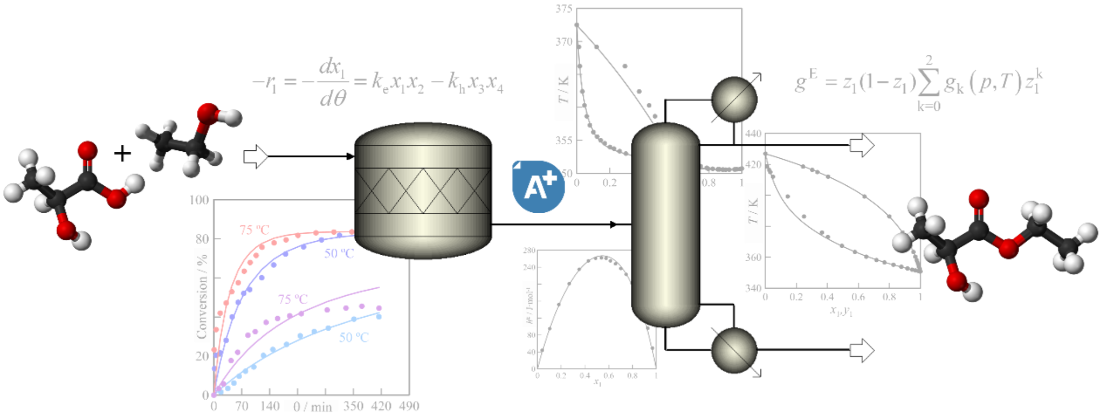
Ethyl lactate (**EL**) is a bio-solvent that is employed in various industrial sectors [1], exhibiting a comparable level of efficiency to other conventional solvents. The usual synthesis route for its production entails the esterification of lactic acid with ethanol, both renewable raw materials [1]. Nevertheless, this approach requires the use of homogeneous acid catalysts, such as H_2SO_4 or H_3PO_4, operating under elevated temperatures, which can potentially cause corrosion problems in the equipment and generate waste in the stages of ester purification and catalyst recovery. One of the challenges in the production of **EL** is posed by the reaction when the heterogeneous catalysts are employed, which are less environmentally aggressive and equally efficient. For the research carried out, a bibliographic repository was previously elaborated, the address of which will be presented in the final version of the work.

To achieve a more sustainable production of **LE**, the synthesis and purification of **LE** using Amberlite-15 resin were investigated. The esterification reaction was conducted in the absence of a solvent within a batch-reactor, utilizing the aforementioned catalyst. The kinetics was performed at two temperatures and atmospheric pressure, considering two other variables: a ratio of $x_{0,\text{alcohol}}/x_{0,\text{ácido}}=1$ and $x_{0,\text{alcohol}}/x_{0,\text{ácido}}=1.8$, checking that the reaction is faster, with a conversion closer to 80 %, when the second ratio is used at 75 ºC. To develop the purification stage, the vapor-liquid equilibria (VLE) at atmospheric pressure of the binaries ethanol+ethyl lactate and ethanol+water were measured. The remaining required information on VLE was estimated using the UNIFAC-DM approach [2]. The thermodynamic study was completed with the experimental determination of the volumetric (v^E) and energetic (h^E) mixing properties of the two aforementioned systems. The kinetic data were correlated using a reversible second-order rate law, while the properties, v^E, h^E and VLE, were correlated with a semi-empirical model widely used by us. The obtained information was utilized to simulate the **EL** production process with the commercial simulator Aspen Plus© to evaluate the technical feasibility of the proposed production route. The results showed that the purification of **LE** according to the proposal route is feasible, resulting a purity of 98% (w/w) of the **LE** and a recovery of 87% (w/w). Consequently, the authors conclude that this work represents a valuable contribution to the advancement of this particular process, extensible to other cases of ester production.



Acknowledgments

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Simulated Moving Bed Reactor for 1,1-Diethoxybutane Synthesis

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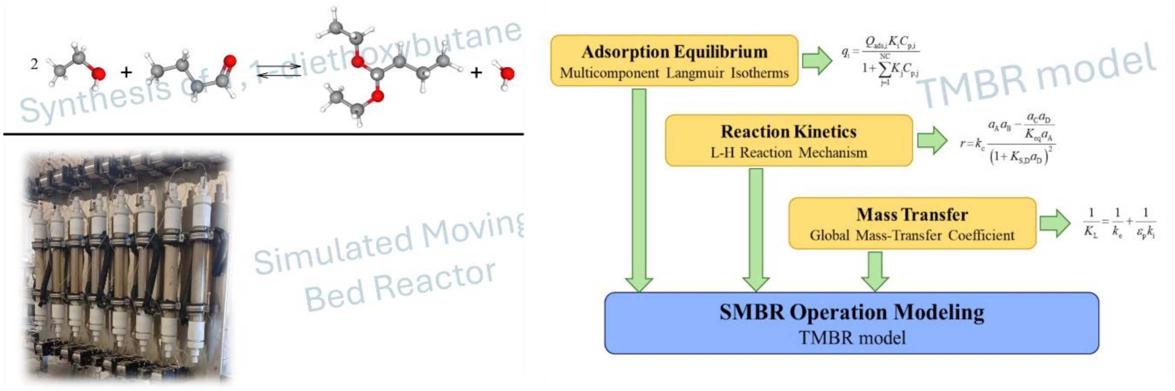
Acetals are obtained in the reaction of an alcohol with the corresponding aldehyde in an acidic medium, a process usually referred as acetalization. Its use is directed towards various applications, hence its interest in various sectors of the chemical industry, including mainly the petrochemical and food industries [1]. The traditional acetalization method has numerous problems, such as: low conversion of reagents, the possible appearance of secondary reactions, difficulty in recovering the catalyst, generation of environmental problems due to the difficulty in separating the final unreacted substances, etc. Some of the problems mentioned, especially the use of the acid catalyst, can be solved by proposing alternative synthesis processes. That is, the replacement of the catalyst is one of the first actions that must be considered. An example is the use of acidic carbon [2], to avoid the use of H_2SO_4, other more usual cases are the use of resins or enzymes as catalyst. In these cases, the reaction occurs with certain improvements in its development. On the other hand, the improvement of advanced experimental systems that integrate the separation of the reactor and the product in a single unit is also of interest. In this sense, one of these new technologies is the Simulated Moving Bed Reactor (SMBR) that uses heterogeneous catalysts. The SMBR simulates a countercurrent flow of the liquid and solid phases by dividing the solid phase into a series of fixed bed columns and periodically changing the position of the inlet and outlet streams by controlling a set of valves. This change of position in the same direction as the liquid phase simulates the movement of the solid phase in the opposite direction [3].

SMBR technology was used to synthesize 1,1-diethoxybutane (DEB), from ethanol and butyraldehide in columns packed with Amberlyst®15. Modeling was performed with the True Moving Bed Reactor (TMBR) version of the combined TMB-SMB model to represent the reaction/separation process and to select the best experimental conditions for the process. Two different operating modes were tested: run I, with incomplete resin regeneration, and run II, with incomplete desorbent cleaning. The best conversion obtained was 94 % for run II but with low refining purity, ≈ 66%. However, the best refining productivity was 3.7 $\mathrm{kgL^{-1}day^{-1}}$ for run I, with a conversion close to 88 %. These results show that the SMBR unit is competitive and efficient for the synthesis of 1,1-diethoxybutane and that the process used can be extended to other acetals. In addition, the kinetic study suggests that the performance of the operation can still be improved by modifying the conditions established for run I and run II.



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Industrial By-Products for Biogas Production

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Abstract

The global energy demand has significantly increased in recent years due to population growth, rapid urbanization, and socio-economic advancements. [1,2] With approximately 80% of the global energy supply produced from fossil sources [3], there is an urgent need for sustainable alternatives to address energy security and environmental concerns [1]. Industrial by-products present a valuable opportunity for biogas production. This study aims to review the background and state-of-the-art technologies in utilizing industrial by-products for biogas production, contributing to a more sustainable and circular economy.

This review begins with an overview of the types of industrial by-products commonly used in biogas production, such as agricultural residues, food waste, and sludge from wastewater treatment plants. It then explores the biochemical processes involved in converting these by-products into biogas, emphasizing the role of anaerobic digestion and the factors influencing its efficiency. The review also delves into recent advancements in biogas production technologies, including pre-treatment methods, co-digestion strategies, and innovations in bioreactor design, which have significantly improved the yield and quality of biogas, making the process more economically viable and environmentally friendly.

In conclusion, this review underscores the importance of industrial by-products as a sustainable resource for biogas production. It also identifies key challenges and future research directions to enhance the efficiency and scalability of biogas production from industrial by-products, contributing to the global transition towards renewable energy. The findings of this research are expected to provide valuable insights into the potential of biogas production from industrial by-products and inform policy decisions related to renewable energy and waste management.

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NANOQUÍMICA Y NANOTECNOLOGÍA

Digital Image Colorimetry Smartphone Determination of ZnO NPs

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ZnO NPs have been widely used in cosmetics, medicine, electronics, rubber and other industries due to their large surface area and the redox capacity of Zn^{2+} ions. However, recent studies reported that the presence of ZnO NPs in the natural environment can pose a threat to some algae, plants, microorganisms, invertebrates, vertebrates, and even humans [1,2]. Therefore, the development and improvement of methods for the detection of ZnO NPs is a growing field of study.

Here we report the use of a smartphone colour recognition app to study the response of a chemosensor-modified cellulose paper to the concentration of ZnO NPs. We used a dansyl-based fluorescent probe (λ_{em} = 530 nm under λ_{ex} = 340 nm), which displays an N,N,O donor set as well as a sulphonamide group suitable to bind the Zn^{2+} ions present on the NPs surface (Figure 1). We record the continuous colour change of the chemosensor-modified cellulose paper from light green to bluish green under 340 nm ultraviolet light, when the ZnO NPs concentration increases from 0.0 to 0.4 ppm. This has allowed us to determine ZnO NPs, without the need to use a spectrofluorometer.

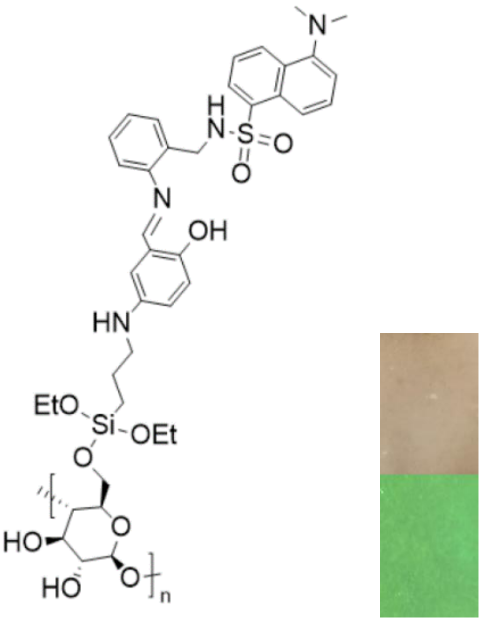

Fig.1. Left: Schematic representation of the chemosensor-modified cellulose paper. Right: Paper colour under both natural light (top) and UV light of wavelength 254 nm (bottom)

Acknowledgments

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Detection of CuO NPs in ethanol-water solution using a fluorescent probe

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Due to the widespread use of CuO nanoparticles in fields as diverse as biomedicine, industrial catalysis, gas detection or electronics, the risk of human exposure is nowadays increasing, which could lead to short- or long-term toxicity. In vitro and in vivo studies have shown that CuO NPs cause oxidative stress, cytotoxicity, genotoxicity, immunotoxicity, neurotoxicity and inflammation in bacteria, algae, fish, rodents and human cell lines[1,2]. Therefore, it is imperative to advance the detection of CuO NPs using rapid, simple and highly sensitive techniques, characteristics for which fluorescent probes stand out.

In this work, the use of a fluorescent probe carrying a dansyl group and a binding domain arranged to bind to the Cu^{2+} ions of the NPs was studied. Figure 1 shows the emission band of the probe at a wavelength of 530 nm when excited with UV light (l_{ex} = 340 nm). The binding of the probe to the Cu^{2+} ions results in a linear decrease of the emission intensity with increasing concentration of the CuO NPs. This information, transferred to a calibration line, allows the quantification of CuO NPs with good sensitivity and linearity.

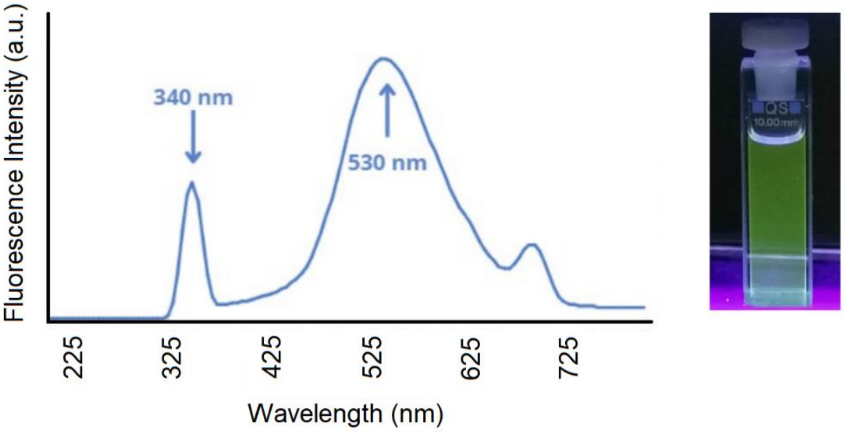

Figure 1. Left: Fluorescence spectrum of the probe. Right: Emission of the probe with l_{ex} = 254 nm.

Acknowledgments

We would like to thank the Ministerio de Ciencia, Innovación y Universidades of Spain (FOODNANORISK, reference PID2021-125276NB-I00), and Xunta de Galicia (Grupo de Referencia Competitiva, reference ED431C 2022/029).

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Does quercetin protect intestinal cells from silver nanoparticle-induced pro-inflammatory effects?

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Silver nanoparticles (AgNP) have become one of the most widely used nanomaterials across a variety of applications. Their use in the food industry has been particularly prevalent due to their antimicrobial properties, helping to ensure product quality and safety. However, the increased use of AgNP has led to inevitable exposure, especially via the oral route, making the intestine susceptible to their potential adverse effects. Several reports in the literature describe the general pro-inflammatory effects of AgNP [1].

This study aimed to investigate two key aspects: first, the in vitro pro-inflammatory effects of 5 nm and 50 nm AgNP coated with polyvinylpyrrolidone (PVP) on an intestinal epithelial cell line (C2BBe1), and second, the potential protective effects of quercetin, a flavonoid known for its antioxidant and anti-inflammatory properties.

Our findings demonstrated that exposure to both sizes of PVP-AgNP resulted in cellular damage, as observed through transmission electron microscopy (TEM). Moreover, PVP-AgNP caused a significant reduction in cellular metabolic activity, as determined by the MTT assay. Additionally, exposure to both sizes of AgNP led to increased expression of inducible nitric oxide synthase (iNOS) and elevated nitric oxide levels ($^{\bullet}$NO), which was detected indirectly using the Griess reaction. Notably, quercetin effectively mitigated these harmful effects.

In conclusion, this in vitro study suggests that quercetin can protect intestinal cells from the deleterious effects induced by AgNP, highlighting its potential as a protective agent for intestinal health in the context of AgNP exposure.

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Synthesis and characterization of ZnO nanostructures using olive leaf extract for prospective application in food packaging

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Nanomaterials (NM), particularly ZnO NM, have shown great potential in food packaging due to their strong stability, effectiveness against UV light and cost efficiency. Moreover, they are widely recognized as antimicrobial agents and are among the most commonly used nanofillers in the food packaging sector [1]. Olive leaf extract (OLE), a valuable by-product of the olive oil industry, contains powerful antioxidant and antimicrobial compounds, making its combination with ZnO NM a promising solution for active food packaging [2].

In this study, ZnO and ZnO+OLE NM were (bio)synthesized using two distinct sol-gel methodologies, each tailored to produce flower- and sheet-shaped particles [3]. In addition, for the latter, two syntheses were carried out with different ultrasound frequencies to investigate the impact on NM properties. The ZnO NM, ZnO+OLE NM and OLE were characterized by a wide range of techniques, including SEM-EDS, XRD, FTIR, nitrogen adsorption-desorption isotherms, DSC, GC-MS and HPLC.

The ZnO and ZnO+OLE NM were successfully synthesized, resulting in particles with the expected morphologies, as confirmed by SEM images. EDS analysis confirmed the purity of the ZnO NM while XRD analysis validated their crystalline structure. FTIR spectra of the ZnO and ZnO+OLE NM showed the characteristic Zn-O stretching band. A comparison of the spectra from OLE and ZnO+OLE NM confirmed the presence of the extract in the particles. Nitrogen adsorption-desorption isotherms revealed that increasing ultrasound frequency during the synthesis of flower-shaped particles promoted a significant increase in the specific surface area. DSC analysis indicated that OLE was not thermally degraded during the synthesis, as the degradation temperature of 218.5ºC was not reached. The volatile compounds identified from OLE by GC-MS included ketones, phenols, aromatic esters, terpenes and furan derivatives, as expected. The quantification (HPLC) of oleuropein in OLE, the main compound responsible for the antioxidant and antimicrobial properties, showed a content of 11.47%, which is close to the 15% value provided by the supplier.

Based on the properties of the synthesized particles, incorporating ZnO+OLE NM into food packaging films offers a promising approach to enhancing their functionality, including protection against pathogens and preservation of organoleptic properties, thus extending food quality and shelf life [1].

Acknowledgments
This work is financed by national funds from FCT - Fundação para a Ciência e a Tecnologia, I.P., in the scope of the project UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences (UCIBIO), the project LA/P/0140/2020 of the Associate Laboratory Institute for Health and Bioeconomy (i4HB), the project UIDB/50006/2020 of the Associate Laboratory for Green Chemistry (LAQV/REQUIMTE) and the project UIDB/50016/2020 of the Centre for Biotechnology and Fine Chemistry/Catholic University of Portugal (CBQF/UCP). FCT/MCTES is also acknowledged for funding through the Individual Call to Scientific Employment Stimulus with the reference 2022.02651.CEECIND/CP1724/CT0011 (C.M.G.) and the PhD grant with the reference 2023.04416.BD (S.P.).

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Engineered bioactive casein micelles for hypertension treatment

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Hypertension, a major risk factor for cardiovascular disease, remains one of the leading causes of death and disability worldwide. Cardiovascular diseases, including heart attacks, strokes, and other circulatory conditions, account for a significant burden on global health systems. In recent years, there has been a growing interest in natural compounds, particularly polyphenols, for their potential role in managing hypertension. Among these, epigallocatechin-3-gallate (EGCG), a prominent polyphenol found in green tea, has garnered attention for its ability to regulate blood pressure. However, despite its promising biological properties, EGCG is highly susceptible to degradation and exhibits poor bioavailability, limiting its therapeutic effectiveness.

To address these challenges, the objective of this study was to develop a nutraceutical capable of regulating blood pressure by encapsulating EGCG in casein nanoparticles (CNPs), which could improve its stability and controlled release. Casein, a milk-derived protein, was isolated from raw bovine milk using isoelectric precipitation. Following extraction, the EGCG was encapsulated by resuspending the casein in EGCG solutions, forming CNPs designed to enhance EGCG's bioavailability.

The formulated nanoparticles were characterized for their size, morphology, and encapsulation efficiency. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) analyses revealed that the mean particle size of the CNPs was (216 ± 4) nm. Encapsulation efficiency, assessed using UV-Vis spectroscopy, was found to be approximately (99 ± 2)%. Notably, these properties remained stable over a 3-week storage period, indicating that the CNPs provided a durable and efficient encapsulation platform for EGCG.

Additionally, the release profile of EGCG from the CNPs was studied at 37 ºC, mimicking physiological conditions. Results indicated that the CNPs facilitated a controlled and sustained release of EGCG, which is advantageous for maintaining consistent therapeutic levels of the compound over time.

To evaluate the potential antihypertensive effects of the CNPs, two key assays were performed: the ABTS radical scavenging assay to measure antioxidant activity, and the inhibition of angiotensin-II (Ang II) converting enzyme (ACE) to assess their ability to interfere with a critical pathway in blood pressure regulation. The results demonstrated that encapsulating EGCG in CNPs significantly enhanced its antioxidant capacity, contributing to a reduction in oxidative stress—a key factor in the development of hypertension. Moreover, the CNPs themselves exhibited the ability to inhibit ACE, suggesting that both EGCG and the CNPs had complementary mechanisms in promoting blood pressure regulation.

HUVEC were used to assess the effectiveness of CNPs in ROS inhibition, once it is possible to gain valuable insights in contexts directly associated with hypertension, given the role of these cells in the regulation of vascular function. Thus, the capacity of the formulations to inhibit the oxidative damage induced by Ang II was also analysed, and demonstrate significant effectiveness in countering the oxidative impact.

The developed CNP-EGCG formulations show great promise as a nutraceutical for hypertension management. By enhancing the stability, bioavailability, and sustained release of EGCG, and by providing inherent antioxidant and ACE-inhibiting properties, CNPs represent an innovative approach to potencially improve the therapeutic potential of polyphenols for cardiovascular health..

Funding
This work received financial support from FCT and Ministério da Ciência, Tecnologia e Ensino Superior through the project PTDC/BAA-AGR/4923/2021 'NanoProMilk'.

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Sustainable nanomaterials from biomass: potential for scale-up and commercialization in the near future

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The growing demand for sustainable materials but with high added performance, has led to the search for alternative strategies through the combination of two concepts: the use of sustainable biomass as raw materials and the obtaining of micro/nanomaterials improving sustainability. Nanotechnology has then emerged as a crucial field in science and engineering, offering innovative solutions in several disciplines.

Micro and nanocellulose are advanced materials derived from cellulose, the most abundant organic polymer on Earth, which can be easily obtained on a micro/nanometric scale through physical, chemical and/or enzymatic processes. These materials are characterized by their micro/nanoscale dimensions, high strength-to-weight ratio, and unique properties such as sustainability, lightweight strength, barrier properties, biocompatibility and biodegradability. These properties make them ideal candidates for use in multiple fields such as medicine, pickering emulsifiers, wood adhesives, adsorption, environmental remediation, filtration, papermaking, oil and gas drilling, energy materials, sensors, and biosensors [1].

However, its scaling up for commercial applications faces several challenges such as i) resource and energy intensive processes that require the optimization of the conversion processes into micro/nanocellulose; ii) associated production cost; iii) homogeneity of physical and chemical properties; iv) drying to avoid the cost associated with the transport of high amount of liquid; v) market opening to potential commercial applications; vi) lack of regulations on nanomaterials.

NANOCEL TECHNOLOGY, through the NACELUP project, has explored the potential for scaling up the production of nanomaterials from renewable biomass sources, highlighting advances in extraction and processing technologies. The economic and ecological benefits of biomass use have been considered, highlighting its role in fostering circular economies and reducing environmental impact. The challenges and opportunities of the transition from laboratory-scale production to industrial-scale production, with special emphasis on achieving process economy, as well as an environmentally sustainable process with high quality and reproducible products, have been considered.

Fig.1. Change of scale for the production of nanomaterials: form 6L/h to 100 L/h.

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QUÍMICA DE POLÍMEROS

Viscosidad intrínseca y peso molecular viscosimétrico medio de diferentes quitosanos

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El quitosano es un biopolímero procedente de la quitina con usos crecientes en los sectores químicos, agrícolas y médicos. La quitina está formada por monómeros de N-acetil-D-glucosamina que después de un proceso desacetilización se convierte en quitosano. En diversas aplicaciones el tamaño molecular del quitosano es clave para las características funcionales. Un método para la determinación del tamaño de un polímero es a través de la viscosidad intrínseca ($[\eta]$, dL·g^{-1}) que se evalúa en régimen de concentración diluido. Así, se puede asumir que no existen interacciones entre moléculas, por lo que la viscosidad intrínseca mide el volumen hidrodinámico del polímero [1]. La viscosidad intrínseca se puede obtener a través de las ecuaciones de Huggins (1) y Kraemer (2) o de Fedors (3) [2]:

$$\frac{\eta_{es}}{C} = [\eta] + k' [\eta]^2\, C \qquad (1) \qquad \frac{\ln \eta_r}{C} = [\eta] + k'' [\eta]^2\, C \qquad (2) \qquad \frac{1}{2(\eta_r^{0,5} - 1)} = \frac{1}{C[\eta]} - \frac{1}{C_{max}[\eta]} \qquad (3)$$

donde $\eta_{es} = \frac{\eta - \eta_s}{\eta_s}$ es la viscosidad específica, $\eta_r = \frac{\eta}{\eta_s}$ la viscosidad relativa, con η la viscosidad de la disolución con una concentración de polímero C (g dL^{-1}), ηs la viscosidad del disolvente, k' y k'' las constantes de Huggins y Kraemer y C_{max} la concentración teórica en la que se considera que las interacciones son significativas. La viscosidad se determinó a 25ºC en un viscosímetro capilar automático tipo Ubbelohde (Schott). La ecuación de Mark-Houwink-Sakurada (4) relaciona el peso molecular viscosimétrico de polímeros, M_v (kDa), con la viscosidad intrínseca:

$$[\eta] = K\, M_v^{\alpha} \qquad (4)$$

donde K y α son constantes de cada polímero-disolvente y que, para el quitosano-disolvente empleado, tienen valores de 0,076 mL g^{-1} y 0,76, respectivamente [3].

Se caracterizaron 2 quitosanos comerciales (Sigma) de medio (MPM) y bajo (BPM) peso molecular y 4 aislados de cefalópodos (3 de *Illex* y 1 de *Loligo*) [4]. Los quitosanos se disolvieron en tampón acetato (pH 4,5; 0,3 M CH_3COOH/0,2 M CH_3COONa) en un rango de concentraciones de 0,025 a 1,000 g L^{-1} después de eliminar la humedad de las muestras por secado a vacío (10 kPa y 70ºC) hasta equilibrio. La evaluación de la viscosidad intrínseca y el peso molecular viscosimétrico medio a través de los modelos de Huggins-Kraemer y de Fedors arrojó una excelente concordancia para cada uno de los quitosanos evaluados. Los rangos de la $[\eta]$ y M_v variaron en amplios rangos, entre 3,79 y 15,4 dL g^{-1} y 73,1 y 466,4 kDa, respectivamente. Se obtuvieron 4 grupos de quitosanos según diferencias significativas ($P < 0,05$), estando conformados el primero por el *Illex* BPM, el segundo por el *Loligo* y el Sigma BPM, el tercero por el *Illex* APM y el Sigma MPM y, por último, el cuarto por el *Illex* MPM. Los resultados muestran la concordancia entre los modelos de Huggings y Kraemer y de Fedor para la estimación de tamaños moleculares de polímeros.

Tabla. Viscosidad intrínseca y peso molecular viscosimétrico medio de quitosanos

	Huggins-Kraemer		**Fedors**	
Quitosano	**$[\eta]$, dL·g^{-1}**	**M_v (kDa)**	**$[\eta]$, dL·g^{-1}**	**M_v (kDa)**
Sigma MPM	11,1±0,5^{c}	300,4±18,3^{c}	11,1±0,7^{c}	302,9±24,6^{c}
Sigma BPM	7,52±0,71^{b}	180,1±22,5^{b}	7,52±0,94^{b}	180,8±26,1^{b}
Illex APM	11,5±0,3^{c}	314,4±11,9^{c}	11,5±0,1^{c}	314,9±3,3^{c}
Illex MPM	15,4±0,4^{d}	462,7±15,8^{d}	15,4±0,4^{d}	466,4±17,4^{d}
Illex BPM	3,79±0,37^{a}	73,3±9,4^{a}	3,79±0,26^{a}	73,1±6,9^{a}
Loligo	7,69±0,31^{b}	186,3±9,9^{b}	7,69±0,17^{b}	186,1±16,1^{b}

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Empleo de sarmientos procedentes de la poda de vid para la fabricación de pasta de papel y cartón, VINEBOX

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La incorporación de sarmientos de vid en el proceso de producción de pasta de celulosa se presenta como una aplicación novedosa y alineada con la estrategia de ENCE al incorporar una materia fibrosa y sostenible en un producto diferenciado, celulosa Naturcell, con menor huella hídrica y de carbono, que refleja un compromiso con la sostenibilidad, la economía circular y la excelencia en calidad.

La definición de las condiciones del proceso de producción de pasta de celulosa que permitan la incorporación de los sarmientos en el proceso productivo debe alcanzar una calidad óptima para emplearse en dicha industria (escala laboratorio y piloto), poniendo el foco en los parámetros clave de la industria papelera (Factor H, tiempo procesos, nº KAPPA alcanzado, etc.) y en la definición de las formulaciones de papel (grado de refinado, encolado, agentes de retención, cargas minerales, etc) para la fabricación exitosa de prototipos de bobinas de papel que a su vez sirvan para la producción de etiquetas y cajas de cartón.

Aunque existen investigaciones que han abordado la problemática generada por los residuos de la poda de la vid [1], este logro supone la obtención de dos productos de utilidad para la propia industria vitivinícola, suponiendo un claro ejemplo de economía circular, donde los residuos generados en el viñedo se terminan convirtiendo en materias primas para nuevos productos.

En concreto, las innovaciones tecnológicas de este proceso abarcan la obtención de pasta de celulosa, cartón y etiquetas a partir de una materia prima considerada un residuo y no utilizada previamente para estos fines, donde se optimizan los procesos de extracción de celulosa que se utilizan posteriormente para la producción de papel y cartón y además, se estudia como la composición inicial de los sarmientos y el proceso de extracción afectan a la calidad de los papeles obtenidos con el fin de seleccionar aquellos procesos que supongan una mejora económica (reducción de costes de procesado) o tecnológica (mejora de las propiedades de materiales finales).

Al considerar esta materia prima para la producción de papel y cartón, permite reducir los problemas de gestión de residuos de la poda de la vid mediante una valorización en cascada, cumpliendo con la nueva Ley 7/2022 de residuos y suelos contaminados para una Economía Circular, que no permite la quema de residuos vegetales generados en el entorno agrario. Por tanto, esta investigación original y novedosa permite la obtención de fibras lignocelulósicas de papel para la producción de papel y cartón para envases de botellas vino y fabricación de etiquetas [2].

Agradecimientos
El proyecto VINEBOX (jun 2022-nov 2024) está cofinanciado por la Unión Europea y por el Centro para el Desarrollo Tecnológico y la Innovación (CDTI) con fondos FEDER. Consorcio liderado por Bodega Matarromera S.L. junto con Pago de Carraovejas y ENCE y que cuenta con la colaboración de IATA-CSIC, ITENE y Papelera de Brandia entre otros..

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Gelatine-alginate hydrogels: evaluation of swelling and 3D-printability targeting wound healing applications

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Hydrogels are three-dimensional networks characterised by a high-water retention capacity and permeability to hydrophilic substances. These materials typically comprise hydrophilic polymer chains and hold chemical or physical crosslinking [1]. This study aimed to develop and characterise gelatine-alginate hydrogels prepared using different concentrations (gelatine: 2, 4 and 5%; alginate: 2.5, 4 and 5%), selected for their biocompatible and biomimetic properties, which are helpful for wound healing applications. After preliminary 3D printing tests, the most promising samples prepared without crosslinking were used to study the effects of two combined crosslinking agents (transglutaminase (TGase) at different concentrations followed by calcium chloride ($CaCl_2$) at a fixed concentration). The objectives were to improve the mechanical properties upon swelling and to allow 3D printing targeting wound healing prototyping.

The samples that demonstrated the best printability without crosslinking were ALG2.5GEL4 and ALG4GEL4, maintaining structural integrity with minimal deformation, as shown in Fig. 1. To analyse the influence of TGase, different concentrations (10%, 20%, 30%, and 40%, relative to the gelatine mass) were tested, followed by crosslinked in a 0.2M $CaCl_2$ solution. The sample using 10% TGase showed the best printability results. Swelling analysis of the lyophilised hydrogels was performed in phosphate-buffered saline (PBS) (pH 7.4) and a phthalate buffer (pH 5), revealing that the ALG2.5GEL4 sample exhibited a higher degree of swelling in both pH media compared to ALG4GEL4. Additionally, TGase-induced chemical crosslinking reduced the swelling capacity of both hydrogels in the two evaluated media, as shown in Fig. 2.

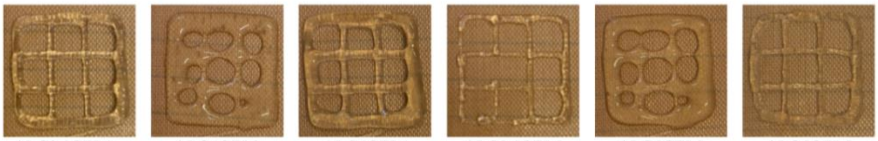
ALG2.5GEL4 ALG4GEL2 ALG4GEL4 ALG2.5GEL5 ALG5GEL2 ALG5GEL5

Fig.1. Hydrogel 3D printing tests of gelatine-alginate samples without crosslinking.

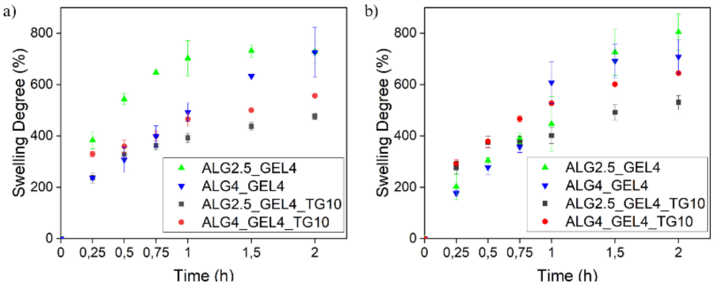

Fig.2. Swelling degree of ALG2.5GEL4 and ALG4GEL4 in PBS solution (a), in phthalate buffer solution (b).

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Recent advances in biodegradable polymers for fishing gear manufacturing

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About 1643 tonnes of fishing gear, mainly nets and ropes are rejected into the sea through ports of Spain every year [1]. They are manufactured from polyamide and high-density polyethylene, which does not biodegrade and more than 90% get deposited in the sea bed. This has resulted in notable presence of plastics in living beings [2].

Application of biodegradable fishing gears as an alternative to replace the polymers made from petroleum products is a sustainable solution. But it is necessary to develop polymers with better durability and rate of degradation.

This work presents the biodegradable polymers which is used for the manufacture of fishing gears. It elaborates the primary raw materials, methods used for the manufacturing, and the new initiatives in the market for replacing non biodegradable fishing gears.

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POL09

Lignina kraft de ENCE para la fabricación de espumas de poliuretano y poliuretanos termoplásticos

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Dentro del proyecto DICKENS, ENCE ha buscado el desarrollo de espumas de poliuretano y de poliuretanos termoplásticos (Thermoplastic Poly-Urethanes, TPUs) a partir de polioles (como biomatrices) derivados de lignina Kraft, para su aplicación principalmente en la fabricación aditiva. La lignina posee grupos hidroxilo, tanto alifáticos como fenólicos, que son muy reactivos, lo que facilita el uso directo de la lignina como matriz para bio-composites de poliuretano (PU). Sin embargo, el uso directo de la lignina tiene sus limitaciones, principalmente debidas a la baja reactividad real que muestra. Esta baja reactividad se debe sobre todo a los impedimentos estéricos debidos a la complejidad estructural de la molécula que impide que los grupos hidroxilo estén accesibles. El método más estudiado para obtener un poliol de lignina para utilizar como matriz en bio-composites es la oxipropilación de lignina con óxido de propileno (PO) en medio básico (fig.1)[1]. Otra de las reacciones más estudiadas se basa en la oxipropilación de la lignina con oxido de propileno y algún otro polímero que consiga mejorar las propiedades del poliol de lignina final.
Sin embargo, debido a los problemas de toxicidad de los epóxidos, se hace necesario el desarrollo de métodos con reactivos oxialquilantes seguros, no- tóxicos y eco-ambientales, como los carbonatos orgánicos cíclicos (fig.2). [2]

Los TPUs sintetizados se transformaron en un filamento para impresoras 3D de modelado por deposición fundida (FDM) mediante un proceso de extrusión por fusión a 180 ~ 220°C y posteriormente se caracterizaron a través análisis reológicos (viscosidad, MFI), químicos (FTIR, GPC), térmicos (DSC, TGA y DMA) y mecánicos (dureza Shore y esfuerzo de tracción).

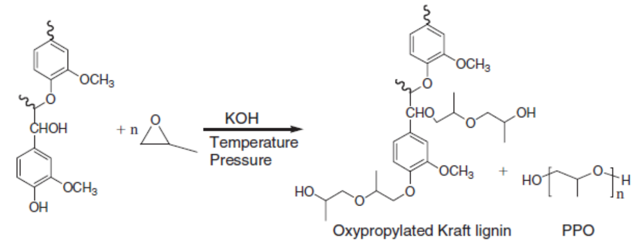

Fig.1. Esquema reacción oxipropilación

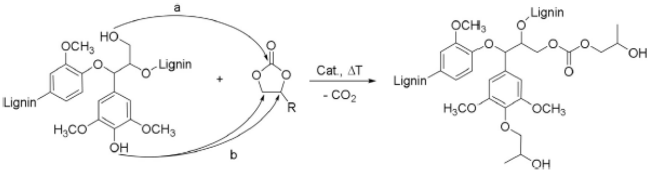

Fig.2. Oxialquilación de lignina.

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QUÍMICA ANALÍTICA

Isothiazolinones: Chemical and ecotoxicological screening

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Biocidal products have been widely used for a long time and remain among the most effective solutions for the control of unwanted organisms that are harmful to human health or that cause damage to natural or manufactured materials [1]. Due to their inherent properties, biocidal products, can pose harm to humans, and the environment and as a result, the EU has established stringent rules and procedures to minimize these risks [2].

Isothiazolinones are a group of heterocyclic sulphur-containing compounds that exhibit excellent broad-spectrum antimicrobial activity against gram-positive, gram-negative bacteria and fungus at low concentrations and over a wide range of pH. Because of their fungicidal, bactericidal, and algacidal properties, isothiazolinone-type biocides are used in many consumers (detergents, shampoos, soaps, or shower gels) and construction (paints, varnishes) products [3].

After use of these products, isothiazolinone-like compounds are released as organic pollutants directly (while using personal care products and cleaning agents or by leaking isotiazolinone-containing materials such as coatings or paints) or indirectly into aquatic ecosystems through wastewater treatment plants. Due to the side effects, they can have on aquatic organisms, it is essential to understand their fate and potential ecological risk in the aquatic environment [3].

Monitoring of chemicals in the aquatic environment by chemical analysis alone cannot completely assess and predict the effects of chemicals on aquatic species and ecosystems. The assessment of aquatic toxicity is an important component of the environmental hazard and risk assessment of all types of chemicals and is therefore included in several pieces of EU chemicals legislation.

In the present work, a preliminary evaluation of isothiazolinone-type biocides' antimicrobial and ecotoxicity activity was carried out. The results obtained will be presented in this communication.

Acknowledgements

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End-of-life plastics from vineyards. A hot spot of pesticides in the terrestrial environment

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Compared to other horticultural practices, viticulture employs a low volume of plastic material per cultivated surface. However, most of the used items are small in size, relatively unexpensive and/or difficult to recover once they lost their function due to weathering, or mechanical breakup. So far, we have reported the accumulation of different kinds of fungicides in polypropylene (PP) guard tubes and polyethylene (PE) materials collected from vineyards suffering a high pressure of fungi infections in the Northwest of Spain [1].

In this project, different kinds of plastic items were collected in two different geographic regions: Galicia (Spain) and Zurich (Switzerland), characterized by IR spectroscopy and analysed for pesticide residues (mainly fungicides) by LC-MS/MS; soil samples collected during the same sampling campaign were also analysed to obtain a comparison between the total pesticide concentrations in both matrices . In addition to PP and PE, we identified residues of aged polyvinyl chloride (PVC) polymers in soils from vineyards. Extraction of sorbed compounds from this kind of waste needs to be adapted to the composition of each polymer. Thus, while PP and PE showed a good stability in contact with polar and non-polar solvents, PVC fragments were dissolved in halogenated solvents, resulting in the formation of slurries difficult to process further.

Irrespective of the composition of the plastic waste (PP, PE and PVC), fragments collected from vineyards contained high concentrations of different pesticides, and even of some of their known environmental transformation products. Levels of pesticides prevailed not only in samples collected at the end of the production cycle of vines (autumn), but also in those wastes sampled at the end of winter in vineyards from both geographic regions. Most of the pesticides found in plastics were also present in soil; although, at lower concentrations. Depending on sampling sites, total pesticide residues in soil and plastic items ranged between 12.38-132.9 ng/g and 1760-8219 ng/g, respectively. The ratios between the sum of all pesticide concentrations in plastic and soil varied between 26 and 409. These results point out to these aged, fragmented plastic pieces as heavily pesticide polluted spots. Likely, plastic fragments contribute to an increasing stability of sorbed pesticides compared with those associated to top-soil particles. This increase stability in plastics can lead to their accumulation and subsequent, and uncontrolled release into the environment, causing unexpected damage to non-target organisms.

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Estudio de la distribución de fungicidas orgánicos en el sistema uva-suelo-vino

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Compatibilizar la sostenibilidad económica y medio ambiental de la viticultura es uno de los mayores retos que afronta este sector. En el contexto actual de cambio climático, con drásticas variaciones en las condiciones ambientales en breves espacios de tiempo, considerando además la escasa implantación de los nuevos híbridos resistentes a enfermedades en el sector vitivinícola español, el uso de fungicidas resulta crucial para controlar las pérdidas económicas derivadas de las infecciones causadas por los hongos en el viñedo. En este escenario, la selección de principios activos debe tener en cuenta, no solo su eficacia, sino también el riesgo de transferencia al producto final: vino, así como su persistencia en los suelos agrícolas.

En esta presentación se muestran los resultados obtenidos en dos experimentos de campo en los que se han aplicado dos estrategias diferentes para el control de infecciones sobre el viñedo. Cada uno de los experimentos ha considerado dos estrategias diferentes, en las que se combinaron diferentes grupos de fitosanitarios para el control de las principales enfermedades que afectan al viñedo: mildew, oidio, *black rot* y botritis. Los experimentos de campo se han llevado a cabo en parcelas experimentales situadas en las D.O. de Ribeiro y Rías Baixas, sobre variedades de uva tinta (Brancellao) y blanca (Albariño). El control de los residuos de fungicidas se ha llevado a cabo sobre tres matrices diferentes: suelos de viñedo, tomados al final de la campaña agrícola y a comienzos de la siguiente primavera; uva en vendimia; y vino. Su determinación se ha llevado a cabo mediante cromatografía líquida combinada con espectrometría de masas en tándem.

Los resultados obtenidos han permitido identificar varios patrones de comportamiento diferentes de los principios activos empleados. Por un lado, se han identificado compuestos con elevados factores de transferencia de uva a vino, poco persistentes en los suelos (ej. iprovalicarb, fenpyrazamine y fenhexamide), con vidas medias inferiores al periodo de reposo otoño-invierno del viñedo; compuestos persistentes en suelo y transferibles a vino (ej. Azoxystrobin); así como compuestos solamente estables en una de las matrices anteriores. En el caso de compuestos persistentes en suelos, se ha estudiado su distribución a dos profundidades diferentes: 0-15 cm y 15-30 cm. En este caso, para un mismo residuo se han encontrado diferentes porcentajes de penetración en las dos parcelas. Considerando que en ambos casos se trata de suelos de tipo *Franco*, se considera que la cantidad de precipitaciones y la inclinación de cada una de las parcelas pueden determinar su mayor o menor penetración en los suelos. Se han identificado además pesticidas procedentes de campañas anteriores, presentes en los suelos de las parcelas experimentales objeto de estudio. En ocasiones se trata de fungicidas que han perdido su autorización de uso, o que son candidatos a sustitución a finales del año en curso.

Agradecimientos
Este estudio ha sido financiado con cargo a la convocatoria de transición ecológica y digital, financiada con fondos Next Generation, dentro del proyecto VITICONTROL (ref. TED2021-129962B-C42). V.F. agradece un contrato pre-doctoral al proyecto anterior.

La huella del empleo de plaguicidas en el polietileno de uso agrícola

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La industria agrícola depende ampliamente del uso de materiales plásticos para optimizar y mejorar la eficiencia en los cultivos, reduciendo así la demanda de agua y las tasas de aplicación de herbicidas. Entre ellos, el polietileno (PE) es el polímero más utilizado en aplicaciones como cubiertas de invernaderos, acolchados, mangueras de riego, tubos fitosanitarios y cintas de atar. Estos productos están expuestos a una gran variedad de pesticidas, especialmente fungicidas e insecticidas, que se aplican a los cultivos. Dependiendo de las propiedades de estos compuestos, los plaguicidas pueden quedarse en la superficie del material o ser absorbidos por el plástico, acumulándose particularmente en el polietileno de baja densidad, a lo largo de varias campañas agrícolas. Al final de su vida útil, estos productos pueden contener concentraciones de plaguicidas incluso más altas que las presentes en el suelo y cultivos adyacentes [1].

En el contexto de la economía circular, el reciclaje de plásticos agrícolas se propone como una estrategia sostenible para reducir el impacto ambiental al final de su ciclo de vida, evitando la generación de micro y mesoplásticos que son difíciles de recuperar del entorno. Estos fragmentos pueden ser transportados a otros compartimentos ambientales mediante escorrentía, erosión del suelo, o indirectamente a través de la ingestión y excreción por fauna silvestre y de granja.

El objetivo principal de esta comunicación es presentar los resultados obtenidos en el estudio de la presencia de residuos de pesticidas en PE de uso agrícola al final de su vida útil, así como evaluar la potencial transferencia de estas sustancias a las materias primas producidas a partir de PE reciclado. Se presentan también resultados de migración de plaguicidas presentes en mangueras de PE, nuevas y envejecidas, al agua durante el riego, y se investiga la eliminación de los plaguicidas durante el tratamiento térmico del PE. Con esta finalidad, se ha analizado la presencia de plaguicidas en extractos obtenidos de PE agrícola envejecido, artículos nuevos fabricados con plástico virgen y plástico reciclado. El análisis de estas muestras se realizó mediante cromatografía líquida acoplada a espectrometría de masas en tándem (LC-ESI-MS/MS), tomando como base una preselección de 40 pesticidas basada en datos de uso y presencia en suelos agrícolas. En este póster se presentarán datos de concentraciones, comparaciones entre diferentes tipos de plásticos y fuentes, así como recomendaciones futuras.

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Identificación y cuantificación de saponinas en muestras silvestres de *Quillaja saponaria* Mol. mediante HPLC-PDA

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Quillaja saponaria Mol. (Quillay) es un árbol nativo de Chile, conocido por sus valiosos metabolitos secundarios conocidos como saponinas [1,2], los que son principalmente utilizados en la industria farmacéutica y alimentaria [3]. Por ello, se implementó un método de cromatografía líquida de alta resolución con detector de arreglo de diodos (HPLC-PDA) [4]. Se cuantificó la cantidad de saponinas totales y se identificó la presencia de cuatro saponinas de interés (QS7, QS17, QS18 y QS21) en muestras de hojas y tallos de Quillay obtenidas en la Región de Valparaíso, Chile. Se probaron 3 métodos de extracción: sonicación, maceración y reflujo; determinando que el método por reflujo es el más eficiente para extraer saponinas de muestras de follaje de Quillay silvestre, presentando un mayor porcentaje de saponinas de 22,81% y una menor variabilidad de CV = 1,27%. Adicionalmente, se identificaron las saponinas de interés con valores entre 5-9% del total de saponinas cuantificadas (Fig1). Se logró determinar parámetros cromatográficos para las 4 saponinas identificadas (número de platos teóricos: N; altura de platos teóricos: H; resolución cromatográfica: R_S; factor de asimetría A_s y factor de capacidad: k´) (Tabla 1) y los parámetros de linealidad, precisión y sensibilidad cumpliendo los criterios de aceptación establecidos para linealidad (*t*cal>*t*tab), precisión (Chv>CV) y sensibilidad para las muestras silvestres de *Quillaja saponaria.*

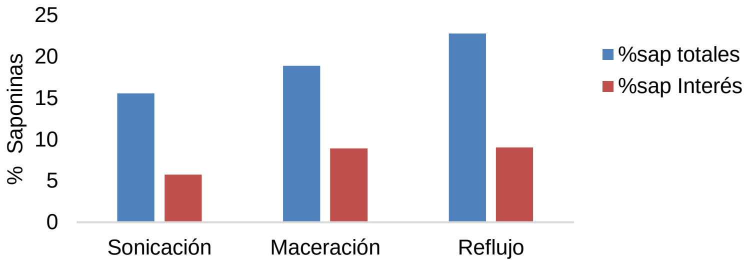

Fig. 1. Porcentaje de Saponinas Totales y de interés, en muestras silvestres de *Quillaja saponaria* Mol.

Tabla 1. Parámetros cromatográficos (HPLC-PDA) para las saponinas de interés.

Parámetro	QS7	QS17	QS18	QS21
N	513	6194	7543	5690
H	0,099	0,040	0,033	0,044
R_s	5,88	3,66	6,46	3,35
A_s	1,2	1,0	1,0	1,6
k'	1,72	2,06	2,14	2,78

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Optimización de condiciones de separación por HPLC mediante inteligencia artificial

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La separación cromatográfica de fármacos se considera un proceso clave dentro de la industria farmacéutica, por lo que su optimización resulta fundamental. La inteligencia artificial también constituye un campo de investigación de gran interés en la actualidad debido a los múltiples avances recientes que se están produciendo en cuanto a su aplicación en procedimientos cromatográficos clásicos [1]. Por ello, en este trabajo se propone la puesta a punto de la metodología basada en la inteligencia artificial para optimizar del proceso de separación de cinco fármacos beta bloqueantes mediante cromatografía de líquidos de alta eficacia HPLC.

Los beta-bloqueantes son fármacos empleados de manera muy habitual en terapia cardiovascular principalmente para controlar la contracción cardiaca y la vasodilatación [2]. En este trabajo se estudian, en concreto, los beta bloqueantes acebutolol, atenolol, labetalol, nadolol y propranolol. A partir de los cromatogramas obtenidos se evaluó la calidad de la separación cromatográfica teniendo en cuenta el tiempo de retención, el área de los picos cromatográficos y la resolución de los mismos, considerando variaciones en (i) el porcentaje de modificador orgánico en la fase móvil, (ii) el pH de dicha fase y (iii) el caudal volumétrico bajo el cual se introduce la fase en el cromatógrafo.

Para la aplicación de la inteligencia artificial, y con los datos experimentales recogidos bajo condiciones conocidas, se entrenaron varias redes neuronales artificiales cuyo objetivo es devolver las condiciones experimentales que permitan optimizar la separación cromatográfica. Por un lado, se desarrolló una red neuronal que devolvió de manera simultánea las tres condiciones experimentales que optimizaban la separación, mientras que por otro lado se desarrollaron tres redes independientes especializadas en cada una de dichas condiciones con el fin de comparar los resultados obtenidos. Los límites empleados por la red para cada una de las condiciones experimentales se muestran en la Tabla 1. Las principales diferencias obtenidas se centraron en el pH de la fase móvil, mientras que, para las condiciones restantes, los valores obtenidos fueron idénticos: mientras que la red independiente fijó el pH óptimo en 3.75, la red conjunta lo hizo en 2.65. En cuanto al modificador orgánico, ambas redes devolvieron un 30% de dicho compuesto y un caudal volumétrico de 1.1 mL/min.

Una vez obtenidos estos resultados, se evaluó la optimización experimentalmente en el laboratorio. En ambos casos, no se logró la optimización completa de la separación, debido a que dos de los fármacos no son separados completamente, es decir, la resolución de sus picos fue ligeramente menor que 1. En base a estos resultados los próximos pasos se centran en la mejora y depuración del código informático de las redes neuronales artificiales.

Tabla 1. Variables de control codificadas y sin codificar.

Condición	pH	Porcentaje de acetonitrilo	Caudal volumétrico[a]
Límite superior	8	100	1.5
Límite inferior	2	0	0.5

[a] Medido en mL/min

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Aplicación de un Diseño Central Compuesto para la optimización de separaciones mediante HPLC

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La optimización de procesos de separación mediante HPLC se trata de un proceso complejo en el que influyen gran variedad de variables de control, muchas de las cuales dependen de las condiciones experimentales. Gracias al diseño de experimentos (DOE) se puede conocer la importancia de los distintos factores sobre la optimización, además de disminuir en gran medida el número de pruebas necesarias para conocer esta información respecto a las requeridas para llevar a cabo un diseño factorial convencional o procedimiento de investigación clásico, en el que se modifican uno a uno los factores hasta encontrar un resultado óptimo [1].

El Diseño Central Compuesto, CCD, se trata de una metodología del tipo superficie de respuesta que permite la optimización de los valores de los factores en un experimento. Este tipo de DOE consiste en la obtención de ecuaciones matemáticas y el uso de herramientas estadísticas que permiten relacionar una respuesta de interés con la variación de una serie de variables de control. Dentro de los métodos de segundo orden, el CCD mostrado en la Figura 1 se trata del diseño de experimentos más comúnmente utilizado por ser rotable y por presentar una región de operación mayor que la empleada inicialmente debido a que presenta dos puntos estrella. [2]. De esta manera obtenemos diseños con 5 niveles para cada uno de los factores. Los valores reales y codificados para las variables de control correspondientes al CCD empleado se muestran en la Tabla 1. Una vez conocidos los valores de las variables de control a probar en el laboratorio gracias al diseño, se obtuvieron las respuestas experimentales, que en este caso se corresponden con 1) el mayor tiempo de retención de los cinco analitos en un cromatograma y 2) la menor resolución entre picos del cromatograma.

A continuación, se empleó el programa informático Stat-Ease para obtener la ecuación de optimización del modelo CCD más adecuado y, con ella, el punto óptimo sugerido. El objetivo planteado en el diseño consiste en maximizar la resolución y minimizar el tiempo de retención. Tras dicha optimización, los resultados fueron satisfactorios.

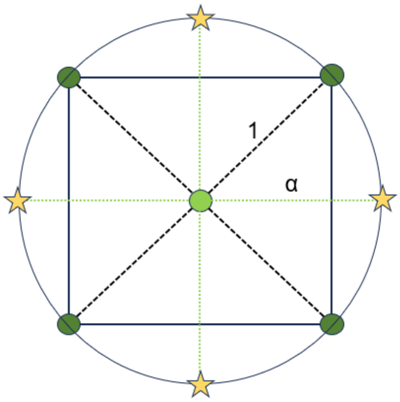

Fig.1. Representación gráfica de los puntos empleados en un CCD.

Tabla 1. Variables de control codificadas y sin codificar.

Variable	-α	-1	0	1	α
pH	2.98	4.00	5.50	7.00	8.02
% acetonitrilo	18.20	25.00	35.00	45.00	51.80
Caudal volumétrico[a]	0.66	0.80	1.00	1.20	1.34

[a] Medido en mL/min

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Curcumin-containing paper based analytical devices for boron determination in environmental waters

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The combination of paper-based analytical devices with everyday communications and information technology equipment offers new opportunities for the development of straightforward, rapid and cost-effective analytical strategies [1]. In this vein, the present contribution reports on the development of a non-instrumental quantitative colorimetric assay for boron determination based on its reaction with curcumin, typically used as a qualitative spot test [2]. The proposed colorimetric assay involves the formation of rosocyanin, a cationic 2:1 complex formed by reaction of boric acid and the immobilized curcumin molecules in acidic media, followed by addition of a microvolume of diluted alkaline media to the PAD, thus leading to a color change from red to blue-green attributed to the formation of quinoid structures that significantly enhanced the selectivity of the assay. Both a scanner and a tablet camera were found suitable for digitization of the PAD prior to the analysis by an open-source image processing and analysis program. Remarkably, the assay can be carried out in less than 1 min with minimal consumption of sample and reagents. The proposed assay represents and advantageous alternative to the standard method 4500-B, a colorimetric method based on the formation of the red-colored product rosocyanin after acidification and evaporation of a boron-containing sample, followed by washing with 95% ethyl alcohol [3]. Both curcumin and ethanolic extracts of the Indian specie and medicinal plant *Curcuma longa L*. were successfully implemented in PADs, showing quantitative recoveries (93-105%) when applied to the determination of boron in wastewater and seawater samples.

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QA24

Photochemical synthesis of carbon dots: Applications in analytical chemistry

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Carbon quantum dots (CDs) have received a great deal of attention in the last decade due to their exceptional optical properties, low toxicity, biocompatibility and their great potential for applications in various areas. In general, these nanomaterials exhibit broad excitation spectra, narrow symmetric emission spectra, good quantum yield, size-dependent luminescence, high chemical stability, resistance to photobleaching, high water solubility and easy functionalization, making them ideal for the design of fluorescent probes and detection devices [1]. Furthermore, CDs have the advantage of being synthesized from natural, non-toxic precursors such as carbohydrates, offering a more environmentally friendly alternative to the widely used semiconductor quantum dots (QDs) that contain heavy metals such as cadmium or lead in their composition. One of the most relevant lines of research in the field of CD synthesis focuses on developing more sustainable, faster and cheaper synthesis routes than conventional methods such as hydrothermal and solvothermal synthesis, microwave treatment or thermal carbonization. Among the emerging techniques, photochemical synthesis routes have proven to be particularly efficient, as they allow CDs to be obtained in short time intervals and without extreme conditions of pressure or temperature. In addition, the use of natural precursors as a carbon source for CD synthesis, including carbohydrates present in plants and other renewable resources, contributes to the reduction of environmental impact and the advancement of 'green chemistry' [2]. A crucial aspect in the design of CDs is the ability to modify their surface and dop them with elements such as nitrogen (N), sulphur (S) or phosphorus (P), which significantly improves their photoluminescent properties [3]. Doping with heteroatoms introduces new active sites on the CDs, increasing their quantum yield.

In general, procedures for the detection of different chemical species based on the use of CDs as fluorescent probes require two steps: i) synthesis and purification of the CDs; ii) recognition of the analyte. This can be simplified by implementing strategies that allow both steps to be carried out simultaneously. Thus, our research group has developed photochemical routes based on the integration of CD synthesis and detection of the analyte of interest in a single step [3,4]. These procedures eliminate the need for time-consuming and tedious procedures to purify and stabilize the newly synthesized CDs, greatly shortening the time required to perform the assay. The analytical response of the CDs is based on analyte-induced changes in the properties of the luminescent nanomaterial, including the increase or decrease of fluorescence intensity (turn-on or turn-off) through energy transfer or charge transfer processes. Applications developed by our research group for the detection of periodate (IO_4-) in water, hydrogen peroxide (H_2O_2) in personal hygiene products and antioxidants (ascorbic acid and glutathione), using CDs as a fluorescent probe, are presented here [3,4].

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A paper-based analytical device for the simultaneous scanometric determination of nitrite and sulfide in environmental waters

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The synergistic combination of paper-based analytical devices (PADs) with everyday IT and communication devices have brought renewed interest in the development of analytical systems that allow to perform rapid, low-cost and on-site analysis [1]. However, the reduced sensitivity of PADs represents a serious limitation to their use for determination of environmentally relevant compounds present at trace levels. A number of strategies have been reported in the literature to overcome this drawback and, particularly, the implementation of PADs in three-phase microseparation approaches has been demonstrated [2]. The present work reports on the development of a miniaturized method for the simultaneous scanometric determination of nitrite and sulfide [3]. The basis of the method consists on the selective formation of colored products in physically separated detection zones of a single cellulose substrate when exposed to volatile analyte derivatives. Thus, the simultaneous determination of the anions by the proposed method involved: i) *in situ* conversion of nitrite and sulfide into hydrogen sulfide and nitrogen oxides, respectively; ii) selective trapping of the volatiles in two differentiated detection areas containing Griess reagent and a Cu(II) salt, respectively; and iii) acquisition of analytical responses (mean color intensity in G and B channels) by digitization of the PAD and further processing. Under optimal conditions, the limits of detection were 54.7 and 4.8 ng/mL for nitrite and sulfide, respectively, whereas the repeatability, expressed as relative standard deviation, was found to be below 7% (n=6) in both cases. The proposed approach showed increased sensitivity when compared with PADs reported in the literature for nitrite or sulfide determination. The applicability of the method was finally assessed by the analysis of environmental waters, showing satisfactory recoveries (95.5-104.6%).

Acknowledgments

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Rapid and eco-friendly chromatographic method for the determination of polyphenolic compounds in leaf water extracts

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Polyphenolic compounds represent a large group of substances that can be found in environmental waters (rain, river, sea water, etc.) due to the contribution from both the biogenic and anthropogenic sources. Plants produce these compounds during their development in response to various environmental conditions, including UV radiation, infections, etc. [1]. A diverse range of polyphenols has been identified at varying concentrations, depending on the specific plant species studied and the part of the plant examined (foliage, rhizomes…). High-performance liquid chromatography with diode array detector coupled to mass spectrometry (HPLC-DAD-MS) has proven to be an effective analytical tool for determine a large number of compounds in plants like *Eucalyptus globulus Labill.* (EG), using chromatographic separations of more one hour [2]. Other authors have focused on analyzing only a few of the more relevant phenolic compounds using shorter separations times (35 minutes) [3]. This work has two main objectives: i) to optimize a rapid and eco-friendly chromatographic method for the separation of a large number of compounds, particularly hydroxybenzoic and hydroxycinnamic acids; and ii) to apply the optimized method to investigate the release of these compounds from the leaves of EG and Iberian autochthonous trees (IAT) into water, in order to assess their potential phytotoxic effects.

An ecofriendly method was optimized by reversed-phase liquid chromatography with DAD using a C18 monolithic column and a low percentage of organic modifier (acetonitrile) at a low flow rate of 0.4 mL/min. Three model compounds (gallic acid, *p*-coumaric acid and pyrogallol) were used for the separation, Unlike other reported methods, in this work the sample was acidified rather than the mobile phase in order to achieve optimal resolution between neutral and acidic compounds. Additionally, a short analysis time of 12 min was achieved using gradient elution. The method was validated, yielding limits of detection of 30 ng/mL for gallic acid and 10 ng/mL for coumaric acid, with inter-day and intra-day precision values below 5%. When applied to leaf water extracts, the method successfully quantified gallic acid at significantly different concentrations in the two extracts: 10 mg/L in EG and 0.1 mg/L in AIT. The recoveries for both compounds (gallic acid and *p*-coumaric acid) in the two extracts ranged from 71% to 104%. Pyrogallol was not detected. However, other polyphenols were identified, including derivates of chlorogenic acid and ellagic acid (with absorption maxima at 255 and 360 nm), flavonols (showing two maxima around 250-260 and 350-360 nm), and glycoside derivates of gallic acid (at 220 and 270 nm). It is important to note that the profile of detected polyphenols differed between the two extracts. Therefore, future studies could reveal qualitative and quantitative differences in the released compounds, which may help establish distinct behaviors in both natural environments.

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SMART SAMPLING PROCEDURE FOR METAL IONS ASSESSMENT IN DYNAMIC WATER SYSTEMS

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Water bodies are dynamic systems, and the presence of metal ions must be a target of spatial-temporal monitoring. The adverse effects of metal ions are well documented, not only for those which display toxic, carcinogenic, mutagenic and teratogenic effects for living organisms like lead, cadmium, mercury, arsenic and chromium but also for zinc, iron and copper, if present in high concentrations. In aquatic systems, they can be present in different forms, namely by the chelation of their metal ions with inorganic or organic ligands, making their toxicity dependent on the respective form. The real-time monitoring is rather cumbersome as current methods rely on transport to off-site laboratories, disrupting the sample characteristics due to pH and redox potential change and exposure to oxygen, light or temperature shifts, leading to diverse chemical equilibria shifts. In this context, a project, denominated Aqua_Smart, was designed with the main aim of devising an integrated smart sampling and automatic monitoring of toxic metal ions in aquatic systems.

The idea is to devise microtubes (cartridges-like tubes) packed with novel sorbents (SPE) to collect the samples. These can be moved to specific sampling points and used in onboard campaigns. The sorbent material can be enriched with analytes by perfusing the sampling device with a large water volume, along with interferents removal; then, the enriched plug is eluted for measurement. The analytical determination is to be based on flow-based techniques with miniaturized optical detection to make the apparatus portable equipment. The whole process, sampling/preparation/measurement, will become automated, enabling the real-time monitoring of various metal species in water bodies. Within the scope of this project, a cartridge packed with a sorbent material for cadmium sampling and enrichment was developed. Additionally, a sequential injection method, using cartridges to discriminate between the different analytes, was also developed for the multiparametric determination of copper, zinc, and manganese determination in water.

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Separación de proteínas mediante electroforese offgel en mostras de algas expostas a nanopartículas de prata

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O estudo da proteómica de algas é un tema de interese actual debido ás aplicacións que presentan as proteínas no ámbito farmacéutico ou cosmético. Do mesmo xeito que as proteínas das algas mariñas, as nanopartículas de Ag (AgNPs) tamén son obxecto de estudo debido á súa utilidade en campos como a biomedicina ou a industria. Isto provoca un aumento da súa presenza no medio ambiente e a bioacumulación polos organismos mariños.

O obxectivo desta investigación é analizar as proteínas presentes en mostras de algas vermellas (*Palmaria palmata*) e algas verdes (*Ulva sp*.), previamente expostas a AgNPs. A extracción e precipitación das proteínas logrouse aplicando un método de tratamento con fenol sobre as algas previamente homoxeneizadas con N_2 líquido. Os pellets obtidos foron sometidos a unha electroforese offgel para separar as fraccións de proteínas en función do seu punto isoeléctrico (pI). Mediante esta técnica para cada mostra se separaron 24 fraccións nunha disolución buffer sobre unha tira de xel de gradiente inmobilizado (IPG Dry Strip pH 3-10, GE Healthcare Life Science).

Unhas vez obtidas estas fraccións offgel realizouse outra separación para cada fracción mediante electroforese LOC (*Lab On a Chip*) para separalas proteínas segundo o seu peso molecular e cuantificalas co Bioanalizador 2100 de Agilent. O estudio da precisión do método de cuantificación LOC mostrou unha boa precisión con valores de desviación estándar relativa menores do 6% tanto para as medidas do tamaño como as de concentración. Nas mostras, observáronse rangos de tamaño e concentración de proteínas de 13,6 a 224,1 kDa e de 1,1 a 426,5 ng μL^{-1} para a alga vermella, e de 13,9 a 223,6 kDa e de 2,3 a 353,9 ng μL^{-1} para a alga verde.

Todas as fraccións offgel mostraron contido proteico salvo a fracción 24 (pI 9,89 a 10) da alga vermella e a 16 (pI 7,76 a 8,1) na alga verde. O contido total de proteínas foi maior na mostra de Ulva sp., así coma o contido de prata total determinado posteriormente por Espectrometría Atómica de Atomización Electrotérmica (ETAAS).

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Determinación de elementos críticos tecnolóxicos en cunchas de moluscos mediante Espectrometría de Masas con Plasma de Acoplamento Indutivo

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Os Elementos Críticos Tecnolóxicos (*Technology Critical Elements, TCEs*) teñen gran relevancia na actualidade debido a que son esenciais para o desenvolvemento de novas tecnoloxías e produción de enerxías limpas. Este grupo está formado por distintos elementos considerados críticos debido a súa escaseza na Terra sumada á dificultade de extracción e separación do resto de elementos. Por iso, o estudo da concentración dos TCEs en distintos medios é de notable interese para a Unión Europea.

O obxectivo deste traballo é a determinación de TCEs (Y, Rh, In, La, Ce, Pr, Nd, Eu, Sm, Tb, Gd, Dy, Er, Tm, Yb, Ta, Pt, Ga, Ge, Nb, Ru, Te, Ho e Lu) e outros elementos de interese (Li, Cu, Tl e U) en cunchas de moluscos de diferentes especies: mexillóns, ameixas e vieiras. As cunchas son residuos de orixe mariña producidos en Galicia en elevadas cantidades debido ao consumo dos bivalvos como alimento.

Para a determinación dos TCEs empregouse a Espectrometría de Masas con Plasma de Acoplamento Indutivo (ICP-MS) previamente realizada a pulverización das cunchas e unha dixestión ácida asistida por microondas con HNO_3 (69% v/v) e H_2O_2 (33% v/v). A medida realizouse en modo KED empregando o He como gas de colisión evitando así as interferencias poliatómicas. A calibración realizouse mediante o método de adición estándar no rango de 0,5 a 100 $\mu g\ L^{-1}$ para todos os elementos, excepto para Li e Cu cun rango de 1,25 a 250 $\mu g\ L^{-1}$.

Avaliáronse as características analíticas do método, obtendo límites de detección comprendidos entre 0,1 ng g^{-1} para Lu ata 14,4 ng g^{-1} para Te. O método presentou unha boa precisión obtendo desviacións estándar relativas inferiores ao 5% para todos os elementos. Como non se contaba con material de referencia certificado, empregouse a medida da recuperación analítica para avaliar a exactitude do método, obtendo valores en torno ao 100 % para todos os elementos estudados .

Os resultados obtidos mostraron que os elementos Pt, Ge, Te e Ta estaban por debaixo do límite de cuantificación en todas as mostras. O Li, Cu, Y, Nd, La e U son os elementos que se atoparon nunha maior concentración nas cunchas analizadas, nun rango que foi dende 0,02 ata 84,1 $\mu g\ g^{-1}$.

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CONTAMINACIÓN DE COMBUSTIBLE DIESEL

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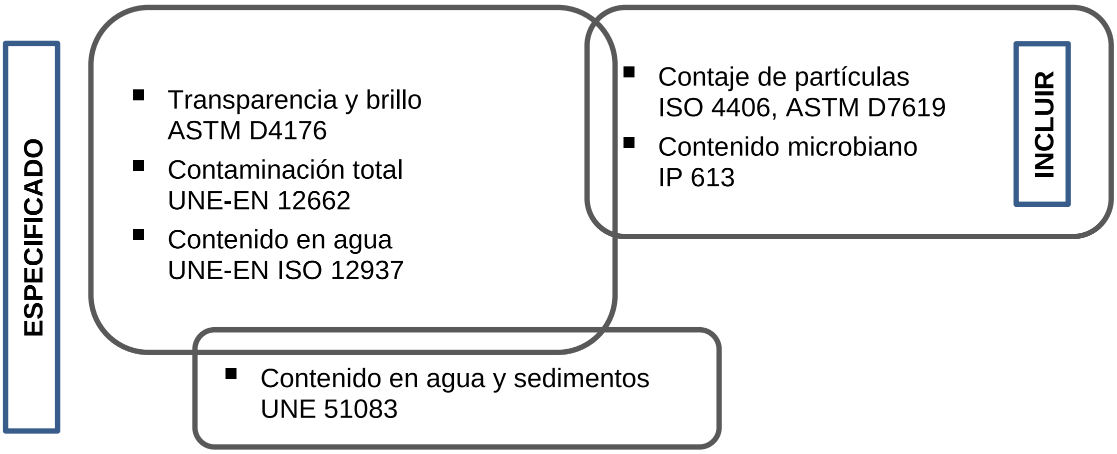
“Lo que no se puede ver puede hacer daño”: Los métodos de análisis de combustible presentes en sus especificaciones de control de calidad cuentan una historia, pero puede que esta no sea la historia completa.

El combustible que sale de la refinería es el combustible más limpio que jamás haya existido, pero a medida que realiza su viaje desde la refinería hasta el depósito, se lo traslada a través de varios contenedores, se lo expone a la humedad y se vuelve susceptible al aire sucio; el combustible, y esto es inevitable, se contaminará. Los contaminantes más comunes que se encuentran en el combustible son partículas de distinta naturaleza, agua, otros productos del petróleo o sus residuos y crecimiento microbiano.

La contaminación del combustible puede provocar tiempos de inactividad no planificados, riesgo para la seguridad humana y averías costosas.

En especificación existen determinadas pruebas para asegurar la limpieza del combustible, pero alguna de ellas como la prueba de “transparencia y brillo” método estándar de análisis de la contaminación del combustible, es un procedimiento en el que al ser el ojo humano el responsable de detectar la limpieza es totalmente subjetivo.

Tras múltiples y exhaustivos ensayos sobre combustible diésel se he llegado a la conclusión de que se debería establecer un protocolo que permitiese garantizar la limpieza del combustible, incluyendo en el control de calidad algunos ensayos más allá de los actualmente especificados para considerar adecuado el combustible para su uso en aquellos equipos y/o motores a los que va a ser destinado:



ESPECIFICADO

- Transparencia y brillo
  ASTM D4176
- Contaminación total
  UNE-EN 12662
- Contenido en agua
  UNE-EN ISO 12937

- Contaje de partículas
  ISO 4406, ASTM D7619
- Contenido microbiano
  IP 613

INCLUIR

- Contenido en agua y sedimentos
  UNE 51083

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BOE 41 17/02/2006
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BOE 215 04/09/2010
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Heliyon, Volume 8, Issue 4, e09264
Published online 2022 Apr 9. doi: 10.1016/j.heliyon.2022.e09264
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Sonda raciométrica composta por pontos quânticos de carbono e de $AgInS_2$ para a determinação fotoluminescente e visual de ácido ibandrónico

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A deteção visual tem adquirido grande relevância nos últimos anos, com a investigação focada no desenvolvimento de metodologias analíticas rápidas, económicas e fáceis de manusear, aplicáveis na monitorização in situ de diversos analitos, desde poluentes a contaminantes alimentares, fármacos e biomarcadores [1]. Este estudo apresenta o desenvolvimento de uma plataforma de deteção raciométrica baseada na combinação de pontos quânticos de carbono (CDs) e de $AgInS_2$ passivados com ácido tiomálico (TMA-$AgInS_2$ QDs) para a deteção de ácido ibandrónico (IBAN), um fármaco da classe dos bisfosfonatos, amplamente utilizado no tratamento de doenças ósseas.

A plataforma de deteção raciométrica utilizou CDs, com emissão azul, que se mantiveram quimicamente inertes na presença de IBAN, e TMA-$AgInS_2$ QDs, com emissão laranja, cuja intensidade foi inibida com o aumento da concentração de IBAN. A razão entre as intensidades de fotoluminescência (PL) permitiu a deteção sensível de IBAN em amostras farmacêuticas, com valores de recuperação entre 98% e 103%. A abordagem ratiométrica oferece vantagens, como a compensação de variações ambientais e a redução de interferências, tornando a deteção mais precisa e robusta. Além disso, foi proposta uma abordagem de deteção visual, através da modulação de cor de laranja para azul, possibilitando um teste de triagem rápida de IBAN sem necessidade de equipamento sofisticado. Esta é a primeira vez que QDs ternários livres de cádmio foram usados para deteção visual, demonstrando o seu potencial como alternativa ambientalmente segura.

A plataforma desenvolvida permitiu uma deteção eficiente e precisa de IBAN em formulações farmacêuticas. A combinação de CDs com $AgInS_2$ QDs mostrou ser promissora para criar metodologias analíticas sustentáveis, oferecendo uma alternativa verde e não tóxica às tecnologias convencionais baseadas em cádmio. Além disso, a abordagem visual proposta oferece uma ferramenta de triagem rápida e eficaz para a monitorização de IBAN.

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Desenvolvimento de um processo FRET utilizando pontos quânticos de $AgInS_2$ e nanopartículas de ouro para a deteção de betabloqueadores.

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Neste estudo, foi desenvolvido um sistema de deteção baseado na transferência de energia por ressonância de fluorescência (FRET) para monitorizar o atenolol, um β-bloqueador amplamente utilizado, em formulações farmacêuticas. A utilização de pontos quânticos (QDs) de $AgInS_2/ZnS$ passivados com D-penicilamina como dadores de energia, combinada com nanopartículas de ouro estabilizadas com cisteamina (CA-AuNPs) como aceitadores, permitiu criar uma plataforma sensível e seletiva para a análise de atenolol. Com esse objetivo, distintos pares doador-aceitador sob diferentes condições de reação foram cuidadosamente estudados, visando otimizar a eficiência do processo FRET e, consequentemente, aumentar a sensibilidade da metodologia. Verificou-se que a presença de uma camada de ZnS em torno do núcleo ternário dos QDs, aliada ao uso de cisteamina como agente estabilizante das AuNPs em vez do citrato, favoreceu um processo FRET mais eficiente.

A interação eletrostática entre os ligandos na superfície das nanopartículas permitiu a ocorrência do processo FRET, resultando na inibição da fotoluminescência (PL) dos QDs. A influência de vários fármacos β-bloqueadores no processo FRET foi analisada detalhadamente. Observou-se que o atenolol e o nadolol induzem a agregação das CA–AuNPs através de interações por pontes de hidrogénio [1], o que reduz a sobreposição espectral entre o dador e o aceitador. Esta alteração impede o processo de FRET, resultando na restauração da emissão dos QDs. Assim, foi possível desenvolver um método para a determinação do atenolol que permite restaurar a emissão dos QDs de forma dependente da concentração. O método apresentou uma relação linear entre a recuperação do sinal de PL e a concentração de atenolol até 11,22 mg L^{-1}, com um limite de deteção de 1,05 mg L^{-1}. O sistema de deteção foi aplicado com sucesso na análise de atenolol em formulações farmacêuticas, com valores de recuperação entre 97,4% e 104,3%, comprovando a sua exatidão e precisão.

Este trabalho demonstra o potencial dos $AgInS_2/ZnS$ QDs como sensores eficientes em plataformas FRET, oferecendo uma alternativa mais ecológica e menos tóxica relativamente aos QDs convencionais baseados em cádmio. A metodologia desenvolvida mostrou-se sensível, simples e aplicável à análise de atenolol em produtos farmacêuticos, com resultados confiáveis. Este avanço abre portas para o desenvolvimento de sistemas analíticos mais seguros, sustentáveis e de fácil implementação em diferentes áreas da química analítica.

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Plastic antibodies as a Revolutionary Recognition Element in Electrochemical Protein Sensing

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Electrochemical sensors are highly effective for protein detection due to their sensitivity, specificity, and rapid response times [1]. Their compact design and potential for miniaturization make them suitable for point-of-care diagnostics, allowing for on-site testing without the need for complex laboratory infrastructure. Additionally, they reduce the need for extensive sample preparation.

The choice of *recognition element*, that converts the interaction event into a measurable electrical signal, is critical to the performance of electrochemical sensors [2]. They can be biological (antibody, nucleic acid) or synthetic (molecularly imprinted polymer (MIP) or aptamer). Antibodies (Fig. 1A), while widely used for their high specificity, are susceptible to instability and raise ethical concerns due to their reliance on animal sourcing. Aptamers (Fig. 1B), short synthetic nucleic acids, offer a promising alternative with their high specificity and stability, but their production costs remain a barrier to widespread adoption. DNA-based genosensors (Fig. 1C) are very specific but prone to interference from impurities in complex biological samples, limiting their application in certain scenarios.

Nowadays, there is still a growing need for developing methods that reduce dependence on traditional approaches. Plastic antibodies, or MIPs, are transforming electrochemical sensing for protein detection. These synthetic recognition elements are designed to mimic natural antibodies by creating highly specific binding sites for target proteins. They are obtained by using the target protein as a template during polymerization of monomers, and once the template is removed, the polymer retains cavities that selectively rebind the analyte (Fig. 1D) [3]. Compared to natural antibodies, MIPs offer greater stability and can operate effectively in a wide range of conditions, including variations in pH and temperature. They are cheap alternative and do not require animal exploitation for production [4]. MIPs have been successfully applied in electrochemical sensing for targets such as cancer biomarkers, human proteins, and pathogens (e.g., viruses, bacteria) [5]. The development of MIP-based sensors, including electrodes' surface modifications, the choice of monomer, polymerization approaches, template elution, and detection methods are reviewed in the scientific poster.

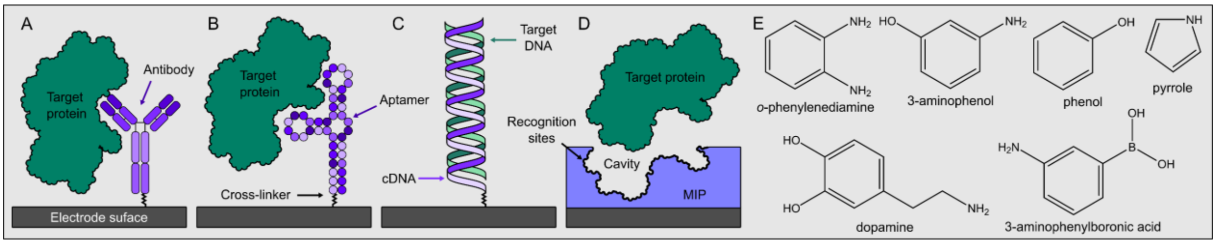

Fig.1. Recognition elements in protein detection: A – antibody (immunosensor), B – aptamer (aptasensor), C – single-stranded DNA (genosensor), D – molecularly imprinted polymer (MIP-sensor); E – common functional monomers in the synthesis of molecularly imprinted polymers

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ANÁLISE DE EXTRACIÓNS EN FASE SÓLIDA APLICADAS A CANNABINOIDES SINTÉTICOS

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Presentamos un traballo experimental e computacional xa que consideramos que aquelas investigacións nas que se realizan simultáneamente unha análise teórica e unha análise experimental permiten estudar unha hipótese de partida con maior profundidade.

Neste traballo realízase, en paralelo, unha análise teórica e experimental para determinar cal dos tres cartuchos de extracción en fase sólida é máis válido para extraer tres cannabinoides sintéticos da mostra de plasma: o CP47,497, o CP55,940 e o JWH-073.

A nivel teórico, estúdanse as enerxías de interacción aplicando o método do funcional da densidade (DFT) entre os monómeros que conforman os cartuchos de SPE e os cannabinoides sintéticos probando diferentes posibilidades de interaccións.

A nivel experimental, optimízase un método cromatográfico para poder detectar e cuantificar os cannabinoides. Posteriormente, deséñanse e optimízanse os protocolos de extracción das SPE para poder realizar un tratamento de mostra acorde coas características dos cannabinoides. Elabóranse tres rectas de calibrado, unha por cartucho, e calcúlase o rendemento de cada tipo de extracción.

Mediante as dúas vías de análise, chégase á conclusión de que o mellor cartucho de extracción é o OASIS MCX.

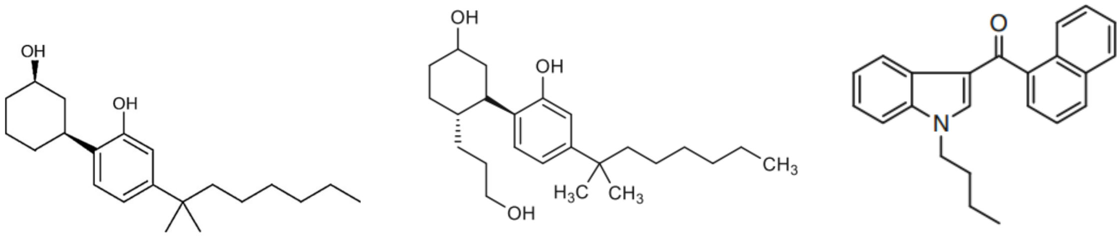

Fig.1. Cannabinoides sintéticos empregados neste estudio.

Development of genosensors for pharmacogenomic targets in the neuropsychiatric diseases: A CYTED project

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The GenoPsySEN thematic network project, approved by CYTED (https://cyted.org/GENOPSYSEN), involves institutions, hospitals, biotech and social companies, as well as researchers from Iberoamerican countries.

The principal goal of the GenoPsySENS network project is to develop electrochemical and optical genosensors able to detect single nucleotides polymorphisms (SNP), namely the most allelic variants of CYP2C19 and CYP2D6, that affect drug response in neuropsychiatric diseases. For that, researchers from Mexico and Brazil are genotyping these SNP to establish a pharmacogenomic database of Ibero-American populations. Then, it is intended to design and develop electrochemical and optical genosensors to evaluate easily and quickly these SNP at the medical appointment.

The planned activities fall under the following instruments: a) Mobility program; b) Training and dissemination program; c) Publicity materials; d) Workshops and seminars, e) Postgraduate courses and f) Organization of International Conferences and discussion forums.

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Detecting neurological pharmacogenetic altering SNS CYP2D6 by electrochemical genosensors

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Epilepsy is a serious neurological disorder which affects every aspect of a patient's life. Unfortunately, only a few suppressive medicines are available, and a complete cure for the disease has not been found yet. In fact, there is high variability in the response to antiepileptic treatment across people with epilepsy. Genetic factors significantly contribute to such variability. Recent advances in the genetics and neurobiology of epilepsies are establishing the basis for a new era in the treatment of epilepsy, focused on each individual and their specific epilepsy. Variation in response to antiepileptic drug treatment may arise from genetepilepsy in a range of gene categories, including genes affecting drug pharmacokinetics, and drug pharmacodynamics, but also genes held to cause the epilepsy itself. Therefore, development of a multi-task solving novel smart biosensing systems is urgently required.

Recently, the GenoPsySEN thematic network has approved by CYTED (REF. 223RT0141) involving institutions, biotech and social companies and investigators from Argentina, Brazil, Colombia, El Salvador, Mexico, Spain, Paraguay, Portugal, and Uruguay. Through mechanisms of cooperation that seek scientific and technological results transferable to the Ibero-American Public Health Systems, it aims to incorporate the consortium's expertise in electronics, electrochemistry, nanomaterials, pharmacogenomics, cell lines, molecular biology, and neurosciences, into the successful development of genosensors, for the detection of genetic variations that affect drug response in neuropsychiatric diseases.

This work aims to design and develop an electrochemical genosensor able to detect the most relevant allelic variant of CYP2D6 (figure 1) in Iberoamerican patients being treated with antiepileptic drugs metabolized by these genes (https: //cpicpgx. org/guidelines/).

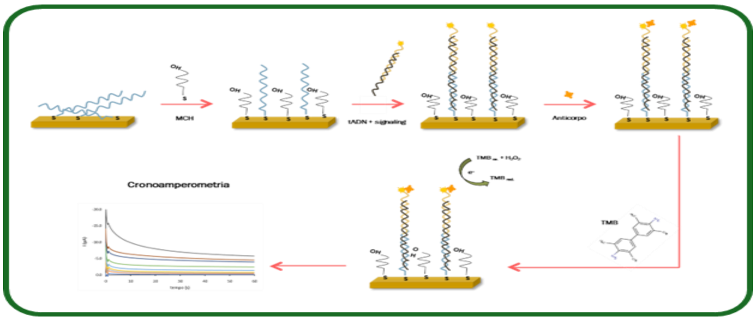

Fig. 1 – Develop of genosensors designed to evaluate SNP CYP2D6.

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DETERMINACIÓN DE LA BIOACCESIBILIDAD DE METALES Y METALOIDES EN MICROPLÁSTICOS MEDIANTE ICP-MS/MS

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Los microplásticos, MPs, pequeñas partículas de polímeros se han convertido en una preocupación global debido a su presencia en ecosistemas acuáticos y terrestres, su resistencia a la degradación [1] y sus posibles efectos adversos sobre la salud. Estas partículas, a menudo imperceptibles a simple vista, se forman tanto por la degradación de plásticos más grandes como por su producción directa en tamaños diminutos. Por esta razón, se plantea la necesidad imperante de desarrollar un método que permita determinar con precisión la fracción de especies nocivas, como algunos metales traza, que se liberan de los microplásticos presentes en alimentos durante el proceso de digestión humana.

En el presente trabajo, se han realizado ensayos de bioaccesibilidad de metales y metaloides en MPs [2]. Las disoluciones gastrointestinales empleadas contienen componentes que simulan la saliva, los jugos gástricos, el fluido duodenal y la bilis. Los ensayos de bioaccesibilidad se realizaron poniendo en contacto entre 0.2 y 2 g de muestra (MPs de polietileno de baja densidad, obtenidos a partir del material de referencia ERM®-EC680m del IRMM, Bélgica) con los jugos digestivos ya nombrados durante un tiempo determinado y en condiciones de temperatura y oscuridad controladas. Una vez completado el proceso se determinó, por una parte, la cantidad de metales y metaloides liberada a la disolución (bioaccesibilidad gastrointestinal) y, por otra, la cantidad retenida en la muestra mediante digestión ácida por microondas. Cabe destacar, que los ensayos se realizaron siguiendo dos métodos, un método que simulaba el sistema digestivo humano en condiciones de ayuno (UBM) y otro método que simula el sistema digestivo humano en condiciones de alimentación (Versantvoort) [3].

Para realizar la determinación de los elementos objetivo se ha empleado un espectrómetro de masas en tándem con fuente de ionización de plasma acoplado inductivamente (ICP-MS/MS) empleando gas He como gas de colisión para eliminar los iones poliatómicos de algunos de los elementos [4]. Los resultados han demostrado que la bioaccesibilidad de elementos tales como el Zn, Br y As, fueron elevadas, tomando entre 50 y 100%, respectivamente. Mientras, para elementos como el Pb, Cd, Cr, Sn y Sb estos parámetros tomaron valores menores que 10%, 1%, 12%, 4% y 2%, respectivamente.

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DETERMINACIÓN DEL PERFIL ELEMENTAL EN BIOMASA MEDIANTE ICP-MS/MS

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La determinación de metales en biomasa, como las algas, es esencial para el control medioambiental, ya que estas especies actúan como bioacumuladores de metales pesados y otros elementos traza presentes en el agua. Debido a su capacidad de adsorción y bioacumulación, las algas reflejan de manera precisa las concentraciones de metales como Pb, Cd, Ni, entre otros, sirviendo como indicadores directos de la contaminación antropogénica y su distribución en los ecosistemas acuáticos [1,2]. Esta información es vital para evaluar riesgos ambientales, ya que la acumulación de metales en las algas puede tener consecuencias significativas en las cadenas tróficas.

La determinación del contenido de metales y metaloides en biomasa constituye un reto analítico, dada la complejidad de sus matrices y la necesidad imperante de detectar concentraciones extremadamente bajas con alta precisión y exactitud. En este trabajo, se ha empleado un espectrómetro de masas en tándem con fuente de ionización de plasma acoplado inductivamente (ICP-MS/MS) empleando gas He como gas de colisión con el fin de eliminar las interferencias espectrales causadas por la presencia de iones poliatómicos [3]. Además, para realizar el análisis multielemental en matrices complejas, se empleó la digestión ácida, un proceso que disuelve la muestra en ácidos fuertes, como ácido nítrico o clorhídrico, para descomponer la matriz y eliminar compuestos inorgánicos insolubles. Para mejorar la reproducibilidad, reducir el tiempo de preparación de la muestra y minimizar la pérdida de analitos volátiles, este procedimiento se llevó a cabo en contenedores cerrados y con digestión asistida por microondas. Los resultados mostraron la presencia de elementos como Ba, Cd, Cr, Cu, Fe, Li, Mn, Ni, Ti y Zn, con concentraciones que varían entre 400 µg/kg y 15 mg/kg para Ba y Mn, respectivamente.

Asimismo, se realizó la caracterización del agua de cultivo de las algas. La determinación del contenido de cloro libre y total, según la norma UNE-EN ISO 7393-2 [4], es esencial para evaluar la calidad del agua, ya que el cloro puede modificar la fisiología de las algas y su capacidad de absorber metales. Adicionalmente, la determinación de la demanda química de oxígeno (DQO) permite evaluar la carga orgánica [5], lo que afecta la disponibilidad de oxígeno disuelto y a la salud del ecosistema acuático.

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Voltammetric profile of psychedelic phenethylamine derivatives

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Phenethylamines (PEA) refer to a class of substances that can have stimulant, and/or hallucinogenic effects depending on the position and identity of functional group substituents on the phenethylamine core [1]. This class of substances with documented psychoactive and stimulant effects and include amphetamine, methamphetamine, MDMA, catecholamines, synthetic cathinones, and other substances. The phenethylamines also include ring substituted substances such as the ‘2C series’, ring substituted amphetamines such as the ‘D series’ (e.g. DOI, DOC), benzodifurans (e.g. Bromo-Dragonfly, 2C-B-Fly) and others (e.g. p-methoxymethamphetamine (PMMA)).

The acute adverse effects of phenethylamines including agitation, hallucinations, drowsiness, confusion, mydriasis, aggression, hyperthermia, hypertension, and tachycardia, with more severe long-term adverse effects including acute psychosis, seizures, coma, cerebral edema, long-lasting severe neurological impairment, serotonin syndrome, prolonged respiratory failure, renal failure, multi-organ failure, etc. [2].

Seizures of phenethylamines were first reported from the United States and European countries and since 2009 substances such as 2C-E, 2C-I, 4-FA and PMMA have been commonly reported by several countries in different regions. Other phenethylamines increasingly reported to UNODC since 2011 include 4-FMA, 5-APB, 6-APB and 2C-C-NBOMe.

There is a need to increase the ability of forensic science and toxicology laboratories to identify these substances as well as their precursors and metabolites. The electrochemical techniques are quite versatile and adapt very well to laboratory or field conditions for a preliminary screening of target drugs since they are effective and powerful analytical tools, encompassing the advantages of instrumental simplicity, moderate cost and portability.

Continuing our efforts to better understand the biotransformation of controlled psychoactive substances, in the present work we present and compare the voltammetric profile of a series of phenethylamines. The results obtained will be presented in this communication.

Acknowledgements

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QUÍMICA FÍSICA

Kinetic Study of Methionine Nitrosation Reaction. Risk of its Consumption as a Dietary Supplement

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Methionine (Met) is an essential amino acid that plays a fundamental role in multiple biological functions in the body and must be obtained through diet or supplements. Methionine participates in protein synthesis, which is why it is highly consumed by athletes, in liver detoxification, immune system strengthening, regulation of gene expression, cardiovascular health, production of neurotransmitters and formation of collagen and elastin, essential components of connective tissue, skin and hair [1]. Recent studies have shown that its consumption as supplement can also have adverse effects such as the growth of tumors in cancer patients or excessive homocysteine production, which may lead to cardiovascular disorders [2].

$NaNO_2$ is added as a preservative to cured meats to enhance their organoleptic properties and prevent botulism. Ingested methionine can react with $NaNO_2$ under the acidic conditions of the stomach, leading to the formation of the corresponding nitroso compound.

In previous research of our working group, the alkylating potential of the nitrosation products of leucine, isoleucine, and methionine was investigated. The behavior of methionine in both the nitrosation and alkylation reactions differed from that of the other amino acids, suggesting a change in the mechanism, likely due to the sulfur atom in methionine's structure. For this reason, we decided to conduct a systematic study of methionine nitrosation. Since the HNO_2/NO_2^- system (hereinafter referred to as nitrite, Nit) shows a maximum in the absorption spectrum at $\lambda = 371$ nm, nitrite was selected for kinetic monitoring of the reaction, since at this wavelength it is the only species present in the reaction medium that shows significant absorption.

Firstly, the experimental rate equation was determined. For every experiment, we maintained constant pH, temperature and the ionic strength. To determine the order with respect to nitrite concentration, a key point in the research, the integration method was applied under different conditions: a) equal initial reactant concentrations, $[Met]_0 = [Nit]_0$; b) a large excess of methionine, $[Me]_0 >> [Nit]_0$; and c) different concentrations of the reactants, but without a large excess of one over the other, $[Me]_0 \neq [Nit]_0$. Next, the influence of medium acidity, temperature, and ionic strength on the reaction rate was studied.

The following conclusion can be drawn:
i) The experimental rate equation is: $r = k_{exp}$ [Met][Nit]. The first-order dependence on nitrite concentration indicates $H_2NO_2^+/NO^+$ as the effective nitrosating agent. Previous studies on α-amino acid nitrosation with primary amino groups found a second-order dependence on [Nit], suggesting N_2O_3 as the active nitrosating species [3].
ii) A proposed mechanism involves nitrosation of methionine's sulfur, followed by transfer of the nitroso group to the primary amino group, forming a diazo compound. This compound loses N_2, leading to the formation of a lactone, the effective alkylating agent.
iii) Methionine supplementation should be approached with caution due to the risk of alkylating DNA nitrogenous bases, potentially leading to tumor and cancer formation."

Acknowledgements:
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QUÍMICA INORGÁNICA

Luminescente Europium(III) complexes supported on silica derived from rice waste

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Rice is the second most consumed food item globally and its demand is expected to increase accordingly to the growth of world population.[1] The use of industry wastes goes accordingly to the 2030 Agenda for Sustainable Development, that aims to balance three areas of sustainable development: economic, social, and environmental.

Rice husk (RH) is a very important residue composed of 70-80% organic substance (e.g. cellulose, lignin, etc) and 20% inorganic components (silica, alkalis and trace metals). The controlled combustion of RH leads to the formation of rice husk ash (RHA) its composition can vary, but for complete combustion of RH almost pure silica (> 95%) can be obtained [1]. RHA can be used in different sectors as cement and concrete industry, construction of lightweight materials, steel industry, agriculture [2].

Silica, which is transparent to light, and can be easily modified, allowing further functionalization with various functional groups making it an ideal matrix for the immobilization of luminescent complexes. Although there are several reports on silica luminescent materials, only few reports can be found in the literature on the use of silica derived from RHA.

In this work, RHA was used as silica support, were a pyridyl type group was immobilized (RHA-py). Subsequent reaction with $Eu(btfa)_3(H_2O)_2$ [Hbtfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedione] resulted in a organic–inorganic hybrid material presenting luminescent properties $Eu(btfa)_3(H_2O)$@RHA-py.

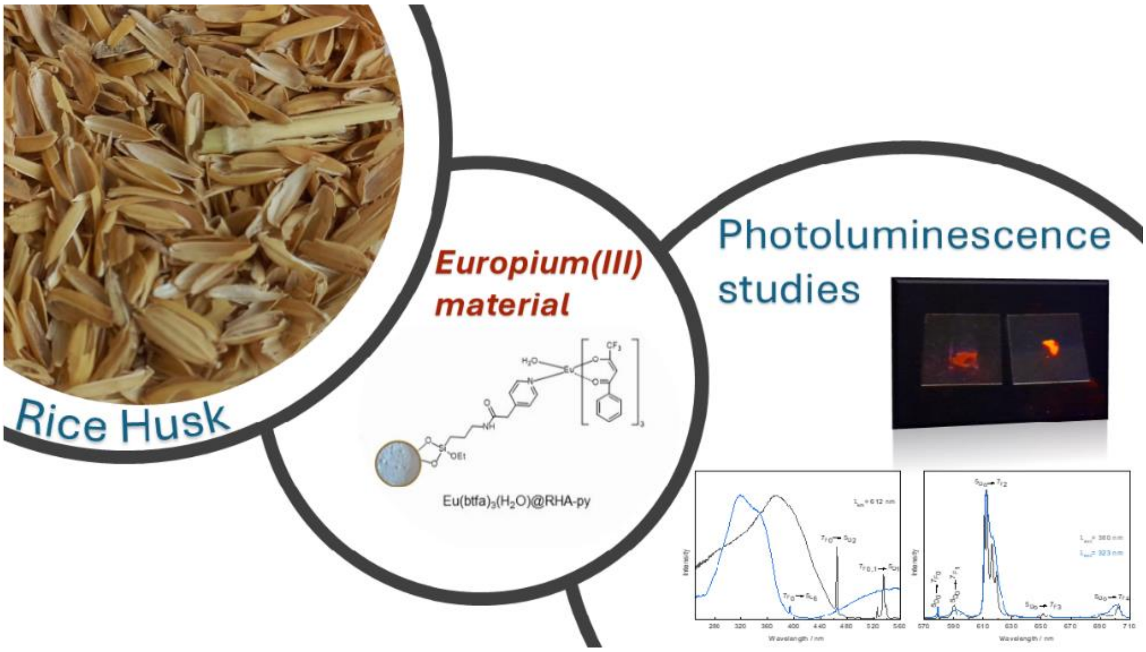

Fig.1. Schematic representation of the organic–inorganic hybrid material prepared from rice husk, and some photoluminescence features.

Agradecimientos
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020), financed by national funds through the FCT (Fundação para a Ciência e a Tecnologia) / MCTES (Ministério da Ciência, Tecnologia e Ensino Superior) (PIDDAC). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC).

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Implications of the cyclometalation in the coordination of crown ethers

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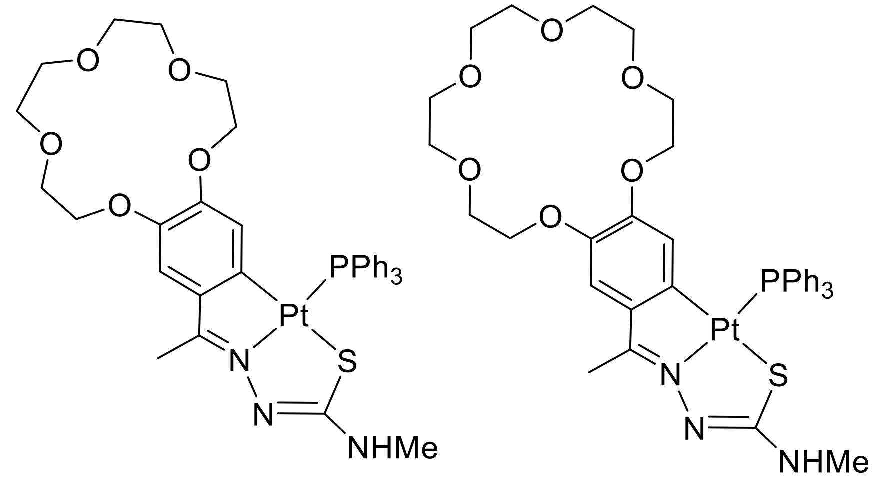
Crown ethers are a class of macrocyclic ligands known for their size-selective interactions with cations. For this reason, their main application is as sensors, usually as part of more complex structures with increased selectivity.[1,2] On the other hand, cyclometalated compounds are a very stable family with many applications. Several studies have been carried out to combine these two functionalities and explore the potential new applications,[3] but the modification of the sensing activity caused by cyclometallation has not been fully determined.



Scheme 1: Compounds studied in this work

In this paper, we present the detailed computational study of a series of platinocycles bearing a crown ether in their structure using density functional theory (**Scheme 1**). Firstly, we have analyzed the different configurations adopted both in the gas phase and in solution. Then, following the methodology described by Achazi *et al.* in 2016,[4] we have determined the affinity of each compound towards the desired cations.

Finally, we performed time-dependent DFT to predict the UV/Vis spectra and to evaluate the possible modifications after coordination. We found that cyclometallation has little effect on the ability of the crown ethers to trap cations.

Agradecimientos
We thank the *Axudas a proxectos de investigación nos distintos ámbitos científicos co obxectivo de impulsar a actividade científica dos grupos de investigación*. May 2024. Vicerreitoría de Política Científica. Universidad de Santiago de Compostela (USC).

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Structural study of two heterodinuclear compounds bearing a cyclometalated moiety

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Palladacycles are a family of compounds well-known for their high stability and wide range of applications. Although in recent years they have been increasingly used as anticancer agents and in other biological application,[1] their main application is as catalysts in the cross-coupling reactions such as Suzuki-Miyaura or Heck couplings.[2] When a thiosemicarbazone is used as ligand, the resulting palladacycle bears extra coordination positions in its structure. It could therefore be used as a metalloligand to incorporate a second metal. This leads to bimetallic structures which may be hetero- or homodinuclear depending on the reaction conditions. This second coordination tends to be labile, and these species are being investigated as potential new catalytic family.

In this publication we present the complete theoretical study of two heterodinuclear species bearing a palladacycle moiety by means of DFT study. The species, named **PdRh** and **PdPt**, are the result of the incorporation of Rh(I) and Pt(II), respectively, into the palladacycle moiety. The synthesis and characterization were previously done in our group.[3] For each compound, four conformers corresponding to two limit structures in the cyclometalated ring conformation were studied. The results showed that the relative energy of the compounds was influenced by the position of the NHR group of the thiosemicarbazone and that the relative energy differences were due to steric hindrance more pronounced in the case of **PdPt**.

Agradecimientos

We thank the *Axudas a proxectos de investigación nos distintos ámbitos científicos co obxectivo de impulsar a actividade científica dos grupos de investigación*. May 2024. Vicerreitoría de Política Científica. Universidad de Santiago de Compostela (USC).

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Use of half-lantern cyclometalated Pt(II)-Pt(II) complexes as down-converting filters: synthesis and properties.

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Luminescent materials, in particular those based on rare earth metals, have become a mainstay in various areas such as optoelectronic devices, biological applications and chemical probes. As rare earth metals are expensive, harmful for the environment and limited, in this area, transition metal complexes based on cyclometalated ligands have emerged as a promising alternative [1]. Recently binuclear cycloplatinated complexes have shown to be efficient NIR emitters attributed to a MMLCT excited state associated to an *intramolecular* Pt···Pt interaction [2], which can be additionally tailored by the bulkiness of the bridging ligands.

In this study, a novel series of binuclear Pt^{II}-Pt^{II} complexes, $[Pt(piq)(N\^{}S)]_2$, has been developed utilizing 1-phenylisoquinoline (piq) as the cyclometalating group and varying the thiolate bridging ligands (N^S = Spy **1**, Spy-CF_3 **2**, S-Q, (Q=quinoline) **3**, Spy-N **4**). The complexes have been fully characterized, including X-ray for **1**, **2** and **3**, and their optical and electrochemical properties investigated. Theoretical calculations have also been carried out to explain and understand the experimental results. Complexes **1**, **2** and **3** have been used as color down-converting filters to fabricate orange-red HLEDs devices.

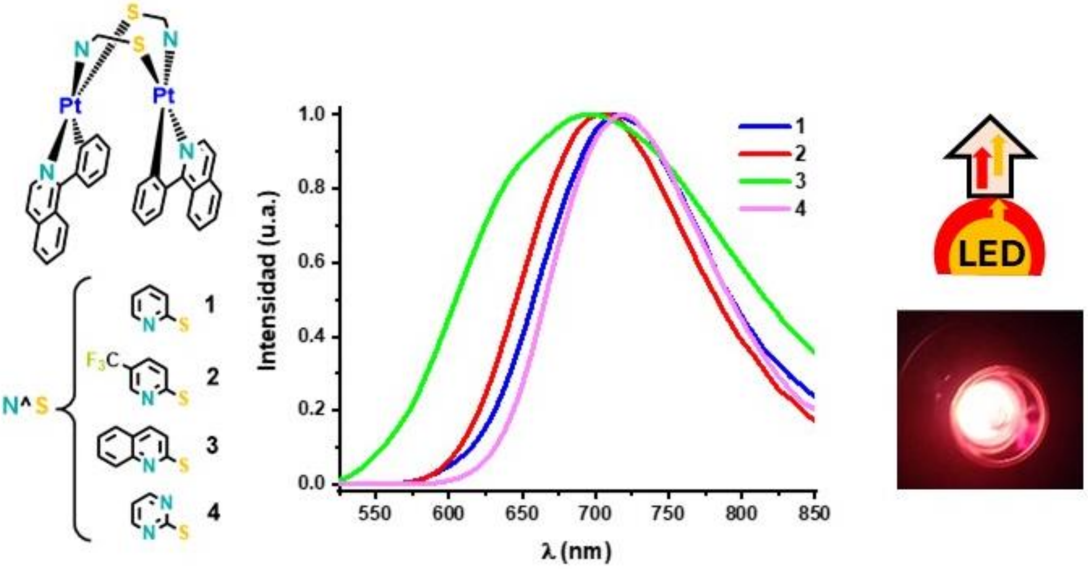

Fig.1. Scheme of the complexes, emission band profiles in PMMA films and a photograph of a down-converting device

Acknowledgements

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Study of the influence of the hydrogen bonds in the interaction of cooper complexes with DNA

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The interaction of DNA with small molecules can occur through different forms**.** The increase of DNA concentrations on a solution of the compound under study for the determination of the intrinsic binding constant, K_b, using Benessi-Hildebrand equation [1] can visualize the type of these interactions.

We have synthesized two cooper (II) complexes derived from hydrazide-hydrazones, A and B. The structure of this complexes is represented in the diagrams of the Fig. 1. The complexes were characterized by elemental analyse, IR and MS spectroscopies and X-ray diffraction of monocrystal. The complexes present flat structures but with different heteroatoms and functional groups. Complex A is a pyridoxal derived and complex B contain a hydroxyl derived from salicylaldehyde. Complex A contain a fluorophenyl group and complex B a furyl group.

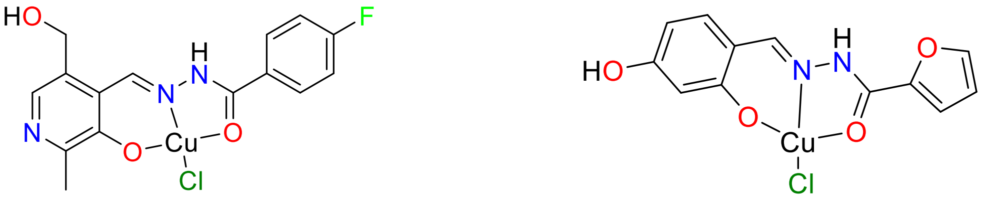

Fig.1. Scheme of the cooper (II) complexes, A to the left and B to the right, used to study the interaction with DNA

We studied the interaction of the two cooper complexes with DNA by UV-Visible spectroscopy, Fig. 2. The hypochromic effect takes place when the molecule and DNA interacts, mainly by intercalation. When we observe, mainly electrostatic interactions between the complex and DNA, hyperchromic effect is observed that reflects the corresponding changes in the conformation and structure of the DNA.[2] In our study, we can observe that in complex A, the principal type of interaction is by intercalation between the nitrogenous bases of DNA and in complex B, electrostatic or hydrogen bonds interactions are the most important.

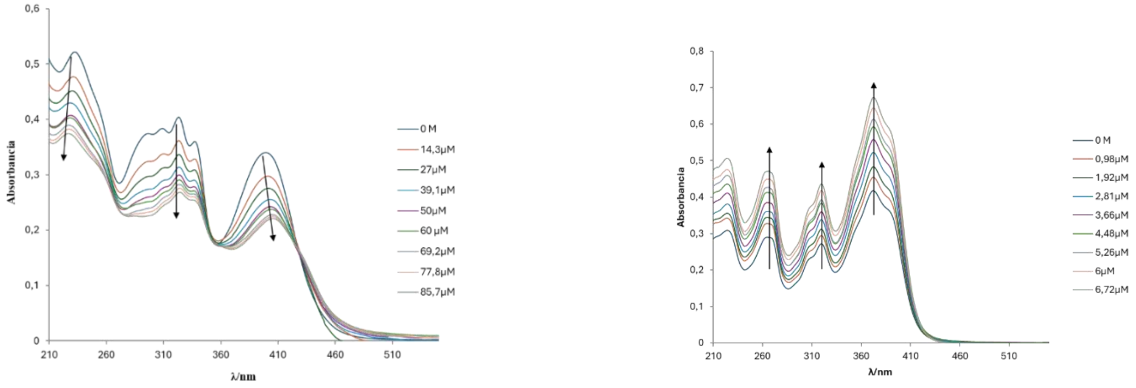

Fig. 2. Absorption spectra of the cooper (II) complexes, with a concentration of 37,6 μM for the complex A and 22μM for the complex B, in 10% EtOH/H_2O solution, in the presence of increasing amounts of DNA.

Acknowledgments
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Thermal, dielectric and optical properties of $[(CH_3CH_2)_3N(CH_2X)]_2[MnCl_4]$ ionic plastic crystals

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In recent years, hybrid metal halide materials, composed of organic cations and metal halide anions, have garnered significant attention within the scientific community. These materials exhibit a multiresponsive behavior to various external stimuli, such as temperature, electric and magnetic fields, light, and pressure, along with a range of functional properties including ferroelectricity, magnetism, optoelectronics, and barocaloric effects.[1] Notably, these properties and responses can be fine-tuned by modifying both the organic and inorganic components.[2] The structural configurations of these materials vary from extended three-dimensional networks to low-dimensional systems, depending on the specific pairing of metal halide anions with organic cations.

Among these, Mn^{2+}-based halide hybrids have emerged as promising candidates for light-emitting technologies, owing to their environmental friendliness, stability, tunable luminescence, nonlinear optical behavior, and high photoluminescence quantum yield (PLQY).[3] It is well-established that Mn^{2+} luminescence is strongly influenced by its coordination geometry. For instance, Mn^{2+} in an octahedral coordination emits red light, whereas zero-dimensional (0D) Mn^{2+} halides, featuring isolated tetrahedral $[MnX_4]^{2-}$ (X = Br, Cl) units, produce green emission with a large Stokes shift and PLQY values reaching up to 90%.[4]

In this study, we focus on two novel 0D hybrid tetrachloromanganate (II) compounds with the general formula $[(CH_3CH_2)_3N(CH_2X)]_2[MnCl_4]$ (X = Cl or Br), incorporating large, polar, quasi-spherical cations. These molecular cations possess a rigid inner structure and a flexible outer region, characterized by significant rotational mobility due to the presence of rotatable C–N and C–C bonds. This structural feature provides an interesting opportunity to introduce new functionalities to the tetrachloromanganate (II) anions.

In this work, we describe the synthetic methods for both compounds, and their crystal structures were elucidated using variable-temperature single-crystal X-ray diffraction or synchrotron powder X-ray diffraction. Additionally, we explored their responses to various external stimuli, including temperature changes, light exposure, and alternating electric fields. Our findings demonstrate significant responsiveness to these stimuli, suggesting that 0D hybrid tetrachloromanganate (II) compounds are multifunctional materials with potential applications beyond traditional light-emitting technologies.

Acknowledgments

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QI17

Inclusion compounds of cucurbit[8]uril and η^5-cyclopentadienyl molybdenum(II) tricarbonyl complexes for controlled release of CO

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In the present study [1], a monosubstituted cyclopentadienyl half-sandwich molybdenum(II) tricarbonyl complex $[(\eta^5\text{-}C_5H_4CO_2CH_3)Mo(CO)_3CH_3]$ (**1**) and its 1:1 inclusion compound with cucurbit[8]uril (**1**@CB8) were prepared. Both compounds were characterized by several tecniques (elemental and thermogravimetric analyses, powder X-ray diffraction, diffuse reflectance UV–vis, solid-state $^{13}C\{1H\}$ MAS NMR, FT-IR, and Raman spectroscopies). The CO-release profiles of **1**, **1**@CB8 and, for comparison, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3]$ (**2**) and **2**@CB8, were determined using the standard myoglobin assay. For assays performed in the dark and under physiological conditions (10 mM PBS, pH 7.4, 37 °C), complex **1** undergoes thermally assisted spontaneous CO release after 6 h of incubation (0.5 equiv. of CO). The half-life ($t_{1/2}$) for **1** (325 min) shows that it is a slow releaser when compared to complex **2** ($t_{1/2}$ = 25 min). CO release from **1** was promoted by exposure to UV light (λ = 365 nm; 0.9 equiv. of CO; $t_{1/2}$ = 85 min), establishing the complex as a photochemically activated CO-releasing molecule (photoCORM). For **1**@CB8, $t_{1/2}$ for photo-assisted CO release increased to ca. 7 h, and for **2**@CB8 the dark-release $t_{1/2}$ increased to 165 min, showing that molecular acceptors like cucurbiturils can be used effectively as second-sphere ligands to modulate the CO release profile of CORMs.

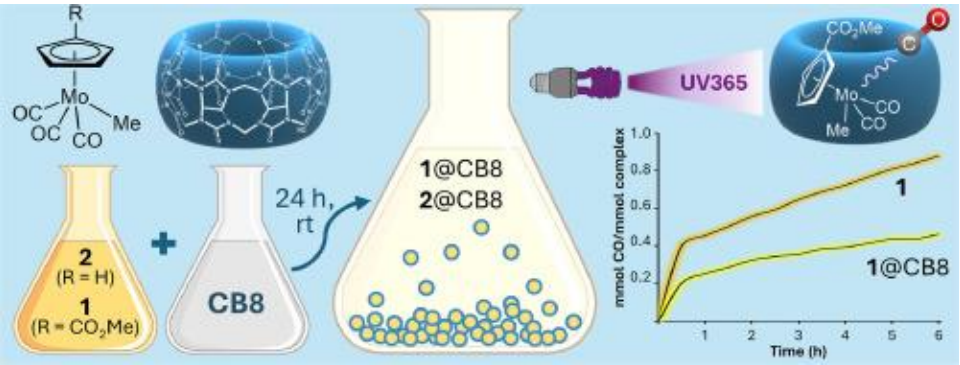

Fig.1. Inclusion compounds studied in this work, showing the CO release profiles for **1** and **1**@CB8.

Acknowledgments

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Synthesis of a silver achiral mesocate architecture

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Mesocates or *meso*-helicates are metallosupramolecular architectures formed by the self-assembly of, at least, two organic threads coordinated to two metal ions [1]. The main characteristic of this class of structure lies in the absence of chirality compared with the related chiral helicates, as in the mesocates the ligands do not cross each other [2]. Meso-helicoidal architectures could be relevant materials due to their potential properties such as magnetic, luminescent, or biological [3].

In the present work, we report the obtention of a silver *meso*-helicoidal architecture (Fig 1) based on an azine ligand (named LP) that possess two triphenylphosphine groups. The compound was fully characterized by different characterization techniques such as mass spectrometry, elemental analysis, infrared spectrometric and X Ray diffraction.

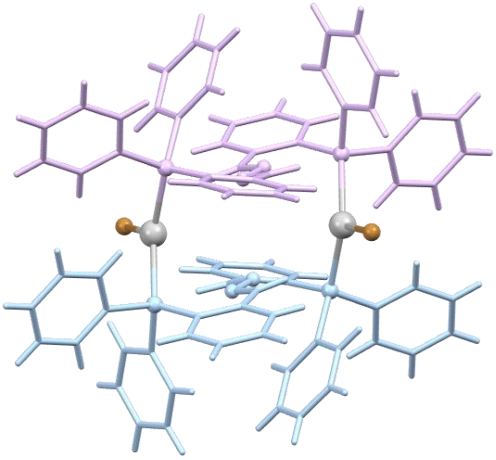

Fig.1. Representation of the *meso*-helicoidal architecture [$Ag_2(LP)_2$] derived from the phosphino-azine ligand (LP)

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Síntese dun ligando tiosemicarbazona funcionalizado cun grupo carborano-iminofosforano

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Os compostos coñecidos como tiosemicarbazonas (TSCs) constitúen un conxunto de ligandos moi versátiles e prometedores en química de coordinación, xa que están consideradas de gran interese farmacolóxico debido as súas diversas propiedades biolóxicas como a súa actividade antiparasitaria, antimicótica, antiviral, antibacteriana e antitumoral, entre outras [1,2]. Debido a isto, hoxe forman parte de moitos compostos bioloxicamente activos [3].

A pesar da gran variedade de derivados de TSCs estudados, na bibliografía non se atopa ningún exemplo de derivados de tiosemicarbazona que conteñan un grupo carborano ou un grupo iminofosforano nalgunha das súas posicións, a pesar das interesantes e potenciais aplicacións farmacolóxicas que estes poderían presentar.

Tendo en conta isto, nesta comunicación preséntase o primeiro exemplo dun potencial ligando tiosemicarbazona funcionalizado cos dous grupos mencionados anteriormente, carborano e iminofosforano (Figura 1).

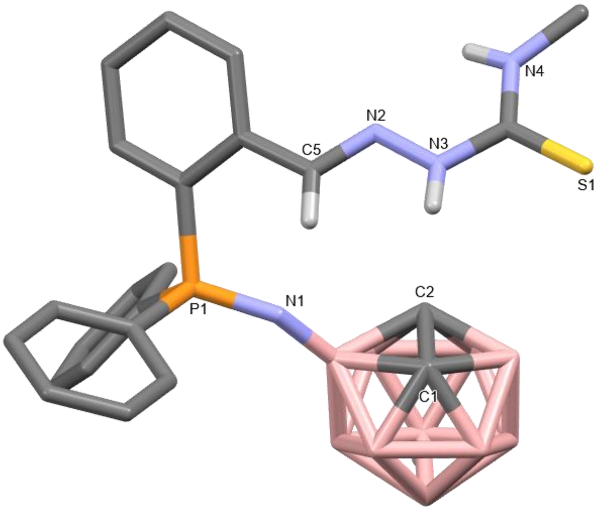

Fig.1. Ligando carborano-iminofosforano derivado de tiosemicarbazona.

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Modificación dun ligando *bis*carbamato para o estudo do seu comportamiento coordinativo

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As arquitecturas metalosupramoleculares de tipo helicatos acadaron unha gran relevancia debido a súa habilidade para envolver ó ADN, o que se relaciona co procedemento de recoñecemento celular[1] e polo seu potencial como novos fármacos anticanceríxenos ou como sistemas de liberación de fármacos.[2] Asimesmo, sobresaíron nos campos da catálise, a Bioloxía Molecular, Química dos Materiais, entre outros.[3–5]

No noso grupo de investigación empregouse unha metodoloxía electroquímica para estudar o comportamento coordinativo dun ligando *bis*carbamato, derivado dun espazador de piridina, e obtivéronse arquitecturas de tipo helicato dinucleares.[6] Nesta comunicacións continúase con dito estudo coordinativo, pero, neste caso, modificando os grupos colgantes do ligando orixinal para ver se isto afecta a arquitectura final dos compostos.

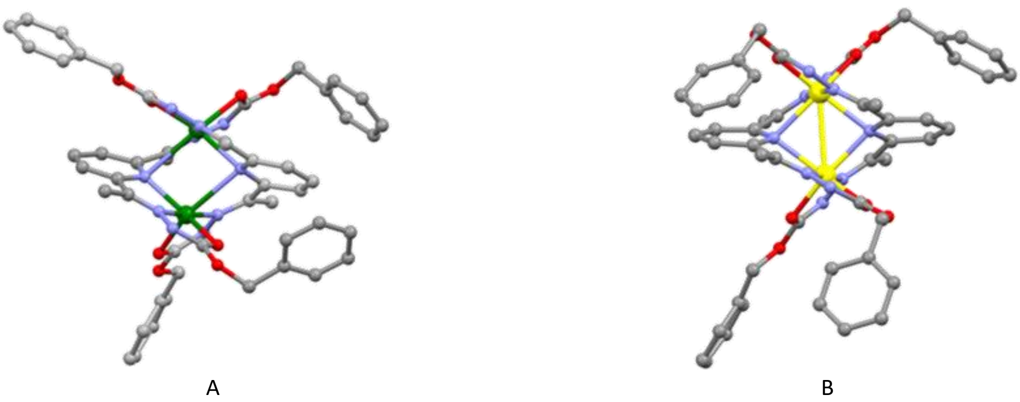

Fig.1. Estruturas de raios X dos helicatos dinucleares $[Cu_2(L^3)_2]$ (A) e $[Ni_2(L^3)_2]$ (B)

Agradecimientos

Consellería de Cultura, Educación e Ordenación Universitaria, Xunta de Galicia, 9 2023GRCGI-1584 (ED431C 2023/02). Ministerio de Ciencia e Innovación, Proxecto PID2021- 10 127531NB-I00 (AEI/10.13039/501100011033/ FEDER, UE) e METALBIO (RED2022-134091-T).

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Luminescent cationic cyclometalated $\mathrm{Pt^{II}}$ complexes with rigid diphosphines

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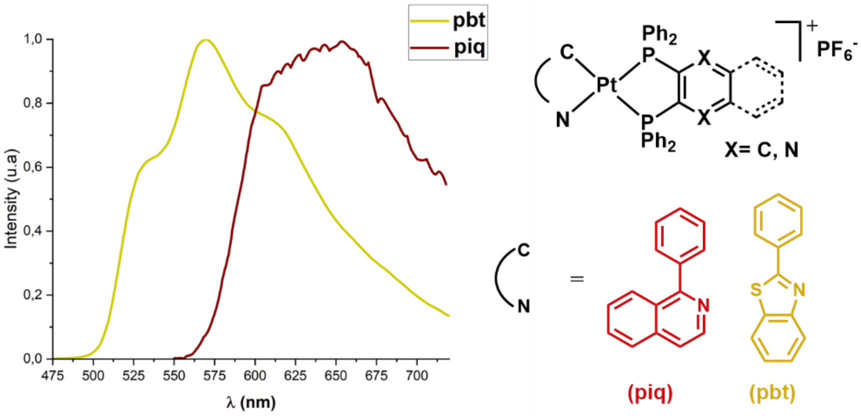
In the search of novel phosphorescent materials based on transition metal complexes, cyclometalated Pt(II) derivatives had and still have a prominent space.[1] Their rich spectroscopic and photophysical properties allow their implementation in diverse fields such as biomarkers and optoelectronic devices. These photophysical properties can be modulated by the change in the electronic nature of the cyclometalated ligand and also with the introduction of rigid, strong sigma donating ancillary co-ligands.[2] Among these, diphosphines combine a rigid bonding feature that ensures stability, while gifting the complexes thus prepared $[\mathrm{Pt(C^\wedge N)(P^\wedge P)}]^+$ with a positive charge, which is of great interest for their potential application in, for example, Light Emitting Electrochemical Cells (LECs).[3]

In this study, we report a new series of mononuclear cationic cyclometalated $\mathrm{Pt^{II}}$ complexes with C^N = 1-phenylisoquinolinate (piq), 2-phenylbenzothiazolate (pbt) and diphosphine ligands $[\mathrm{Pt(C^\wedge N)(P^\wedge P)}]^+$ [P^P = 1,2-bis(diphenylphosphine)benzene (dppbz), 2,3-bis(diphenylphosphine)pirazine (dpppyz) and 2,3-bis(diphenylphosphine)quinoxaline (dppQx)]. The compounds have been fully characterized using mass spectrometry, NMR and X-ray diffraction. Finally, their optical properties have been studied and the origin of their bright orange-red emissions rationalized on the basis of the characteristics of the ligands employed.



Absorption and emission band profiles in solid state at 298 K with dppbz. Scheme of the presented complexes.

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Transforming PET of a plastic bottle into new molecules with potential antimicrobial activity

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Plastic production and its massive use is a huge problem in our world, with major consequences for soil, water, and air pollution. Although the discovery of plastics had a lot of positive effects, such as providing a barrier against moisture, air and contaminants from food, beverages and pharmaceuticals, plastic packaging is mainly used for the short-term being discarded afterwards leading to massive waste [1].

Polyethylene terephthalate (PET), a commodity plastic, is formed by two monomers: ethylene glycol and terephthalic acid (Figure 1). After obtaining recycled PET monomers through depolymerization, regardless of the method employed, these molecules can be used as a feedstock to synthesize other compounds with higher added value [1].

The urgent demand for effective antibiotics to fight bacterial resistance mechanisms has driven the development of new antimicrobial agents that offer high potency, greater specificity, and reduced toxicity [2]. Metal complexes are undergoing clinical development for the treatment of cancer, malaria, and neurodegenerative diseases. However, their potential as antimicrobial agents had received limited attention [3].

When plastic is dumped into the ocean, exposure to seawater leads to its degradation, complicating recycling through conventional methods. As a result, much of the plastic collected on beaches ultimately ends up in landfills. Our group is collaborating with Ílhavo City Council and some local school groups to collect plastic on beaches and coastal areas. To reduce plastic waste, we are establishing a method for depolymerizing PET plastic, allowing the reuse of this material through the development of metal complexes based on terephthalate derivatives and the study of their potential antimicrobial properties.

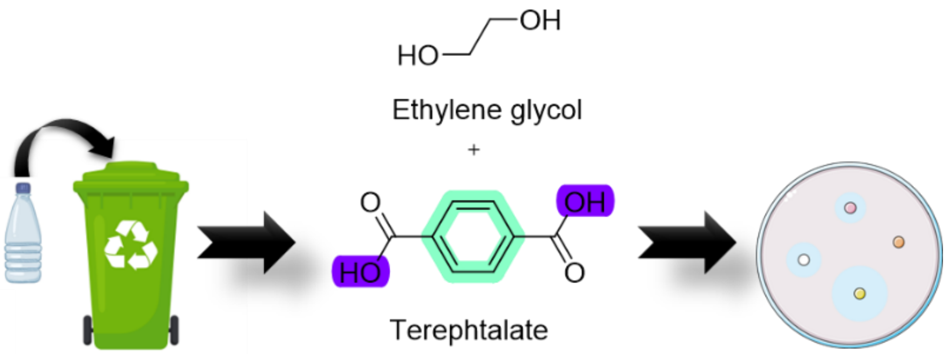

Figure 1: Terephthalate derivatives obtained from PET as new molecules with potential antimicrobial activity.

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QUÍMICA ORGÁNICA

Síntesis de Nuevos Análogos de Brasinoesteroides benzoilados en C-22 con distintos sustituyentes y su potencial actividad en el crecimiento vegetal

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Los Brasinoesteroides (BRs) son hormonas vegetales que participan en diferentes procesos de la planta, como la elongación del tallo, expansión celular, entre otros efectos. El primer BRs aislado y caracterizado completamente en 1979 corresponde a la brasinólida (**1**), que fue extraída desde *Brassica napus* y estudiada debido a que algunos extractos de su polen producían un poderoso efecto de elongación en el tallo del frijol [1].

Si bien, los BRs son posibles de encontrar en las hojas, polen, flores y semillas de la planta, sus concentraciones detectadas en estas fuentes naturales son muy bajas [2], por lo tanto, la síntesis de nuevos análogos cobra una vital importancia, donde algunos ya han sido patentados como sustancias promotoras del crecimiento vegetal [3]. Debido a la gran cantidad de estudios que se han realizado desde la década de los 80' en adelante, se han logrado identificar ciertas características estructurales importantes en los BRs que aumentan considerablemente la actividad biológica en el crecimiento vegetal como la presencia de grupos funcionales oxigenados en los anillos A y B y la incorporación de anillos aromáticos en la cadena lateral [4].

En base a lo anterior, en esta investigación se ha planteado una ruta sintética a partir del compuesto comercial ácido hiodeoxicólico (**2**) para la obtención de ocho nuevos análogos de Brasinoesteroides con la presencia de los grupos funcionales cetona en C-3 y C-6 (anillos A y B respectivamente) y grupos benzoilo en C-22 (cadena lateral) con diferentes sustituyentes en posición *para* del anillo aromático (**3a**-**h**), para así estudiar el efecto modulador en la actividad biológica y sus interacciones con el receptor de brasinoesteroides BRI1. Todos los análogos y compuestos intermedios fueron caracterizados por técnicas espectroscópicas de IR, RMN y EM.

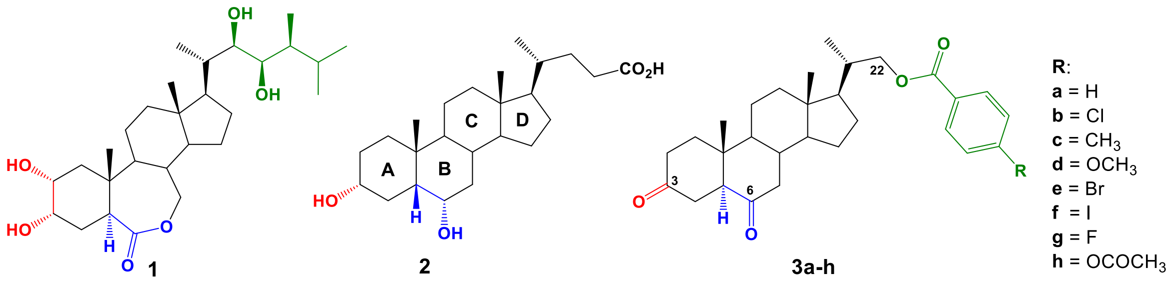

Figura 1. Estructuras de: brasinólida (**1**), ácido hiodeoxicólico (**2**) y nuevos análogos de brasinoesteroides **3a**-**h**.

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Preparation of Bis(silyl)peroxide

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Over the past century, silicon organic peroxides have emerged as valuable organometallic peroxides in organic synthesis, due to their thermal stability and long shelf life compared to traditional organic peroxides. The synthesis of bis(silyl)peroxides (BSPs, **Figure 1**) is relatively straightforward and well-established, typically involving the reaction of a chlorosilane with a hydrogen peroxide source, such as a hydrogen peroxide-urea complex, in the presence of a base, along with other methods that often rely on concentrated hydrogen peroxide solutions.[1,2] Silicon organic peroxides serve as synthetic building blocks in various oxidative processes using metal catalysts, selective alkylations, and as radical initiators with applications ranging from organic synthesis to materialC chemistry. Their reactivity is influenced by the strength of the peroxy bond and the experimental conditions, including temperature, irradiation, catalysts, additives, and nucleophiles, facilitating reactions through ionic or radical pathways.[3-6]

Although the preparation of BSPs has been documented in the literature, the yields obtained for isolated products are often not reported. In this study, we will detail our methods of preparation, isolation, and characterization of BSPs, along with the outcomes of our efforts to enhance the yields.

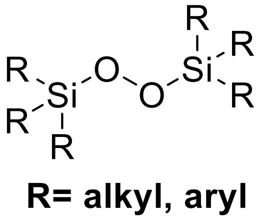

Fig.1. General structure of bis(silyl)peroxides.

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Novel On-Site Oxidation Protocol for the *N*-Hydroxylation of Melanostatin Neuropeptide Using Cope Elimination

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N-hydroxylated peptides have gained recent attention due to their unique conformational and physicochemical properties, which can profoundly impact biological activity.[1] However, the incorporation of *N*-hydroxyproline into peptides has remained a challenge, often requiring protection and deprotection steps that lead to a low atom economy and increased waste of solvents and reagents. This work presents an innovative approach to *N*-hydroxylation of proline (Pro) in peptides through an on-site oxidation strategy utilizing Cope elimination. In this work, this methodology was applied to the synthesis of an *N*-hydroxylated analog of Melanostatin (MIF-1, Figure 1), an endogenous tripeptide.

The key to this method is to avail the dual functionality of the *N*-(cyanoethyl) group, which serves as both a protecting group during peptide synthesis and as a leaving group in the subsequent oxidation step. The synthetic route begins with *N*-(cyanoethyl)-L-proline, which is coupled through classical peptide synthesis strategies to form a MIF-1 Pro mimetic. Following the peptide coupling, treatment with *m*-chloroperbenzoic acid induces Cope elimination with *N*-hydroxylation at Pro residue.

This one-step oxidation proceeds under mild conditions with excellent yield (93%), avoiding the need for additional deprotection steps. Comparative studies demonstrated that early introduction of the *N*-(cyanoethyl) group provided superior overall yields (78%) compared to late-stage introduction (41%).

The methodology was successfully applied to synthesize *N*-hydroxy-MIF-1, representing the first *N*-hydroxylated analog of this neuropeptide. This on-site oxidation strategy via Cope elimination offers a valuable new tool for selective *N*-hydroxylation of Pro residues in peptides, potentially enabling the development of novel bioactive compounds.

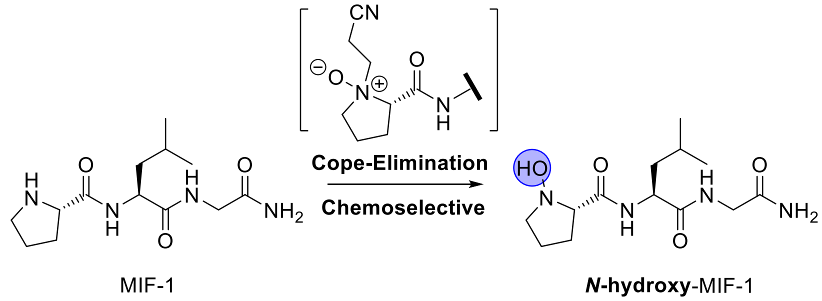

Fig.1. On-site oxidation of MIF-1 by Cope-elimination.

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Synthesis and Characterization of Neutral- and Cationic-Substituted Zinc(II) Phthalocyanine Dyes

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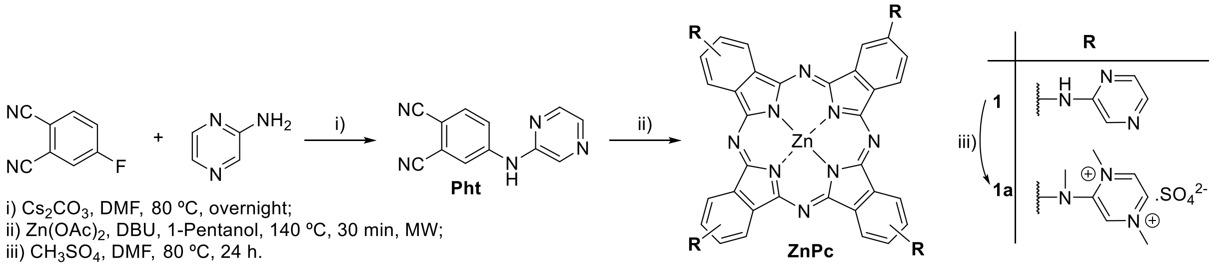
The development of new phthalocyanine (Pc) derivatives has been a challenging area for synthetic researchers, aimed at exploring their applicability across various scientific and technological fields. Pc dyes are photoactive molecules capable of absorbing and emitting light over a wide range of the UV-Vis spectrum [1,2]. Nevertheless, the low solubility of this class of compounds poses a major challenge for their application in various fields, particularly in biomedical contexts [3]. Incorporating pyrazine/pyrazinium units into Pc structures may be an effective strategy to enhance their solubility in different media [4,5]. In this communication, we will report and discuss the synthesis and characterization of pyrazine-substituted phthalonitrile (**Pht**) and the corresponding zinc(II) phthalocyanine derivatives (**ZnPcs 1** and **1a**) – Figure 1. A comparative analysis will be conducted between the neutral (**ZnPc 1**) and the cationic (**ZnPc 1a**) substituted phthalocyanines. The NMR, absorption, emission spectroscopy, and mass spectrometry will be analyzed for the prepared dyes.



i) Cs_2CO_3, DMF, 80 °C, overnight;
ii) $Zn(OAc)_2$, DBU, 1-Pentanol, 140 °C, 30 min, MW;
iii) CH_3SO_4, DMF, 80 °C, 24 h.

Fig.1. Pyrazine phthalonitrile (**Pht**), pyrazine zinc(II) phthalocyanine (**ZnPc 1**) and pyrazinium zinc(II) phthalocyanine (ZnPc **1a**).

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Strategies for the synthesis of key metabolites of cathinone derivatives pentedrone and methylone

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New psychoactive substances pose a significant public health threat since they were first marketed as legal alternatives to illicit drugs, readily available online and with limited information regarding their properties. Among these substances, synthetic cathinones are widely consumed due to their psychostimulant effects, with methylone and pentedrone being representative examples of the ones used in the USA and Europe [1].

The metabolism of synthetic cathinones has been extensively studied and is well-documented in literature. For instance, the metabolic pathways of methylone include *N*-demethylation, *O*-demethylation and β-keto reduction leading to the formation of key metabolites such as nor-methylone, dihydroxymethcathinone (DHMC) and dihydromethylone, respectively [2]. Similarly, metabolites resulting from *N*-demethylation and β-keto reduction have been reported for pentedrone, namely nor-pentedrone, dihydropentedrone and nor-dihydropentedrone [3]. While synthetic cathinones have been widely studied, information regarding the biological effects of their metabolites is still limited. For further investigation into these metabolites, their synthesis is essential.

In this work, diverse strategies have been applied to synthesize the above-mentioned metabolites. As an example, the synthesis of dihydropentedrone and dihydromethylone was successfully performed by β-keto group reduction of the respective cathinone using sodium borohydride with good yields (64-96%) [4]. The total synthesis of other metabolites is ongoing. The structure elucidation of metabolites and intermediates has been confirmed using spectroscopic methods, such as IR, ^1H and ^{13}C NMR.

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Synthesis, enantioseparation and absolute configuration of a benzyl 2-hydroxyoctanoate precursor for cyclic peptides

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Marine cyclic peptides are very promising for the development of new therapeutic agents due to their unique structures, chemical properties, and interesting biological activities, such as antimicrobial [1]. Among the many described antimicrobial marine cyclic peptides, Unnarmicins A and C are outstanding examples. Both inhibit the fungal ABC transporters whose overexpression is the cause of the highest levels of multi-drug resistance of pathogenic fungi [2].

In a recent work, a series of unnarmicin analogues were designed and docked against a CaCdr1p efflux pump to select the most promising compounds [3]. The virtual hit compound, emerging from this structure-based virtual screening, resulted from the assembly of a tetrapeptide linked to a (*R*)-2-hydroxy fatty acid comprising an octanoic chain.

Herein, initial steps towards the synthesis of the most promising analogue are described. The synthesis, enantioseparation and absolute configuration determination of an aliphatic benzyl 2-hydroxyoctanoate precursor were taken to obtain the desired enantiomer with high enantiomeric purity. The synthetic reaction was successfully carried out, achieving a yield of 58% and the structure was established by IR, ^{1}H NMR and $_{13}$C NMR techniques. Chiral liquid chromatography was chosen for enantioseparation using a Lux Amylose-1® column and 100% ethanol as mobile phase. Favourable enantioseparation and resolution were achieved, with α and Rs values of 1.60 and 3.26, respectively. The enantiomeric ratio values for both enantiomers were higher than 99%. The absolute configuration of the enantiomers was determined by electronic circular dichroism (ECD) with the aid of theoretical calculations. The first eluted enantiomer was identified as the (*R*)-enantiomer.

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Bifurcaria bifurcata macrolga parda (Phaeophyceae) productora de sustancias antimicrobianas

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Bifurcaria bifurcata R. Ross 1958 macroalga parda (Phaeophyceae) del orden Fucales (fucoides) es una especie perenne dominante y ampliamente distribuida a lo largo de la costa atlántica europea [1,2]. Los recursos de *B. bifurcata* en Europa son muy abundantes, aunque todavía no se han explotado, en contraste con otros fucoides como *Ascophyllum nodosum* (Linnaeus) Le Jolis 1863 y *Fucus* spp. que ya se explotan comercialmente para varias aplicaciones industriales [3]. Además, se ha observado que las poblaciones de *B. bifurcata* han aumentado su abundancia y/o ampliado su área de distribución a lo largo de la costa norte de España en el contexto actual de calentamiento global [4]. Se ha demostrado que los extractos de *B. bifurcata* son una fuente prometedora de diterpenos lineales bioactivos [5].

En un trabajo anterior, establecimos las propiedades antioxidantes de los extractos de *B. bifurcata* analizando el efecto de los extractos de *B. bifurcata* en células Caco-2 sometidas al efecto de estrés oxidativo del tert-butil hidroperóxido (tert-BOOH). Los resultados de este estudio indican que el extracto de *B. bifurcata* ejerce un efecto antiapoptótico que protege a las células Caco-2 contra el estrés oxidativo inducido por el tert-BOOH. Este efecto antiapoptótico se asoció con una menor generación de ROS, una menor producción de NO y una inducción eficaz de enzimas antioxidantes. Todas estas propiedades biológicas convierten a los extractos de *B. bifurcata* en interesantes candidatos para la quimioprotección celular. Por lo tanto, los productos aislados a partir de extractos de *B. bifurcata* pueden contribuir a la protección contra enfermedades en las que el estrés oxidativo se ha implicado como factor causal o contribuyente, o como alternativas potencialmente eficaces a los agentes oxidantes en la industria de los alimentos funcionales [6].

El objetivo del presente estudio fue evaluar el contenido químico de extractos orgánicos seleccionados de *B. bifurcata* recolectados en Cantabria (España) y purificar e identificar los metabolitos secundarios producidos por esta especie y evaluar la actividad antimicrobiana de los metabolitos aislados.

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Synthesis of siderophore-antifungal conjugates as an innovative strategy to tackle multidrug resistance

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The growing issue of antifungal resistance in human fungal pathogens poses a significant challenge in modern medicine [1]. There is an urgent need to explore new strategies beyond conventional therapies to address this problem. Recently, siderophores have emerged as a promising avenue to tackle resistance [2]. This novel approach has garnered considerable attention in medicinal chemistry and antimicrobial drug discovery, although it has yet to be fully explored for fungal infections. The potential for conjugating siderophores with antifungal agents offers a "Trojan Horse" strategy, leveraging microorganisms' iron transport systems to deliver antifungal drugs directly into the cell, providing an effective solution against multidrug-resistant pathogens [3].

In a previous work, one hit compound emerged (**Fig.1**) from a synthetic library of six different siderophore mimetics, showing the highest affinity for Fe(III). Thus, the present work involves the design, synthesis, and lead generation of new siderophore-antifungal conjugates for treating antifungal infections using the selected siderophore. First, the siderophore was obtained in a straightforward amide coupling reaction between 2,3-bis(benzyloxy)benzoic acid, a moiety frequently found in naturally occurring siderophores, and commercially available L-DOPA, as building blocks. The siderophore mimetic was condensed with a linker to be further conjugated with structurally diverse antifungal compounds. The structure elucidation of all the synthesized compounds was established by nuclear magnetic resonance (NMR) spectroscopy.

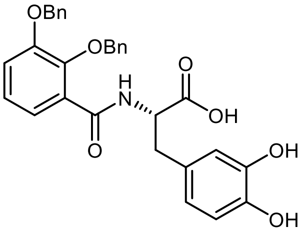

Fig.1. Bis(benzyloxy)benzoic acid siderophore mimetic.

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Synthesis and optical properties of a new rhodamine–thiazolothiazole conjugate

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The development of fluorescent molecules is crucial for advancing scientific research and technological applications across multiple fields including bioimaging, environmental monitoring, solar cells, and organic light-emitting diodes (OLEDs) [1].

Rhodamines are well-known fluorescent dyes characterized by their exceptional photophysical properties, which include high molar absorptivity, strong fluorescence in the visible spectrum, and variable quantum yield and fluorescence lifetime, depending on the solvent [2]. Another important class of fluorophores is the thiazolo[5,4-*d*]thiazoles (TzTz), characterized by a rigid, coplanar structure composed of two fused thiazole rings, an extended π-conjugated system, and high environmental stability [3].

In this work, we present a novel fluorescent conjugate that combines these two important classes of fluorophores: rhodamines and thiazolo[5,4-*d*]thiazoles (TzTz). The newly synthesized compound (Rhod–TzTz–Rhod) features a central TzTz unit connected via phenyl bridges to two rhodamine B hydrazide units (Fig. 1). The synthesis and structural characterization of this novel conjugate, as well as its photophysical properties, pH-dependent fluorescence, and metal ion sensitivity will be discussed.

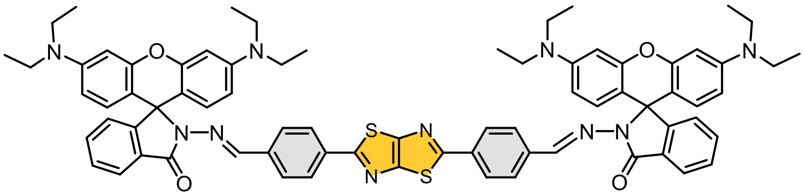

Fig.1. Novel fluorescent conjugate Rhod–TzTz–Rhod.

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Synthesis of new acridone derivatives with G-Quadruplex DNA Stabilization Properties

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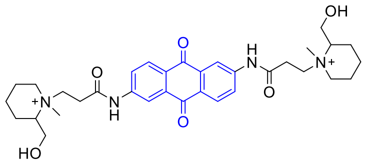
Cancer is one of the leading causes of mortality worldwide and the numbers are expected to increase around 40% in next two decades with high incidence in male population. The evidence that telomerase, tumour suppressor genes and oncogenes are closely associated with the initiation and progression of tumours, justifies their use as targets for the development of new anticancer drugs [1].

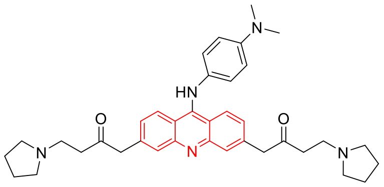
The use of interactive ligands that target secondary DNA structures, such as G-quadruplexes (G4), found in telomeres and in the promoters of most human oncogenes, is considered a promising anticancer strategy. This approach can contribute to downregulating transcription or blocking telomere elongation in cancer cells by stalling the DNA replication machinery [2].

Several organic compounds have been evaluated as G4 stabilizers and as potential anticancer drugs. The first G4 organic ligand described was the 2,6-diaminoanthraquinone derivative [2]. Other examples are BRACO and CX-5461 (Figure 1), the latter is already in clinical phase trials and presented favorable interactions with the G4 DNA and direct correlations with the tumors' growth control [3].

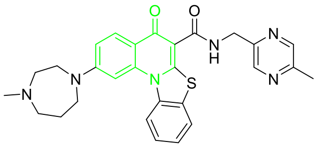
In line with our interest in developing new heterocyclic compounds with the ability to stabilize G4 structures [4], we report here the synthesis and characterization of a neutral and a cationic derivative based on the acridone scaffold (Fig. 1). The synthetic strategy, photophysical characterization, and ability of the two new acridone derivatives to stabilize G4 structures in the telomeric and c-*myc* oncogene DNA sequences will be discussed.



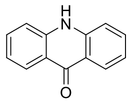
2,6-diaminoanthraquinone derivative



BRACO-19



CX-5461/Pidnarulex



acridin-9(10*H*)-one

Fig. 1. Structure of efficient G4 stabilizing ligands.

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A New and Efficient Approach to the Synthesis of Red-shifted Aminoimidazole Azo Dyes with Potent Antimicrobial Activity

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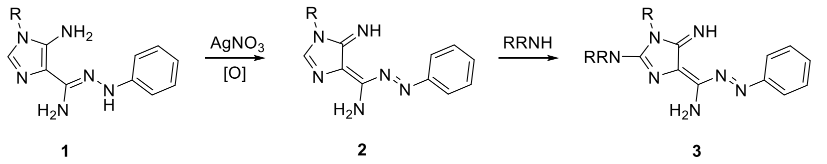
Azo dyes are the most important synthetic colorants in textile industry, printing, and paper manufacturing. They are also common building blocks of materials with potential applications in the areas of optical storage media, drug delivery, liquid crystals, nonlinear optics, and chemosensors [1]. The world's production of industrial azo dyes essentially involves azobenzene derivatives, which commonly exhibit colours in the yellow-red range. However, replacing one or both benzene moieties with heterocyclic units affords functional advantages and unusual spectral properties, such as enhanced colouring properties, tinctorial strength, thermal stability, and a desired solvatochromic behavior [2]. The incorporation of heterocycles in azo dyes offers a broader structural diversity and additional H-bonding interactions, which usually enhance the bioactivity [3]. Imidazole nucleus has become one of the most important synthons in medicinal chemistry and has demonstrated particular relevance in the design of new imidazole-based antifungal agents [4]. However, imidazole-containing azo dyes with antimicrobial activity are limited in the literature.

The conventional syntheses of imidazole azo dyes mainly involve coupling of diazonium salts with the more electron-rich nucleophile segments. A novel route to obtain 2-aminoimidazole azo dyes with unique substituents pattern in the imidazole unit have been previously reported. The reaction pathway (**Figure 1**) starts with the preparation of the azoimidazole **2** from amidrazones **1**. Reaction of **2** with secondary amines affords the 2-amino azoimidazoles **3** [5]. This new class of azoimidazoles (**3**) exhibits vibrant magenta - violet colours, showed potent antimicrobial properties against infectious yeasts, and no cytotoxicity was detected for concentrations lower than 16 □g□mL^{-1}. However, the method required the presence of highly amounts of the expensive $AgNO_3$ catalyst, suffered from the unwanted formation of secondary products and additional purification steps to remove contaminants and the solid Ag^0 were required. In this communication, a simpler method has been developed where a catalytical amount of a more sustainable and accessible catalyst was used, and the products were isolated in higher yields with no need for further purification. Additional details will be presented and discussed.



- *Candida krusei:* MIC and MLC ≥ 4 μg.mL^{-1};
- *Cryptococcus neoformans:* MIC and MLC ≥ 2 μg.mL^{-1}.

Figure 1 – Synthesis of halochromic & antimicrobial 2-aminoimidazole azo dyes **3** from amidrazone precursors **1** [5].

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New Red-shifted Aminoimidazole Azo Dyes with Halochromic Properties: Colorimetric Studies

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Halochromic molecules have received significant attention for smart materials development due to their capacity to exhibit a visual colour change when exposed to pH variations stimuli [1]. Although azobenzenes have been more extensively studied as photochromic dyes, aminoazo dyes have been usually used as pH indicators because significant spectral differences can be found between their acid and base forms. In general, the $\pi\pi^*$ band of the parent azobenzene is found in the UV-region (~320 nm), and the presence of amino substituents can red-shift this band to > 400 nm [2]. Changes in pH lead to protonation of azo compounds, which can occur in the nitrogen of the azo-group or at peripheral nitrogens, resulting in a shift of its absorption spectrum and consequent colour change [3]. Incorporating heterocyclic moieties in azo dyes affords unusual spectral properties over conventional azobenzenes, such as enhanced colouring properties, tinctorial strength, thermal stability, and higher bathochromic effects [4]. However, reported imidazole-containing azo dyes are limited in the literature and exhibit yellow-red colours, like classical azobenzenes. In addition, it is important to note that no prior reports were found on red-shifted imidazole-based azo dyes exhibiting halochromic properties.

A novel route to obtain 2-aminoimidazole azo dyes with unique substituents pattern in the imidazole unit have been previously reported [5]. This new class of azoimidazoles exhibits vibrant colours that change from magenta to deep blue as the pH decreases. In addition, they showed potent antimicrobial properties against infectious yeasts, and no cytotoxicity was detected for concentrations lower than 16 $\mu g \cdot mL^{-1}$. Recently, new derivatives were prepared and their colorimetric and halochromic properties were studied. We found that this class of 2-aminoimidazole azo dyes, in fact, can exist in three different ionization forms, showing three distinct colours (**Figure 1**). As previously reported, the neutral form exhibits a vibrant magenta colour. When one equivalent of acid is added a violet form is obtained, and when an excess of acid is further added, the colour changes to a brillant red. In this communication, the experimental results of the study will be presented and discussed.

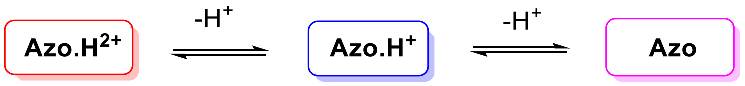

Figure 1 – Halochromic 2-aminoimidazole azo dyes**:** colours of the three different ionization forms.

Acknowledgements
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Synthesis of building blocks for further design of fluorescent probes for enantioselective quantification of amino acids

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The process of discovery of amino acids (AAs) began more than two centuries ago when proteins were put in boiling acid, were broken down, and simple substances were obtained and isolated over time, many of which were identified as AAs [1, 2]. For a long time, it was believed that the proteins of living systems were composed only of AAs in the L configuration, with the D-amino acids (D-AAs) being associated with "non-natural" molecules, creating the doubt of the possible presence of this homochirality in organisms [2-5]. Nevertheless, many discoveries involving D-AAs were made since 1935 until now [2]. Nowadays, all D-AAs have been detected in various locations of the human body, such as the brain tissue, kidneys, liver, blood, urine, cerebrospinal fluid, teeth, eye lens, among others. Despite this, high or low levels of several D-AAs have been associated with several diseases, including neurodegenerative disorders, and can be used as biomarkers for early diagnosis or therapy [2, 4, 6, 7].

Considering this important application, this work describes the synthesis of different fluorophore building blocks to be associated to a chiral unit for further design of fluorescent probes for detection and quantification of D-AA and D/L AA ratios. One of the synthetic strategies considers the substitution of positions 2 and 7 of the xanthone nucleus with amine groups, resulting in a precursor containing a functional handle for a subsequent bond of the chiral structure. This transformation was achieved through nitration and reduction reactions, using potassium nitrate and tin chloride, respectively. The 3,6-dihydroxyxanthone was also synthesized in one-step synthesis by heating the 2,2',4,4'-tetrahydroxybenzophenone at high temperature. The 3,6-dihydroxyxanthone has also the appropriate features to be applied as a fluorophore building block. The structures of these synthetic units were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. The fluorophore building blocks are intended to serve as the base for future studies aiming enantioselectivity coupling with both D- and L-amino acids in human biological fluids. These studies will provide crucial insights into the enantioselective binding properties and potential diagnostic applications for diseases associated with the presence of D-amino acids.

Acknowledgements
This work is financially supported by UIDB/04423/2020 and UIDP/04423/2020 (Group of Marine Natural Products and Medicinal Chemistry and by CESPU, projects grant number XANTAAL-GI2-CESPU-2022 and XRED-AA-GI2-CESPU-2023.

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Enantioseparation of Nadifloxacin by Amylose based Chiral stationary Phase

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Antibiotic residues have been detected in various environmental matrices, such as surface water and even drinking water (1). Although present at low levels (µg/L, ng/L), the occurrence of antibiotics in the aquatic compartments may have huge implications due to their possible uptake and biomagnification through the food chain, as well as due to their contribution for dissemination of antimicrobial resistance (2). Fluoroquinolones (FQs) are antibiotics that are widely used to treat bacterial infections in both humans and animals. Their excessive use has become worrying for the scientific community since FQs are very recalcitrant in the environment.(3) Although environmental assessment of chiral pharmaceuticals is of utmost importance, there is a lack of knowledge about enantioselective ecological processes and influence of these behaviors in the different environmental compartments (4)Nadifloxacin (NDF) is a chiral (racemic FQ) antibiotic, used worldwide for acne vulgaris and other skin infections (5). The (*S*)-enantiomer of the NDF corresponds to the levonadifloxacin (LNDF). knowledge about enantioselective ecological processes and antimicrobial resistance of NDF is missing. In order to further investigation of the enantioselective in antimicrobial resistance of NDF it is crucial to hand the pure enantiomers. This work describes the optimization conditions of the enantioseparation of NDF in semi-preparative scale using an amylose based chiral stationary phase. The strategies were adopted in terms of developing a more environmentally friendly method of separation, like substitute the trifluoro acetic acid for formic acid and isopropanol for ethanol in the mobile phase. Both enantiomers of NDF were achieved with high enantiomeric purity.

Acknowledgements
This work is financially supported by national funds through the FCT/MCTES (PIDDAC), under the projects 2022.02842.PTDC – STAR - STereoselective environmental processes in Antibiotics: role for Resistance, with DOI 10.54499/2022.02842.PTDC (https://doi.org/10.54499/2022.02842.PTDC) and 2022.08738.PTDC, PTDC with DOI 10.54499/2022.08738.PTDC (https://doi.org/10.54499/2022.08738.PTDC) and also supported by UIDB/04423/2020 and UIDP/04423/2020 (Group of Marine Natural Products and Medicinal Chemistry).

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Synthesis of cationic diketopyrrolopyrroles for biological applications

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Diketopyrrolopyrroles (DPP) are a family of organic pigments that have been drawing scientists' attention due to their fascinating properties. Initially these compounds were used as pigments and dyes for plastics, but nowadays they are indispensable in optical and electronic devices and are being evaluated as biological probes and as photosensitizers for the photodynamic inactivation of microorganisms, for example [1–3].

In this communication, we present the synthesis of two cationic DPP derivatives that will be used as photosensitizers. After the *N*-alkylation of a starting DPP with a dibrominated alkylating agent, reaction with phosphine derivatives afforded the expected dicationic derivatives **3** and **4** (Fig.1) [4]. The photophysical properties and biological activity of the new compounds will be evaluated.

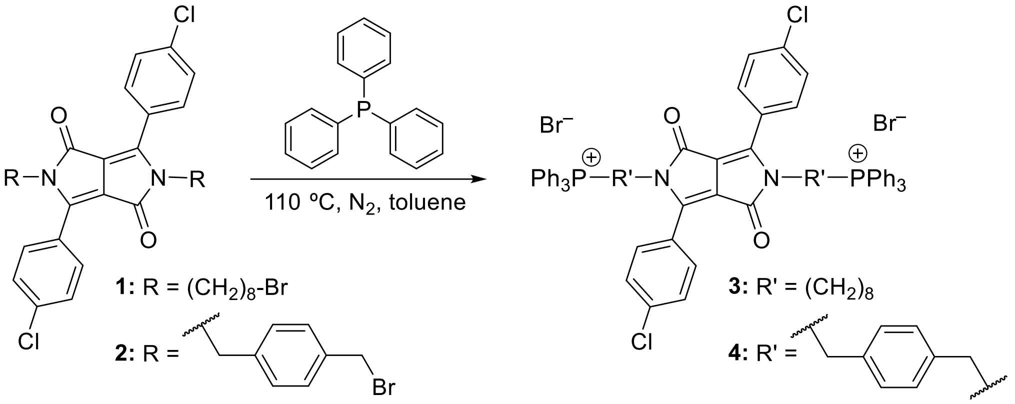

Fig.1. Reaction scheme for the cationic DPP derivatives.

Acknowledgments
Thanks are due to the University of Aveiro and Fundação para a Ciência e a Tecnologia for the financial support to the LAQV-REQUIMTE (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020). Thanks are also due to the Portuguese NMR and Mass networks.

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Selective Synthesis of Novel Imidazole-based Amidrazones and Hydrazonoyl Cyanides with Anticancer Activity:
A Mechanistic Study

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Imidazoles are an important class of heterocycles extensively represented in natural and synthetic molecules.[1] Their key roles in vital processes have stimulated the synthesis and biological evaluation of a large number of novel imidazole derivatives.[1,2] Thus, incorporation of this moiety in organic scaffolds has been an important synthetic strategy in drug design.[2] Similarly to imidazoles, hydrazones are also relevant structural motifs in drug discovery due to their pharmacological properties,[3] which include anticancer activity.[4] Amidrazones are an important class of hydrazone-containing molecules due to their wide use as precursors for the synthesis of five-, six- and seven-membered heterocyclic systems, particularly 1,2,4-triazoles, thiatriazoles and 1,2,4-triazine derivatives, and tetrazole.[4] In addition, a great number of amidrazone-based molecules exhibit a broad spectrum of biological activities. On the other hand, although hydrazonoyl cyanides have attracted significant interest in medicinal chemistry as they have been widely used as synthetic precursor for pyrazoles, 1,2,3-triazoles and 1,2,4-triazoles, limited methods can be found in the literature for the synthesis of these highly functionalized synthetic precursors.

Novel hybrid heterocyclic compounds that combine the imidazole ring with bioactive piperidine, morpholine or piperazine heterosystems, through a hydrazone unit, were easily obtained from our pipeline by two competitive pathways. Starting from 5-amino-4-cyanoformimidoyl imidazoles and 1-aminopiperidine, 4-aminomorpholine or 1-amino-4-methylpiperazine, under mild acidic media, led to the selective synthesis of 5-aminoimidazole 4-carboxamidrazones, whereas the corresponding 4-hydrazonoyl cyanides were obtained under stronger acidic conditions. The compounds were screened against colorectal cancer HCT116-p53 wt cell line, and significant IC_{50} values were obtained.
Thus, to understand the mechanisms underlying the selective preparation of these two significant classes of imidazole derivatives, mechanistic studies using experimental and theoretical assays were carried out. The experimental and *in silico* data obtained in this study will be presented and discussed.

Acknowledgements

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Efficient Microwave-Assisted Solid-Phase Peptide Synthesis of a Granzyme B Substrate on 2-Chlorotrityl Chloride Resin

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The 2-chlorotrityl chloride resin (2CTC) is a widely used acid-sensitive linker for the synthesis of linear peptides with protected side chains. The side-chain protection enables precise labelling along the peptide backbone, facilitating the incorporation of Förster Resonance Energy Transfer (FRET) pairs. This versatility allows for the application of various labelling techniques targeting peptides. 2CTC resin offers several key advantages: (i) it supports racemization-free attachment of the initial amino acid, preserving peptide integrity; (ii) it prevents diketopiperazine formation, which is critical when glycine or proline is the first residue; and (iii) it allows for cleavage under mild acidic conditions, preserving side-chain protecting groups for subsequent modifications [1,2]. However, its susceptibility to ester bond hydrolysis, especially at elevated temperatures, can result in premature cleavage from the solid support, requiring careful optimization of synthesis conditions. Despite these limitations, 2CTC resin remains an effective tool for the synthesis of long or difficult peptides [2,3].

Microwave-assisted solid-phase peptide synthesis (MW-SPPS) enhances peptide synthesis by offering faster reaction rates, higher crude yields, reduced racemization, and simplified purification processes. This method is particularly advantageous for synthesizing long or challenging peptide sequences [4].

In this study, we present a fast and efficient MW-SPPS protocol using 2CTC resin, following the 9-fluorenylmethyloxycarbonyl/tert-butyl (Fmoc/*t*Bu) strategy, to synthesize the protected heptapeptide **1** (KIEPDAL) (Figure 1). This peptide serves as a substrate for Granzyme B (GzmB), a serine protease which plays an important role in target cell apoptosis when released by cytotoxic T lymphocytes or natural killer cells [5]. The synthesized peptide will be conjugated with a suitable FRET pair to develop GzmB-targeted probes for therapy and medical imaging.

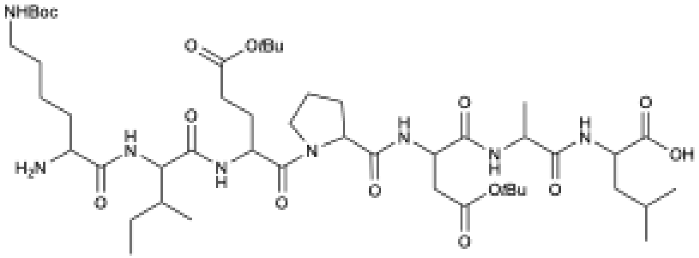

Fig.1. Structure of the Granzyme B substrate **1**.

Acknowledgements
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Thienothiophene-based dyes for DSSC applications.

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Thiophene-based π-conjugated systems are characterized by efficient electron transfer, moderate band gap, and structural versatility. Fused thiophenes, such as thienothiophenes, represent a promising class of π-bridge due to their extended molecular conjugation, high stability, ring planarity and S-S interactions.[1] Due to these properties, fused thiophenes have attracted significant interest in the fields of organic photovoltaic cells (OPVs),[2,3] organic field-effect transistors (OFETs) [4] and dye sensitized solar cells DSSCs.[1,5]

Considering the promising properties of dyes containing the thienothiophene nucleus in DSSCs, a family of compounds containing this moiety in their π-bridge has been synthesized. The design features a D-π-$(A)_2$ structure, where the π-spacer is extended by attaching a phenyl or a thiophene group. Phenothiazine and carbazole donor groups were also introduced into these molecules. The compounds were applied in DSSC devices to evaluate their photovoltaic performance, with values ranging from 1.39 to 1.96 %. Photophysical and electrochemical studies were conducted to correlate the obtained photovoltaic efficiencies with the structural modifications.

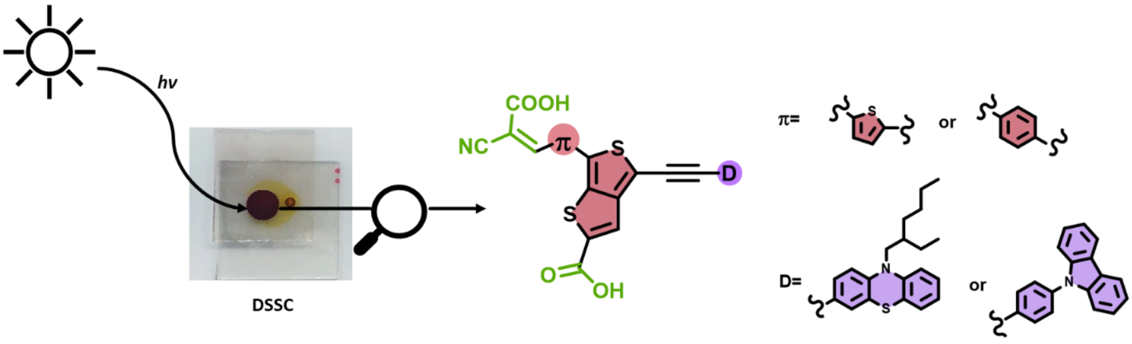

Fig.1. Schematic representation of the synthesized thienothiophene-based organic dyes.

Acknowledgments
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A simple on-off optical chemosensor of biologically relevant ions derived from benzofuran-2-carbohydrazide

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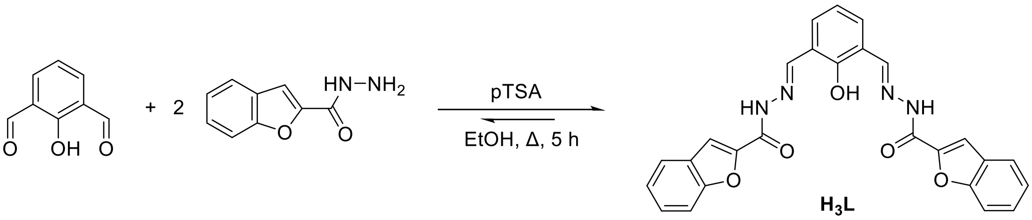
In the last decade, fluorescent and colorimetric chemosensors have become an important research area in supramolecular chemistry and have attracted much attention due to their simplicity, high selectivity and sensitivity in fluorescent assays. The development of molecular sensors for selective cation or anion sensing is critical for a wide range of relevant environmental, biological and diagnostic applications [1].

Hydrazone ligands have been extensively studied in recent decades due to their important biological properties and their versatility in coordination chemistry with different metal ions [2]. In recent years, the use of hydrazone ligands as chemosensors has been investigated with promising results [3].

In this work, we present a *bis*-hidrazone H_3L ligand capable of acting as a colorimetric and fluorescent chemosensor of important biological ions. This compound was obtained by an imine condensation reaction between 2-hydroxyisophthalaldehyde and benzofuran-2-carbohydrazide (Scheme 1) and has been fully characterized by different techniques, including X-ray diffraction [4].



Scheme 1. Synthesis of *bis*-hydrazone ligand H_3L.

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QUÍMICA Y SALUD

Novel avenues into adipogenesis inhibition: optimization and validation of an in vitro methodology to study the role of flavonoids in 3T3-L1 adipocyte cell line differentiation

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In recent years, obesity has escalated to pandemic proportions, with the World Obesity Federation predicting that nearly 3.3 billion adults will be affected by this condition in 2035. This alarming trend has intensified scientific efforts to unravel obesity mechanisms and identify new compounds that can mitigate the metabolic complications associated with this condition. Obesity, characterized by abnormal or excessive fat accumulation due to excessive calorie intake, is a major risk factor for cardiovascular diseases, cancer, and diabetes mellitus, potentially reducing life expectancy by 5 to 20 years, depending on the severity of the condition and the presence of comorbidities. Polyphenols are naturally occurring compounds distinguished by the presence of multiple phenol units. Among them, flavonoids are well known for their diverse biological effects, which include anti-inflammatory, antioxidant, antidiabetic, and anti-obesity activities. Due to their structural diversity, flavonoids have attracted attention for their anti-adipogenic potential.

Adipogenesis, the process by which preadipocytes differentiate into adipocytes (fat cells) through a series of molecular and cellular transformations, involves the accumulation of lipid droplets within the cell. In this work, an optimized methodology was applied to enhance the differentiation of 3T3-L1 Mouse Embryonic Fibroblasts (ATCC CL-173) into adipocytes. Furthermore, the potential anti-adipogenic effect of a set of flavonoids was investigated using an Oil Red O staining kit for the selective staining and detection of neutral lipids in cultured cells. Additionally, the quantitative determination of triacylglycerols (TGs) was performed using an enzymatic colorimetric assay with a commercial kit. Resveratrol, a natural polyphenol with confirmed clinical effects on weight and fat mass reduction through the inhibition of preadipocyte differentiation, was used as a positive control (Figure 1). Our results validate resveratrol's ability to inhibit the differentiation of 3T3-L1 pre-adipocytes and indicate that the presence of certain groups within flavonoids may contribute to decreasing the TGs content, suggesting their potential as promising anti-obesity compounds.

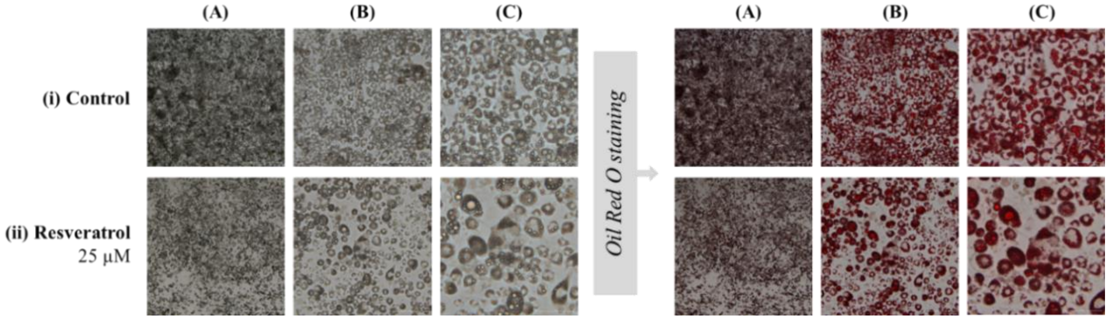

Figure 1. *Effects of resveratrol on adipogenesis and growth of differentiating 3T3-L1 cells. 3T3-L1 pre-adipocytes were induced to differentiate using induction media in the absence (i) and presence of 25 μM resveratrol (ii) over an 8-day period. Cellular lipid content was assessed using Oil Red O staining solution, and images were captured on day 8 at 4x (A), 20x (B), and 40x (C) magnification under color brightfield microscopy.*

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Unravelling the influence of indolenine-derived squaraine dyes' alkyl chains on HSA detection

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Protein detection and quantification plays a fundamental role in clinical diagnosis since changes in protein concentrations are usually associated with pathologies. Hence, proteins have been used as diagnostic markers for over 150 years [1]. Despite the availability of numerous methods for serum proteins detection and quantification, fluorescent dye-binding methods typically offer greater selectivity, sensitivity and simplicity, as well as faster and more precise results [2].

Squaraine dyes are 1,3-disubstituted structures of squaric acid. These compounds present a resonance-stabilized donor-acceptor-donor skeleton, consisting of a central ring of four carbon electron acceptors and two electron-donating terminal groups that, depending on whether they are of the same nature, allow the classification of the dye as symmetrical or asymmetrical, respectively [3]. Squaraine dyes have aroused the interest of researchers as possible probes for serum proteins detection and quantification due to their photochemical and photophysical properties such as the increased fluorescence intensity after non-covalent binding to biomolecules, with the main advantage being that non-covalent binding affects the biomolecules functional activity to a lesser extent than covalent binding [4].

This communication aimed to assess the potential application of two indolenine-derived squaraine dyes (Fig. 1.) as fluorescent probes for human serum albumin (HSA), unravelling the influence of different alkyl chains in the dyes´ detection and quantification capacity. The fluorimetric assays, performed with constant dyes´ concentrations and variable HSA concentrations (ranging from 0,0 µM to 3,0 µM), revealed a good interaction between each dye and the referred protein, visible through the linearity between HSA concentrations and the fluorescence intensity obtained at the maximum emission wavelength. Based on experimental results, it was possible to determine that dye 2 had the best fluorescent probe properties.

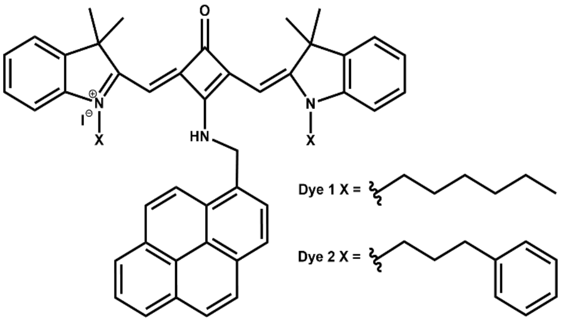

Fig. 1. Structure of the dyes used on HSA fluorimetric detection and quantification.

Acknowledgements
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From Ayurveda to ADHD: *Bacopa monnieri* Gummies as a Natural Therapeutic Option

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Attention Deficit Hyperactivity Disorder (ADHD) is the most prevalent neurodevelopmental disorder in school-aged children, characterized by hyperactivity, inattention, and impulsivity [1]. A key challenge in this disorder is the fact that treatments mainly involve psychostimulant medications, raising concerns about long-term efficacy and side effects [1]. Thus, alternative therapeutic approaches, particularly phytotherapy, are needed. *Bacopa monnieri*, a nootropic herb used in Ayurvedic medicine for centuries, has shown promising in managing ADHD. It is associated with memory, cognitive function, and executive processes improvement. The herb's therapeutic potential is linked to saponin compounds, especially bacoside A, which exert antioxidant effects and modulate neurotransmitter pathways [2]. This study aimed to develop and characterize a gummy formulation incorporated with *B. monnieri* extract, addressing the gap in alternative treatments for ADHD in children. Firstly, a hydroethanolic extract enriched with bacoside A was produced, characterized and quantified using HPLC-DAD. The antioxidant capacity was evaluated through thiobarbituric acid reactive substances (TBARS) and oxygen radical absorbance capacity (ORAC) assays. Subsequently, a pectin-based gummy formulation was optimized (60% sugar, 1% pectin, 0.875 % citric acid and water q.s 100%), and incorporated with 25 mg of the *B. monnieri* extract. The concentration of bacoside A in each gummy was quantified by HPLC-DAD. The gummies were also assessed for physicochemical properties and textural profile, and compared with a commercially available product where applicable. The findings confirm that the hydroethanolic extract of *Bacopa monnieri* was rich in bacoside A (64.303 mg/g extract) and exhibited promising antioxidant activity, with an ORAC value of 2544.578 ± 104.131 µmol Trolox equivalents per gram of extract and a TBARS EC_{50} of 0.077 mg/mL. The gummies were successfully enriched with bacoside A, reaching a concentration of 1.049 ± 0.044 mg per gummy. In terms of technological parameters, *B. monnieri* gummies displayed satisfactory characteristics when compared to a commercial product. Specifically, *B. monnieri* gummies had good mass uniformity (1.408 ± 0.090 g), and lower pH (2.797 ± 0.123 vs. 3.899 ± 0.178) than commercial gummies. Regarding texture, *B. monnieri* gummies exhibited lower firmness (835.46 ± 103.14) compared to the commercial gummies (1633.09 ± 334.45), with similar springiness values (30.54 ± 7.01 for *B. monnieri* gummies vs. 31.04 ± 1.65 for commercial gummies). However, our gummy formulation had a higher water activity (0.780 ± 0.009) compared to the commercial product (0.511 ± 0.002), while both had similar total water content (21.767 ± 0.274% for *B. monnieri* gummies vs. 21.175 ± 0.056% for commercial). Additionally, the color measurements for *B. monnieri* gummies were L* 22.987 ± 0.470, a* -0.037 ± 0.015, and b* 1.347 ± 0.042. Given the successful production of these gummies, future studies should focus on investigating their effectiveness in alleviating ADHD symptoms.

Acknowledgments
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Downregulation of COX-2 expression in human leukocytes by 2-styrylchromones

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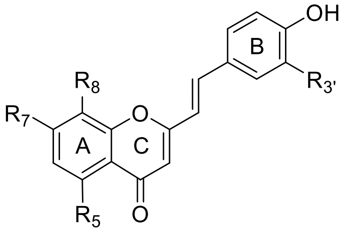
Cyclooxygenase-2 (COX-2) is an inducible enzyme that plays a pivotal role in the inflammatory process, participating in the biosynthetic pathway of prostaglandins. Its expression is predominantly triggered by inflammatory stimuli, leading to its upregulation in various inflammatory cells, including endothelial, epithelial, and immune cells. Leukocytes, which include neutrophils, eosinophils, basophils, monocytes, and lymphocytes, are essential mediators of the inflammatory response [1]. Therefore, identifying molecules capable of modulating COX-2 expression in these cells is crucial to regulate inflammation. 2-Styrylchromones (2-SC) are a class of oxygen heterocyclic compounds, characterized by a chromone core to which a styryl group is attached. Their biological properties have garnered significant attention from the scientific community, although their anti-inflammatory effects remain poorly described in the literature [2]. In this context, freshly isolated human leukocytes were exposed to 13 structurally related 2-SC to evaluate their influence on lipopolysaccharide (LPS)-induced COX-2 expression via western blot analysis [3].

Several of the studied 2-SC were able to downregulate COX-2 expression with 2-SC **6** to **9** being the most effective at reducing LPS-induced COX-2 expression. 2-SC **6** displayed the strongest inhibition, reducing the expression by 57 ± 6% at 6.25 µM and 71 ± 3% at 25 µM. These results suggest that the presence of a catechol group at C-3' and C-4' on the B-ring is important to inhibit COX-2 expression, while the presence of methoxy groups on the A-ring does not promote a reduction in COX-2 expression. In conclusion, 2-SC may affect COX-2 expression and hold potential as scaffolds for the development of new anti-inflammatory drugs.



1 $R_5 = R_7 = R_8 = R_{3'} = H$
2 $R_5 = OH; R_7 = R_8 = R_{3'} = H$
3 $R_5 = R_8 = R_{3'} = H; R_7 = OH$
4 $R_5 = R_7 = OH; R_8 = R_{3'} = H$
5 $R_5 = OH; R_7 = OCH_3; R_8 = R_{3'} = H$
6 $R_5 = R_7 = R_8 = H; R_{3'} = OH$
7 $R_5 = R_{3'} = OH; R_7 = R_8 = H$
8 $R_5 = R_8 = H; R_7 = R_{3'} = OH$
9 $R_5 = R_7 = R_{3'} = OH; R_8 = H$
10 $R_5 = R_8 = H; R_7 = OCH_3; R_{3'} = OH$
11 $R_5 = R_7 = OCH_3; R_8 = H; R_{3'} = OH$
12 $R_5 = H; R_7 = R_8 = R_{3'} = OH$
13 $R_5 = H; R_7 = R_8 = OCH_3; R_{3'} = OH$

Fig.1. Chemical structure and substitution pattern of the tested 2-SC.

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Caracterización físico química das mesturas de viño, caolín e auga do Balneario de Laias

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O obxectivo desta comunicación é caracterizar mesturas de viño tinto, arxila de caolín e auga termal para posibles aplicacións cosméticas. O traballo baséase no uso ben documentado de arxilas e polifenoles en cosmética. O viño, co seu alto contido de polifenoles, ofrece unha fonte prometedora destas moléculas beneficiosas. Ademais, as arxilas teñen a capacidade de absorber moléculas, incluídos os polifenoles.

As mesturas preparáronse con viño tinto da Ribeira Sacra, caolín do Vimianzo e auga mineromedicinal do Balneario de Laias.

En primeiro lugar, a arxila enriqueceuse con viño. Para iso, o viño mesturouse coa arxila e deixouse madurar durante 36 horas. A continuación, filtrouse, separando o viño sobrante da arxila enriquecida. A arxila enriquecida deixouse secar a temperatura ambiente durante 48 horas. Os peloides preparáronse cun 73% de caolín enriquecido e un 27% de auga mineromedicinal do Balneario de Laias.

As propiedades estudiadas son: o pH utilizándose un pH-metro Hanna modelo HI 8424 [1], a densidade utilizando un picnómetro (Álamo 25 ml) [2], a condutividade térmica medida con un analizador de propiedades térmicas KD2 Pro [3], a calor específica determínase utilizando un microcalorímetro Calvet [4], a difusividade térmica avalíase a partir da densidade, a calor específica e a condutividade térmica como se describe en Casas et al, 2013 [1]. Tamén se realizou unha análise do contido de carbono, nitróxeno, xofre e hidróxeno nas mostras de caolín, viño, caolín enriquecido e o viño filtrado despois do contacto co caolín. Esta análise levouse a cabo nos Servizos de Apoio á Investigación (SAI) da Universidade da Coruña, utilizando un analizador elemental FlashEA112 (ThermoFinnigan).

Na figura 1 móstranse os resultados das propiedades físicas comparadas coas da bibliografía. Os resultados da análise química mostran un aumento no contido de carbono e hidroxeno no caolín enriquecido e unha diminución no viño, o que supón absorción de materia orgánica no caolín procedente do viño.

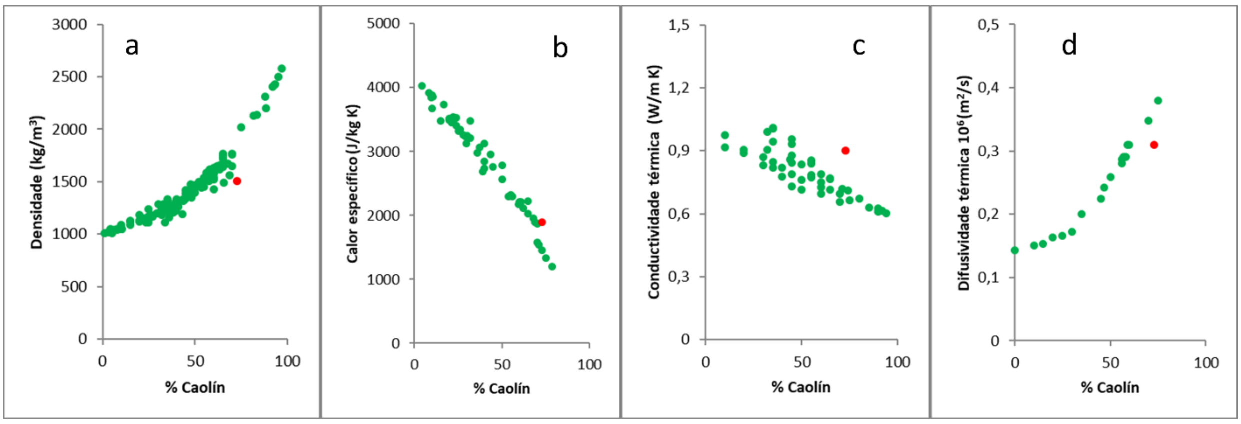

Fig.1. Propiedades físicas do peloide, a) densidade; b) calor específico, c) conductividade térmica, d) difusividade térmica. Puntos verdes: valores da bibliografía. Punto vermello: valor medido neste traballo.

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Pyrimido[5,4-*d*]pyrimidines as efficient and specific anticancer agents in the osteosarcoma 143B cell line

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Pyrimido[5,4-*d*]pyrimidines are heterocyclic compounds recently shown to possess antimicrobial, anti-inflammatory, and anticancer properties [1-3]. Osteosarcoma, a type of bone cancer, has poor disease outcomes, particularly in cases of recurrence, underscoring the need for novel therapeutic drugs [4].

To address the versatility and promising anticancer activity of pyrimido[5,4-*d*]pyrimidines, we aimed to identify novel compounds as potential anticancer agents for osteosarcoma. Ten structurally related pyrimido[5,4-*d*]pyrimidines (**Fig. 1**) were synthesized with different substituents in position C4 of the heterocycle and screened for their anticancer potential in the human osteosarcoma 143B cell line. After exposing cells to the compounds (0 – 16 µM, 48 hours), the inhibition of cell viability and growth was assessed using the resazurin and sulforhodamine B assays. The most active compounds were evaluated in MRC-5 healthy lung cells for potential toxicity. Six compounds strongly inhibited osteosarcoma cell viability and growth, with IC_{50} values of 1 – 16 µM. Despite toxicity to osteosarcoma, three compounds showed low toxicity to healthy cells. Notably, the most selective compound [R = 3-(3´-pyridinylCONH)C_6H4] demonstrated no significant toxicity to healthy cells at the tested concentrations.

These promising results point to pyrimido[5,4-*d*]pyrimidines as therapeutic agents for osteosarcoma. Further studies are needed to elucidate their mechanism of action and confirm anticancer efficacy.

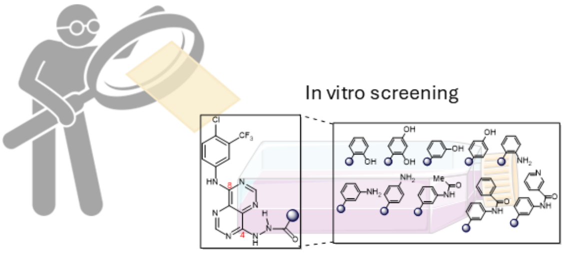

Fig.1. Scaffold and substituents of the tested compounds.

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Produção de Pontos de Carbono Fluorescentes com Potencial Antioxidante a partir dos Ouriços da Castanha

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A castanha é um fruto sazonal proveniente do castanheiro (*Castanea sativa* Mill.) que possui elevada riqueza nutricional, apresentando o seu consumo benefícios inegáveis para a saúde. A sua composição é elevada em hidratos de carbono e fibras não digeríveis que estimulam o desenvolvimento de bactérias probióticas no intestino, contribuem também para a regulação dos níveis de colesterol e de resposta à insulina. A presença de uma vasta diversidade de vitaminas, minerais e compostos fenólicos conferem ainda a este alimento notáveis propriedades antioxidantes e de proteção celular [1].

Portugal destaca-se a nível mundial como produtor de castanha, registando-se as maiores taxas de produção na região norte do país, nomeadamente na zona da Serra da Padrela, Terra Fria e Soutos da Lapa, regiões demarcadas com Denominação de Origem Protegida (DOP) e com grande impacto na economia regional [1,2]. Contudo, a indústria agroalimentar de processamento de castanha gera grande quantidade de resíduos, nomeadamente castanhas apodrecidas, cascas e polpas provenientes do descasque, ouriços e folhas [3], os quais apresentam altos teores de matéria orgânica e compostos com elevado valor nutricional, cuja valorização por processos eficientes poderá contribuir para mitigar potenciais problemas ambientais, promovendo a economia circular.

A implementação de processos sustentáveis na obtenção de pontos de carbono (PsC) fluorescentes a partir da valorização de resíduos com elevado teor em carbono de diferentes origens (*e.g.* desperdícios agrícolas, domésticos e industriais) tem sido largamente explorada nas últimas décadas [4].
Os nanomateriais produzidos têm revelado excelentes propriedades óticas (*e.g.* fotoestabilidade e rendimento quântico), boa solubilidade em água, baixa citotoxicidade e relevante biocompatibilidade, conferindo-lhes potenciais utilizações em áreas muito diversificadas, nomeadamente aplicações biológicas [5].

Na presente comunicação serão apresentadas as propriedades espetroscópicas (FTIR, UV-Vis e fluorescência) de PsC obtidos por tratamento hidrotérmico em diferentes condições, recorrendo a aquecimento convencional em reator de alta pressão e em mufla, utilizando como matéria-prima ouriços da castanha, bem como avaliado o seu potencial antioxidante pelo método do radical ABTS.

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Aplicação de Pontos de Carbono derivados de Biomassa de Microalgas cultivadas em Resíduos Alimentares como Sondas Fluorescentes em Imagiologia

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Os pontos de carbono (PsC) integram uma subclasse de nanomateriais que se caracterizam por possuírem um núcleo de carbono com hibridação sp^2/sp^3 contendo diferentes grupos funcionais à sua superfície, estruturas com dimensões inferiores a 10 nm e morfologia *quasi*-esférica [1]. Produzidos por métodos simples e sustentáveis a partir de uma ampla variedade de matérias-primas com elevado conteúdo em carbono provenientes de fontes sintéticas, naturais ou de resíduos de diversas origens, estas nanopartículas destacam-se pelas suas propriedades óticas, baixa toxicidade, elevada biocompatibilidade, fotoestabilidade e solubilidade em água, sendo atualmente explorada a sua aplicação tecnológica em áreas distintas como a catálise, a optoelectrónica, a remediação ambiental, a imagiologia, entre outras [2].

As microalgas são microrganismos unicelulares e fotossintéticos, que crescem em sistemas aquáticos de água doce ou salgada, sendo capazes de produzir uma vasta gama de metabolitos primários e secundários, intra e/ou extracelulares, tais como proteínas, hidratos de carbono, lípidos, vitaminas e pigmentos e cuja síntese é influenciada pelas condições de crescimento. Esta diversidade de biocompostos torna a sua biomassa uma matéria-prima com elevada carga orgânica potencialmente útil para a síntese de vários compostos de alto valor acrescentado [3,4]. Atualmente, um dos maiores desafios dos sistemas de cultivo de microalgas é o desenvolvimento de estratégias que promovam a utilização de meios de cultura baseados em recursos alternativos, sustentáveis e de baixo custo (*e.g.* resíduos alimentares) que permitam aumentar a relação custo-benefício destes bioprocessos [5].

No presente trabalho será apresentada a produção sustentável *via* tratamento hidrotérmico com aquecimento convencional de PsC fluorescentes bioativos a partir da biomassa da microalga *Chlorella vulgaris* (BM-Cv), cultivada em meio de cultura enriquecido com resíduos alimentares e a sua posterior aplicação como marcadores celulares fluorescentes em ensaios de citotoxicidade *in vivo* acompanhados por microscopia de fluorescência utilizando como organismo modelo o microcrustáceo *Artemia salina*.

O estudo desenvolvido reflete não só a valorização da BM-Cv, como dos resíduos alimentares de baixo valor que suplementam o meio de crescimento, emergindo como uma alternativa económica e mais sustentável para a produção de microalgas. A composição do meio de cultura inviabiliza a incorporação da BM-Cv em alimentos para consumo humano, tornando sua aplicação na síntese de PsC uma solução inovadora.

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Biophysical characterization of a dual-action peptide for wound healing

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Antimicrobial resistance is a spiralling worldwide concern, as ineffective treatment of infections may lead to serious or even life-threatening conditions. Alternatives to conventional antibiotics have been explored to fight this problem, e.g. antimicrobial peptides [1].

Recently, Gomes *et al.* designed peptide-based constructs, aiming at their application for the treatment of infected wounds, providing antimicrobial action and faster healing. Peptide IL-PP4 combines an antibacterial ionic-liquid (IL) with the collagen-boosting peptide (PP4, with amino acid sequence KTTKS), exhibiting in vitro antibacterial, antifungal, and collagenesis inducing activity [2].

In this work, we aim at understanding the biophysical profile and the mechanism of action (MOA) of IL PP4 against Gram(+) and Gram(-) bacteria, using POPC:POPG (1:1) and total extract of *Escherichia coli* liposomes as bacterial mimetic model systems. Peptide bacterial membrane interaction was studied through the determination of the partition constant by spectrofluorimetry, and by dynamic light scattering and confocal laser scanning microscopy experiments, to understand possible aggregation effects in lipid vesicles [3]. Atomic Force Microscopy was further used to elucidate the MOA of the peptide against *Staphylococcus aureus* ATCC 29213 and *E. coli* ATCC 25922.

Biophysical and microscopical results revealed that IL PP4 has a different MOA in Gram(+) and Gram(-) bacteria. In *E. coli*, IL-PP4 induces aggregation and disaggregation of lipid vesicles, establishing electrostatic interactions and adsorption on membrane surface, and subsequent penetration, possibly acting by the "carpet model". In *S. aureus* no aggregation effects were observed, and the results point out for a "toroidal-pore model".

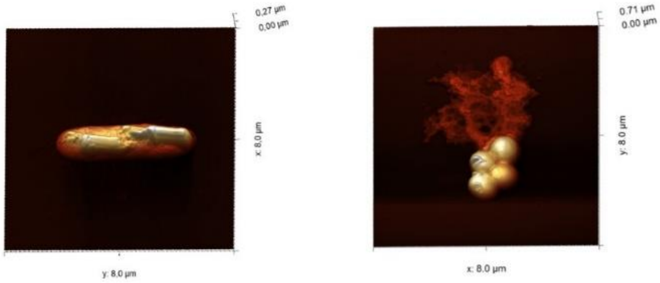

Fig.1. Representative AFM images of the antibacterial effect of peptide IL-PP4 on *E. coli* ATCC 25922 (left) and *S. aureus* ATCC 29213 (right).

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Highly fluorescent 2-amino-6-cyanopurines as new bioimaging tools for studying yeast vacuoles

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Fluorescent nucleobase analogues (FNAs) have been extensively used for scientific and biomedical purposes owing to their relevant photophysical properties. In this study, five newly synthesized 2-amino-6-cyanopurines were evaluated for their fluorescent probing and imaging capabilities using *Saccharomyces cerevisiae* as model organism. The new compounds, which were synthesized using highly efficient cost-effective methods, show unique photophysical properties compared to other FNA, such as longer absorption and emission wavelengths, environment-sensitive emission, and unprecedented brightness [1]. The new 2-amino-6-cyanopurines specifically accumulate in vacuoles of living yeast cells. Vacuole staining requires active cell metabolism (glucose/energy dependency), since it was not evident in ethanol-fixed (dead) cells, as well as when cells energy metabolism was challenged through (i) starvation or by (ii) inhibiting glycolysis and ATP production with the glucose analogue, 2-deoxyglucose, or with the metabolic uncouplers, NaN_3 and NaF [2,3].

The new purine derivatives stand as auspicious vacuole fluorescent probes for advanced microscopy cell imaging, as they are non-toxic toward the model organism, are easy-to-obtain, and may be a cost-effective alternative to commercially available fluorescent dyes. To our knowledge, these are the first FNAs capable to stain intracellular structures (e.g. vacuoles) in living cells. Their photophysical properties makes them suitable for monitoring vacuolar function, dynamics, and stress responses. Their applications range from basic research about autophagy, aging, and stress tolerance, to practical uses in industrial fermentation, environmental sensing, and disease modelling. In a research field mostly populated by green- and red-emitting fluorophores, the blue-emitting purines herein presented allow for new fluorophore combinations in multiplex imaging, while paving the way for new nucleobase-inspired probes emitting in the visible light spectrum.

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Composição e Bioatividade de Algas *Nori*, *Wakame* e *Kombu* Comercializadas em Portugal

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As macroalgas apresentam grande potencial como fonte de matérias-primas para diversas indústrias. Devido à sua composição bioquímica, exibem várias propriedades com efeitos preventivos e benéficos para a saúde, nomeadamente atividades antioxidante, anti-inflamatória, antibacteriana, anticoagulante e antitumoral, podendo assim ser consideradas “superalimentos” [1,2].

No entanto, estes organismos possuem capacidade de biorremediação através de processos de bioabsorção e bioacumulação, retendo nas suas células compostos tóxicos presentes no meio onde se desenvolvem, pelo que quando transformadas em alimentos, a presença de contaminantes nas macroalgas, pode representar um potencial risco para a saúde do consumidor, invalidando os benefícios já identificados [3,4].

Para o presente estudo, foram selecionadas três algas das mais populares, nori (*Porphyra* spp.), wakame (*Undaria pinnatifida*) e kombu (*Laminaria* spp.), sendo as duas primeiras normalmente utilizadas na preparação de *sushi*, adquiridas em locais de venda ao público de bens alimentares, em Portugal, tendo em consideração a origem da sua produção (Ásia).

A composição mineral das amostras foi avaliada por fluorescência de raios X por energia dispersiva e a quantificação de biocompostos, nomeadamente lípidos, polissacáridos, açúcares redutores e compostos fenólicos totais, foi realizada após extração por multietapas (água fria, água em ebulição, condições alcalinas e ácidas). Os extratos obtidos foram avaliados *in vitro* quanto ao seu potencial antioxidante e antibacteriano, e no que respeita ao seu efeito citotóxico contra linhas celulares animais (3T3, Vero e S180).

Este trabalho revelou a presença de macro e micronutrientes essenciais, bem como de elementos tóxicos (*e.g.* estrôncio e arsénio), comprometendo a qualidade e a segurança destes alimentos. No entanto, os extratos obtidos exibiram atividade antioxidante, propriedades antibacterianas e baixa citotoxicidade, demonstrando elevado potencial na sua utilização como alimentos funcionais, quando desenvolvidos em condições controladas. Desta forma, a premência de soluções inovadoras e sustentáveis para a alimentação e saúde humanas requer o estudo aprofundado da composição e propriedades exibidas por este tipo de produtos alimentares.

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Polyurea dendrimers as inhibitors of urease activity in *Helicobacter pylori*

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Helicobacter pylori is a Gram-negative bacteria responsible for the widespread of gastrointestinal diseases and is one of the most common bacterial infections globally. Due to increasing bacterial resistance to available antibiotics, standard treatments face significant limitations [1]. One promising approach is the development of urease inhibitors, with a broad range of natural, synthetic, and semi-synthetic compounds being explored as potential new drugs. In this context, dendrimers, polymers with a well-defined 3D structure and high batch-to-batch reproducibility, have shown promise as antimicrobial agents.

Our research group has successfully developed polyurea (PURE) dendrimers with nanomolar antimicrobial activity [2,3] specifically designed to target urease in *H. pylori*. These dendrimers are particularly promising due to the unique mobility of the Flap region at the entrance of urease's active site, which allows macromolecules like dendrimers to deeply penetrate the enzyme's cavity [4,5]. The synthesis of these amino acid-based dendrimers was performed using solvent-free melting methods, offering a sustainable, cost-effective, scalable, and straightforward process. Additionally, the fluorescent properties of the dendrimers provide an alternative method for quantifying urease activity [6-8]. Further spectroscopic studies are being conducted to explore urease conformational changes due to dendrimer interactions.

Preliminary results suggest that dendrimers surface conjugated with amino acid groups, particularly sulphonamide and thiourea, show enhanced activity against *H. pylori*. PURE dendrimers demonstrated better urease inhibition, using the Berthelot reaction method, than control thiourea and non-modified dendrimers. Therefore, this study provides valuable insights for the development of new urease inhibitors.

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Photodynamic efficiency of porphyrins with attached *N*-Donor units incorporated into PVP-based formulations

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Antibiotic resistance is a pressing public health issue caused by inappropriate prescribing and the overuse of antibiotics. Over 35,000 deaths occur annually in Europe due to antibiotic-resistant infections, with projections of up to 10 million deaths by 2050 [1]. Antimicrobial photodynamic therapy (aPDT) is a promising alternative or complementary strategy to traditional antimicrobial methods. This approach relies on the light-activation of a photosensitizer (PS) in the presence of dioxygen to generate reactive oxygen species (ROS), namely singlet oxygen ($^1O_2$), which selectively destroys pathogen cells such as viruses or bacteria [2,3]. aPDT offers broad-spectrum, minimal side effects, and simultaneous targeting of multiple cellular components, making it effective against a wide range of microorganisms, including antibiotic-resistant strains [4]. Porphyrins are key PS for efficient microorganism eradication due to their unique properties, which can be manipulated through functionalization for specific applications [5].

In this communication, we will present the incorporation of a series of Zn(II) complexes of *trans*-A_2B_2-type porphyrins, modified with nitrogen-based donor moieties directly attached to the porphyrin core *via* a C–N bond, into polyvinylpyrrolidone (PVP) formulations. The photodynamic activity of the resulting PVP-based formulations was assessed against the Gram-positive model *Staphylococcus aureus*.

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Development of Melanostatin Neuropeptide Conjugates for Application in Parkinson's Disease Therapy

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Melanostatin (MIF-1, Figure 1) is a short endogenous neuropeptide that acts as a positive allosteric modulator (PAM) of dopamine D_2 receptors (D_2R) and displays therapeutic potential for the treatment of dopamine-related disorders, such as Parkinson's disease (PD). However, this neuropeptide exhibits unfavorable pharmacokinetic properties such as poor gastrointestinal absorption and susceptibility to proteases of the central nervous system (CNS), hampering its clinical translation.[1,2] This project aims to overcome these limitations by using a conjugation strategy to enhance the lipophilicity and PAM potency of MIF-1. To this end, amantadine (Am, Figure 1) was selected for conjugation via an amide bond at the *C*-terminal position of this neuropeptide (Figure 1) using classical peptide synthesis strategies.[3]

Following this strategy, the lipophilicity was substantially increased as determined by the classical shake-flask method and compared to *in silico* predictions using cheminformatics software available at SwissADME. While conjugate **2** displayed a higher affinity for the organic phase than MIF-1, the partition coefficient was not determined for conjugate **1** due to the formation of emulsions.[3]

Pharmacological functional assays were performed for the determination of PAM activity at human-derived D_2R using transfected mammalian cells by monitorization of cyclic adenosine monophosphate (cAMP) mobilization. In these assays, conjugates **1** and **2** promoted a 3.3- and 4.9-fold increase in dopamine potency at 0.01 nM, respectively, while MIF-1 was only active at the highest concentration tested (1 nM).[3]

These findings suggest that conjugation with amantadine effectively enhances the pharmacological potential of MIF-1, offering a promising strategy for treating dopamine-related disorders.

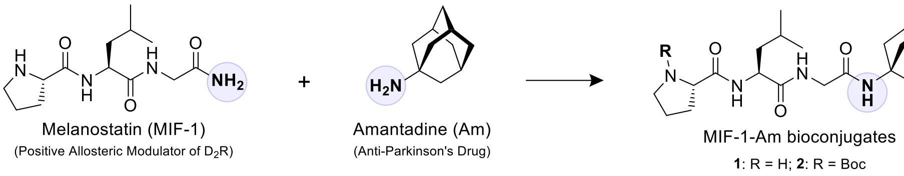

Figure 1. Chemical structures of MIF-1, amantadine, and conjugates **1** and **2**.

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Chalcone derivatives as potential antimitotic agents: synthesis and antitumor screening assays

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Antimicrotubule agents are among the most effective chemotherapeutic drugs against many cancer types. Unfortunately, adverse side effects and resistance have limited their usage, underscoring the need for new antimitotic drugs [1]. At "Laboratório de Química Orgânica e Farmacêutica da FFUP/CIIMAR," one of the study goals is to find novel small molecules with potential anticancer activity, both synthetic and natural. From a library of compounds emerged the synthetic prenylated chalcone PC2 showing potent anti-growth activity against different tumor cell lines (GI ≤ 10 μM), being this effect associated with antimitotic effect [2]. Herein, aiming to improve the antimitotic effect and to perform structure activity relationship studies (SAR), the synthesis and antiproliferative activity evaluation of PC2 analogues, possessing prenyl and amine groups was carried out. Chalcones were obtained by Claisen-Schmidt condensation of previously prepared acetophenones with prenyl or amine groups with appropriately substituted benzaldehydes in basic medium. The antiproliferative activity in three cancer cell lines was evaluated using the sulforhodamine B assay, being identified some chalcones with promising activity.

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Development of Chondroitin Sulfate-loaded Chitosan/Hydroxyapatite Scaffolds Targeting Bone Regeneration

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Bone tissue has a high capacity for healing, but large-size defects require intervention [1]. Chondroitin sulphate (CS) can create a favourable environment for growth factors, which can help tissue repair. This makes CS an attractive option to combine with artificial scaffolds, like chitosan/hydroxyapatite (CH/HAp) scaffolds. These scaffolds mimic bone composition and are gradually resorbed by the body, facilitating natural regeneration without requiring surgical removal [2].

In this study, scaffolds were prepared using 30% of CH (organic component) and 70% of HAp (inorganic component), mimicking the typical bone organic:inorganic ratio (30:70) [3]. Different concentrations of CS were tested, maintaining the HAp concentration fixed. The prepared samples are shown in Fig. 1. Supercritical CO$_2$ (scCO$_2$) was used to remove the acetic acid introduced for CH solubilisation. The samples were characterised by thermal analysis (TG), density, and swelling to assess scaffold structure and composition, targeting future cell adhesion and biocompatibility tests. TG results confirmed that scCO2 effectively removed the acid, ensuring the biological viability of the scaffolds. The density values (~0.05 g/cm^3) and swelling capacities (2.79–3.24 g/g) were consistent with literature data. Overall, the CS-incorporated scaffolds are promising materials for bone regeneration.

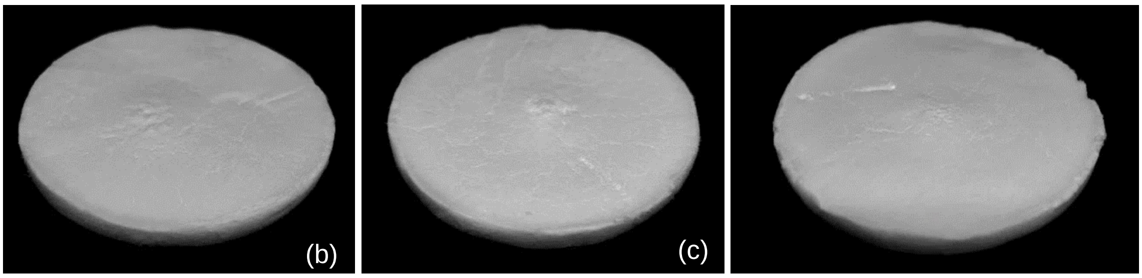

Fig.1. CH/CH scaffolds added with CS (a) 1%, (b) 2.5% and (c) 5%.

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Synthesis of chalcone-kojic acid hybrids with potential skin health promoting effects

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Melanogenesis, which supports homeostasis and photoprotection, is the process of synthesizing melanin, the pigment found in human skin, eyes, and hair. However, melasma, postinflammatory melanoderma, solar lentigines, and malignancy are examples of dermatological diseases caused by aberrant overproduction of this pigment [1]. Among several enzymatic reactions involved in melanogenesis, the rate-limiting step is catalysed by tyrosinase [1]. Therefore, the search of tyrosinase inhibitors is an important strategy to the discovery of bioactive compounds with skin health promoting effects.

Kojic acid has long been used in cosmetics for its skin-lightening properties, attributed to the inhibition of tyrosinase. Nevertheless, it has several drawbacks such as low stability, and increased susceptibility to sunburn. As a result, several alternatives to kojic acid have been developed [2].

Chalcones are a group of natural products with a wide array of biological activities, such as antioxidant and anti-inflammatory, revealing also skin health promoting effect [3]. Taking these into account, the synthesis of new kojic acid-chalcone hybrids by click chemistry reaction could result in the discovery of new tyrosinase inhibitors with potential skin-lightening properties. Herein, some kojic acid-chalcone hybrids with a 1,2,3-triazole linker were synthesized by click chemistry and their structures were elucidated by nuclear magnetic resonance. In the future, the anti-tyrosinase activity will be evaluated by a spectrophotometric assay.

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Challenging invasive fungal infections:
Development of innovative electrochemical nanogenosensors to detect *Candida spp.*

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Despite the considerable advances in the prevention and treatment of fungal infections, invasive fungus such as *Candida spp.,* continues to be one of the major causes of morbidity and mortality [1]. The Global Action Fund Infections reported that, annually, more than 300 million people are infected with fungal infection, from these, about 1.5 million ends up dying. *Candida albicans* is the most important fungal 66
opportunistic pathogen, it can cause superficial or invasive infections [1,2]. *Candida*, often, causes superficial infections, per example in skin or mucous membranes with simple and effective treatment, however, also can break to the bloodstream and disseminate to internal organs [3].

It has been observed among high-risk patients such as allogeneic stem-cell transplant recipients and with acute leukemia receiving high-dose chemotherapy [4]. These patients are at a heightened risk of developing infections due to the suppression of their immune system during the transplantation process. The diagnosis of systemic fungal infections persists as a problematic issue. Therefore, the development of more efficient, sensitive and specific methods for early diagnosis is need.

In this study, an easy, rapid, and accurate detection methods for fungal infections in patients undergoing hematopoietic stem cell transplantation (HSCT) was designed. To address this challenge, it was developed an electrochemical nanogenosensor for the detection of *Candida albicans*.This nanogenosensor was assembled in an innovative low-cost electrochemical paper based analytical devices (ePAD). A sandwich hybridization reaction was used to enhaced the sensitivity of the electrochemical signal.

Preliminary results demonstrated that using this nanogenosensors it was possible to detect Candida spp., in synthetic fungus sample. Despite these results, the optimization of the nanogenosensor in terms of quantifying *Candida albicans* is being carried out, which will be validated in future studies.The applicability in hospital environment relatively to sensitivity, accuracy, quickness response, challenges and opportunities will be discuss in future developments.

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Discovery of Hybrid Glypromate Conjugates with Neuroprotective Activity Against Paraquat-Induced Toxicity

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Paraquat is a highly toxic herbicide known to cause fatal injuries if mishandled.[1] Due to its intrinsic toxicity and the lack of effective treatments, paraquat is deemed as a major health concern in developing nations, where restrictions to its use are scarce.[1] In addition, long-term exposition to this neurotoxin can result in severe adverse effects, namely having a higher propensity to develop some motor symptoms resembling Parkinson's disease.[1]

Glypromate (glycyl-L-prolyl-L-glutamic acid) is an endogenous neuropeptide derived from the insulin-like growth factor-1 (IGF-1) that is present in brain tissues.[2] This small neuropeptide has been demonstrated to hold great potential to tackle neurodegenerative disorders, such as Parkinson's and Alzheimer's diseases, through several *in vitro* and *in vivo* assays.[2] However, the peptide nature of Glypromate hinders its clinical application due to its low oral bioavailability.[2]

In this work, a new series of peptide conjugates of the Glypromate neuropeptide is reported to explore the interplay of annular constriction and neuroprotective activity.[3] To this end, a bicyclic scaffold was used as an L-proline and L-pipecolic acid surrogate in addition to functionalization of glutamate residue with relevant active pharmaceutical ingredients (amantadine, memantine, and (*R*)-1-aminoindane).[3]

Using differentiated SH-SY5Y cells with a dopaminergic phenotype, a conjugate functionalized with (*R*)-1-aminoindane counteracted the toxicity elicited by paraquat ($p < 0.0001$) while Glypromate was found to exacerbate the neurotoxicity.[3] Altogether, this work adds new insights into Glypromate research by demonstrating that chemical conjugation and annular constriction are effective strategies to tune neuroprotective responses against different neurotoxic stimuli, paving the way for the development of new multitarget neurotherapeutics, as well as unveiling the unprecedented potential of Glypromate derivatives in countering paraquat-induced toxicity.

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Discovery of Hybrid Glypromate Conjugates with Improved Activity Against Protein Aggregation Induced by A$\beta_{25\text{-}35}$ in Neuronal Cells

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Neurodegenerative disorders comprise a series of heterogeneous conditions that affect millions of people worldwide, representing a significant health burden in both developed and developing countries.[1] Without disease-modifying treatments currently available, the development of effective neurotherapeutics is a health priority.[1]

Glypromate, also known as glycyl-L-prolyl-L-glutamic acid or GPE, is an endogenous neuropeptide derived from the insulin-like growth factor-1 (IGF-1) that can be found in brain tissues.[1] This tripeptide has been demonstrated to hold great potential to tackle neurodegenerative disorders, such as Parkinson's and Alzheimer's diseases, as demonstrated by several *in vitro* and *in vivo* studies.[1] However, the clinical translation of Glypromate is halted by its low oral bioavailability and negligible permeation across the blood-brain barrier, as a consequence of its intrinsic peptide nature.[1]

In this work, a new series of peptide conjugates of the Glypromate neuropeptide is disclosed by functionalization of glutamate residue with relevant active pharmaceutical ingredients, namely amantadine, memantine, and (*R*)-1-aminoindane.[2] In addition, a bicyclic scaffold was used as an L-proline and L-pipecolic acid surrogate to study the interplay of annular constriction and neuroprotective activity.[2]

Using non-differentiated SH-SY5Y cells, two Glypromate conjugates, functionalized with amantadine, significantly reduced protein aggregation induced by A$\beta_{25\text{-}35}$, outperforming both Glypromate by a 2-fold activity enhancement ($p < 0.05$), and an equimolar mixture of Glypromate and amantadine ($p < 0.0001$).[2] Altogether, this work adds new insights into Glypromate research by demonstrating that chemical conjugation and annular constriction are effective strategies to tune neuroprotective responses against different neurotoxic stimuli, paving the way for the development of new multitarget neurotherapeutics, as well as demonstrating the potential of Glypromate derivatives in countering protein aggregation in neuronal cells.

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Composición de ácidos grasos y potencial antioxidante del aceite de andiroba

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El aceite de andiroba se extrae de las semillas de *Carapa guianensis,* un árbol nativo de las regiones tropicales de América Central y del Sur, especialmente de la selva amazónica. Conocido por sus propiedades medicinales y cosméticas, el aceite de andiroba ha sido utilizado tradicionalmente por las comunidades indígenas durante siglos. Es rico en compuestos bioactivos que le otorgan una variedad de aplicaciones terapéuticas [1]. El aceite de andiroba promueve la cicatrización de heridas al mejorar la actividad de los fibroblastos y la síntesis de colágeno. Su rico contenido de ácidos grasos esenciales ayuda a restaurar la barrera natural de la piel y acelera la curación de heridas, quemaduras y úlceras, lo que lo convierte en un ingrediente valioso en aplicaciones dermatológicas. En la industria cosmética, el aceite de andiroba es valorado por sus propiedades hidratantes y calmantes para la piel. Se puede encontrar en formulaciones de cremas, lociones y productos para el cuidado del cabello, donde actúa como emoliente, mejorando la textura de la piel y la manejabilidad del cabello. Su potencial antienvejecimiento, atribuido a su actividad antioxidante, ayuda a proteger la piel del daño oxidativo causado por factores ambientales como la radiación ultravioleta [2]. A pesar de la amplia gama de aplicaciones potenciales de este aceite, sigue estando poco explorado por la industria y la comunidad científica. Por ello, este trabajo se llevó a cabo con el objetivo de hacer una caracterización del perfil de ácidos grasos y evaluar la actividad antioxidante del aceite de andiroba.

El perfil de ácidos grasos se analizó mediante cromatografía de gases con detección por ionización de llama tras la derivatización de la grasa bruta y el potencial antioxidante se determinó mediante el ensayo de la actividad de captación de radicales DPPH y del poder reductor. El estudio demostró que la fracción lipídica del aceite de andiroba estaba constituida principalmente por los ácidos oleico, palmítico y linoleico, y mostró actividad antioxidante en el método *in vitro* de DPPH y poder reductor. Esta investigación ha contribuido a aumentar los conocimientos sobre el potencial de este aceite y podría abrir nuevas perspectivas para su aplicación en diferentes sectores. Sin embargo, se necesitan más estudios para evaluar todo el potencial del aceite, que podría tener un amplio espectro de aplicaciones medicinales y cosméticas, convirtiéndose en un valioso agente terapéutico.

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Avaliação de biomarcadores de dano renal em bombeiros com participação ativa num fogo controlado urbano

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A rotina diária do bombeiro acarreta diversos fatores de risco, *i.e.*, stress físico e térmico, desidratação, assim como a exposição a vários poluentes libertados durante os fogos [1]. Estes fatores de risco potenciam o desenvolvimento de danos na saúde dos bombeiros, nomeadamente no sistema urinário [2,3]. No entanto, a avaliação da função renal dos bombeiros continua muito pouco caracterizada. Este estudo determina as concentrações de creatinina e cistatina-C, biomarcadores de disfunção renal precoce, e os níveis de cobre, molibdénio e chumbo, na urina de bombeiros portugueses com participação ativa num fogo controlado urbano.

Foram recolhidas 3 amostras de urina de 13 bombeiros (homens; 25,7 ± 1,93 anos; índice de massa corporal 23,9 ± 2,08 kg/m^2; 62% fumadores) antes, após e na manhã seguinte à sua participação num fogo controlado urbano. Os participantes preencheram um questionário de caracterização individual e assinaram um consentimento informado previamente revisto e aprovado pela Comissão de Ética da Universidade do Porto. Os níveis de creatinina foram determinados pelo método colorimétrico de Jaffe, e as concentrações de cistatina-C foram quantificadas por ensaios de imunoabsorção enzimáticatécnica (ELISA; Human Cystatin C, Quantikine ELISA Kit, R&D Systems, Minesota, EUA). Os níveis de metais foram determinados por espectrometria de massa acoplada com plasma indutivo. Os dados obtidos foram tratados estatisticamente (SPSS, versão 28.0, Armonk, NY, EUA) considerando o valor de $p \leq 0,05$ como significativo.

Em 38% dos bombeiros foi observado um aumento de 1,5 vezes (pós- *versus* pré-exposição) na concentração de creatinina após o fogo. A concentração de cistatina-C foi significativamente mais alta no período pós-fogo [52,9 (45,7 - 63,0) ng/mg creatinina, $p<0,001$], e na manhã seguinte ao evento [53,3 (44,3 - 62,4) ng/mg creatinina, $p=0,002$], do que na urina pré-fogo [36,2 (28,5 – 43,9) ng/mg creatinina]. Os níveis de cobre e molibdénio também aumentaram após o fogo (5,00 *versus* 5,30 µg/g creatinina e 37,90 *versus* 50,50 µg/g creatinina, respetivamente). Em 62% dos bombeiros, foi observado um aumento nas concentrações de chumbo após o combate ao fogo.

Os resultados preliminares obtidos demonstram que a avaliação de biomarcadores de dano renal pode auxiliar na deteção precoce de alterações e/ou disfunção da atividade renal resultantes da participação ativa em combate a incêndios. De forma a suportar os resultados obtidos, os futuros estudos de biomonitorização devem ser alargados a um número superior de participantes e incluir outros biomarcadores de disfunção renal precoce.

Financiamento

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QUÍMICA TEÓRICA

A machine learning-based approach to understand dynamic topological changes of the charge density

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Coupling *ab inito* Molecular Dynamics (AIMD) with Quantum Theory of Atoms in Molecules (QTAIM) is a proven strategy for gaining interesting insights on chemical reactions[1,2]. One particularly interesting approach being the development of bond-breaking/bond-forming phenomena under the framework of catastrophe theory[3]. Unfortunately, such an approach is limited by the ability to carry out extended AIMD simulations, as well as the computational effort involved in processing the simulation trajectory under QTAIM.

This work presents the first few applications of a Machine Learning (ML) based strategy to allow for an extended sampling and analysis of several chemical systems as well as its subsequent analysis under QTAIM. The proposed protocol relies on two ML models and two levels of theory for the exploration of the Potential Energy Surface (PES): a fast method which is applied to steered AIMD simulations of the system(s) of interest, and a higher level, used for refining the shape of the PES. As detailed in Fig. 1, the first ML model then refines the PES by learning the response curve of the two electronic structure methods. The timestamp of each point along the trajectory is then modified to account for the updated energy barriers and valleys. Then, a second, multi-purpose, ML model is responsible for learning a set of relevant features of the topology of the charge density requested. Results are given for some example systems, together with some benchmarks regarding the computational effort of this approach.

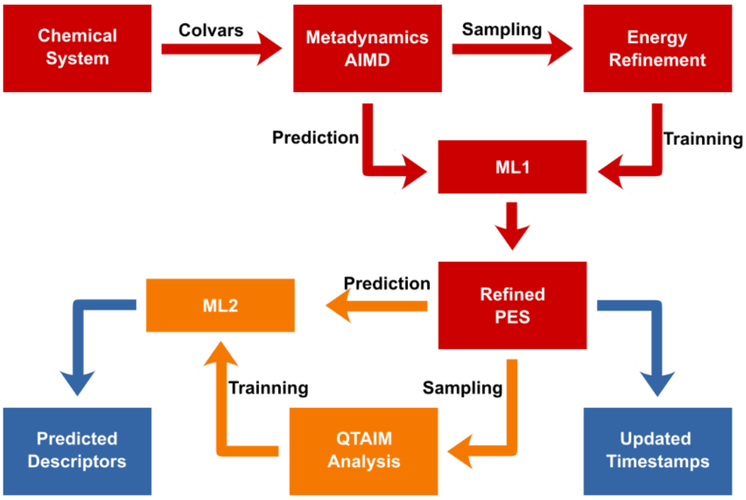

Fig.1. Schematic representation of the proposed AIMD/ML/QTAIM/ML protocol for enhanced exploration of the PES and the dynamical changes in the topology of the charge density.

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Hansen solubility parameters of ionic liquids from inverse gas chromatography data

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In light of the global increase in demand for more sustainable processes, ionic liquids (ILs) have emerged as a promising solution to replace conventional solvents. Given their widespread use in various applications, from catalysis to separation processes, the proper characterization of ILs is crucial for optimizing their performance and ensuring their sustainable use [1].

The main objective of this study is thus to determine the Hansen Solubility Parameters (HSP) of ILs, which are essential for predicting solubility and miscibility, directly impacting the efficiency of ILs in different processes [2]. To achieve this, two approaches are employed:

- Determining the HSP of ILs by using the solubility of different organic molecules in these ILs and calculating the HSP using the conventional method;

- Combining experimental activity coefficients at infinite dilution, γ^{∞}, obtained through inverse gas chromatography with theoretical modeling to calculate the HSP.

In both approaches, the Hansen Solubility Parameters in Practice (HSPiP) software will be used [2, 3].

Imidazolium-based ILs with the chloride anion (Cl^-) are investigated, focusing on the impact of increasing the IL cation chain length on the HSP. Additionally, this study compares the two approaches, highlighting the benefits and limitations of each.

By bridging the gap in understanding IL behavior, this study provides valuable insights into their practical applications across various fields, with a focus on fundamental properties.

Acknowledgments

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The challenges of Claisen-Schmidt condensation with polyhydroxylated subtracts.

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The Claisen–Schmidt condensation has been the primary method for synthesizing chalcones for over a century, valued for its simplicity, broad substrate scope, mild conditions, and favorable atom economy. However, this reaction presents challenges, especially with polyhydroxylated acetophenones, where the reaction may either not proceed or become sluggish, often accompanied by side reactions. [1] To address these issues, protection and deprotection strategies are commonly employed, but these steps negate the method's inherent advantages. [2] Consequently, efforts have been directed toward developing a protocol to synthesize a novel polyhydroxylated *bis*-chalcone **3** from a polyhydroxylated acetophenone **1**, without relying on initial protection steps (Figure 1). Despite testing various catalytic systems, the reaction was unsuccessful.

To gain deeper insights into the limitations of this process, DFT calculations were performed to evaluate the nucleophilicity of starting material **1** under base, acid, and metal-mediated catalysis mechanisms. Models with and without hydroxy groups were used to test the hypothesis that competing nucleophiles were hindering the reaction.

Preliminary results indicate that in a strong basic medium, full deprotonation of all phenol groups occurs, leading to heightened competition between nucleophilic sites, where phenolates outcompete enolates. Although complexation with lithium and calcium cations was predicted to reduce the nucleophilicity of the phenolates, it failed to sufficiently suppress the reactivity of the remaining phenolate, resulting in undesired side reactions.

In acidic medium, enols showed superior nucleophilicity compared to phenols. However, the acidic conditions also facilitated isomerization of the *bis*-chalcone, increasing the risk of degradation or undesired cyclization.

This communication discusses the various factors contributing to the reaction's failure, with ongoing studies on the energy profiles of different mechanisms to elucidate the reaction's limitations further when competing nucleophiles are present.

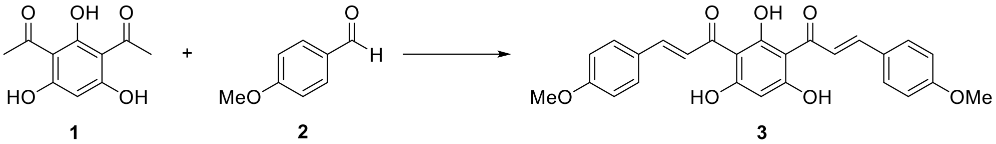

Fig. 1. Attempted synthesis of the polyhydroxylated bis-chalcone **3**.

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SEGURIDAD QUÍMICA

EVALUACIÓN DE LA EXPOSICIÓN A AGENTES QUÍMICOS

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El R.D. 374/2001[1] sobre la prevención de los riesgos derivados de la presencia de agentes químicos en el trabajo, establece que la evaluación de la exposición debe hacerse, con carácter general, por medición de las concentraciones ambientales de dichos agentes químicos en el puesto de trabajo; pero también establece una alternativa a la evaluación cuantitativa cuando “el empresario demuestre claramente por otros medios de evaluación que se ha logrado una adecuada prevención y protección”: una evaluación cualitativa.

En este trabajo se realiza una evaluación de la exposición a agentes químicos en el puesto de trabajo de “Técnico de laboratorio”, conforme a lo establecido en el R.D.374/2001.

La metodología utilizada es:

1. Evaluación cualitativa y simplificada del riesgo por inhalación (II). Modelo COSHH Essentials (Control of Substances Hazardous to Health).
2. Evaluación cuantitativa basada en la norma UNE-EN 689:2019+AC:2019 [2].

Un técnico de laboratorio a lo largo de su jornada laboral, ocupa en ControlQ_LABCOMB:

☐ aproximadamente una hora en limpieza de material.
☐ aproximadamente 6 horas en “análisis de gasolina”, analizando en ese tiempo 3 muestras.
☐ aproximadamente 6 horas en “análisis de gasóleo”, analizando en ese tiempo 2 muestras.

Para cada uno de los agentes químicos presentes, los trabajadores están expuestos a pequeñas cantidades de los mismos, de orden de los mililitros. Para la gasolina y gasóleo muestras objeto de los ensayos, pero también agentes químicos con potencial peligrosidad por inhalación, la cantidad utilizada es mediana, del orden de litros.

Los datos manejados en el estudio muestran que se superan los valores límite o que resulta probable que se superen en algunas ocasiones. La situación se considera como no aceptable y se deberá proceder a su corrección mediante la implantación de medidas específicas de prevención, protección y vigilancia de la salud, de acuerdo con lo dispuesto en los artículos 5, 6 y 7 del RD 374/2001.

Fig.1. Variables que pueden considerar los métodos cualitativos de evaluación.

Referencias

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ControlQ_LABCOMB: EVALUACIÓN DE LA EXPOSICIÓN AL RUIDO

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En el real y diario funcionamiento de un laboratorio químico existen distintos agentes que actúan directamente sobre la seguridad y salud de los técnicos e investigadores que en ellos desarrollan su actividad.

La Agencia Europea para la Salud y Seguridad en el Trabajo (EU-OSHA, 2006) reconoce que la pérdida auditiva por ruido es la enfermedad profesional que con mayor frecuencia se presenta en Europa, y aconseja una mayor atención a los factores de riesgo combinados en los trabajadores expuestos a ruido elevado y compuestos químicos.

Dado el tipo de muestras manejadas y equipos empleados en ControlQ_LABCOMB, debido a la existencia de riesgo combinado, se consideró relevante realizar una evaluación de la exposición al ruido [1] ya que, en el laboratorio, existen dos equipos que ocasionan un considerable ruido ambiental durante su funcionamiento: la vitrina de gases y un criotermostato de refrigeración en funcionamiento continuo durante la jornada laboral.

La evaluación se realizó siguiendo el siguiente esquema:
Etapa 1. Selección de la estrategia: medición basada en muestreos durante el trabajo.
Etapa 2. Mediciones.
Etapa 3. Cálculo del nivel de exposición diario equivalente y su incertidumbre expandida.
Etapa 4. Cálculo de la atenuación de los protectores auditivos.
Etapa 5. Comparación con los valores límite.

- En la determinación de la exposición real del trabajador al ruido, se tuvieron en cuenta la atenuación que procuran los protectores auditivos individuales utilizados por los trabajadores:

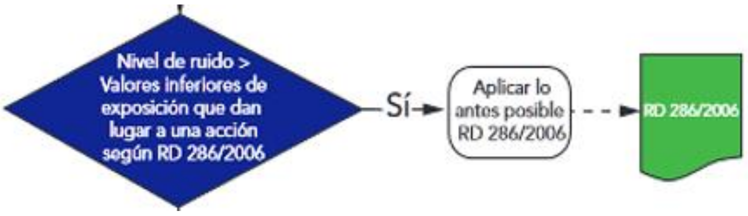
86 dB < 87 dB(A) → no se supera el valor límite de exposición

- Para los valores de exposición que dan lugar a una acción no se tuvieron en cuenta los efectos producidos por dichos protectores:

90,2 dBA > 85 dBA → se supera el valor superior de exposición que da lugar a una acción

El Real Decreto 286/ 2006 [2] establece los valores límite de exposición y los valores de exposición que dan lugar a una acción, referidos a los niveles de exposición diaria y a los niveles de pico. La superación de cada uno de los niveles de referencia conlleva asumir una serie de medidas específicas.

Fig.1. Requisitos legales_Exposición al ruido



Referencias

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