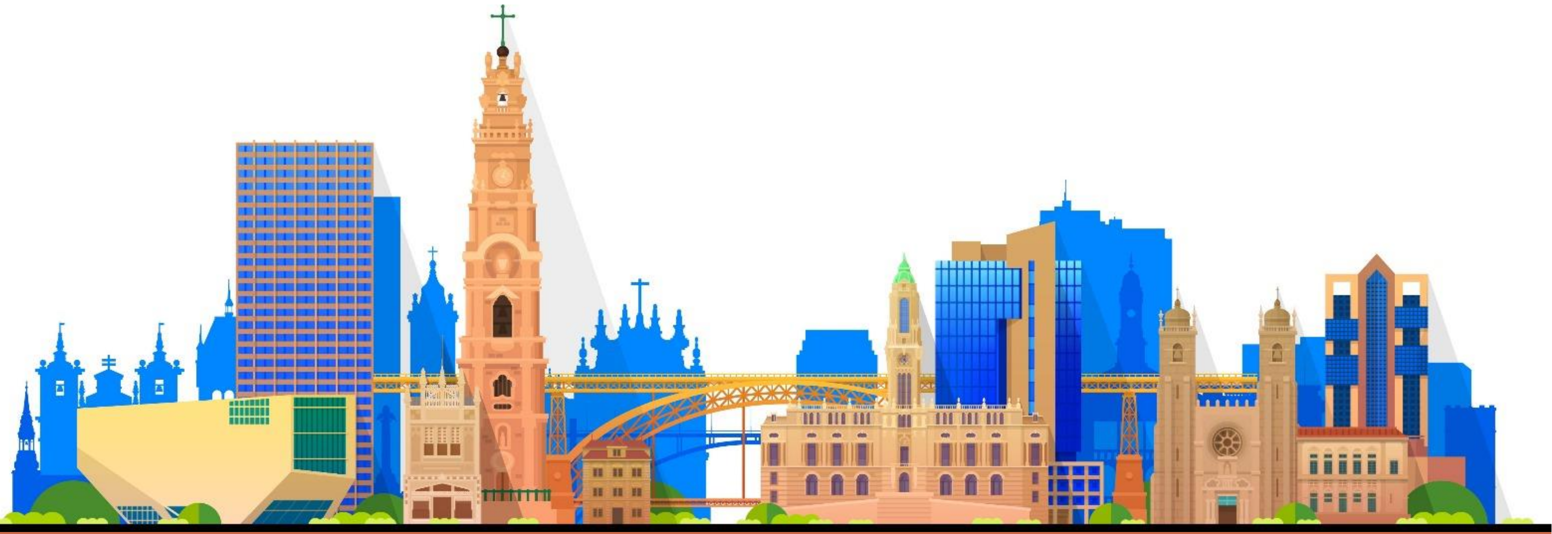

III REUNIÃO DO GRUPO DO CARBONO

LIVRO DE RESUMOS

26-27 MARÇO 2024

PORTO, PORTUGAL

Grupo do Carbono

Sociedade Portuguesa de Química

EuChemS
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FICHA TÉCNICA

TÍTULO

III Reunião do Grupo de Carbono

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Este livro de atas foi produzido a partir dos trabalhos submetidos diretamente pelos autores. Apenas foram introduzidas pequenas alterações de edição, o que não alterou o conteúdo científico. Os autores são responsáveis pelo conteúdo científico dos seus trabalhos.

PREFÁCIO

A III Reunião do Grupo do Carbono (III RGC) decorrerá de 26 a 27 de março de 2024 na Faculdade de Engenharia da Universidade do Porto, no Porto. O evento é organizado pela Universidade do Porto, com o apoio do Laboratório de Processos de Separação e Reação - Laboratório de Catálise e Materiais (LSRE-LCM), dos Laboratórios Associados ALiCE e REQUIMTE e da Sociedade Portuguesa de Química (SPQ).

A III RGC pretende ser um ponto de encontro com o objetivo de privilegiar a divulgação de trabalhos que envolvam fundamentos, desenvolvimentos e aplicações de materiais de carbono nas mais variadas áreas do conhecimento científico, estimulando a criação de novas colaborações entre grupos multidisciplinares. Foram desenvolvidos esforços para juntar neste encontro investigadores provenientes das áreas da química, da física, dos materiais e respetivas engenharias com o objetivo de criar um grupo de carbono transversal e representativo de todas as unidades de investigação que em Portugal têm atividade em materiais de carbono, nas suas diferentes alotropias. Em 2028, *The World Conference on Carbon – Carbon 2028,* que é o maior evento mundial nesta área do conhecimento, será organizado em Portugal pelo Grupo do Carbono que deverá ter a capacidade de mostrar a dinâmica da investigação portuguesa nesta vertente científica.

O programa da III RGC integra duas sessões plenárias, em que temos o privilégio de contar com dois investigadores que são uma referência mundial na área do carbono, os professores Alain Celzard da Universidade de Lorraine e Diego Cazorla da Universidade de Alicante; 5 comunicações convidadas, por investigadores nacionais que são líderes em distintas linhas de investigação envolvendo materiais de carbono; e inclui ainda diversos tipos de comunicações orais e em painel no sentido de proporcionar um evento de elevada qualidade científica.

O Grupo do Carbono decidiu atribuir pela primeira vez nesta edição o Prémio Melhor Tese de Doutoramento na área do carbono, destinado a um recém-doutorado de nacionalidade portuguesa ou que tenha obtido o grau de doutor numa universidade portuguesa no período compreendido entre 1 de janeiro de 2022 e 31 de dezembro de 2023. O vencedor desta edição foi o doutor André Torres Pinto com a tese "Optimised 2D carbon materials activated by artificial light and electrical current for catalytic water and wastewater treatment".

A Comissão Organizadora agradece a todos os participantes, com a expectativa de que esta seja uma reunião que permita criar pontes nesta área do conhecimento e reforçar a ligação às atividades do Grupo do Carbono. Uma palavra final de agradecimento a todas as empresas e instituições que apoiaram a realização deste evento.

Porto, 26 de março de 2024
M. Fernando Pereira

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SRE CM Laboratory of Separation and Reaction Engineering Laboratory of Catalysis and Materials

ALiCE Associate Laboratory in Chemical Engineering

LAQV requimte Laboratório Associado para a Química Verde

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INFORMAÇOES GERAIS

LOCAL

A III Reunião do Grupo do Carbono decorrerá na Faculdade de Engenharia da Universidade do Porto, no Porto.

RECEPÇÃO

O acolhimento para levantamento da documentação da reunião e informações estará localizada junto à sala B032, entrada pelo Piso 1 do edifício B da Faculdade de Engenharia da Universidade do Porto, no horário indicado no programa.

COMUNICAÇÕES ORAIS

As comunicações plenárias terão duração de 45 minutos, as comunicações orais convidadas de 30 minutos, e as comunicações orais de 15 minutos, estando incluído o período de discussão em todos os casos.

COMUNICAÇÕES ORAIS FLASH

As COF terão a duração de 5 minutos sem qualquer período de discussão. Estas deverão conter no máximo 4-5 diapositivos, devendo o primeiro mencionar o número do poster, o título do trabalho, os autores e correspondente afiliação; e o último conter as principais conclusões do trabalho.

COMUNICAÇÕES EM PAINEL

As dimensões máximas dos painéis serão de 90 cm de largura x 120 cm de altura, aconselhando-se a dimensão A0 para o poster. Pede-se aos autores para estarem presentes junto dos painéis durante a sessão de discussão. Os posters deverão ser removidos pelos autores da comunicação.

EQUIPAMENTO DE PROJEÇÃO

A sala das comunicações orais está equipada com computador (Microsof Office) e sistema de projeção. Cada orador deverá transferir o ficheiro (em PowerPoint) da sua apresentação para o computador da sala pelo menos, no limite, na sessão anterior.

JANTAR DO EVENTO

O jantar da III Reunião do Grupo de Carbono será no dia 26 de março, pelas 20:30, no Restaurante O Comercial - Palácio da Bolsa.

PROGRAMA CIENTÍFICO

PROGRAMA CIENTÍFICO

	Terça-Feira, 26 março 2024	**Quarta-Feira, 27 março 2024**
09:30		CPL2 ::: Diego Cazorla
09:45		
10:00		
10:15		**CC3 ::: Clara Pereira**
10:30	**Registo**	
10:45		**Coffee Break**
11:00	**Sessão de Abertura**	
11:15		**CC4 ::: Conceição Paiva**
11:30	CPL1 ::: Alain Celzard	
11:45		CO3 ::: Ana Cristina Estrada
12:00		CO4 ::: Ana S. Mestre
12:15	**CC1 ::: Adélio Mendes**	CO5 ::: Cláudia Batista Lopes
12:30		CO6 ::: Marta Amaral Andrade
12:45	**Almoço**	**Almoço**
14:15	**CC2 ::: Inês Matos**	**CC5 ::: Pedro Alpuim**
14:30		
14:45	**Prémio Melhor Tese** ::: André Torres-Pinto	CO7 ::: Antonio J. Paleo
15:00	CO1 ::: Artur M. Pinto	CO8 ::: Gabriel Bernardo
15:15	CO2 ::: Gil Gonçalves	CO9 ::: Mariana Martins da Silva
15:30	**COF ::: Comunicações Orais Flash (Estudantes de Doutoramento)**	**Coffee Break**
15:45		
16:00		CO10 ::: Ana Sofia Monteiro Silva
16:15		CO11 ::: Rui S. Ribeiro
16:30	**Apresentações em Painel & Coffee Break**	CO12 ::: Diana M. Fernandes
16:45		CO13 ::: Joana S. Teixeira
17:00		**Sessão de Encerramento**
17:15		
17:30	**Assembleia geral de sócios do Grupo do Carbono**	
17:45		
18:00		
18:15		
18:30		
20:30	**Jantar do Evento**	

CPL: Comunicação Plenária (45’) • CC: Comunicação Convidada (30’) • CO: Comunicação Oral (15’) (incluindo discussão)

TERÇA-FEIRA, 26 MARÇO 2024

10:30 – 11:00	**Registo**
11:00 – 11:30	**Sessão de Abertura**
11:30 – 12:15	**CPL1 ::: Alain Celzard** *3D printing of carbon-based materials: update on the state of the art*
12:15 – 12:45	**CC1 ::: Adélio Mendes** *Carbon Molecular Sieve Membranes: From Science to Technology and Beyond*
12:45 – 14:15	Pausa para Almoço
14:15 – 14:45	**CC2 ::: Inês Matos** *Porous carbon: efficient and sustainable material for catalysis for fine chemicals*
14:45 – 15:00	**Prémio Melhor Tese Doutoramento na área do Carbono** **André Torres-Pinto** *Optimised 2D carbon materials activated by artificial light and electrical current for catalytic water and wastewater treatment*
15:00 – 15:15	**CO1 ::: Artur M. Pinto** *Carbon nanomaterials in biomedicine: with focus on graphene-based materials*
15:15 – 15:30	**CO2 ::: Gil Gonçalves** *Cutting-edge carbon-based nanomaterials in the fight against cancer*
15:30 – 16:30	**Comunicações Orais Flash (Estudantes de Doutoramento)**
16:30 – 17:30	**Apresentações em Painel & Coffee Break**
17:30 – 18:30	**Assembleia geral de sócios do Grupo do Carbono**

20:30	**Jantar do Evento ::: Restaurante O Comercial - Palácio da Bolsa**

QUARTA-FEIRA, 27 MARÇO 2024

09:30 – 10:15	**CPL2 ::: Diego Cazorla** *Carbon as catalyst, catalyst support and catalyst promoter. An example with oxygen reduction reaction*
10:15 – 10:45	**CC3 ::: Clara Pereira** *Exploring the Boundless Potential of Hybrid Carbon Nanomaterials in Smart Energy Harvesting and Storage Textile Technologies*
10:45 – 11:15	Coffee Break
11:15 – 11:45	**CC4 ::: Conceição Paiva** *Surface modification of carbon nanomaterials and dispersion in polymers*
11:45 – 12:00	**CO3 ::: Ana Cristina Estrada** *Carbon-based heterostructured BiVO4 photocatalysts for the degradation of contaminants of emerging concern*
12:00 – 12:15	**CO4 ::: Ana S. Mestre** *Insights on the regeneration of activated carbons exhausted with pharmaceutical compounds*
12:15 – 12:30	**CO5 ::: Cláudia Batista Lopes** *Magnetic graphite-like nanoplatelet composites: from synthesis to application in water treatment*
12:30 – 12:45	**CO6 ::: Marta Amaral Andrade** *Engineered pine nut shell powdered activated carbons for advanced drinking water treatment: is particle size important?*
12:45 – 14:15	Pausa para Almoço

QUARTA-FEIRA, 27 MARÇO 2024

14:15 – 14:45	**CC5 ::: Pedro Alpuim** *Neurotransmitter detection with graphene aptasensor multitransistor chips*
14:45 – 15:00	**CO7 ::: Antonio J. Paleo** *Electric properties of cotton fabrics prepared with Pyrograf® III carbon nanofiber-based inks*
15:00 – 15:15	**CO8 ::: Gabriel Bernardo** *Tuning the pore network nanomorphology of cellulose precursor films to produce Carbon Molecular Sieve Membranes*
15:15 – 15:30	**CO9 ::: Mariana Martins da Silva** *Thermoplastic polyurethane composites with single walled carbon nanotubes for soft actuators*
15:30 – 16:00	Coffee Break
16:00 – 16:15	**CO10 ::: Ana Sofia Monteiro Silva** *High performance PEEK/MWCNT nanocomposites with enhanced electrical conductivity for the production of spun fibres by melt-spinning*
16:15 – 16:30	**CO11 ::: Rui Sérgio da Silva Ribeiro** *Bottom-up construction of Fe–N–C active centers: Towards sustainable oxygen reduction reaction electrocatalysts*
16:30 – 16:45	**CO12 ::: Diana Mónica de Mesquita Sousa Fernandes** *Shrimp shell-derived biochars as efficient electrocatalysts for oxygen reactions*
16:45 – 17:00	**CO13 ::: Joana Filipa dos Santos Teixeira** *The Influence of CNT@Metal Sulfide Hybrid Electrode Materials in Thermally-Chargeable Textile Supercapacitors*
17:00 – 17:30	**Sessão de Encerramento** Entrega do Prémio Melhor Comunicação em Painel

COMUNICAÇÕES ORAIS FLASH | Terça-feira, 26 de março 2024 | 15h30 – 16h30

COF1	Experimental design tools to maximize RNA capture with oxidised nanodiamonds	Pedro Filipe Lopes Ferreira
COF2	Acidic functionalization of MWCNTs: insights on their antibiofilm activity against E. coli and S. aureus	Marisa C. L. Gomes
COF3	NO reduction over carbon xerogel supported catalysts	Patrícia Sofia Ferreira Ramalho
COF4	Extending the catalytic potential of carbon-based macrostructured catalyst for continuous water treatment systems	Ana Sofia Guedes Gorito dos Santos
COF5	Abatement of toluene from gaseous streams by Fenton's reaction over N-doped carbon materials	Emanuel Filipe da Silva Sampaio
COF6	Assessment of surface-modified activated carbons as catalysts in the ozonation of emerging pollutants	Diego Armando Montenegro Apraez
COF7	Effect of heteroatom doping in biochar's catalytic performance towards oxygen electroreduction	Renata Teixeira Correia de Matos
COF8	Nanostructured SiO_2-supported Ni-Fe catalysts loaded onto a planar slab reactor for stable catalytic methane splitting	Luís Daniel Martins Alves
COF9	Enhancing the electrochemical performance of electrochromic textile supercapacitors using PEDOT:PSS and oxidized MWCNTs	Gabriela Pinto de Queirós
COF10	Innovative Thin Multilayer Thermally-Chargeable Textile Supercapacitors	Ana Rita Correia e Sousa

COMUNICAÇÕES PLENÁRIAS

3D printing of carbon-based materials: update on the state of the art

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As an insoluble, infusible and non-weldable material, carbon is a priori unsuitable for 3D printing. However, in recent years, spectacular progress has been made in the additive manufacturing of carbon, which has gradually been able to embrace a growing number of processing technologies (Fig. 1).

This communication, based on a former review published in 2021 [1], aims to present an up-to-date state of the art of 3D printing techniques applied to carbon materials. If the use of carbon as a filler in 3D-printed polymers is not new, and some useful reminders will be made on this subject, this presentation will mainly deal with the preparation of pure carbon materials through modern additive manufacturing methods. It will be clearly shown that, depending on the techniques implemented, the number of steps, the physical and textural properties, but also the final dimensions of the object thus produced and the resolution of its geometrical details can be extremely different. Consequently, the applications of these new materials will also be very varied, and most often one technique will not be able to replace another according to the intended purpose.

The advantages and shortcomings of the different techniques of additive manufacturing of pure carbon components will be presented, and examples of recent achievements will be given, demonstrating the full potential of carbon 3D printing, which still has much room for development.

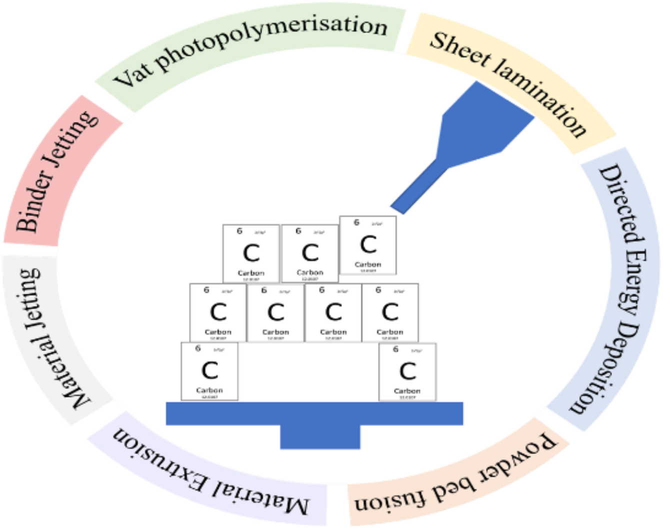

Fig.1. Overview of 3D printing techniques already successfully used to process carbon materials for various applications.

Funding

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References

[1] P. Blyweert, V. Nicolas, V. Fierro, A. Celzard, Carbon, 183 (2021) 449

Carbon as catalyst, catalyst support and catalyst promoter. An example with oxygen reduction reaction

Emilia Morallón[2], Diego Cazorla-Amoros[1,*]

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Carbon materials exhibit unique properties that make them useful in an extraordinary large number of technological applications. The unique (and different) properties that can be found for carbon materials are due to their diversity in structure. From the structure point of view, and focusing only on sp2 carbon materials, materials with long-range and short-range orders can be found what explains the large family of carbon materials. The second factor that determines the properties of the carbon materials is the surface chemistry, which is determined by the concentration of intrinsic defects and the presence of heteroatoms. Then, the combination of both structure and surface chemistry results in an enormous collection of materials with properties that can be tailored for many different applications.

Among the different applications of carbon materials their use in industrial catalytic processes is very well known for more than 100 years. Recently, the development of electrochemical energy storage and production devices has impressively raised the interest in carbon materials. In this field, the role of carbon materials as catalyst or catalyst support is outstanding and strong research and technology development efforts are being done trying to optimize the performance of electrochemical technologies, which are still far from industrial requirements.

In the specific application of energy generation through fuel cells or metal-air batteries, one important limitation is the oxygen reduction reaction (ORR) which occurs in the cathode due to the sluggish kinetics of the reaction. This requires the use of high amounts of precious metals that impedes the deployment of the technology. In this sense, research on new catalysts either based on metal-free carbon materials or non-precious metal-based catalysts are subject of strong research trying to find catalysts that can substitute precious metals. Carbon materials, due to their unique properties, may have different roles in the ORR and they can be catalyst, catalyst support and promoter of catalytic activity. In this talk, we will present examples of the three mentioned functions of the carbon materials in ORR, that will show the great interest in designing at the nanoscale the structure and chemical composition of the material to boost the catalytic properties. On one hand, the role of carbon as catalyst will be illustrated with N-doped carbon materials and the discussion will be focused on the nature of the active sites. Carbon as catalyst support will be exemplified with Fe-phthalocyanine catalyst supported on functionalized carbon nanotubes. Finally, the need of the carbon material to boost the catalytic activity of metal perovskites will be presented.

COMUNICAÇÕES ORAIS CONVIDADAS

Carbon Molecular Sieve Membranes: From Science to Technology and Beyond

Adélio Mendes[1,2*], Tiago Araújo[1,2], Gabriel Bernardo[1,2]

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Carbon molecular sieve membranes (CMSM) produced from the carbonization of casting cellulose were reported only recently after the seminal article by Mendes [1]. This new route opened the doors for the development of tailor-made low-cost CMSMs, using a renewable and abundant resource. A solution of Emimac:DMSO (30:70 wt.%, Emimac = 1-ethyl-3-methylimidazolium acetate) is used to dissolve the cellulose (9.2 wt.%) at 90 °C by magnetic stirring for *ca*. 2 hours. This solution is then used for casting the membranes as flat sheets or as hollow fibers. The pore size distribution and surface chemistry can now be tailored using different pathways, namely i) regeneration conditions and solvent; ii) carbonization atmosphere, iii) carbonization end temperature; and iv) surface modifying additives. Ceramic additives are also used to control the shrinkage rate of the membranes during the carbonization process and the pore size distribution. The CMSMs display oxygen chemisorption, which makes them age rather quickly, and an "S" shape adsorption isotherm of water vapor, which p roduces the blockage of the pores at relative humidities above ca. 30 %. These challenges were addressed, the first passivating the surface using propylene and the second making the CMSM more hydrophilic. Finally, the separation performance of a membrane to a binary gas mixture is normally characterized based on the permeability to the faster gas and the ideal selectivity. These parameters are then compared with the upper bond Robeson plot, inserting the new values in a plot. This makes the comparisons complicated and the update of the Robeson plots even more complicated. The authors suggested for the first time the use of the so-called Robeson Index [2], which is a merit figure of the gas separation compared with the original upper bond Robeson plot, but everything condensed into a single number easily updated.
Table 1 displays the performance of the best-performing membranes for two critically relevant gas separations: a) oxygen enrichment from air (OEA) [3] and b) hydrogen extraction from a hydrogen/methane mixture [4]. It can be concluded that cellulose-based CMSMs are a very promising gas and vapor separation technology.

Table 1. Performance of the best-performing membranes for O_2/N_2 and H_2/CH_4 separation

Permeability / barrer				**Selectivity / -**		**Robeson Index**		
L_{H2}	L_{O2}	L_{N2}	L_{CH4}	**α(O_2/N_2)**	**α(H_2/CH_4)**	**θ(O_2/N_2)**	**θ(H_2/CH_4)**	**Ref.**
544			0.21		3498		100	4
	333	6.37		53.8		12.3		3
Production cost of OEA > 96 %: 83.8 €·tonO_2^{-1} – Cost of cheapest competing technology, cryogenic distillation: *ca*. 100 €·tonO_2^{-1}								
Production cost of H_2 > 99.8 % and a recovery of 96%: 0.26 €·kgH_2^{-1} – Cost of cheapest competing technology (PSA): >3 €·kgH_2^{-1}								

Acknowledgements

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References

[1] S.C. Rodrigues, M. Andrade, J. Moffat, F.D. Magalhães, A. Mendes, J. Membrane Science, 572 (2019) 390.
[2] T. Araújo, G. Bernardo, A. Mendes, Molecules, 25 (2020) 3532
[3] T. Araújo, T.S. Lopes, G. Bernardo, A. Mendes, Journal of Membrane Science 694 (2024) 122430
[4] T. Araújo, G. Bernardo, A. Mendes, Journal of Membrane Science 693 (2024) 122337

Porous carbon: efficient and sustainable material for catalysis for fine chemicals

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How to maintain necessary products and living standards while increasing sustainability, resource efficiency, and zero waste production? – This is one important challenge faced by Europe in the circular economy goal. This is relevant in all day-to-day goods but particularly challenging in health-related products such as pharmaceuticals, or in ensuring access to clean drinking water [1]. Porous carbon materials may play an important role in this context.

Porous carbons are extremely environmental-friendly materials with an increasing number of applications in different domains. Besides applications related to environmental engineering, such as water treatment and air and gas purification, carbon materials have found application in areas as diverse as drug delivery, catalysis, chromatography systems, energy storage, among others.
For many of these applications, custom-tailored properties such as surface area and controlled porosity, chemical and thermal stability, electronic conductivity, easy heteroatom doping, and tunable surface chemistry are very relevant to their performance [2,3].

In this presentation, the work devoted to the development of new highly porous carbon materials following different synthetic methodologies and using different precursor materials, including biomass and waste will be presented, and its application in heterogeneous catalysis.

Pharmaceuticals are often associated with high cost and/or low yields of production making them less accessible to those in need. A new technological approach based on the circular economy principals can be of high impact. [4]
In this context researching new and sustainable chemical processes becomes very pertinent and catalysis a pivotal element of development. The search for new feedstocks and the need for efficient use of resources will necessarily comprise biomass valorization.
Thus, their application as catalysts in the synthesis of relevant nitrogen heterocyclic systems, quinolines or benzodiazepines - molecules with a variety of pharmaceutical applications such as antidepressant medicines.

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References

[1] European Commission; Innovation, D.-G. for R. and Material Resource Efficiency - Targeted scenario N°11. 2018, doi:10.2777/147443.
[2] E. Pérez-Mayoral, I. Matos, M. Bernardo, I.M. Fonseca, Catalysts 9 (2019) 133- 168; doi:10.3390/catal9020133
[3] E. Pérez-Mayoral, I. Matos, M. Bernardo, M. Ventura, M. Fonseca, Catalysts 2020, 10, 1407; doi:10.3390/catal10121407
[4] Godino-Ojer, M., Morales, V.R., López Peinado, A.J., Matos, I., Pérez-Mayoral, E., Catalysis Today, 2023, 419, 114160 https://doi.org/10.1016/j.cattod.2023.114160

Exploring the Boundless Potential of Hybrid Carbon Nanomaterials in Smart Energy Harvesting and Storage Textile Technologies

Clara R. Pereira[1,*], Joana S. Teixeira[1,2], Gabriela P. Queirós[1,2], Rui S. Costa[2], Marta S. Nunes[1,2], André M. Pereira[2]

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The burgeoning markets of IoT and wearable electronics have sparked a quest for smart multifunctional energy technologies seamlessly integrated into clothing for a diversity of applications, encompassing Healthcare, Protection, Fashion, and Defense. Thermally-chargeable textile supercapacitors are of prime interest for self-powered wearables since they are able to convert the low-grade wasted heat from the environment or human body into electrical energy and, simultaneously, store the produced electrical energy [1]. Multifunctional textile supercapacitors merging energy storage with dynamic color-switching properties are another emerging class of smart energy technologies that are opening promising prospects for real-time monitoring of energy consumption and high-visibility safety clothing [2,3].
Hybrid electrode nanomaterials composed of carbon nanostructures functionalized with redox-active transition metal oxides/sulfides and/or electrically-conductive polymers have been fostering the advance of these smart technologies owing to the synergy between their structural, textural and electrochemical properties.
In this work, we will provide an overview of the progress on the development of innovative all-in-one energy harvesting/storage textile technologies, glow-in-the-dark and electrochromic textile supercapacitors (Fig. 1). The boundless potential of functional and hybrid carbon-based nanomaterials as building blocks for the development of such intelligent systems will be highlighted. The journey from the conceptualization and design of these engineered nanomaterials through eco-sustainable and scalable processes, their integration onto textile substrates and assembly into versatile multi-tasking systems will be presented. Finally, the assessment of the electrochemical performance and feasibility of the developed technologies to power electronic devices will be showcased.

Fig. 1. A) Thermally-chargeable textile supercapacitor (T-TCSC), B) Glow-in-the-dark textile supercapacitor and (C) Electrochromic textile supercapacitor.

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References

[1] R. S. Costa, A. L. Pires, A. M. Pereira, C. R. Pereira, Journal of Power Sources, 587 (2023) 233712.
[2] L. Manjakka, L. Pereira, E. K. Barimah, P. Grey, F. F. Franco, Z. Lin, G. Jose, R. A. Hogg, Progress in Materials Science 142 (2024) 101244.
[3] J. S. Teixeira, A. M. Pereira, C. Pereira, Chemical Engineering Journal 426 (2021) 131274.

Surface modification of carbon nanomaterials and dispersion in polymers

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Graphite and graphite-derived nanomaterials present a smooth surface of sp^2 carbon, chemically bonded forming an hexagonal lattice structure. These characteristics, associated with the excellent thermal, electrical and mechanical properties of graphite-derived materials, make them interesting for a wide range of applications. Some applications may require specific surface chemistry, such as in the formation of polymer composites, requiring strong interfaces between polymer and nanoparticle, or for electrochemical sensing, requiring chemical groups that favour specific molecular interactions. The chemical modification of the graphene surface may be achieved through non-covalent or covalent chemistry, the latter being preferred for establishing strong interfaces with polymers. In that case, the organic chemistry of C=C bonds may be used to achieve covalent functionalization of the graphene surface with minimal damage to the nanoparticle surface structure.

The present work reports the covalent modification of graphite-derived nanoparticles, namely carbon nanotubes and graphite nanoplatelets, using non-oxidative, one-pot, simple organic reactions that bond reactive groups such as anhydride [1] and pyrrolidine [2] to the graphene surface. Controlled functionalization may yield functional groups that further react with specific polymers, forming strong polymer/nanoparticle interfaces capable of effective load transfer from the polymer to the reinforcing phase [3], and may facilitate nanoparticle dispersion in the polymer [4]. The covalent functionalization of the graphite-derived nanoparticles and further bonding with specific polymers was performed, and the influence of the surface functionalization on the dispersion of the nanoparticles in polymers was analysed. Figure 1 depicts scanning tunnelling microscopy images of (a) functionalized and (b) polymer bonded carbon nanotubes. A prototype extensional mixer was used that allowed the application of high stress to the polymer melt, evaluate the nanoparticle dispersion along the length of the dispersion process, and evaluate the effect of stress relaxation in the polymer melt.

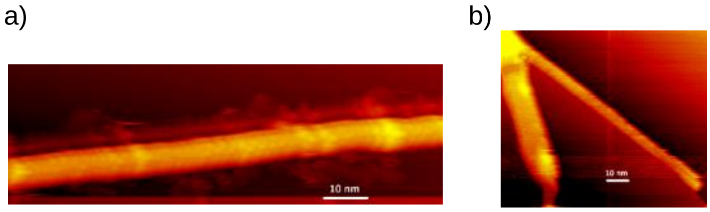

Fig.1. Images of carbon nanotubes obtained by scanning tunnelling microscopy: a) covalently functionalized and b) functionalized and treated with polycarbonate.

Acknowledgements

We acknowledge funding by Portuguese FCT through the National Funds, namely Reference UIDB/05256/2020 and UIDP/05256/2020.

References

[1] R. Araújo, M. F. Proença, C. J. Silva, T. Castro, M. Melle-Franco, M. C. Paiva, S. Vilar-Rodil, J. M. D. Tascón, Carbon, 98 (2016) 421.
[2] M. C. Paiva, F. Simon, R. Novais, T. Ferreira, M. F. Proença, W. Xu, F. Besenbacher, ACS Nano, 4 (2010) 7379.
[3] R. Novais, F. Simon, P. Pötschke, T. Villmow, J. A. Covas, M. C. Paiva, Journal of Polymer Science Part A: Polymer Chemistry, 51 (2013) 3740.
[4] R. M. Santos, C. Vilaverde, E. Cunha, M. C. Paiva, J. A. Covas, Soft Matter, 12 (2016) 77.

Neurotransmitter detection with graphene aptasensor multitransistor chips

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Neurotransmitters play a crucial role in facilitating communication within the neural network, and disruptions in their levels or transmission are implicated in various brain disorders, including depression and schizophrenia. Despite the significance of closely monitoring different neurotransmitters in the brain, the intricate nature of the brain poses a formidable challenge in accurately measuring chemical neurotransmission [1]. This study introduces a neural interface for multiplexed neurotransmitter detection, leveraging graphene multitransistor arrays (gMTAs) functionalized with selective DNA aptamers. The gMTA chip was designed to accommodate six distinct functionalization areas, each featuring a minimum of four micron-sized transistors. Our work started with dopamine detection using a short-strand dopamine-specific DNA aptamer [2]. We successfully discriminated dopamine with exceptional sensitivity in artificial cerebral spinal fluid and brain homogenates, extending our application to a mouse model of Parkinson's Disease, establishing the lowest reported limit of detection for dopamine (1 aM) [3] with gMTAs. The next step was to develop a novel aptamer for glutamate, complementing the existing dopamine aptamer and a previously published serotonin aptamer for multiplexed detection of these three important neurotransmitters within a single gMTA. Notably, our new aptamer demonstrated high selectivity for glutamate over other neurotransmitters (Fig.1,center). Achieving selective functionalization of each set of transistors involved utilizing a custom 3D-printed piece with micron-sized wells and a specially designed fixation method.

To validate the gMTA neural interfaces, we tested physiological buffers and ex vivo brain slices from transgenic mice stimulated optically. Real-time biosensing is carried out in both DC and AC transistor operation modes, utilizing custom-designed electronics and online signal processing. For the next in vivo studies, an implantable probe carrying an LED was also fabricated. The platforms presented in this work hold promise for developing novel neurotransmitter sensors suitable for real-world applications in academic and preclinical pharmaceutical research and clinical diagnosis.

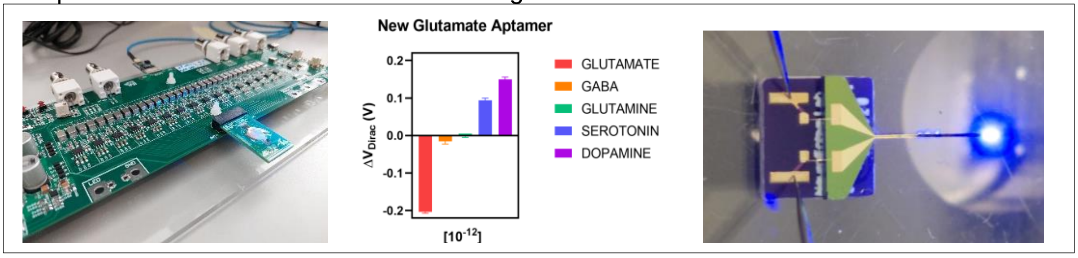

Fig.1. A 32-channel electronic board developed in-house to interrogate the gMTAs in the AC-transistor mode (left); a new glutamate aptamer's selectivity against different neurotransmitters at 1pM concentration in artificial cerebrospinal fluid (center); and an implantable silicon probe with a micro-LED in the ON-state mounted on its shank fabricated at INL (right).

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References

[1] Y. Zhang, et al., Biosensors and Bioelectronics, 189 (2021): 113351.
[2] N. Nakatsuka, K.-A. Yang, J.M. Abendroth, K.M. Cheung, X. Xu, H. Yang, et al. Science.362 (6412) (2018) 319.
[3] M. Abrantes et al., Journal of Nanobiotechnology, 20.1 (2022): 495.

COMUNICAÇÕES ORAIS

Carbon nanomaterials in biomedicine: with focus on graphene-based materials

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Carbon nanomaterials (CNM) have gained great interest in the scientific community and motivated multiple studies in the biomedical field thanks to their unique properties. CNM colloids can be used as multifunctional agents in phototherapy (photodynamic and photothermal therapy (PTT)), targeting cancer and antimicrobial applications. In 2004 graphene was isolated by Geim, Novoselov, *et al*. Nevertheless, the initial investigations employing graphene-based materials (GBM) for cancer PTT were documented only in 2010, while GBM use for PTT against infections was reported in 2013. Remarkable advances have been achieved in the field of nanomedicine and immunotherapy, since it was found that several nanomaterials can modulate the immune response. CNM, including GBM, and also new 2DnMat have a vast potential on the field, however, little is known about the effects of several of those materials in the immune system. A general perspective on the work of our team will be presented, with emphasis on graphene-based materials for phototherapy, immunotherapy, and 3D-printing for tissue regeneration [1-3].

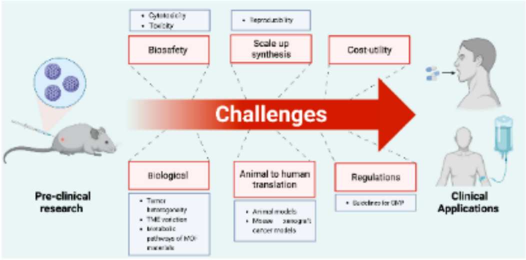

Fig.1. Adapted with permission from [4] Copyright 2023, MDPI.

References

[1] Pinto AM, Pereira AM, Gonçalves IC (2020). Carbon Biomaterials. In Wagner WR, Sakiyama-Elbert SE, Zhang G, Yaszemski MJ (Ed.), Biomaterials Science. An Introduction to Materials in Medicine, 4th ed. San Diego, California: Elsevier. ISBN: 9780128161371.
[2] Amaral SI, Costa-Almeida R, Gonçalves IC, Magalhães FD, Pinto AM. Carbon nanomaterials for phototherapy of cancer and microbial infections. Carbon 2022, 190, 244.
[3] Azevedo S, Costa-Almeida R, Santos GS, Magalhães FD, Pinto AM. Advances in carbon nanomaterials for immunotherapy. Applied Materials Today 2022, 27C, 101397.
[4] Fernandes P, Magalhães FD, Pereira RF, Pinto AM. Metal-Organic Frameworks Applications in Synergistic Cancer Photo-Immunotherapy. Polymers 2023, 15, 1490.

Cutting-edge carbon-based nanomaterials in the fight against cancer

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Carbon is among the most abundant and versatile elements on Earth, existing in a multitude of natural allotropic forms. Taking inspiration from nature, the scientific community embarked on the development of innovative synthetic routes for creating novel carbon nanomaterials. This presentation will delve into the employment of multifunctional nanomaterials, specifically endohedral and/or exohedral functionalized carbon nanostructures, which have proven successful in the realms of cancer bioimaging and therapy. These applications encompass bioimaging techniques such as fluorescence,[1] as well as photodynamic and photothermal therapies. Notably, we will underscore the advancement in nuclear-based therapy with the introduction of a pioneering concept of Lithium Neutron Cancer Therapy (LiNCT).[2] This innovative approach involves carbon nanocapsules (CNCs) that hermetically encapsulate 6Li active NCT nuclides (6Li@CNCs), **Fig. 1**. Impressively, 6Li@CNCs exhibited high cellular biocompatibility (>90%), yet when subjected to neutron exposure, the survival rate plummeted to an astonishing 1.8%.[3] These preliminary findings represent a significant leap forward in paving the way for the clinical implementation of LiNCT.

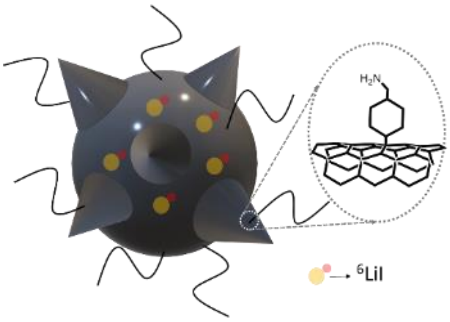

Fig.1. Carbon nanocapsule filled with lithium iodide.

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References

[1] C.I.M. Santos et al. Carbon 166 (2020), 164e174
[2] Lithium filled nanocapsules and the use thereof" Gonçalves G. et al. WO Patent WO2023180615A1
[3] C.I.M. Santos et al., ACS Appl. Nano Mater. 4(12) (2021),13079–13089

Carbon-based heterostructured $BiVO_4$ photocatalysts for the degradation of contaminants of emerging concern

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Heterogeneous photocatalysis based on semiconductors has emerged as a focal point within advanced oxidation processes (AOP) for wastewater decontamination [1]. These methods have been regarded as particularly effective alternatives for eliminating certain harmful organic pollutants, even those present in trace amounts.

Bismuth vanadate ($BiVO_4$) has been investigated as a photocatalyst of interest due to its ability to harvest photons efficiently in the visible spectral region [2]. Particularly, powdered $BiVO_4$ particles show high photochemical stability, good dispersibility, and resistance to corrosion in oxidative conditions. On the other hand, carbon-based materials, which are relatively cheap, can be used as substrates for supported catalysts.

In this context, we have investigated the *in-situ* growth of monoclinic $BiVO_4$ on carbon spheres obtained by the hydrothermal carbonization of κ-carrageenan, a biopolymer extracted from red seaweeds [3]. The carbon-supported photocatalysts were prepared by varying a range of experimental conditions, allowing to selection of materials with exceptional chemical stability and well-defined particle morphology for specific synthesis conditions. The ensuing carbon-supported photocatalysts were then investigated in the degradation of tetracycline (TC) dissolved in water, for distinct operational conditions, such as the presence of H_2O_2 and their reuse in further catalytic cycles. The hybrid photocatalysts described have shown better photocatalytic activity, as compared to the powders of pure monoclinic $BiVO_4$, for similar conditions. The potential application of these hybrid photocatalysts in the degradation of contaminants of emerging concern will be discussed, taking into consideration the results obtained so far for water samples spiked with TC.

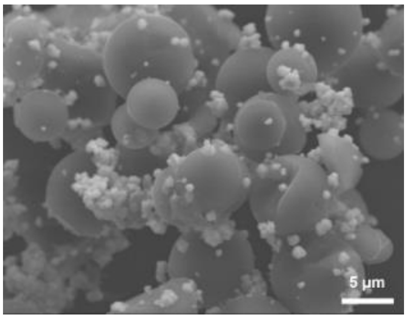

Fig.1. SEM image of carbon spheres decorated with $BiVO_4$ particles.

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References

[1] S. O. Ganiyu, S. Sable S, M. G. El-Din, Chemical Engineering Journal, 429 (2022) 132492.
[2] A. Malathi, J. Madhavan, M. Ashokkumar, P. Arunachalam, Applied Catalysis A: General, 555 (2018) 47.
[3] J. L. Lopes, A. C. Estrada, S. Fateixa, N. A. Sobolev, A. L. Daniel-da-Silva, T. Trindade, Journal of Photochemistry & Photobiology, A: Chemistry 447 (2024) 115174.

Insights on the regeneration of activated carbons exhausted with pharmaceutical compounds

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Regeneration of exhausted activated carbons is mandatory to increase the sustainability of the technologies relying on activated carbon adsorption processes. Besides contributing to decrease the carbon footprint associated to their production, contributes to lower the operational costs and is also of paramount importance to minimize the end-of-life disposal of highly contaminated residues in landfill or their incineration [1]. Granular activated carbons (GACs) performance for pharmaceutical compounds (PhCs) removal from water is dependent on the adsorbent (GAC), adsorbate (PhC) and water matrix [2]. Considering that the regeneration of GACs exhausted with PhCs is only scarcely explored despite their increasing application in full-scale wastewater treatment plants (WWTPs) to control recalcitrant microcontaminants, as is the case of numerous PhCs, it is thus important to address the major factors influencing the regeneration process aiming to identify the PhCs properties (e.g., polarity, solubility, and molecular structure) that allow to predict the regeneration efficiency of a PhC exhausted GAC.

This study explored the regeneration of GACs - 1 commercial and 1 lab-made material - exhausted with pharmaceutical compounds addressing the influence of the adsorbate, the adsorbent and the thermal regeneration process. Caffeine (CAF), paracetamol (PARA) and sulfamethoxazole (SMX) were the pharmaceutical compounds selected, and both thermal regeneration under inert atmosphere or steam were tested. Along with the regeneration efficiency the changes on textural properties and surface chemistry of the regenerated materials were also evaluated. At pH 5 the SMX exhausted GAC presented the lowest regeneration efficiency while CAF allows the highest, regardless the cycle and the atmosphere of the thermal regeneration (steam or N_2). Adsorption data shows the apparent higher affinity of the neutral SMX specie for the GAC what may explain this behavior. Given the complex speciation of SMX, complementary assays were performed at pH 7.6 (pH of wastewater treatment plants effluent) reveling that the anionic SMX specie has lower adsorption affinity and consequently is more prone to regeneration than the neutral SMX (specie present at pH 5).

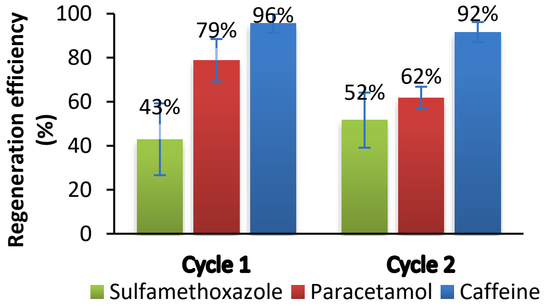

Fig.1. Regeneration efficiency of GAC exhausted with PhCs and regenerated under N_2 flow.

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Acknowledgements

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References

[1] A. S. Mestre, M. Campinas, R. M. C. Viegas, E. Mesquita, A. P. Carvalho, M. J. Rosa. Chapter 17 - Activated carbons in full-scale advanced wastewater treatment. In D. Giannakoudakis, L. Meili, & I. Anastopoulos (Eds.), Advanced Materials for Sustainable Environmental Remediation, 2022, pp. 433-475). Elsevier.
[2] R. M. C. Viegas, A. S. Mestre, E. Mesquita, M. Machuqueiro, M. A. Andrade, A. P. Carvalho, M. J. Rosa, Water 14 (2022) 166.

Magnetic graphite-like nanoplatelet composites: from synthesis to application in water treatment

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Carbon is one of the most abundant elements in the environment and in the human body [1], with the peculiarity of having an extraordinary ability to bind to other elements. Carbon has extensive allotropy, including spherical forms such as buckminsterfullerene and sheets such as graphene. Graphene is a 2D material with a hexagonal structure composed of sp^2-hybridised C atoms, where each carbon atom is covalently bonded to each other in the same plane [2], which has some limitations for water compatible applications, such as poor solubility and agglomeration tendency. [3]. To overcome these limitations, researchers have synthesised structurally similar compounds, such as graphene oxide (GO) and graphite-like nanoplatelets (GNP), which can be produced from carbon sources using simple top-down methods [1].

In this study GNP were investigated for their adsorption capability and ability to enhance the adsorption capacity of various composites with the aim of removing toxic metal ions from water. The GNP are a viable and inexpensive material that can be used as a stable substrate for the preparation of magnetic nanocomposites for water adsorption treatment, thus allowing their use in magnetic separation technologies. The GNPs were decorated with nanoparticles of spinel ferrites (MFe_2O_4, M = Fe, Mn, Co.), giving them the ability to magnetically separate the sorbents when exposed to an external magnetic gradient. The Fe_3O_4/GNPs, $CoFe_2O_4$/GNPs and $MnFe_2O_4$/GNPs composites were synthesised and used for the capture of Hg and As from binary and unary solutions. Among the toxic substances of anthropogenic and natural origin, these elements pose the greatest threat to the environment due to their non-degradable nature, severe toxicity and bioaccumulative character. Arsenic and Hg occupy the 1st and 3rd positions, respectively, in the list of priority hazardous substances for 2019, provided by the Agency for Substances and Toxic Diseases, and therefore their effective removal from water is a priority to achieve the United Nations SDG6.

The pH dependence of the sorption process using these magnetic nanostructures was evaluated for the range 4-9. After 24 h exposure of equal amounts of MFe_2O_4/GNPs to unary solutions of As(III) (1000 µg/L) and Hg(II) (50 µg/L), the results showed that 1) Fe_3O_4/GNPs were the least effective for removal of As(III) or Hg(II) and 2) As(III) removal was higher for the $CoFe_2O_4$/GNPs at pH 7 (90.4%), while $MnFe_2O_4$/GNPs showed a higher efficiency for the removal of Hg(II) at pH 6 (90.6%). In binary solutions, $CoFe_2O_4$/GNPs showed higher efficiency against As(III) with removal percentages close to 90% in ultrapure water and around 80% in tap water, while $MnFe_2O_4$/GNPs preferentially removed Hg(II) (85%) in both matrices. Although the above nanocomposites were prepared by similar methods, those containing Co and Mn ferrites performed better than the Fe_3O_4/GNPs.

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References

[1] Rao, N., Singh, R., and Bashambu, L. Mater. Today Proc., 44 (2021) 608.
[2] Kallumottakkal, M., Hussein, M. I., and Iqbal, M. Z., Front. Mat, .8 (2021) 34.
[3] Joseph, A., Sajith, V., and Sarathchandran, C., Handb. Carbon-Based Nanomater., (2021) 517.

Engineered pine nut shell powdered activated carbons for advanced drinking water treatment: is particle size important?

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The development of advanced drinking water treatment (DWT) processes to tackle the presence of micropollutants in natural waters, such as the case of pharmaceutical compounds (PhCs) and natural organic matter (NOM), that resist to conventional treatments [1], calls for high-performing powdered activated carbons (PACs), as those prepared in EMPOWER+ by physical (steam or CO_2) activation of carbonized pine nut shells (PNS, a by-product of the food industry) [2].

The efficiency of PAC <20 µm and 20-75 µm of PNS-derived PACs, S2 and C3, and of a commercial PAC, obtained by sieving, was evaluated for the adsorption of spiked PhCs and NOM surrogate compounds. Both fractions were characterized regarding textural properties, density, moisture content, pH_{PZC} and particle size distribution, assessed by SEM (Fig. 1) and laser diffraction spectrometry.

Adsorption isotherms revealed the detrimental effect of direct site competing NOM on PhCs removal. PhC removal was faster and higher for PAC <20 µm. The adsorption isotherms were modelled by the Simplified Equivalent Background Compound model (EBCM), and the adsorption kinetics by the Homogeneous Surface Diffusion Model (HSDM), an approach that allowed to predict the PhC removals for a given PAC concentration and contact time. Application in conventional DWT processes (20-75 µm), and in hybrid adsorption-membrane technology (< 20 µm), for advanced DWT, is ongoing.

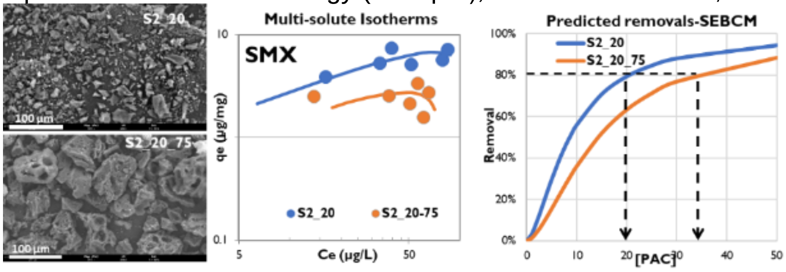

Fig.1. SEM micrographies (left), multi-solute isotherms (centre) and predicted removals (right) for PNS-derived PACs S2<20 and S2_20-75.

Funding

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Acknowledgements

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References

[1] M. Campinas, C. Silva, R.M.C. Viegas, R. Coelho, H. Lucas, M.J. Rosa, *J. Water Process Eng.* 40 (2021) 101833.
[2] A. S. Mestre, R. M. C. Viegas, E. Mesquita, M. J. Rosa, A. P. Carvalho, *J. Hazard. Mat.* 437 (2022) 129319.

Electric properties of cotton fabrics prepared with Pyrograf® III carbon nanofiber-based inks

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The electrical properties of cotton fabrics dip-coated with aqueous inks made from different Pyrograf® III carbon nanofibres (CNFs) contents are analysed in this work. At 30 °C, textiles prepared with the highest content of CNFs (6.4 mg ml^{-1}) show conductivities (σ) of ~ 35 S m^{-1}, and Seebeck coefficient (S) of -6 μVK^{-1}, which means that their majority charge carriers are electrons. From 30 °C to 100 °C, the σ (T) shows negative temperature coefficient (NTC) effect, analysed via the 3D variable range hopping (VRH) model of the charge carriers through a random network of potential wells. Likewise, their *S (T)* shows NTC effect, conveniently depicted by the model used for describing the S (T) of doped multiwall carbon nanotube mats [1]. From these findings, it is deduced that the negative Seebeck in the textiles may come from the impurities found in the as-received CNFs, which may cause sharply varying and localized states at approximately 0.085 eV above their Fermi energy level (E_F). Moreover, the possibility of a slight n-doping onto the most external CNF graphitic shells came from the cellulose fibers of the starting textiles and/or the anionic surfactant´ residuals used for producing the CNF-based aqueous inks is discussed [2, 3].

Funding

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References

[1] Choi YM, Lee DS, Czerw R, Chiu PW, Grobert N, Terrones M, et al., Nano Letters, 3(6), (2003), 839-42.
[2] Paleo AJ, Krause B, Cerqueira MF, Muñoz E, Pötschke P, Rocha AM, ACS Applied Engineering Materials, 1(1), (2023),122-31.
[3] Paleo AJ, Krause B, Cerqueira MF, González-Domínguez JM, Muñoz E, Pötschke P, et al., 16(12), Materials. (2023), 4335.

Tuning the pore network nanomorphology of cellulose precursor films to produce Carbon Molecular Sieve Membranes

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Cellulose has long been recognized as a promising polymer precursor to produce high-performance carbon molecular sieve membranes (CMSM). However, due to the difficulty in processing the cellulosic precursor, the scientific community chose initially to use commercially available cellulose materials. In 2019, Mendes reported for the first time a CMSM produced from the carbonization of spun-cast cellulose precursor films regenerated from an ionic liquid solution [1]. A solution of Emimac:DMSO (Emimac = 1-ethyl-3-methylimidazolium acetate) is used to dissolve the cellulose and for casting the membranes as flat sheets or as hollow fibers. The membranes are then regenerated in a nonsolvent, in a process known as nonsolvent-induced phase separation (NIPS), to produce cellulose precursors. This innovation opened the doors for fine-tuning the pore network nanomorphology of the cellulose precursor, by changing the nonsolvent properties of the regeneration bath. In this work, ionic liquid processed cellulose membranes were prepared by NIPS in different coagulation baths, namely in baths of water-acetone mixtures, ethanol-water mixtures, and water at different temperatures. A small angle neutron scattering (SANS) *in-situ* study of the wet regenerated films shows clearly that their nanostructure depends on the properties of the coagulation bath. A structural transition of cellulose takes place in water-acetone baths at a very low water concentration, while at a higher temperature, the size of nanostructures in the gel-like structure increases. This allows a structural tuning of cellulose membrane precursor and then to obtain CMSM with tuned performance for target gas separations.

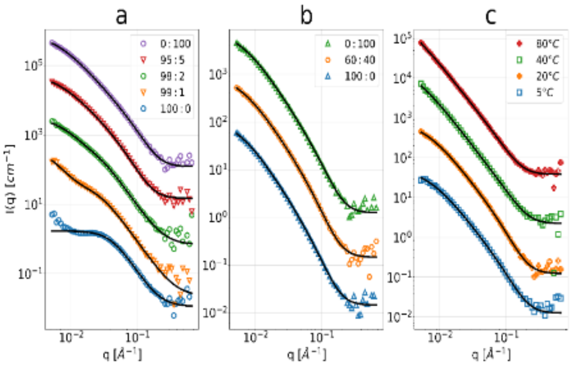

Figure 1. SANS scattering intensity as a function of *q* and respective polymer mass fractal (PMF) or DAB-Lorentzian (DL) fits for cellulose films regenerated in (a) acetone:water bath mixtures at different volume fractions, (b) ethanol:water bath mixtures at different volume fractions, (c) water bath at different temperatures.

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References

[1] S.C. Rodrigues, M. Andrade, J. Moffat, F.D. Magalhães, A. Mendes, J. Membrane Science, 572 (2019) 390.

Thermoplastic polyurethane composites with single walled carbon nanotubes for soft actuators

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Endowing lightweight polymer composites with electrical conductivity brings a wide range of possible applications. The design freedom of polymeric materials is desirable in areas such as aeronautics and automotive industries, simultaneously enabling multifunctionality, for example through sensing possibilities. Carbon nanotubes (CNT), in particular single walled carbon nanotubes (SWCNT), have high electrical conductivity and may assemble a composite structure with electrical conductivity at a very low SWCNT weight content. However, strong Van der Waals forces and CNT entanglement are common issues influencing the final composite properties.

Melt-mixing processing techniques are industrially ready to produce thermoplastic polymer composites, inducing mixing in high viscosity fluids without requiring solvents. Different melt-mixing techniques will have different outputs concerning the distribution and dispersion of CNT in the polymer matrix. The present work consists of the preparation of nanocomposites, specifically a three-component system consisting of SWCNT, polypropylene glycol (PPG), and thermoplastic polyurethane (TPU), to achieve electrical properties (resistivity and Joule heating) and thermal properties (thermal stability and conductivity) using two extrusion techniques – twin-screw extrusion and micro-compounding.

The electrical conductivity was higher for the composites prepared by twin-screw extrusion, comparing composites with similar CNT weight concentrations. Composites produced by micro-compounding did not achieve a temperature variation with the application of tension up to 90 V, as depicted in Figure 1. Composites produced on a prototype mini-extruder display Joule heating effects at the same tension (Figure 1 b, c, and d). Preliminary tests suggest that actuation may be induced by light stimulation.

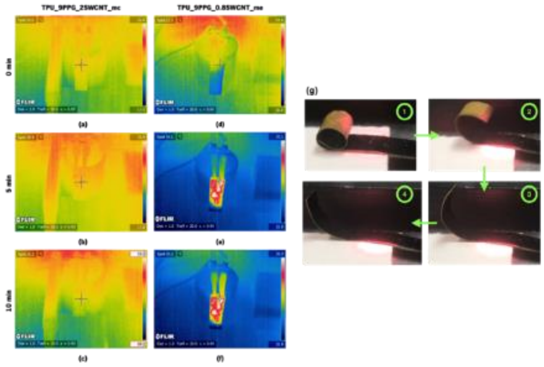

Fig.1. Evaluation of the temperature of TPU/CNT composites produced by micro-compounding (a, c and e) and twin-screw extrusion (b, d and f), at 90 V for 10 minutes. Images of actuation effects of bilayer composites under a NIR laser source (g).

Acknowledgements

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High performance PEEK/MWCNT nanocomposites with enhanced electrical conductivity for the production of spun fibres by melt-spinning

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The increasing interest in high-performance engineering thermoplastics is driven by their ability to offer lightweight and excellent mechanical performance, in a wide temperature range. Poly (ether ether ketone) - PEEK is a representative material of this group of polymers. Given its exceptional properties, PEEK has found wide application as the matrix material for reinforced polymers and nanocomposites. The development of PEEK-based composites intends to meet the requirements of structural applications. However, PEEK is inherently characterized by low electrical conductivity, which restricts its applicability. To enhance its performance, carbon fillers can be incorporated into the PEEK matrix, improving their superior properties [1, 2].

The present work investigates the optimal conditions to prepare PEEK/carbon nanotube (CNT) nanocomposites, dismissing the CNT agglomerate size while maximizing the nanocomposite electrical conductivity. The aim is to achieve PEEK/CNT nanocomposites that are suitable for melt-spinning applications.

Two studies were performed to achieve our goal: (1) The electrical percolation threshold of PEEK/CNT was accomplished with compositions ranging from 0.5 – 7 wt.% CNT. This study showed an electrical percolation threshold between 1 – 2 wt.% CNT (10^7 – 10^2 S/m) and a rheological percolation at 2 wt.% CNT, confirming the formation of a CNT network in the nanocomposite. The number of agglomerates per unit area remains reasonably constant for all MWCNT contents, showing a uniform number of agglomerates formed during processing that increase in size with the increase in MWCNT concentration. Thermal stability were also assessed; (2) The effect of the melt extrusion parameters (screw speed, temperature, and throughput) were studied by the evaluation of CNT agglomerates morphology and nanocomposites rheology and electrical properties. Generally, all processing conditions tested produced nanocomposites with electrical conductivity in the range of 0,50 – 0,85 S/m. The combination of the higher values of screw speed and temperature profile leads to the smaller number of CNT agglomerates with smaller size, although at a slightly lower electrical conductivity. This nanocomposite, presented the lowest value of elastic modulus, perhaps owing to higher matrix degradation and lower connectivity between the agglomerates. From all the process parameters studied, the screw speed was identified to have the higher impact.

References

[1] Zhang, X. Carbon Nanotube/Polyetheretherketone Nanocomposites: Mechanical, Thermal, and Electrical Properties. J. Compos. Mater. 2021, 55 (15), 2115–2132. https://doi.org/10.1177/0021998320981134.
[2] King, J. A.; Tomasi, J. M.; Klimek-McDonald, D. R.; Miskioglu, I.; Odegard, G. M.; King, T. R.; Sutherland, J. W. Effects of Carbon Fillers on the Conductivity and Tensile Properties of Polyetheretherketone Composites. Polym. Compos. 2018, 39 (S2), E807–E816. https://doi.org/10.1002/pc.24250.

Bottom-up construction of Fe–N–C active centers: Towards sustainable oxygen reduction reaction electrocatalysts

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Noble metals employed in conventional oxygen reduction reaction (ORR) electrocatalysts are scarce and costly. Seeking sustainable alternatives to the use of noble metals through the development of more sustainable carbon-based electrocatalysts has thus been the focus of our research.

Combining our recent findings on the application of carbon nanotubes-supported iron phthalocyanine [1], Fe–N-modified hollow carbon spheres [2], and carbon black [3,4] in the ORR, we have moved towards the design of an effective electrocatalyst where single-atom Fe–N active centers surrounded by Fe nanoclusters, N-containing sites, and the high porosity of carbon black contribute to a high electrocatalytic activity and stability towards the ORR [5]. By optimizing the synthesis conditions, we were able to do so by employing only earth-abundant and inexpensive precursors (Fig. 1). This communication reports our contribution towards the advancement of knowledge on the design of affordable and sustainable non-noble metal-containing carbon black electrocatalysts for the ORR.

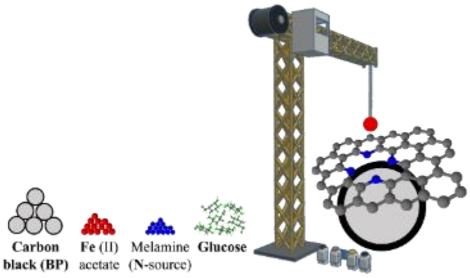

Fig. 1. Representation of the bottom-up construction of single-atom Fe–N active centers at the surface of carbon black through our synthesis methodology employing only broadly available precursors.

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References

[1] R.G. Morais, N. Rey-Raap, J.L. Figueiredo, M.F.R. Pereira, Applied Surface Science, 572 (2022) 151459.
[2] R.S. Ribeiro, A.L.S. Vieira, K. Biernacki, A.L. Magalhães, J.J. Delgado, R.G. Morais, N. Rey-Raap, R.P. Rocha, M.F.R. Pereira, Carbon, 213 (2023) 118192.
[3] M. Florent, T.J. Bandosz, Nanomaterials, 12 (2022) 4432.
[4] G. de Falco, M. Florent, T.J. Bandosz, Carbon, 189 (2022) 230.
[5] R.S. Ribeiro, M. Florent, J.J. Delgado, M.F.R. Pereira, T.J. Bandosz, Nanoscale, 15 (2023) 18592.

Shrimp shell-derived biochars as efficient electrocatalysts for oxygen reactions

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The current global energy crisis, reflected in the depletion of fossil fuels and growth of the environmental pollution has stimulated the development of novel renewable energy storage and conversion technologies as well as of effective and greener catalytic processes for the preparation of important molecules. Electrocatalysis plays a central role enabling a number of sustainable processes for future technologies. The oxygen reduction and evolution reactions (ORR and OER) are two of the crucial energy-related processes in fuel cell and electrolyser systems [1]. For this reason, regarding the real implementation of these technologies, efficient electrocatalysis of these processes is required, stimulating the quest for new, non-expensive, and highly active electrocatalysts during the last years.

Future alternatives may include biochar, a porous carbon-rich solid material produced by the thermochemical degradation of biomass. These materials have attracted increasing interest due to their tunable physical-chemical properties, renewable feedstock, and low production cost [2]. Shrimp shells derived biochars, in particular, have very interesting electrocatalytic properties, originated from the feedstock natural abundance in heteroatoms (e.g. N, S, P) [3].

Herein, we prepared different nitrogen-doped supported cobalt electrocatalysts using two nitrogen precursors (melamine and phenanthroline) and two methods for N-doping (impregnation and ball-milling) [4]. Then, wet impregnation was also used for the functionalization with cobalt. Activation under chemical/physical experimental conditions resulted in high surface areas (BET > 200 m^2/g). By XPS, XRD and SEM/EDS, the successful preparation of the functionalized electrocatalysts was also confirmed. SEM and XPS both showed the formation of highly porous structures, which led to a notable increase in N-functionalization following the doping approach. The ORR electrocatalysts in an alkaline medium showed good performance, with potential onset values of $0.89 \geq E_{\text{onset}} \geq 0.76$ V vs. RHE. Additionally, the materials also showed activity towards OER in an alkaline medium, with overpotential values of about 0.50 V vs. RHE and maximum current densities exceeding 35 mA cm^{-2}.

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References

[1] C. Freire, D. M. Fernandes, M. Nunes and V. K. Abdelkader, ChemCatChem, 10 (2018) 1703-1730.
[2] R. Ramos, V. K. Abdelkader-Fernández, R. Matos, A. F. Peixoto, D. M. Fernandes, Catalysts, 12 (2022) 207.
[3] Y. Ding, S. Huang, Y. Sun, Y. Li, L. Zhu, S. Wang, ChemElectroChem, 8 (2021) 3745.4
[4] I. S. Marques, B. Jarrais, R. Ramos, V. K. Abdelkader-Fernandez, A. Yaremchenko, C. Freire, D. M. Fernandes, A. F. Peixoto, Catalysis Today, 418 (2023) 114080.

The Influence of CNT@Metal Sulfide Hybrid Electrode Materials in Thermally-Chargeable Textile Supercapacitors

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The growth of the smart electronic clothing market has been driven by the integration of the Internet of Things into wearable technologies. Currently, there is a need for self-powered devices that can harness residual energy from various sources (*e.g.*, our own body), transform it into electrical energy, and effectively store the generated energy.[1] The emerging thermally-chargeable supercapacitor (TCSC) technology combines both thermal energy harvesting and electrochemical energy storage functionalities in a single device. The key challenges faced in this technology include the design of solid-gel electrolytes with high ionic conductivity and the understanding of the role of the electrode material in the system.

Herein, novel hybrid carbon@mono/bimetallic sulfide nanomaterials were prepared and used as electrode materials to develop smart textile TCSCs (Fig.1). The hybrids were synthesized through the functionalization of carbon nanotubes (CNT) with mono/bimetallic sulfides (Bi and Zn-based sulfides), by the hydrothermal route. The as-prepared nanomaterials were incorporated into knitted cotton fabrics by the coating process to fabricate the electrodes. Afterward, the TCSCs were fabricated by stacking two different knitted electrodes (one coated with CNT and the other with the hybrids) with a solid-gel electrolyte in-between, in an asymmetric sandwich-type architecture.

In general, the asymmetric TCSC containing bimetallic sulfide presented the best electrochemical performance. The highest energy density of 5.46 μW h cm^{-2} for a power density of 233.18 μW cm^{-2} and a capacitance of 21.75 mF cm^{-2} (at 1 mV s^{-1}) was observed for the asymmetric BiZnS-based device (*vs.* 2.82 μW h cm^{-2}, 171.27 μW cm^{-2} and 21.13 mF cm^{-2} for the symmetric CNT-based TCSC). In the monometallic sulfide group, the ZnS-based TCSC excelled with an energy density of 3.88 μW h cm^{-2} at 247.66 μW cm^{-2} and a capacitance of 19.75 mF cm^{-2}. To study the thermal energy harvesting part, different temperature gradients were applied on each TCSC and the output potential was tracked over time. Preliminary tests have already demonstrated that the devices, simultaneously, harvest and store energy under different temperature gradients.

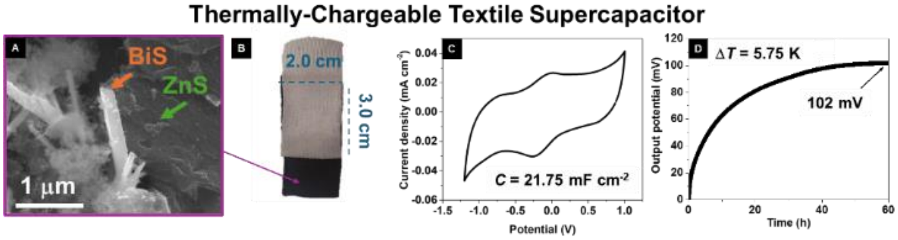

Fig.1 (A) SEM image of BiZnS hybrid nanomaterial; (B) Sandwich-type textile TCSC; (C) *i*-*V* cycle at 1 mV s^{-1} and (D) Thermoionic measurement of the asymmetric BiZnS-based TCSC.

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References

[1] J. S. Teixeira, R. S. Costa, A. L. Pires, A. M. Pereira and C. Pereira, *Dalt. Trans.*, 2021, **50**, 9983–10013.

COMUNICAÇÕES EM PAINEL

Wet peroxide oxidation of paracetamol in continuous mode using DLP 3D-printed carbon monolith as catalyst

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Catalytic wet peroxide oxidation (CWPO) can potentially eliminate a wide range of organic pollutants under mild conditions. However, while effective, metal-based catalysts frequently encounter challenges such as iron leaching. Researchers are exploring metal-free carbon materials to address this, demonstrating promising results in the CWPO process. In this work, a carbon monolith prepared by DLP 3D-printing, according to the methodology described elsewhere [1], was used as a catalyst to degrade paracetamol, chosen as a model organic pollutant, in a continuous CWPO system. The continuous system was assembled as represented in Figure 1(a), and the reaction was carried out at 80 °C, pH 3, PCM concentration of 100 mg L^{-1}, and stoichiometric amount of H_2O_2 for complete pollutant mineralization [2]. The solution was fed to the reactor at 0.75 mL/min, containing the pollutant and the oxidant reagent. The carbon monolith weighs 0.51 g, with 3.92 cm x 0.77 cm.

The results demonstrate that the pollutant concentration in the reactor inlet remained unchanged during the experiment, indicating that the pollutant is not being degraded in the solution used to feed the reactor (Figure 1(b)). Figure 1(b) also shows that in the first 12 h of the reaction, the PCM concentration was oscillating, the same behaviour being observed for TOC removal in Figure 1(d), which is a consequence of the H_2O_2 decomposition in the beginning of the process, as shown in Figure 1(c). After 24 h on stream, all parameters reach a steady state. The results demonstrate the promising application of 3D-printed carbon materials for water remediation, with a carbon catalyst that has no iron on its structure.

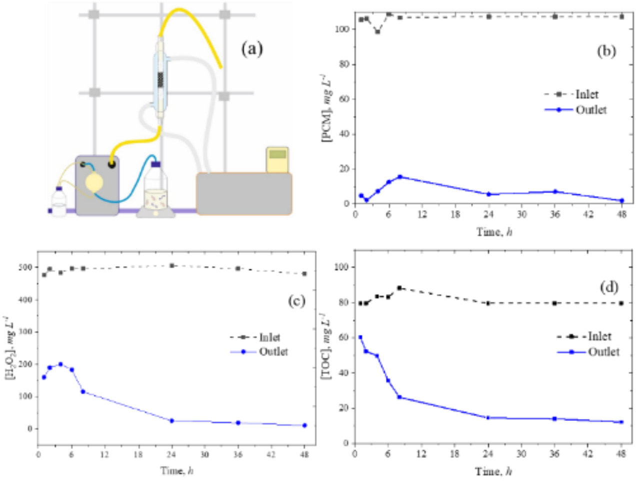

Figure 1. (a) Scheme used for the continuous CWPO system and concentration of (b) PCM, (c) H_2O_2, and (d) TOC during the experiment.

Acknowledgements

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References

[1] H. Steldinger, A. Esposito, J. Gläsel, and B. J. M. M. Etzold, *Advanced Science*, 2019, 6.
[2] A. S. Silva, F. F. Roman, A. Dias, J. L. Tuesta, H. T. Gomes, *J Environ Chem Eng*, 2023, 110806.

Assessment of surface-modified activated carbons as catalysts in the ozonation of emerging pollutants

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Currently, water pollution remediation is a significant challenge, due to the presence of emerging pollutants that prevent better water management practices. Given that, there is an urgent need to find ways to decrease the occurrence of emerging pollutants with low cost techniques and without producing more toxic by-products. Catalytic ozonation is a promising technology, in which the catalyst plays an important role of converting ozone into reactive oxygen species (ROS) capable of degrading even the more persistent pollutants. In this study, activated carbon (AC) was selected as catalyst due to its developed pore structure, large specific surface area, active sites and uniform dispersion of active components on the surface [1]. In addition, AC can be easily tuned to gain more desired characteristics, such as increasing the surface area or incorporating functional groups into the carbon structure [2]. Based on this, AC was modified with different functional surface groups using for that oxygen and nitrogen precursors [3], and the catalytic activity was evaluated in the ozonation of ibuprofen (IBF) and carbamazepine (CBZ).

During catalytic ozonation experiments IBF was degraded into the following by-products: oxamic acid (OXM), oxalic acid (OXL), hydroquinone (HDQ), and benzoquinone (BZQ), whereas CBZ into: oxamic acid (OXM), oxalic acid (OXL), pyruvic acid, and hydroquinone (HDQ) were identified.

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Table 1. By-products identified in the ozonation of IBF and CBZ

Catalyst	Treatment applied to AC	Ozonation of IBF	Ozonation of CBZ
Without catalyst		OXL, OXM, BZQ	OXL, Pyruvic acid, HDQ
AC	None	OXL, BZQ	OXL, Pyruvic acid, HDQ
ACH 400	Thermal treatment at 400 °C	BZQ	OXL, Pyruvic acid
ACH 600	Thermal treatment at 600 °C	OXL, OXM, BZQ	OXL, Piruvic acid
ACH 900	Thermal treatment at 900 °C	OXL, OXM	OXL, OXM
ACM	N-doping with melamine	OXL, BZQ, HDQ	OXL, OXM

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References

[1] J. Yang, L. Fu, F. Wu, X. Chen, C. Wu, Q. Wang, Catalyst, 12 (2022) 1085.
[2] I. Matos, M. Bernardo, I. Fonseca, Catalysis Today, 285 (2017) 194-203.
[3] C.A.L. Graca, R. Zema, C.A. Orge, J. Restivo, J. Sousa, M.F.R. Pereira, O.S.G.P. Soares, Journal of Environmental Management, 334 (2023) 118639.

Extending the catalytic potential of carbon-based macrostructured catalyst for continuous water treatment systems

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The development of macrostructured catalysts for remediation processes is a key-step towards the sustainability of multi-phase environmental systems [1]. Practical applications face great challenges regarding the availability of active centers on catalysts' surfaces [2]. New, renewed and more sustainable approaches, for macrostructured catalysts synthesis, have been studied to enhance their catalytic efficiency when applied in continuous water treatment processes [3]. Bimetallic macrostructured catalysts were prepared through washcoating (WCP) and tested on selective NO_3^- conversion. The obtained results were compared with catalysts synthesized by more established technique (chemical vapor deposition, CVD).

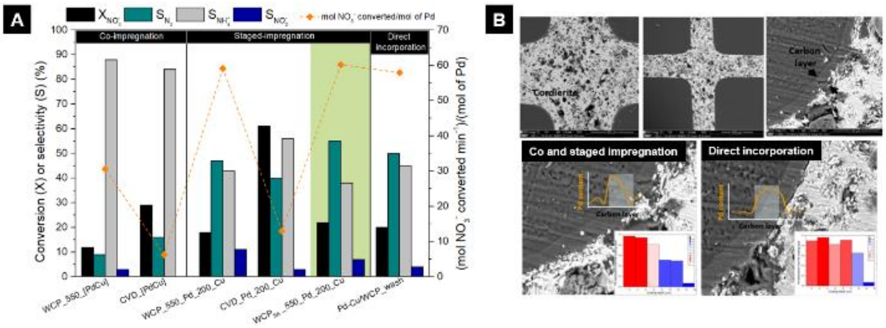

Fig.1. NO_3^- conversion and corresponding selectivities related to Pd present in the catalyst (A) and study on Pd distribution along the coating layer obtained through different synthesis techniques (B).

For macrostructured catalysts synthesis, significant importance lies in two factors: the method for incorporating the carbon support in the macroscopic structure and the impregnation methodology for the metal nanoparticles deposition into the coated structure. CVD allowed the incorporation of a higher carbon loading, although it was a more costly and time-consuming process than washcoating. A staged impregnation methodology proved to be the most efficient approach, allowing a greater availability of active centers to participate in the reaction (metal center more deposited on the periphery of the coating). These catalysts proved to be more active for NO_3^- conversion, as well as, more selective for N_2 formation due to the nanoparticles rearrangement on the carbon structure surface (higher interaction between Pd and Cu centers). Promising results were achieved with the WCP methodology and its transition from using Triton X-100, as a surfactant, to a more environmentally friendly dispersant (sodium alginate, SA) showed no loss of performance offering, this way, an opportunity to become a more sustainable process.

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References

[1] L. Kiwi-Minsker, M. Crespo-Quesada, Chimia (Aarau). 65 (2011) 699.
[2] K. Pirkanniemi, M. Sillanpää, Chemosphere. 48 (2002) 1047–1060.
[3] J. Restivo, C.A. Orge, A.S.G.G. Santos, et al., ACS Appl. Nano Mater. 3 (2020) 5271–5284.

Transforming biomass wastes into ozone-active activated carbons for the efficient degradation of refractory water pollutants

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Cork residues and coffee grounds were transformed into activated carbons (ACs) through physical activation with carbon dioxide (CO_2). The main goal was to potentialize the application of these waste-derived ACs as catalysts in ozonation reactions for water remediation purposes. For that, the key parameters of the physical activation, namely the dwell temperature, dwell time and %CO_2 were optimized according to a Box-Behnken experimental design, considering the catalytic activity of the produced AC in the ozonation of oxalic acid (OXL) as the response. This contaminant was selected as model-pollutant since it is a well-known ozone refractory substance [1].

Table 1 contains the OXL %removal observed after 180 min reaction for each of the produced catalysts. For the activated carbon produced from coffee grounds (ACCGs), it can be verified that increasing the dwell temperature and time, the catalytic activity decreases, since lower OXL %removals were observed. Also for this material, increasing the %CO_2 does not seem beneficial. Thus, an extra assay (Run N) was performed at the lowest dwell temperature and time (500ºC for 1 h) and lowest %CO_2 (30% w/w), and a substantial activity increase was observed for ACCG (OXL removal > 90%).

For the activated carbon produced from cork wastes (ACCKs), increasing the dwell temperature and time also led to some activity loss, while increasing the %CO_2 appears to not affect the ACCK activity. However, the best performance was observed for the ACCK treated at 500ºC, for 2 h and with 70% CO_2. An intriguing observation is that when these OXL removals obtained via catalytic ozonation are contrasted with those observed in adsorption experiments performed with ACCKs, opposite results are achieved, i.e. the most adsorbing materials correspond to the less catalytically active for OXL ozonation. To help support such results, the surface chemistry of these materials also has to be analysed, since it is known that it has a great influence in the decomposition of O_3 [2].

Table 1. Physical activation conditions for ACCG and ACCK and corresponding OXL %removal obtained in catalytic ozonation reactions.

	Run	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**	**N**
	T (ºC)	500	800	500	800	500	800	500	800	600	600	600	600	600	500
	dwell time (h)	1	1	3	3	2	2	2	2	1	3	1	3	2	1
	%CO_2	50	50	50	50	30	30	70	70	30	30	70	70	50	30
OXL % removal	ACCG	36	17	56	25	62	29	45	59	70	50	50	39	16	**97**
	ACCK	72	62	68	65	67	53	**92**	56	87	14	44	27	35	

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References

[1] A. Gonçalves, J.L. Figueiredo, J.M.J. Órfão, M.F.R. Pereira, Carbon, 48 (2010) 4369.
[2] Pereira, M.F.R., Gonçalves, A.G., Órfão, J. J.M. Boletín del Grupo Español del Carbón 31 (2014), 18.

Novel yeast-based carbon rich material as a potential adsorbent of vanillin

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One of the main challenges of the biotechnological production of xylitol from yeast is the detoxification of hemicellulosic hydrolysates, aiming for the partial removal of phenolic compounds that negatively impact the fermentative efficiency of this process [1]. Processes based on adsorbent materials, particularly, activated carbons prepared from vegetal biomass are widely used in this detoxification process allowing to overcome this issue.

This study aims to investigate the properties of a new carbon-enriched material derived from residual yeasts from the xylitol production. The presence of carbon in the yeast cell structure, combined with its availability in nature and in industrial processes, allow us to consider it as valuable precursor for the synthesis of carbon materials, and as final goal for the development of new adsorbent materials for the detoxication step. As raw material, residual yeast (*Saccharomyces cerevisiae*) from the beer production bioprocess was used. The yeast was inactivated, dehydrated, and macerated to obtain a powder texture. Hydrothermal carbonization was performed on dehydrated yeast under different temperatures (170°C, 195°C, and 220°C) with treatment times (3h, 9h, and 15h). The preliminary liquid phase adsorption tests revealed that the hydrochars were not stable materials as some leaching occurred, despite the thoroughly washing step previously made. The hydrochar with the highest carbon percentage was then selected to be submitted to steam activation at 800°C for 30 minutes [2]. The material obtained present a density of 484 kg/m^3, and an apparent surface area of close to 400 m^2/g composed mainly of micropores. Screening tests were conducted under conditions like those used in the xylitol synthesis process (5 mg of carbon material in 5 mL of 120 mg/L vanillin solution) to determine if this carbonaceous material could effectively remove vanillin from aqueous solution. The results shown that the removal attained 15% after 5 min of contact time and 41% after 24 h.

These promising results suggest the possibility of developing an alternative method for detoxifying hemicellulosic hydrolysates by using residual microbial biomass from the beer production, and the study will continue exploring, namely, other activation protocols and extending the liquid adsorption studies to other probe molecules.

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References

[1] S. S. Queiroz, F. M. Jofre, S. I. Mussatto, M. G. A Felipe, Renewable and Sustainable Energy Reviews, 154 (2022) 36.
[2] A. S. Mestre, R. M. C. Viegas, E. Mesquita, M. J. Rosa, A. P. Carvalho. Journal of Hazardous Materials, 437 (2022) 129319.

Marine biomass: a valuable precursor for carbon materials synthesis within the biorefinery concept

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Gelidium corneum, a red seaweed found on European shores [1] is manually harvested at S. Martinho do Porto (Portugal) and sold for industrial agar extraction due to its high quality. Generally, the biomass remaining after agar extraction is disposed of in agricultural fields but can also be a source of numerous bioactive molecules with applications in the health and biotechnological sectors (Fig. 1) [2]. To ensure the sustainability of this valuable resource, exploring alternative uses for this byproduct within a biorefinery framework is crucial, thus aligning with the principles of a circular economy. In this work, the valorization of the residual biomass was studied through the synthesis of chars (also known as biochars) by conventional pyrolysis (slow and fast) and innovative routes (hydrothermal carbonization – HTC and acid-mediated carbonization - AMC) [3]. Further steam activation was also addressed.

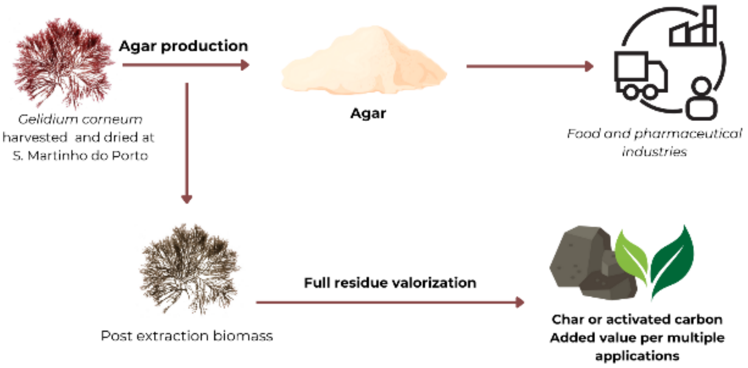

Fig.1. *Gelidium corneum* valorization by a biorefinery approach.

HTC produced the char with the most developed pore structure (BET area up to 36 m^2/g and total pore volume of 0.80 cm^3/g) while pyrolysis and AMC yielded chars with values one order of magnitude lower. Pyrolysis yields a basic surface ($pH_{PZC} \geq 8$ for slow pyrolysis and pH_{PZC} 7.3-9.5) while HTC and AMC originate an acidic surface (pH_{PZC} = 2.6-3.9 and 1.7-1.9, respectively). The chars prepared by innovative protocols present lower ash content than those obtained by pyrolysis (< 5% versus 14-25%, respectively). The hydrochar and acid char-derived activated carbons present BET area ≈ 950 m^2/g but distinct textural properties: while the acid-char yielded an exclusively microporous and dense activated carbon (apparent density 680 kg/m^3), the hydrochar-derived activated carbon is a light material with an apparent density of 194 kg/m^3 and presents a micropore network combined with a relevant external area. The large range of carbon materials prepared from the residues of this seaweed allows to envisage a wide number of applications, namely for the removal of contaminants in liquid or gas phase in the case of activated carbons or soil amendment in the case of the chars.

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References

[1] R. Gaspar, L. Pereira, I. Sousa-Pinto, (2019). Botanica Marina, 62 (2019) 499.
[2] M. Matias, A. Martins, C. Alves, J. Silva, S. Pinteus, M. Fitas, P. Pinto. J. Marto, H. Ribeiro, P. Murray, R. Pedrosa, Antioxidants, 12 (2023) 1684.
[3] A. S. Mestre, A. P. Carvalho, in Porosity—Process, Technologies and Applications, T. H. Ghrib (Ed.), InTech, 2018, 37.

Valorization of wet olive cake onto nanoporous carbons for the removal of pharmaceutical compounds

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The presence of pharmaceuticals and antibiotics in water is a global problem that has increased the demand for activated carbon materials (60% is generated from fossil carbon). The extraction of olive oil produces 20 % olive oil and 80 % wet olive cake (WOC) with 70 % humidity [1]. Portugal and Spain are responsible for half of the global production of WOC (4 to 5 of the 10 million Tm/year produced annually) [2]. Recently, WOC-derived hydrochars exhibited a great potential to remove pharmaceutical compounds in aqueous media [3] thus, to extend their applicability, were herein steam activated and screened for the removal of diclofenac. The most developed textural properties were attained when the hydrochar precursor was previously thoroughly washed to remove soluble salts and organic compounds and further steam activated at temperatures between 700 ºC and 900 ºC (C6 to C10 materials). The results reveal an increase in diclofenac adsorption as the textural properties of the activated carbons increase, with a higher efficiency for the washed hydrochar size with particles below 149µm (burn-off 84%, BET area 596 m^2 g^{-1}, total pore volume 0.58 cm^3g^{-1}, micropore volume 0.21 cm^3g^{-1}, mesopore volume 0.37 cm^3g^{-1}). The most promising materials will be evaluated for the removal of pharmaceutical compounds of different therapeutic classes through kinetic and equilibrium studies.

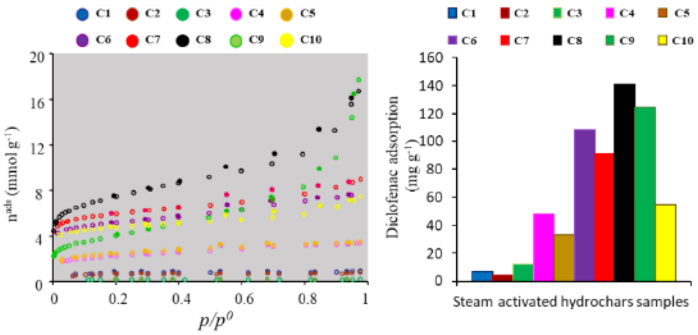

Fig.1. Nitrogen adsorption isotherms of the steam activated wet olive cake derived hydrochars (left) and diclofenac adsorption in the different samples (right).

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References

[1] https://www.interregeurope.eu/good-practices/valorisation-of-by-products-generated-during-the-production-of-olive-oil (Assessed on January 29th, 2024)
[2] Newsletter International Olive Council, 2019 (Assessed on January 29th, 2024)
[3] L. Delgado-Moreno, S. Bazhari, G. Gascó, A. Méndez, M. El Azzouzi, E. Romero. Sci Total Environ 2021, 752, 411838.

Resíduos Lenhocelulósicos como Adsorventes de moléculas Modelo

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Os processos de adsorção são amplamente utilizados para a remoção de uma gama muito diversificada de moléculas. Neste trabalho explora-se a utilização de adsorventes naturais para a remoção de moléculas modelo (corantes, pesticidas e fármacos). As moléculas estudadas foram o azul de metileno, o ácido amarelo 17, o ácido 4-cloro-2-metilfenoxiacético (MCPA), o 4-nitrofenol e o diclofenac sódico (Voltaren) em solução aquosa. Os adsorventes naturais lenhocelulósicos, essencialmente compostos por carbono, incluíram, entre outros, desperdícios de madeiras, pellets de madeira, carvão comercial e cinzas lignocelulósicas. Embora o carvão ativado seja um dos adsorventes preferidos para a remoção deste tipo de moléculas, a sua utilização está dependente do seu custo relativamente elevado. Assim, a procura de adsorventes alternativos, não convencionais e de baixo custo é uma questão de interesse. Este trabalho insere-se neste esforço e avalia aspetos como a remoção de moléculas específicas e os mecanismos de adsorção, incluindo a cinética, a determinação de isotérmicas de equilíbrio e a influência de parâmetros experimentais como: razão massa do adsorvente/volume da solução, pH do meio de adsorção e modificação ácida e básica do adsorvente.

Em particular, o carácter ácido ou básico de um adsorvente pode influenciar significativamente a sua capacidade de adsorção. Para avaliar este possível efeito, os materiais estudados foram submetidos a modificações distintas, ácida e básica, e a sua capacidade de adsorção para moléculas selecionadas foi comparada com os valores correspondentes já obtidos com concentrações iniciais dessas mesmas moléculas específicas no caso dos materiais originais não modificados.

Fig.1. Exemplo de um adsorvente lenhocelulósico não modificado (A), modificado via ácida (B) e modificado via básica (C).

Estas modificações provocaram alterações na estrutura porosa, na química da superfície, na natureza química (ácida, neutra ou básica), na forma, na cor, na estabilidade e, consequentemente, também na composição química elementar das amostras. Os resultados obtidos neste estudo indicam que alguns dos resíduos de base de carbono são potenciais adsorventes na sua forma não modificada, enquanto outras apenas permitem a remoção de moléculas modelo quando modificadas. É de salientar que este trabalho segue uma abordagem de economia circular baseada na utilização de materiais adsorventes de origem natural e renovável.

Referências

[1] E. Tchikuala, P. Mourão, J. Nabais, Activated carbons from angolan wood wastes for the adsorption of MCPA pesticide. In WASTES—Solutions, Treatments and Opportunities II; CRC Press: Boca Raton, FL, USA, (2017) 311.
[2] J. Gomes, B. Azaruja, P. Mourão, Appl. Surf.Sci. 380 (2016) 119.

O projeto LIFE BIOAs em Portugal: do Bagaço de Azeitona ao Adsorvente de Arsénio

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As grandes quantidades de desperdícios lenhocelulósicos geradas em diferentes sectores da atividade humana, da agricultura à indústria, proporcionam uma fonte importante de materiais precursores para a produção de materiais de carbono. Entre eles, os desperdícios de origem vegetal apresentam um enorme potencial para a produção de adsorventes de carbono com possibilidade de aplicação em diferentes domínios, com particular enfoque no tratamento de água.

Nesta comunicação explora-se a utilização de um resíduo biomássico, que por si só constitui um problema ambiental, o bagaço de azeitona, enquanto precursor de biochar. Este material de carbono foi preparado por carbonização hidrotérmica, em condições ambientalmente favoráveis, e sofreu uma modificação por adição de ferro. Esta modificação visou a sua transformação num adsorvente, embora com uma estrutura porosa pouco desenvolvida, com propriedades químicas que o tornam um candidato à utilização em processos de tratamento de água para consumo humano, em particular quando esta apresenta valores de arsénio elevados.

Neste domínio, importa referir que Portugal, um dos maiores produtores de azeite e consequentemente de bagaço de azeitona, tem regiões com águas naturais com elevados teores de arsénio (> 10 µg L^{-1}; Diretiva 98/83/EC) que apresentam um desafio para as entidades responsáveis por assegurar a sua potabilidade para consumo humano.

No cenário descrito, Portugal constitui um campo de experimentação privilegiado para testar esta abordagem e desta forma tentar demonstrar a possibilidade de valorizar um resíduo biomássico pela via da produção de um adsorvente com um preço competitivo quando comparado com os adsorventes comerciais disponíveis no mercado.

Fig.1. Estratégia do projeto LIFE BIOAs.

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Referências

[1] P. Mourão, C. Cassavela, I. Cansado, J. Castanheiro, L. Ribeiro, F. Pagnanelli, Int. J. Environ. Sci. Technol. (2023).
[2] P. Mourao, F. Di Caprio, I. Cansado, J. Castanheiro, I. Falcone, M. Astolfi, P. Altimari, F. Pagnanelli, Chemical Engineering Transactions. 93 (2022) 91.
[3] L. Capobianco, F. Di Caprio, P. Altimari, M. Astolfi, F. Pagnanelli, J. Environ. Manage., 273 (2020) 111164.

4-Fluorophenol degradation: unveiling the role of metal-catalysts

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4-Fluorophenol (4-FP) is a fluorinated organic compound (FOC) with valuable contributions in many industries, but it is a carcinogen compound according to the RTECS (Registry of Toxic Effects of Chemical Substances) standard [1]. Therefore, it is essential to devise a technology for accomplishing the efficient degradation of 4-FP. Catalytic hydrodefluorination is an environmentally friendly and non-destructive approach to cleaving the C-F bond, and thus a potential solution for FOC contamination. The main goal of the present work is to study the catalytic hydrodefluorination of 4-FP using different materials supports and metallic phases.

Four catalysts were synthesized by the incipient wetness impregnation method, employing palladium and nickel as metals on titanium dioxide and carbon nanotubes supports. Catalytic reduction experiments were performed in a semi-batch reactor, where 400 mL of a 100 ppm solution of 4-FP together with 200 mg of synthetized catalysts were fed into the reactor, and a hydrogen flow (100 cm^3 min^{-1}) and stirring (700 rpm) were applied. Samples were collected to quantify 4-FP, phenol and chloride in a high-performance liquid chromatography (HPLC) and ionic chromatography (IC).

Figure 1 illustrates the outcomes of the 4-FP reduction over different catalysts and reaction medium (water or NaOH). No degradation was observed when nickel was employed, but a significant increase in the extent of reduction was noted with palladium. The support also revealed to influence the catalyst's performance, with the ones supported on CNT presenting a higher activity than those supported on a metal oxide (TiO_2). Moreover, the pH of the medium was studied, and a more basic medium revealed a faster degradation for the best catalyst in a non-controlled medium (water).

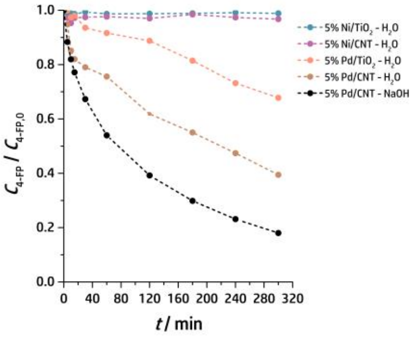

Figure 1. Normalized concentration profile of 4-FP during catalytic hydrodefluorination reaction using water or 2 mM of NaOH as solvent.

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References

[1] X. Wang, P. Wang, Q. Wang, P. Xu, C. Yang, Y. Xin, G. Zhang, Chemical Engineering Journal, 2021, 420 (2021) 127577.

Abatement of toluene from gaseous streams by Fenton's reaction over N-doped carbon materials

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The emission of volatile organic compounds (VOCs) into the atmosphere causes adverse effects on public health and the environment. It is, therefore, crucial to remove/reduce their concentrations from gaseous polluted effluents, particularly from industrial streams [1]. The heterogeneous Fenton reaction is a promising treatment process to efficiently remove organic compounds, including gaseous VOCs, which must, however, be transferred from the gas to the liquid phase wherein oxidation occurs. The heterogeneous Fenton process is based on the generation of hydroxyl radicals by catalytic decomposition of hydrogen peroxide in the presence of iron supported on a solid matrix (e.g. carbon-based materials).

The presence of N-groups on the surface of activated carbon materials has demonstrated to improve their catalytic performance for heterogeneous Fenton's applications [1]. So, the main objective of this work is to evaluate the effect of N-doping over carbon materials with different textural properties (carbon nanotubes – CNT, activated carbon – AC, or xerogels – XG) in the efficiency of gaseous toluene (used as model VOC) removal by adsorption and heterogeneous Fenton oxidation in a bubble reactor. Some results have already been obtained and are shown in Figure 1, proving their potential; further experiments and detailed characterization of the materials are ongoing to better understand and explain their distinct performances.

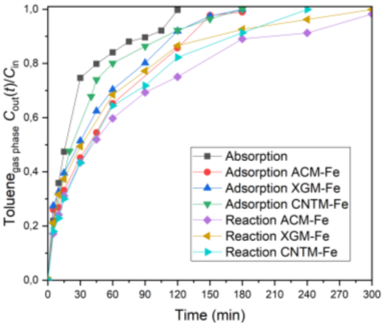

Fig.1. Effect of N-doped carbon-based materials on the ratio between toluene concentration at the outlet and inlet of the bubbling reactor. Experimental conditions: $pH_0 = 3.0$, $[H_2O_2] = 5$ mM, [iron-based catalyst] = 0.75 g dm^{-3}, $Q_{air} = 0.15$ dm^3 min^{-1} at 1 atm and ambient temperature.

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References

[1] E.F.S. Sampaio, C.S.D. Rodrigues, O.S.G.P. Soares, M.F.R. Pereira, L.M. Madeira, Nanomaterials, 12 (2022) 3274.

Graphite-like carbon nitride as photocatalyst for green ammonia production

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Ammonia is vital for fertilizer production, essential for global food supply, and holds promise as a convenient hydrogen carrier, with potential for sustainable energy when produced via zero-carbon methods [1]. This work applies heterogeneous photocatalysis to produce ammonia using visible light, N_2, water, and metal-free catalysts, such as thermally exfoliated graphite-like carbon nitride (GCN-T), easily synthesized from C- and N-rich precursors [2]. This work aims to immobilize these materials in 3D structures made through additive manufacturing, enhancing the technological efficiency of photocatalysis for sustainable ammonia production. Preceding this, several experiments were conducted to study the effect of different catalyst loads (GCN-T) in powdered form on the amount of ammonia produced at the end of one hour reaction using the same concentration of scavenger, methanol (5 mM). From Fig.1(a), it is observed that the concentration of ammonia produced rises with an increase in the catalyst load, reaching an optimum at 1 g/L catalyst load. Followingly, experiments were conducted with a fixed catalyst load of 1g/L using different concentrations of methanol scavenger. Hole scavengers can enhance the photocatalytic activity of the system for ammonia synthesis (Fig.1(b)). Among the initial concentrations tested, the highest rate for ammonia production was attained with 100 mM of hole scavenger. Ongoing work aims to immobilize the GCN catalyst in a 3D structure and conduct reactions using different scavengers to find a favorable way for ammonia production. This innovative approach eliminates the need for catalyst separation and enables the utilization of solar light for reaction activation, highlighting the sustainability of this ammonia production method.

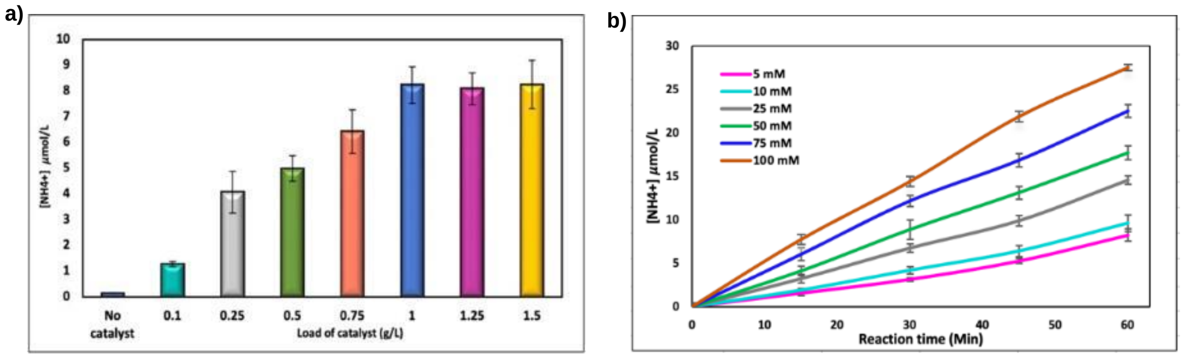

Fig.1. a) Ammonia generation at 1 h reaction using different loads of GCN-T catalyst; (b) Rate of ammonia generation using different concentrations of methanol scavenger.

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References

1. A. Qandil, A. Othman, N.I. Beithou, Journal of Ecological Engineering, 24 (2023), 221-229.
2. M. J. Sampaio, A. R. L. Ribeiro, C. M. R. Ribeiro, R. A. Borges, M. A. Pedrosa, A. M. T. Silva, C. G. Silva, J. L. Faria, Chemical Engineering Journal, 459 (2023), 141617.

Application of biopolymer composite materials for organic dyes removal

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The synthetic dyes are one of the examples of not completely treated by conventional wastewater resource recovery facilities. They can alter the chemistry of water (*e.g.*, pH changes), introduce harmful chemicals into the resultant wastewater or impact a water colouration and disturbs light penetration into water bodies which adversely affects their photosynthesis. This leads to a reduction in dissolved oxygen levels, affecting the entire aquatic biosystem [1,2]. Among advanced removal technologies the photocatalysis has shown great promise, where a semiconductor catalyst is activated upon light irradiation to produce highly reactive oxidative species that can non-selectively degrade pollutants.

In this work, the three-component biopolymer composite materials were prepared and tested as photocatalyst for organic dye removal (Rhodamine B, RhB) The fly ash from coal combustion (CFA) after beneficiation by sieving and magnetic separation leading to fractions: rich in carbon (C-CFA), iron (Fe-CFA) and silica (Si-CFA), was used as support for active sites. The biopolymer composites CFA@CS@$MnFe_2O_4$ and CFA@CS@Fe_3O_4 contain (C-CFA, Fe-CFA or Si-CFA (support), biopolymer (chitosan, CS) linker and Fe_3O_4 or $MnFe_2O_4$ (active centre), were prepared using environmentally friendly approach. The composites, pristine semiconductor NPs (Fe_3O_4 or $MnFe_2O_4$) as well as CFA beneficiated fractions 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 activity in RhB removal, and the best performance was found for composites containing C-CFA fraction (RhB removal 87% during 60 min).

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References

[1] M. Naidu Subramaniam, P. Sean Goh, D. Kanakaraju, J. Wei Lim, W. Jye Lau, A. Fauzi Ismail, Environmental Science and Pollution Research, 29 (2022) 12506.
[2] A. Ashley, B. Thrope, M. R. Choudhury, A. H. Pinto, Environmental Science Water Research &Technology, 8 (2022) 22.

Photocatalytic removal of emerging pollutants using $g\text{-}C_3N_4$ immobilized on cylindrical structures

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The rising consumption of psychoactive medications in modern-day societies directly affects surface waters with adulteration by contaminants of emerging concern [1]. This contamination represents an environmental threat due to its direct impact on the aquatic ecosystem. The refractory character of many of these pollutants avoids their elimination through the current wastewater treatment processes. In this sense, advanced oxidation processes, such as photocatalysis, arise as a suitable technology to overcome this environmental challenge.

This work investigates the evaluation of the photocatalytic performance of carbon nitride ($g\text{-}C_3N_4$, CN) immobilized on cylindrical structures, obtained by additive manufacturing of poly(lactic acid) (PLA) [2], for the removal of selected emerging pollutants, namely venlafaxine (VFX), citalopram (CTP), fluoxetine (FXT), and carbamazepine (CBZ). Moreover, the influence of the precursor (dicyandiamide, D or urea, U) used in the CN synthesis was assessed. The supported CN proved its photocatalytic efficiency in eliminating combinations of psychoactive pharmaceuticals under LED illumination (Figure 1A). On consecutive reuse, the immobilized material exhibited good modular character (Figure 1B) regarding conversion rate. The stability of electronic and optical properties was also confirmed. The advantages of using an immobilized photocatalyst through a simple set-and-use approach in developing this full-scale wastewater photocatalytic treatment are discussed.

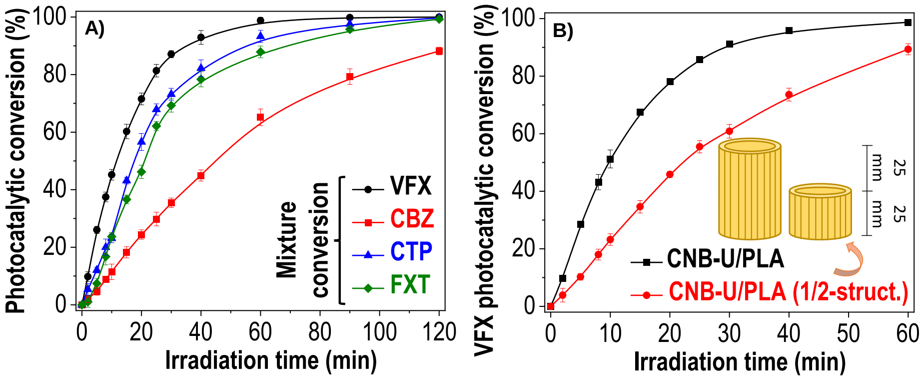

Fig.1. (A) Conversion of a mixture of emerging pollutants using the immobilized CN under LED radiation, and (B) evaluation of the modular character of the supported photocatalyst.

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References

[1] M.d.J.S. Chaves, J. Kulzer, P.d.R. Pujol de Lima, S.C. Barbosa, E.G. Primel, Environ Sci Process Impacts, 24(11) (2022) 1982-2008.
[2] M. Peñas-Garzón, M.J. Sampaio, Y. Manrique, C.G. Silva, J.L. Faria, J. Environ. Chem. Eng., 11(6), 2023, 111343.

Functionalized graphitic-C_3N_4 with enhanced photocatalytic performance for caffeine removal under visible radiation

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Metal-free catalysis, particularly utilizing semiconducting g-C_3N_4 (graphitic carbon nitride, GCN), is currently a highly discussed subject due to its sustainability and promising performance in various crucial reactions. Despite its application as a photocatalyst, the efficacy of g-C_3N_4 under visible light remains constrained, primarily due to slow charge transfer, fast recombination of photogenerated electron/holes pairs (e-/h+), and limited surface area. Consequently, numerous strategies have been explored to enhance its photocatalytic capabilities.

In this study, bulk GCN (BGCN) was synthesized through the thermal treatment of a mixture of urea and melamine. Subsequently, to improve its crystallinity and photocatalytic performance, BGCN underwent further processing at 500 ºC, resulting in the material denoted as TGCN500. A comparative analysis was conducted with another sample obtained through an alternative treatment in ethylene glycol (EG) at 150 ºC, designated as BGCN/EG. EG was chosen due to its high boiling temperature and its active role as a solvent during semiconductor preparation, contributing to the enhancement of optical, structural, and catalytic properties of BGCN [1]. The subsequent treatment of TGCN500 was also explored, involving processing in EG at 150 ºC to produce TGCN500/EG, or subjecting it to a hydrothermal treatment at 150 ºC in water, resulting in TGCN500/H_2O. The materials were further characterized using XRD, FTIR, DRS, and N_2 adsorption at -196 ºC. Photocatalytic performance evaluation of the prepared materials was conducted under visible light, focusing on the degradation of caffeine as a microcontaminant model.

XRD data confirmed the successful synthesis of GCN, with TGCN500/EG exhibiting the highest BET area value (25 m^2/g) and the most promising optical response under visible light. Photocatalytic assays under visible radiation revealed the superior performance of the treated materials, with TGCN500/EG achieving approximately 80% caffeine removal after 180 min of irradiation, while TGCN500 reached around 60%, and BGCN only achieved approximately 20% removal.

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ASM thanks FCT for the Assistant Researcher contract CEECIND/01371/2017 (Embrace Project, DOI 10.54499/PTDC/EQU-EQU/6024/2020).

References

[1] Y. Zhang, P. Zheng, S. Li, H. Guo, X. Hu, Y. Fang, R. Duan, Q. Chen, Colloids and Surfaces A: Physicochemical and Engineering Aspects 676 (2023) 132113.

Photoelectrocatalytic removal of pharmaceuticals from urban wastewaters with metal-free g-C_3N_4

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Sophisticated technologies for eradicating persistent organic contaminants found in effluents from urban wastewater treatment plants (WWTPs) must be investigated to ensure access to clean potable water. Among these contaminants, pharmaceutical substances pose potential threats to both the environment and human life [1]. In this sense, photocatalysis and electrocatalysis emerge as promising alternatives to meet the demand for sustainable wastewater treatment processes. Graphitic carbon nitride (g-C_3N_4) is a metal-free polymer with the possibility of dual activation in both photo- and electrochemical domains. This material has demonstrated notable efficacy as a catalyst for eliminating organic pollutants [2].

In this work, we focused on synthesising and optimising g-C_3N_4 derived from urea, prepared at varying temperatures [3]. Initially, we assessed the electrochemical performance of the resultant materials to identify the most efficient electrocatalyst. Subsequently, we examined the removal of diclofenac, ibuprofen, and fluoxetine in simulated and actual wastewater samples, evaluating its efficiency across photo-, electro-, and photoelectrocatalytic systems. Diverse operational parameters, including electrode type, electrolyte composition, and matrix constitution, were systematically explored to improve the degradation and mineralisation rate [4].

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References

[1] D. Papagiannaki, M.H. Belay, N.P.F. Gonçalves, et al., Chem Eng. J. Adv., 10 (2022) 100245.
[2] W.-J. Ong, L.-L. Tan, Y. H. Ng, et al., Chem Rev., 116 (2016) 7159.
[3] A. Torres-Pinto, A.M. Díez, C.G. Silva, et al., Fuel. 360 (2024) 130575.
[4] A. Torres-Pinto, A.M. Díez, C.G. Silva, et al., Chem. Eng. J., 476 (2023) 146761.

Acidic functionalization of MWCNTs: insights on their antibiofilm activity against *E. coli* and *S. aureus*

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The chemical functionalization of multi-walled carbon nanotubes (MWCNTs) has been described as a powerful strategy to improve the overall antimicrobial and anti-adhesive performance of MWCNT-based surfaces [1]. In this study, the antibiofilm activity of nitric acid-functionalized MWCNT-based composites was evaluated against two common colonizers of medical devices—*Escherichia coli* and *Staphylococcus aureus* [2].

MWCNTs with different acidic levels were firstly obtained via oxidation with nitric acid (f-MWCNTs), followed by thermal treatment at 600 °C. After evaluating the textural properties of MWCNTs, they were incorporated into a poly(dimethylsiloxane) (PDMS) matrix, and the roughness and morphology of the resulting composites were assessed using optical profilometry and scanning electron microscopy, respectively. The antibiofilm performance of MWCNT/PDMS surfaces was determined by quantifying culturable *E. coli* and *S. aureus* cells after 24 h of biofilm formation. Furthermore, the cytotoxicity of MWCNT/PDMS composites was tested against a human kidney (HK-2) cell line.

The results revealed that the antimicrobial activity of MWCNTs incorporated into a PDMS matrix can be efficiently tailored through nitric acid functionalization, and it can be increased by up to approximately 50% for f-MWCNT samples heated at 600 °C. These samples are characterized by the absence of surface carboxylic groups and the presence of redox activity of carbonyl groups. Furthermore, the synthesized composites did not impact HK-2 cell viability, confirming the biocompatibility of MWCNT composites.

Altogether, these results indicate that f-MWCNT-based surfaces have the potential to be applied in the construction of medical devices and implants.

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References

[1] R. Teixeira-Santos, M. Gomes, L.C. Gomes, F.J. Mergulhão, iScience, 24 (2021) 102001.
[2] M. Gomes, R. Teixeira-Santos, L.C. Gomes, F. Sousa-Cardoso, F.M. Carvalho, A.R. Tomé, O.S.G.P. Soares, K.A. Whitehead, F.J. Mergulhão, Antibiotics, 12 (2023) 1620.

NO reduction over carbon xerogel supported catalysts

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Reducing nitrogen oxide (NOX) emissions is crucial due to its environmental effects, such as global warming, acid rain and impacts on human health. The need for advanced technologies and effective catalysts is vital to comply with stricter environmental regulations. Selective Catalytic Reduction (SCR) converts NOx to N_2 with a catalyst [1]. Carbon-based catalysts exhibit high activity at low temperatures, highlighting selective catalytic reduction with carbon (SCR-C) as an excellent alternative to reduce NOx, without the need for an external reducing agent [2,3]. The main objective of this work is to study the reduction of NO using carbon xerogels (XG) as a catalyst or as a support for the metallic phases.

Carbon xerogels were synthesized through the conventional sol-gel approach using formaldehyde and resorcinol with 2 different pH values (XG_5.3 and XG_6.9). Furthermore, nitrogen-carbon xerogels were prepared using melamine as a nitrogen source incorporated into the polymer matrix by the sol-gel process (XG_M_5.3 and XG_M_6.9). They were then carbonized at a temperature of 800 ºC. After preparing the carbon support structure, the metallic phase (copper and potassium) was introduced using the incipient impregnation method. The textural and chemical properties of the materials were characterized by N_2 adsorption at -196 °C, inductively coupled plasma-optical emission spectrometry (ICP-OES), and elemental analysis (EA). NO reduction experiments were performed in a fixed-bed, U-shaped flow reactor using 0.2 g of sample, a flow rate of 100 cm^3 min^{-1}, and a concentration of NO in He of 1000 ppm.

The textural properties of XG are strongly affected by the preparation pH. Increasing the synthesis pH, the specific surface area decreases (S_{BET} of XG_5.3 = 643 m^2 g^{-1} and S_{BET} of XG_6.9 = 464 m^2 g^{-1}). Samples containing melamine and impregnated with metal show a decrease in specific surface areas due to blocking access to surface porosity during analysis. Therefore, the influence of the specific surface area, the amount of nitrogen and the type of metal incorporated were evaluated for the reduction of NO. Carbon xerogels with different pH (XG_5.3 and XG_6.9) have low catalytic activity for NO reduction. The addition of copper improves the performance, achieving 96% and 40% conversion for XG_5.3@Cu and XG_6.9@Cu, respectively. The introduction of nitrogen groups on the surface further amplifies the activity, resulting in 99% and 70% reduction for XG_M_5.3@Cu and XG_M_6.9@Cu. The addition of potassium to copper in both types of support significantly improves the catalytic performance, with XG_M_5.3@CuK being the most efficient, achieving 100% NO reduction at 375 °C. The results show that the pH of XG synthesis interferes with the catalytic activity of NO reduction, the surface area, the amount of nitrogen, and the incorporation of metal, determining the effectiveness of NO reduction.

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References

[1] S. Bahrami, A. Niaei, M.J. Illán-Gómez, A. Tarjomannejad, S.M. Mousavi, V. Albaladejo-Fuentes, Journal of Environmental Chemical Engineering, 5 (2017) 4937-4947.
[2] M.J. Illán-Gómez, S. Brandán, C. Salinas-Martínez de Lecea, A. Linares-Solano, Fuel, 80 (2001) 2001-2005.
[3] P.S.F. Ramalho, O.S.G.P. Soares, J.L. Figueiredo, M.F.R. Pereira, Catalysis Today, 418 (2023) 114044.

Experimental design tools to maximize RNA capture with oxidised nanodiamonds

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The research in the RNA-based therapeutics field has rapidly grown with exciting results supporting their application to different diseases. However, the large-scale production of RNA remains technically difficult and expensive. RNA production is achieved through multi-step processes that require effective manufacturing strategies and precise quality control, which should result in a highly pure product for pharmaceutical use [1]. Within the intricate process, recovery and purification are the most high-burden steps, being time-consuming and an economic challenge, mainly due to the abundance of impurities with characteristics similar to RNA [2]. As such, this study aims to improve, simplify, and find a more cost-efficient method for capturing and recovering RNA.

The use of carbon-based nanomaterials for capturing RNA emerges as a promising option. Among these materials, nanodiamonds (NDs) have unique physical and chemical properties, making them highly attractive in the biomedical field. NDs have a large specific surface area, chemical resistance, magnetic and optical properties, and are easy to produce on a large scale [3]. Additionally, their surface reactivity allows their properties to be tailored, promoting specific interactions with the target product [3]. Compared to other carbon-based nanomaterials, such as fullerenes and carbon nanotubes, NDs are one of the most biocompatible forms [3].

The first screening focused on using non-functionalized, hydrogenated, oxidised, and aminated NDs, as well as microdiamonds, to assess their efficacy in the adsorption and recovery of RNA while promoting electrostatic and hydrophobic interactions. All materials, except for the oxidised NDs (NDs-ox), exhibited high RNA adsorption ability when promoting both interactions. However, RNA recovery was impossible to achieve. In contrast, NDs-ox did not adsorb RNA when electrostatic interactions were promoted, but when adjusting the experimental conditions to establish hydrophobic interactions, the RNA adsorption was dependent on the ionic strength of the equilibration buffer. Moreover, using these conditions allowed RNA's successful recovery by lowering the ionic strength or including a mild surfactant solution. Further, an experimental design was implemented to optimise the RNA adsorption and recovery. This involved the variation of the RNA concentration, the ionic strength of the equilibration buffer, and the time of contact between the sample and the NDs-ox. According to the experimental design, at the optimal conditions, it is possible to capture and recover approximately 68 of the 100 µg of applied RNA.

Overall, the findings highlight the potential of NDs-ox in effectively capturing RNA, streamlining the pre-purification process. This method distinguishes itself by its simplicity, efficiency, and reliability, showcasing promising prospects for applications in RNA-related studies for biomedical purposes.

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References

[1] Ponchon, L., et al., Nat Protoc, (2009) 4(6).
[2] Carapito, R., et al., Separation and Purification Technology, (2023) 315.
[3] Garifo, S., et al., Frontiers of Materials Science, (2021) 15(3).

H_2O_2 production promoted by glucose oxidase immobilised onto graphitic carbon nitride

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Glucose oxidase (GOx) is an oxidoreductase enzyme of glucose oxidation into hydrogen peroxide (H_2O_2) and gluconic acid. GOx has attracted increased interest in several industries. For instance, it is known for its antioxidant, preservative, and stabiliser properties in the food industry. Moreover, GOx is widely used in glucose testing kits to quantify glucose levels in industrial and biological samples (e.g., blood and urine). However, the practical use of GOx in its free form has numerous limitations, such as low stability and single-use restriction. The immobilisation of GOx onto nanoparticle catalysts is a viable and promising solution to address these issues. Immobilisation onto solid supports facilitates the reuse of the enzyme and enhances its stability and kinetic properties, while maintaining its intrinsic catalytic activity [1]. This work aims to use thermally exfoliated graphitic carbon nitride (GCN-T) for the first time as support for GOx immobilisation and the production of H_2O_2. Easily synthesised by earth-abundant elements (i.e., C, N, and H), GCN-T has outstanding biocompatibility, stability, photocatalytic activity, and tunable functionalisation, all of which provide a unique set of interesting properties for its use in various fields [2]. After obtaining the optimal immobilisation conditions, the bioconjugate´s capacity for H_2O_2 production was investigated. Different operating conditions, such as glucose concentration, dissolved oxygen, and pH were evaluated. The results indicate the superior performance of GCN-T as a support for GOx, achieving immobilisation yields of 90%. The bioconjugate exhibited exceptional reusability, maintaining 81% of its activity after 10 cycles, and revealed enhanced thermal stability at higher temperatures than the free enzyme. A maximum of 3.9 mM H_2O_2 was produced using a GCN-T/GOx bioconjugate load of 0.1 g L^{-1}.

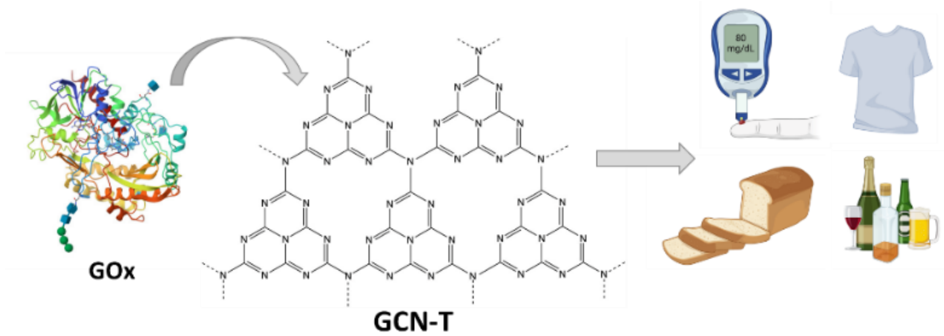

Fig.1. Immobilisation of glucose oxidase onto GCN-T and its industrial applications.

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References

[1] M. Wang, D. Wang, Q. Chen, C. Li, Z. Li, J. Lin, Small, 15 (2019)
[2] S. Deshmukh, K. Pawar, V. Koli, P. Pachfule, ACS Appl. Bio Mater., 6 (2023), 1339-1367.

Oxidative desulfurization of a simulated fuel using carbon nanotubes from plastic waste

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Sulfur is an inherent atom in crude oil composition. However, its presence in fuels is concerning, as it is responsible for giving rise to SO_x and particulate matter upon combustion [1]. Typically, S removal from fuels is carried out by reacting the fuel with hydrogen under high pressure (5-200 bar) and temperatures (), a process called Hydrodesulfurization (HDS). HDS is, however, ineffective for removing certain types of compounds, specifically compounds containing a thiophenic ring. Oxidative desulfurization (ODS) emerges as an alternative that can be carried out at milder operating conditions (1-2 bar and <150 °C). In this work, carbon nanotubes (CNTs) derived from simulated plastic solid waste were applied as catalysts in the ODS of dibenzothiophene (DBT). The CNTs were grown over a $NiFe_2O_4/Al_2O_3$ substrate and considering a mixture of polyolefins (low- and high-density polyethylene (LDPE and HDPE), and polypropylene (PP)), in a 35:25:40 mass basis (LDPE:HDPE:PP). After synthesis, the sample was washed with H_2SO_4 [2], leading to CNT-P. CNT-P was used in the ODS of DBT at 70 °C, considering acetonitrile as the extractant phase in an 80:20 fuel-to-extractant volume ratio, $[H_2O_2]_0$ = 15.1 g L^{-1}, [cat] = 2.5 g L^{-1}. The results are reported in Figure 1. As can be seen, the non-catalytic run (N.C.) did result in ca. 44% of DBT removal, ascribed to mass transfer. Nevertheless, using a catalyst resulted in a much more relevant removal (ca. 73% of removal). In the presence of CNT-P, DBT is converted into DBT-5-oxide (Fig. 1b) and later into DBT-5,5-dioxide (Fig 1c), indicating that CNTs derived from a mixture of polyolefins can be interesting catalysts for fuel purification.

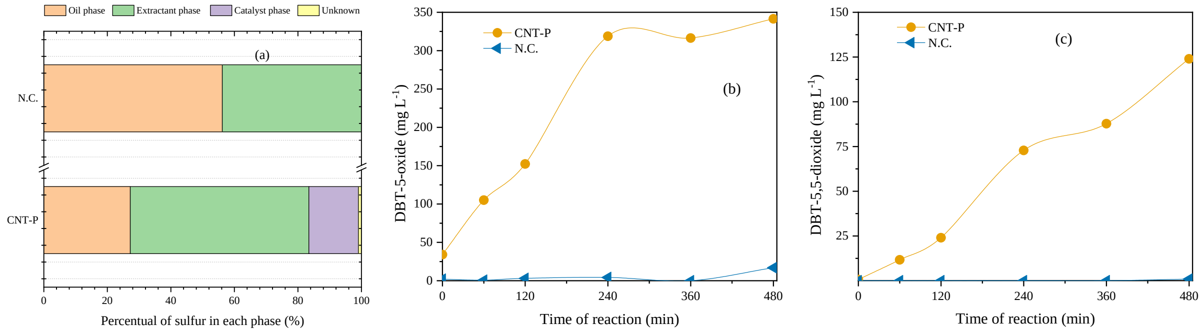

Figure 2. (a) Sulfur balance at the end of reaction and evolution of (b) DBT-5-oxide and (c) DBT-5,5-dioxide.

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References

[1] Roman FF, Diaz de Tuesta JL, Silva AMT, Faria JL, Gomes HT. Carbon-Based Materials for Oxidative Desulfurization and Denitrogenation of Fuels: A Review. Catalysts 2021;11(10):1239.
[2] Roman FF, De Grande Piccinin L, Santos Silva A, Diaz de Tuesta JL, Freitas IVK, Vieira A, et al. Carbon Nanomaterials from Polyolefin Waste: Effective Catalysts for Quinoline Degradation through Catalytic Wet Peroxide Oxidation. Catalysts 2023;13(9):1259.

Nanostructured SiO_2-supported Ni-Fe catalysts loaded onto a planar slab reactor for stable catalytic methane splitting

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Catalytic methane splitting (CMS) has the ability for fast cost-effective energy decarbonization. This reaction produces hydrogen and graphitic carbon from methane: $\mathrm{CH_4(g) \rightleftharpoons 2H_2(g) + C(s)}$. CMS is widely accepted to be structure-sensitive over metal surfaces, requiring the use of nanoparticles, stabilized on a ceramic support [1]. However, the metal nanoparticles may be removed from the support during the growth of the carbon allotropes – tip growth. Alternatively, carbon may grow over the nanoparticles – base growth [2]. A set of Ni and Fe-based catalysts supported on mesoporous SiO_2 were synthesized and the carbon growth mechanism assessed. The metal phase was deposited by incipient wetness impregnation exclusively inside pores. The confinement of the particles was made to promote base-growth mechanisms. Different amounts of Fe were added to regulate carbon dehydrogenation and diffusion [3]. Figure 1 displays the carbon allotropes formed from CMS over the nickel and the nickel-iron alloy catalysts, at 750 °C, feeding pure CH_4 at 1 bar. It was seen that the catalyst without Fe (catalyst A) produced bamboo-shaped carbon nanotubes, characteristic of the tip-growth mechanism. However, when Fe was added (catalysts B and C), multi-walled carbon nanotubes were created, indicating a shift in mechanism. None of the characterized nanotubes from catalyst B present metallic particles on their tips, strongly suggesting that the base-growth mechanism was successfully promoted. In contrast, the carbon filaments produced over catalyst C contain metallic particles enclosed in the round tips.

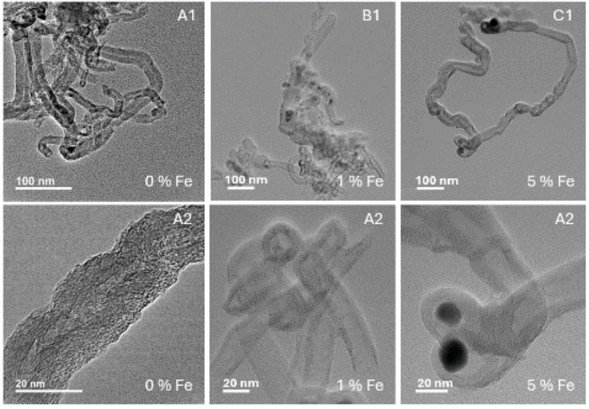

Figure 3 – Carbon allotropes produced during CMS at 750 °C and 1 bar: A1 and A2 - Ni/SiO_2; B1 and B2 - NiFe/SiO_2, 1 % Fe in metal phase; C1 and C2 - NiFe/SiO_2, 5 % Fe in metal phase.

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References

[1] Gonzalez I, et al. J Phys Chem C 2012; 116:21577-87
[2] Alves L, Pereira V, et al. Renew Sustain Energy Rev 2021; 137:110465
[3] Arevalo RL, et al. Sci Rep 2017;7:13963

Definição das condições ótimas da reação de hidrogenação de CO_2 a hidrocarbonetos com catalisador metálico de carbono

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O aumento da população e o crescimento económico têm impulsionado significativamente o consumo de energia, resultando num crescimento exponencial das emissões de dióxido de carbono (CO_2) (81% dos gases de efeito estufa) para a atmosfera e contribuindo para o aquecimento global [1]. A hidrogenação catalítica do CO_2 tem mostrado ser uma tecnologia promissora para valorizar o CO_2. Embora tenham sido registados avanços notáveis na conversão do CO_2 em produtos contendo apenas um átomo de carbono (C_1), a hidrogenação do CO_2 a produtos com 2 ou mais átomos de carbono (C_{2+}) apresenta desafios adicionais devido à inerticidade do CO_2, e só recentemente tem sido estudada apesar de apresentar interesse económico e ambiental superior [2]. Este trabalho teve como principal objetivo determinar as condições ótimas da reação de hidrogenação de CO_2 a hidrocarbonetos (C_2-C_4) através da síntese modificada de *Fischer-Tropsch* (FTS) usando catalisadores bifuncionais suportados em nanotubos de carbono.

Em todos os ensaios utilizou-se um catalisador sintetizado com 8 %m/m de ferro e 20 %m/m de cobre impregnados em nanotubos de carbono (CNT) (Fe_8Cu_{20}/CNT). A reação ocorreu num reator *Microactivity-Reference* (PID) e a análise dos produtos foi realizada num cromatógrafo Micro GC *Fusion Gas Analyzer*. Na Tabela 1 estão descritos os ensaios realizados para a determinação das condições ótimas de reação, onde se variaram os parâmetros em estudo: temperatura (T), pressão (P), razão de caudais dos reagentes (Q_{H2} / Q_{CO2}), caudal total dos reagentes (Q_{total}) e massa de catalisador ($m_{catalisador}$).

Tabela 1. Condições reacionais utilizadas nos ensaios catalíticos.

Condições Reacionais	**T / °C**	**P / bar**	**Q_{H2} / Q_{CO2}**	**Q_{total} / $cm^3\ min^{-1}$**	**$m_{catalisador}$ / mg**
Ensaio Temperatura	250, 300, 350, 400, 450	15	3 H_2 : 1 CO_2	30	200
Ensaio Pressão	350	10, 15, 20, 25, 30	3 H_2 : 1 CO_2	30	200
Ensaio Razão Caudal	350	20	3 H_2 : 1 CO_2 2 H_2 : 2 CO_2 1 H_2 : 3 CO_2	30	200
Ensaio Caudal Total	350	20	3 H_2 : 1 CO_2	30, 50, 100, 150	200
Ensaio Massa de Catalisador	350	20	3 H_2 : 1 CO_2	30	200, 500, 1000

Os resultados desde trabalho permitiram concluir que o catalisador tem melhor desempenho quando avaliado à temperatura de 350 ºC, pressão de 20 bar, razão de caudais de 3 H_2 : 1 CO_2, caudal total de 30 cm^3 min^{-1} e 500 mg de massa de catalisador, onde se verificou uma conversão de CO_2 de 42 % e 26 % de seletividade a produtos C_2 a C_4.

Agradecimentos

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Referências

[1] Fan, W. K., Tahir, M., Environ. Chem. Eng., 2021, 9(4), 105460.
[2] Roy, S., Cherevotan, A., ACS E. Let., 2018, 3(8), 1938–1966.

Bimetallic catalysts supported on CNT-Al_2O_3 composites for the hydrogenation of CO_2 into methanol

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Carbon dioxide (CO_2) is one of the main products of fossil fuels combustion, the world's primary energy resource and, as a greenhouse gas, its emissions contribute massively to climate change. Therefore, it is essential to develop processes capable of converting CO_2 into valuable products [1]. The hydrogenation of CO_2 into methanol is an appealing research area since methanol is an alternative to fossil fuels. Thus, it may enable the decline of CO_2 emissions and eliminates the release of harmful products, such as NO_x or SO_2 [1,2]. This reaction has thermodynamic limitations, as it is favored at high pressures and low temperatures [3]. Although CO_2 activation is promoted at relatively high temperatures, the selectivity for methanol decreases, with an increase in secondary products, as the *reverse water-gas shift* secondary reaction becomes predominant [3, 4].

This study aims to assess the catalytic performance of Copper (Cu) and Zinc (Zn) bimetallic catalysts supported on pristine Activated Carbon (AC) and Carbon Nanotubes (CNT), and on composites with different proportions of CNT and Aluminum Oxide (Al_2O_3). The catalysts were prepared by incipient wetness impregnation and the composites by a ball milling treatment. The catalytic experiments to evaluate CO_2 conversion were conducted at 250 °C and 30 bar (GHSV = 24 000 cm^3/g h) with a Microactivity Reference reactor from PID Eng & Tech. The resulting gaseous products were analyzed with a Micro GC from Inficon. Along with the catalytic tests, the catalysts were also characterized by different techniques, such as H_2-Temperature Programmed Reduction and N_2 Physisorption at −196 °C.

Preliminary catalytic experiments demonstrated that the catalyst supported on pristine CNT, CuZn/CNT, achieves better catalytic results (higher CO_2 conversion) than the catalyst supported on pristine AC, CuZn/AC, leading to the preparation of catalysts supported on CNT:Al_2O_3 composites. The catalyst, CuZn/CNT-Al_2O_3 (70:30), achieved a better catalytic result than the catalyst CuZn/CNT, confirming the benefits of combining the properties of CNT materials and metal oxide on composites, turning this approach an interesting toolbox for developing highly efficient catalysts for this reaction.

Acknowledgements

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References

[1] I. U. Din, M. S. Shaharun, M. A. Alotaibi, A. I. Alharthi, A. Naeem, Journal of CO_2 Utilization, 34 (2019) 20.
[2] Q. Tan, Z. Shi, D. Wu, Industrial & Engineering Chemistry Research, 57 (2018), 10148
[3] H. Bahruji,M .Bowker, G. Hutchings, N. Dimitratos, P. Wells, E.Gibson, W. Jones, C. Brookes, D. Morgan,G. Lalev, Journal of Catalysis, 343 (2016) 133.
[4] O. Tursunov, L. Kustov, Z. Tilyabaev, Journal of the Taiwan Institute of Chemical Engineers, 78 (2017) 416.

Sustainable production of aviation fuels directly from palmitic acid

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In recent years, there has been a growing effort to reduce the use of fossil fuels, particularly in the transport sector. In this sense, biomass appears to be a sustainable alternative that could replace oil derivatives, such as petrol and diesel, due to its low cost [1,2,3].

In this work, the process of converting palmitic acid (a model compound from microalgae) through hydrodeoxygenation (HDO) reaction was studied, where the main objective was the formation of hydrocarbons in the aviation fuels range (C_8-C_{16}). To this end, bi- and monometallic catalysts composed of 1-4% Mo and 2.5-10.5% Ru supported on carbon nanotubes (CNT) were synthesized. Catalytic tests were carried out, in which 0.5 g of palmitic acid, 50 mL of solvent (decane or dodecane) and 0.25 g of catalyst were introduced into a batch reactor (Parr Instruments) under stirring at 150 rpm and H_2 pressure of 30 bar. After heating to 350 ºC, the reaction was started and carried out for 6 h, after which the reaction mixture was analysed by gas chromatography-mass spectrometry (GC-MS Shimadzu TQ-8040 NX). The prepared materials were characterised by temperature-programmed reduction (TPR) and N_2 adsorption isotherms. The conversion of palmitic acid and the yield of hexadecane (C_{16}) were calculated, and the effects of the support (CNT and CNT_{ox}), solvent and metal content were assessed.

Based on the results obtained, the catalyst metal content proved to be a determining factor to obtain a higher C_{16} yield. Thus, the catalysts with a higher metal content, namely 2.5%Ru-10.5%Mo/CNT_{ox} and 2.5%Ru-10.5%Mo/CNT, allowed to attain the best results: 60.2% and 57.6% yield of C_{16}, respectively. Among the prepared monometallic catalysts, 10.5%Mo/CNT and 2.5%Ru/CNT_{ox}, the former led to the formation of 29.7% yield of C_{16} and 84% conversion of palmitic acid, while the latter resulted in a C_{16} yield of 3.1% and complete palmitic acid conversion. As for the other parameters evaluated, it was concluded that the use of CNT_{ox} as support and decane as solvent did not significantly affect the results obtained.

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References

[1] R. Ding, Y. Wu, Y. Chen, H. Chen, J. Wang, Y. Shi, M. Yang, Catalysis Science & Technology, 6 (2016) 2065.
[2] X. Li, M. Lin, R. Li, Q. Lu, M. Yang, Y. Wu, Fuel, 332 (2023) 126139.
[3] M. Zhang, Y. Hu, H. Wang, H. Li, X. Han, Y. Zeng, C.C. Xu, Molecular Catalysis, 504 (2021) 111438.

Catalytic deoxygenation of palmitic acid using Co-Mo supported on carbon nanotubes

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The growing need for ecologically friendly aviation solutions is driving the development of renewable jet fuel. In this perspective, lipid sources are especially important since they include fatty acids with carbons in the aviation fuel range (C_8-C_{16}) [1]. However, their direct use as fuel is not feasible due to the elevated oxygen content, resulting in deterioration of the physical and chemical properties. Therefore, a catalytic hydrotreatment process is necessary [1,2]. In this context, this work focused on the evaluation of the catalytic performance of Co-Mo supported on carbon nanotubes (CNT) in the deoxygenation of palmitic acid (lipid-based feedstock model compound).

For this purpose, bimetallic catalysts (metal loadings of 2.5 and 10.5 % of Co and Mo, respectively) were prepared by incipient wetness impregnation. CNTs and oxidized CNTs (CNT_{ox}) were used as supports. After this procedure, the materials were thermally treated in a N_2 flow at 600 ºC for 3 h and reduced in H_2 at the same temperature and time. The prepared catalysts (Co-Mo/CNT and Co-Mo/CNT_{ox}) were characterized by N_2 adsorption, X-ray diffraction, temperature programmed reduction, elemental analysis, ICP-OES and point of zero charge. Reactions with 0.25 g of each catalyst were performed in a stainless steel batch reactor (100 mL) using 0.5 g of palmitic acid diluted in 50 mL of *n*-decane at 350 ºC, 30 bar of initial H_2 pressure, using a stirring rate of 150 rpm for 6 h. The final liquid products were analysed by GC-MS (Shimadzu TQ8040-NX). After that, the conversion of palmitic acid and the yields of hexadecane (C_{16}) and pentadecane (C_{15}) were determined. In addition, a reaction under the same conditions described above using a commercial catalyst (Co-Mo/Al_2O_3 , metal loadings of 2.5 and 10.5 % of Co and Mo, respectively) was carried out.

After 6 h of reaction, the carbon-supported metal catalysts were effective, with 67.7 and 81.8 % C_{16} yield over Co-Mo/CNT and Co-Mo/CNT_{ox}, respectively. The yields for C_{15} production were the same for both catalysts - 8.1 %. The addition of oxygenated groups to the surface of CNT improved the catalytic performance of Co-Mo/CNT_{ox} in the hydrodeoxygenation reaction, and a complete palmitic acid deoxygenation was achieved. Despite the commercial catalyst's lower acidity and the presence of micropores, the higher Co concentration in the material may have contributed to a larger C_{16} production (83.2 %) compared to Co-Mo/CNT. The high loads of Co and Mo oxides on the commercial catalyst and the high acidity of Co-Mo/CNT_{ox}, offered comparable performance in terms of C_{16} production after 6 h of reaction.

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References

[1] P. Mäki-Arvela, M. Martínez-Klimov, D.Y. Murzin, Fuel, 306 (2021) 121673.
[2] M. Zhang, Y. Hu, M. Wang, H. Li, X. Han, Y. Zeng, C. C. Xu, Molecular Catalysis, 504 (2021) 111438.

Ni-W catalysts for cellulose-derived ethylene glycol one-pot synthesis: advancing sustainable production

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To help with issues of global environmental problems and diminishing fossil fuel reserves, lignocellulosic biomass is attracting attention as raw-material for the production of green chemicals [1,2]. One of the most interesting routes for its valorisation is the one-pot hydrolytic hydrogenation into valuable chemicals, such as ethylene glycol (EG) [3,4]. EG is an alcohol with two –OH groups, widely used in pharmaceutical, cosmetic, food, dye, plastic and automobile industries, which allows it to be considered a high-value market product [5].

In this work, the direct hydrolytic hydrogenation of cellulose to EG was evaluated using Ni and W mono- and bimetallic catalysts supported on carbon nanotubes (CNT). Furthermore, the influence of the metal loading was investigated. In standard tests, 300 mL of water, 750 mg of cellulose (previously ball-milled for 4 h at 20 s^{-1}) and 300 mg of catalyst were introduced into a 1000 mL stainless steel reactor under stirring at 300 rpm. After heating under N_2 to 205 ºC, the reaction was initiated by switching to H_2 (50 bar), and the reaction mixture was analysed by high performance liquid chromatography (HPLC) and total organic carbon (TOC) evaluation. The properties of the synthesized catalysts were characterized by several techniques, such as N_2 adsorption, microscopy (SEM/EDS), XRD, TG, ICP and TPR.

Conversions of cellulose around 100% were reached after 5 h in all experiments, and a synergistic effect was observed between Ni and W, allowing the tuning of the EG yield by changing the weight ratio between both metals. An EG yield over 50% was reached in just 5 h of reaction using 20%Ni-20%W/CNT as catalyst [6]. This result greatly surpassed those previously obtained using Ru-W/CNT under the same conditions [7-9], indicating that a cheaper metal such as Ni can successfully replace the Ru noble metal.

In conclusion, Ni-W/CNT catalysts are efficient for the direct EG production from cellulose, being presented herein as low-cost and sustainable catalytic alternatives.

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References

[1] A.M. Ruppert, K. Weinberg, R. Palkovits, Angewandte Chemie International Edition, 51 (2012) 2564.
[2] H. Kobayashi, Y. Yamakoshi, Y. Hosaka, M. Yabushita, A. Fukuoka, Catalysis Today, 226 (2014) 204.
[3] P. Wataniyakul, P. Boonnoun, A.T. Quitain, M. Sasaki, N. Laosiripojana, A. Shotipruk, Catalysis Communications, 104 (2018) 41.
[4] Z. Xiao, J. Li, H. Wang, Q. Ge, C. Xing, J. Huang, J. Ji, J. Mao, Biomass and Bioenergy, 170 (2023) 106722.
[5] H. Yue, Y. Zhao, X. Ma, J. Gong, Chemical Society Reviews, 41 (2012) 4218.
[6] L.S. Ribeiro, A.L.F. Pires, J.J.M. Órfão, M.F.R. Pereira, Renewable Energy, 200 (2022) 1008.
[7] L.S. Ribeiro, J.J.M. Órfão, M.F.R. Pereira, Bioresourse Technology, 263 (2018) 402.
[8] L.S. Ribeiro, N. Rey-Raap, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira, Cellulose, 26 (2019) 7337.
[9] L.S. Ribeiro, J.J.M. Órfão, M.F.R. Pereira, Industrial Crops & Products 166 (2021) 113461.

Cork-derived activated carbons as electrodes for supercapacitors

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The increasing global energy demand and the gradual depletion of fossil sources have encouraged a growing search for substitute energy sources, such as renewable energies [1]. These types of energy are categorized as environmentally friendly, profuse, and sustainable. Supercapacitors are an emerging technology in the field of energy storage systems that can offer higher power density than batteries and higher energy density than traditional capacitors. Supercapacitor electrode materials such as carbon and carbon-based materials have received increasing attention due to their high specific surface area, good electrical conductivity, and excellent stability [2, 3].

Herein, derived cork-activated carbons were synthesized via a solvent-free physicochemical method [4]. Briefly, cork powder was physically mixed with K_2CO_3 in different mass ratios and heated in a vertical furnace tube under different atmospheres (N_2 and/or CO_2) temperatures, times, and flow rates. Urea was also tested as a nitrogen precursor and mixed with cork and K_2CO_3 before thermal treatment.

The synthesized cork-derived materials showed specific surface areas up to 1210 m^2 g^{-1} with a well-developed microporosity obtained by N_2 adsorption-desorption isotherms. The prepared samples were tested as electrodes in a symmetric two-electrode cell supercapacitor device. Cyclic voltammetry tests (Fig.1), galvanostatic charge-discharge measurements, and electrochemical impedance spectroscopy were used to assess the electrochemical characterization. The method and temperature of preparation originate materials with remarkably different performances.

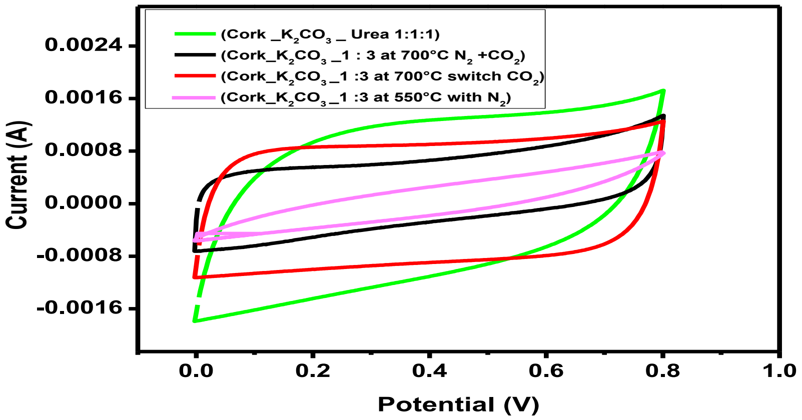

Fig.1. Cyclic voltammograms of selected cork-derived activated carbons measured in a two-electrode cell in 1 M H_2SO_4 at a scan rate of 2 mV s^{-1}.

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References

[1] B. Mufutau Opeyemi, *Energy*, 228 (2021) 120519.
[2] P. González-García, *Renewable and Sustainable Energy Reviews*, 82 (2018) 1393.
[3] Ochai-Ejeh, F. O*., et al., Electrochimica Acta 252 (2017).*
[4] Rensch, Tilo, et al., *ChemSusChem 15.16 (2022).*

Innovative Thin Multilayer Thermally-Chargeable Textile Supercapacitors

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The rapid development in smart electronic technologies has led to an increased focus on real-time sensing capabilities, posing significant challenges in the domains of energy storage and harvesting. This shift has led to new, flexible, and wearable self-powered smart devices.[1] Thermoelectric systems (TEGs), key in energy harvesting, efficiently convert unused thermal energy into electrical energy for low-power electronics, while supercapacitors (SCs) are an effective energy storage solution for such devices. The innovative fusion of TEGs and SCs into a single entity, known as thermally-chargeable supercapacitors (TCSCs), represents a rapidly growing and cutting-edge field. In previous research conducted by our group [2], textile-based SC and TCSCs were successfully produced utilizing carbon-based textile electrodes in a sandwich-type configuration. The focus now shifts to leveraging coating techniques to develop thinner devices, towards seamless integration. In this sense, herein thinner TCSCs were produced with a multi-layer configuration built in a single textile substrate. To accomplish this objective, the solid-gel electrolyte was firstly applied on the fabric, followed by the coating of MWCNT paste onto both sides of the fabric. Constructing this type of device posed the challenge of precisely depositing the electrolyte into specific areas of the textile substrate, a task that was addressed by exploring various coating techniques (Fig. 1).

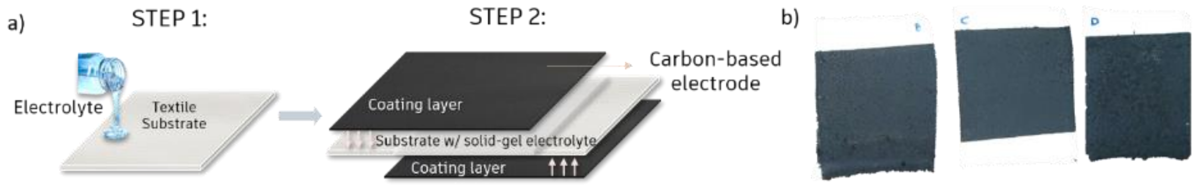

Fig.1. a) Schematic representation of the development of thinner TCSC devices using only one substrate. b) As-produced devices by different coating techniques.

The approach used for electrolyte application influenced how the electrode was integrated into the substrate and the electrochemical performance of the resulting TCSCs. The device with the lowest equivalent series resistance was the one produced by coating (76.6 Ω). Regarding the capacitance, the device produced by drop-coating reached 4.49 mF cm^{-2}, emerging as the most efficient of this study. In conclusion, the one-substrate configuration for TCSCs in textiles is a notable development, potentially leading to more efficient, flexible, and lightweight self-sustaining smart textile technologies. The thermal charging tests are ongoing for the three devices.

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References

[1] J. S. Teixeira *et al*., Dalton Trans., 2021, 50, 9983-1003.
[2] a) R. S. Costa *et al.*, J. Power Sources, 2023, 587; b) J.S. Teixeira *et al.*, J. Chem. Eng., 2021, 426.

Enhancing the electrochemical performance of electrochromic textile supercapacitors using PEDOT:PSS and oxidized MWCNTs

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The critical energy transition involves shifting from fossil fuel-based energy systems to renewable sources and advancing clean energy technologies for a sustainable future. Supercapacitors are a promising energy storage solution due to their long cycle life, high power density and fast charging. A present challenge relies on the development of multifunctional supercapacitors with sensing properties for real-time monitoring of energy consumption. In response to this challenge, electrochromic supercapacitors (ECSCs) are emerging bifunctional devices that integrate the energy storage functionality with the ability to reversibly change color under an applied potential [1].

In this study, symmetric and asymmetric ECSC devices were developed on cotton textile coated with the electrically-conductive electrochromic polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and oxidized multiwalled carbon nanotubes (CNT-O) as electrode materials. The devices were assembled using gel polymer electrolytes, which have high ionic conductivity, flexibility and enable reaching wider potential windows, making them suitable for flexible devices, unlike liquid electrolytes that operate at smaller potential windows [2]. The electrochemical performance of the devices was investigated by electrochemical impedance spectroscopy, cyclic voltammetry and galvanostatic charge/discharge measurements.

All the developed flexible devices could successfully store energy. Concerning the electrochromic properties, the symmetric device based on PEDOT:PSS and the asymmetric device (Fig. 1) showed the most significant color change for potentials higher than |±1.2| V. The asymmetric ECSC presented the best energy storage properties due to the combination of CNT-O-coated electrode with PEDOT:PSS-coated electrode, reaching 23% higher areal capacitance and 41% higher energy density than the symmetric ECSC device based on PEDOT:PSS.
This research enabled the development of textile-based devices with supercapacitive and electrochromic characteristics for future wearable electronic applications, such as healthcare monitoring and flexible electronic displays.

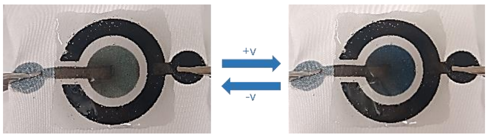

Fig.1. Asymmetric ECSC textile developed using PEDOT:PSS and CNT-O.

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References

[1] Z. Zhao, K. Xia, Y. Hou, Q. Zhang, Z. Ye and J. Lu, *Chemical Society Reviews*, 2021, **50**, 12702-12743.
[2] M. Kotobuki, in Polymer Electrolytes: Characterization Techniques and Energy Applications, ed. A. K. A. TanWinie, and Sabu Thomas, by Wiley-VCH Verlag GmbH & Co. KGaA, 2020.

Carbon supported electrocatalysts for cathode in PEMEL

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Energy demand keeps increasing and is expected to continue with the same tendency, along with population growth. Thus, shifting to green energy production methods becomes necessary to meet demand and comply with carbon neutrality policies. Green hydrogen [1] can be obtained through prominent PEMEL (proton exchange membrane electrolyser) technology allows compact and high-power density electrolysers, using platinum group metals (PGM) as catalysts, making it an expensive technology [2]. Besides, PGM belongs to the critical raw materials (CRM) list, making deploying greener materials even more important [2]. Although the system is only fed with pH-neutral water, the nature of the proton exchange membrane (PEM) makes the water circulating during operation acidic (pH range 3.4-5.6) [3,4]. Thus, besides the obvious high electrochemical activity, catalysts implemented need to be stable in acidic conditions. That is why state-of-the-art catalysts for PEMEL depend on PGM – they present the best relationship between activity and stability under acidic conditions [5]. The research community is making efforts to replace these PGM for cheaper and more sustainable catalysts. To replace the Pt used in the hydrogen evolution reaction (HER), use of transition metal phosphides (TMP) to catalyse the HER is a common approach. These catalysts can be obtained by impregnation of carbon support with solution of metal nitrate followed by calcination. Posterior step is performed to phosphorise the carbon supported metal, obtaining a TMP supported on carbon. In this work, different samples of TMP supported on Vulcan carbon were prepared. Samples with different loadings of metal (iron) were prepared and other phosphorization methods were compared to the red phosphor method. The samples were characterised and electrochemically tested in a simple three-electrode configuration with acidic electrolyte (0.5 M H_2SO_4) since the goal is to screen different catalysts to be implemented in PEMEL. In the future, the best performing catalysts will be coated in a Nafion membrane and tested in a lab-scale PEMEL with active area of 4 cm^2.

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References

[1] IEA, "The Future of Hydrogen," 2019.
[2] European Commission, "Critical Raw Materials Act." [Online]. Available: Critical Raw Materials Act
[3] L. Liu, "Platinum group metal free nano-catalysts for proton exchange membrane water electrolysis," *Current Opinion in Chemical Engineering*, vol. 34. Elsevier Ltd, Dec. 01, 2021. doi: 10.1016/j.coche.2021.100743.
[4] M. Paidar, V. Fateev, and K. Bouzek, "Membrane electrolysis-History, current status and perspective," 2016, doi: 10.1016/j.electacta.2016.05.209.
[5] M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, "A comprehensive review on PEM water electrolysis," *International Journal of Hydrogen Energy*, vol. 38, no. 12. pp. 4901–4934, Apr. 22, 2013. doi: 10.1016/j.ijhydene.2013.01.151.

Transition metal-doped CNT as bifunctional oxygen electrocatalysts

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The negative impacts of fossil fuels on our ecosystems and the growing global energy demand have accelerated the need to employ renewable sources-based technologies to generate electricity. Nowadays, the use of hydrogen as an energy vector is one of the hottest research topics towards achieving a sustainable future and one of the main strategies of the European Commission to achieve climate neutrality [1]. Therefore, hydrogen-based devices play a crucial part in this matter and are required to be optimized to ensure their industrial viability. Accordingly, the unitized regenerative fuel cell (URFC) presents itself as one of the most attractive alternatives to employ hydrogen as an energy vector. This device is comprised of a fuel cell and an electrolyzer, which allows the electrolysis of water to be carried out when the electrical energy production is higher than its demand and, inversely, reconverting the resulting reactants into water and electricity when the renewable energy production is unable to suppress the energy requirements. Nonetheless, the compartmentalization of the URFC into two different pairs of reactions leads to the need for bifunctional catalysts for each pair. The oxygen pair of reactions, oxygen reduction and evolution (ORR and OER, respectively), presents the most sluggish kinetics in comparison to the hydrogen pair and, consequently, requires more investigation. This drawback is usually surpassed by using noble metal electrocatalysts that are scarce and expensive. Therefore, the proper design of widely available and low-cost carbon electrocatalysts can be an interesting and important alternative to reduce the operational costs of the URFC. Moreover, the modification of the material's chemical properties by incorporating transition metals is crucial to enhance the electroactivity of the catalyst. Considering our previous investigations, the use of iron phthalocyanine (FePc) towards ORR and Ni or Co species towards OER has led to individually high electroactivities towards each reaction, whereas the simultaneous presence of FePc and Ni or Co on the same carbon support has led to remarkable bifunctional oxygen electrocatalytic performances [2, 3]. Therefore, the preparation of bimetallic- and trimetallic-doped carbon nanotubes (CNT) derived from FePc, cobalt nitrate, and/or nickel nitrate was studied towards the oxygen reactions. The bifunctionality features of the optimized electrocatalyst are among the best ever reported for carbon-based electrocatalysts and largely surpassed those of conventional noble metal-containing electrocatalysts, making it a good candidate for upscale testing in more industrially relevant applications.

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References

[1] T.M. Gulotta, R. Salomone, F. Lanuzza, G. Saija, G. Mondello, G. Ioppolo, Environmental Impact Assessment Review, 92 (2022) 106698.
[2] R.G. Morais, N. Rey-Raap, J.L. Figueiredo, M.F.R. Pereira, Catalysis Today, (2023) 114057.
[3] R.G. Morais, N. Rey-Raap, J.L. Figueiredo, M.F.R. Pereira, Applied Surface Science, 572 (2022) 151459.

Catalytic applications of N-doped Pd-supported biochar: Haloarene aminocarbonylation and electroreduction of H_2 and O_2

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Biochar has arisen as a promising alternative to conventional carbon materials, such as graphene, carbon nanotubes and activated carbon. Its renewable feedstock origin and low production cost makes it more a sustainable option than fossil fuel derived materials [1]. Furthermore, biochars are generally rich in surface functional groups, which can help anchoring metal particles into their surface without requiring any additional functional step [1]. Indeed, several metal-functionalized biochar catalysts have been reported in the last decades, with a wide range of applications, namely in organic synthesis, biorefinery processes, electrochemical reactions and supercapacitors [1].

The chemical composition, morphology and physical-chemical properties of biochar are reportedly dependent on the choice of the biomass feedstock [1]. Crustacean shells, rich in chitin (a biopolymer containing a high content of N), proteins and minerals (mainly $CaCO_3$) [2,3], are specially promising, as the heteroatoms are mostly preserved during the synthesis and the removal of $CaCO_3$, acting as self-template, lead to the formation of highly porous structures.

Herein, we describe the preparation of shrimp shells-derived biochar through pyrolysis and doping with urea *via* ball milling, and its use as carbon support for the immobilization of palladium by a wet impregnation approach (Pd/N-BCH). The versatility of the obtained material was then successfully demonstrated in: a) catalytic aminocarbonylation of haloarenes for the synthesis of aromatic amides [5]; and, b) energy-related electrochemical processes: hydrogen reduction reaction (HER) and oxygen reduction reaction (ORR), both critical parts in energy conversion devices (e.g. fuel cells and metal-air batteries) [4]. Pd/N-BCH achieved a E_{onset} of 0.81 V vs. RHE and j_L of -3.70 mA cm^{-2} for ORR, as well as good selectivity for the direct reduction to water; in HER, it showed a η_{10} of only 274 mV. In the catalytic aminocarbonylation of iodobenzene, the Pd/N-BCH catalyst, when using xantphos as P ligand, showed high activity and selectivity, with up to a 99% conversion and full selectivity for the carboxamide product. Even in the absence of any P ligand, the catalyst presented moderate activity (30% conversion) achieving both carboxamide (ca. 55%) and ketoamide product (ca. 45%). Therefore, the N-doped Pd-supported biochar showed great potential in a wide array of catalytic processes.

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References

[1] R. Ramos, V. K. Abdelkader-Fernández, R. Matos, A. F. Peixoto, D. M. Fernandes, Catalysts, 12 (2022) 207.
[2] D. Zhao, W. Huang, N. Guo, S. Zhang, C. Xue, X. Mao, Polymers, 11(3) (2019) 409.
[3] Y. Ding, S. Huang, Y. Sun, Y. Li, L. Zhu, S. Wang, ChemElectroChem, 8 (2021) 3745.
[4] C. Freire, D. M. Fernandes, M. Nunes, V. K. Abdelkader, ChemCatChem, 10 (2018) 1703-1730.
[5] L. Damas, F. M. S. Rodrigues, A. C. S. Gonzalez, R. M. B. Carrilho, M. Pineiro, M. M. Pereira, J. Organomet. Chem. 923 (2020) 121417.

Effect of heteroatom doping in biochar's catalytic performance towards oxygen electroreduction

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Electrochemical energy conversion devices such as fuel cells and metal-air batteries have arisen as promising alternatives to fossil fuels combustion. However, both technologies rely on several electrochemical processes, including oxygen reduction reaction (ORR), whose sluggish kinetics and large overpotentials hinders their practical application [1]. These limitations can be overcome by the development of highly effective electrocatalysts.

While currently Pt-based materials are considered the state-of-the-art electrocatalysts towards ORR, heteroatom-doped carbon catalysts arose as promising precious metal-free alternatives [2]. Recently, carbon materials obtained from the pyrolysis of biomass, known as biochars, have attracted interest as highly sustainable catalysts, due to their tunable physical-chemical properties, renewable feedstock, and low production cost [3]. Shrimp shells derived biochars, in particular, have very interesting electrocatalytic properties, originated from the feedstock natural abundance in heteroatoms (e.g. N, S, P) [4].

Herein, N doped and N,S co-doped biochars were prepared through a simple three step route, involving (i) the pyrolysis of shrimp shell waste, (ii) solventless ball milling with the selected dopant and (iii) a second pyrolysis. In order to analyse the effect of different heteroatom sources on the electrocatalytic properties of our biochars, four different N or N,S sources were used: N_6, SN_6, S_3N_2 and S_3N_3. The biochar doped with S_3N_3 achieved the most promising results, obtaining the most positive onset potential (E_{onset}=0.90 V vs. RHE), the highest diffusion-limited current density (j_L=-3.49 mA cm^{-2}) and a number of electrons transferred per O_2 molecule very close to 4 (n_{O2} = 3.62), indicating an excellent selectivity for the direct O_2 reduction to H_2O. Indeed, this material obtained n_{O2} slightly higher than the state-of-the-art catalyst, Pt/C; although the E_{onset} and j_L still need some improvement, it is important to consider that our catalyst is not only completely metal-free but also derived from a common waste.

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References

[1] C. Freire, D. M. Fernandes, M. Nunes and V. K. Abdelkader, ChemCatChem, 10 (2018) 1703-1730.
[2] J. Quílez-Bermejo, E. Morallón, D. Cazorla-Amorós, Carbon, 165 (2020) 434-454.
[3] R. Ramos, V. K. Abdelkader-Fernández, R. Matos, A. F. Peixoto, D. M. Fernandes, Catalysts, 12 (2022) 207.
[4] Y. Ding, S. Huang, Y. Sun, Y. Li, L. Zhu, S. Wang, ChemElectroChem, 8 (2021) 3745.

Composite fibers with high lignin content as precursors for carbon fibers

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Lignin is the second most abundant carbon-based material in nature, and is a residue produced in large scale by the pulp and paper industry [1]. The chemical structure of lignin is complex, rich in aromatic macromolecules based on the reaction of three monolignols, originating different functional groups, isomers and chirality, variations in molecular weight, presence of rigid and soft molecular chain segments, impurities, that hampers the prediction of lignin properties [2]. The highly aromatic nature of lignin makes it a potential source for graphite-based materials such as carbon fibres [3].

The objective of this work is to characterize a softwood lignin in terms of its chemistry and thermal properties, to produce composite fibres with high lignin content and a recycled polymer, and to study the fibre thermal stabilization process, in order to evaluate its potential for further production of carbon fibres.

Two polymers were selected for this study, namely glycol-modified polyethylene terephthalate (PET-G) and a blend of polycarbonate with acrylonitrile-butadiene-styrene (PC/ABS). Softwood lignin was acquired from West Fraser, Canada. The polymers were mixed with lignin at high lignin contents (50-60 wt.%) by melt mixing using twin screw extrusion. Composite filaments were produced and characterized by Infrared and Raman spectroscopies, as well as mechanical testing by dynamic mechanical analysis (DMA). The filaments were tested as produced and after thermal stabilization, carried out in air under tension.

Spectroscopic analysis showed that, typically above 250 °C, the chemical nature and physical structure of the lignin-rich composite fibres begin to change, increasing the aromatic content. The mechanical properties such as the storage modulus increased after the thermal stabilization process.

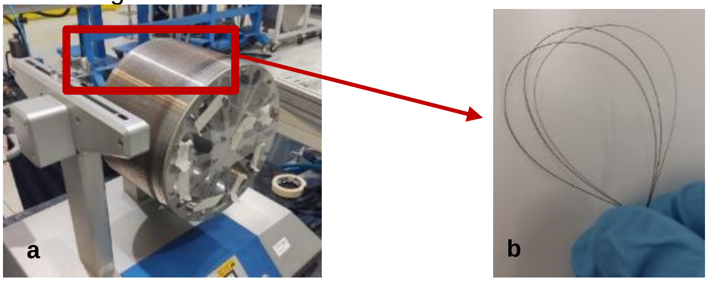

Fig.1. (a) PET-G/Lignin green fibers after the extrusion process; (b) PET-G/Lignin green fibers.

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References

[1] Mahendra Thunga, Keke Chen, David Grewell, Michael R. Kessler,
Bio-renewable precursor fibers from lignin/polylactide blends for conversion to carbon fibers, Carbon, Volume 68, 2014, Pages 159-166.
[2] Bostan, L., Hosseinaei, O., Fourné, R., & Herrmann, A. S., Upscaling of lignin precursor melt spinning by bicomponent spinning and its use for carbon fibre production, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences. 379. 20200334. 10.1098/rsta.2020.0334., 2021.
[3] Wang, S., Bai, J., Innocent, M. T., Wang, Q., Xiang, H., Tang, J., & Zhu, M., Lignin-based carbon fibers: Formation, modification and potential applications, Green Energy & Environment, 2021.

The effect of MWCNT modifications and polymeric pastes in the EMI shielding properties of coated fabrics

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The widespread use of wireless technologies and electromagnetic waves has raised concerns about long-term health effects and electromagnetic interference [1]. The exploration of carbon-based materials for the development of advanced electromagnetic interference (EMI) shields has become a focal point for researchers [2]. The key to developing efficient EMI shields from carbon materials lies in advancing their electrical conductivity and meticulously fine-tuning their physical and chemical properties [3]. In this study, modified multi-walled carbon nanotubes (MWCNT) were prepared through i) ball-milling treatments, targeting structural defects (MWNCT-BM), ii) N-doping through ball-milling MWCNT with a nitrogen precursor, followed by thermal treatment (MWCNT@N) and iii) acidic oxidation treatment to incorporate oxygen-based groups on the MWCNT's surface (MWCNT-O). Then, the modified MWCNT were dispersed in two different polymeric matrixes, polyurethane (PU) or poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), to create coating inks for fabric substrates. Comparing PEDOT_PSS/MWCNT-based coated fabrics with PU/MWCNT-based, an increase of ±20 dB of SE was observed. PEDOT:PSS offers better results than PU regarding the MWCNT dispersion onto the polymeric matrix, providing homogenous coatings and due to its high electrical conductivity, when combined with MWCNT-BM or MWCNT@N, the EMI shielding capability was increased. The same highlighted two coated fabrics achieved SE values above 30 dB, which makes them promise to the healthcare textile industry since they are classified as 'excellent' considering the Committee for Conformity Assessment on Accreditation and Certification of Functional and Technical Textiles classifications [4].

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References

[1] National Cancer Institute. https://www.cancer.gov/about-cancer/causes-prevention/risk/radiation/cell-phones-fact-sheet, 2018
[2] Meng, F., Wang, H. et al. Composites Part B: Engineering. 137 (2018) p. 260-277
[3] Chen, C., Bao, S., et al. Applied Surface Science. 467-468 (2019) p. 836-843
[4] TTS-FA-003, Test Method of Specified Requirements of Electromagnetic Shielding Textiles. 2005. p. 1-4

High performance thermoplastic composites

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Materials used in aerospace and spacecrafts are subjected to extreme environments. To meet these requirements, it’s crucial to develop materials that offer multifunctionality and superior performance, under severe conditions, such as strength, durability and effective electromagnetic shielding.

High-performance thermoplastics are attractive for these applications and provide a great blend of properties that include light weight, high temperature resistance and structural integrity. Thermoplastic composites are used extensively in the aerospace field for structural components, offering an alternative to heavier traditional materials [1;2]. These composites also provide a time-cost efficient production, desirable for these industries, being more advantageous than thermoset-based composites [2].

Due to the outstanding properties of carbon-based materials, the purpose of this study is to use them as reinforcing agents for the development of high-performance thermoplastic composites with enhanced strength, stiffness, and thermal stability. The composites will be produced in a twin-screw extruder, and optimized to ensure an effective dispersion of fillers in the polymer matrix and hence, their reinforcing effect.

References

[1] J. Lynch, Journal of the Science and Technology Organization, 2 (2020) 18-28.
[2] B.Y. Zeyrek, B. Aydogan, E. Dilekcan, et al, Int J Eng Tech & Inf., 3 (2022), 1–6.

Advanced Bi-Component Flexible MWCNT Composite for Smart Textile Applications

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Smart textiles mark a significant technological advancement, but their development must balance traditional textile properties with electronic features [1-3]. This study introduces a flexible, and electrically conductive composite material to meet this challenge. The primary aim was to create a masterbatch combining multi-walled carbon nanotubes (MWCNTs), polypropylene (PP), and thermoplastic elastomer (TPE), optimized for conductivity and flexibility. This blend, suitable for bi-component extrusion processes, exemplifies the role of advanced materials in combining electrical conductivity, mechanical flexibility, and processability, essential for wearable technology.

The masterbatch optimization consisted of balancing MWCNT (2.5, 5, 7.5, and 10 wt.%) and TPE (0, 25, and 50 wt.%) on a PP matrix. The electrical percolation threshold was found between 2.5 and 5 wt.%, with electrical resistivity ranging from (7.64±4.03)104 to (1.15±0.10)10-1 Ω.m. A 25 wt.% TPE addition improved the samples' flexibility, while 50 wt.% TPE decreased tensile strength and impeded the masterbatch cutting process.

The final stage involved integrating the composite filament, with a 5% MWCNT/PP/TPE core and a TPE sheath, into a triboelectric impact detection sensor. This sensor, responding to contact and separation, produced an output voltage of approximately 5 V peak-to-peak per filament and 15 V peak-to-peak with five filaments, under a 100 N force over 78.54 cm². This result underscores the material's potential in smart textiles, representing a significant advancement in merging textile properties with electronic functionalities.

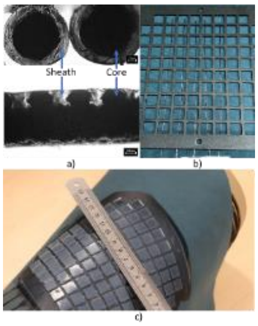

Fig.1. a) Bi-component cross section before and after hot pressing. b) lamination of the filaments on a textile structure and metallic mold for the silicone rubber. c) Triboelectric sensors with 5 laminated filaments.

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References

[1] Mahesh, G., & Sornapudi, S. (2017). Techniques and application of smart textiles. Int. J. Comput. Sci., 5, 10.
[2] S. Maity, K. Singha, and P. Pandit, “Advanced applications of green materials in wearable e-textiles,” in Applications of Advanced Green Materials, Elsevier, 2021, pp. 239–263.
[3] L. Van Langenhove, Smart textiles for medicine and healthcare: materials, systems and applications. Elsevier, 2007.

Analysis of the carbon produced by Ni/Al_2O_3-SiO_2 catalytic films in methane splitting reaction

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Catalytic methane splitting (CMS) emerges as a clean alternative to produce hydrogen, allowing a swift and cost-effective energy decarbonization pathway. This reaction produces hydrogen and multi-walled carbon nanotubes (MWCNT) from methane: $\mathrm{CH_4(g)} \rightleftharpoons \mathrm{2H_2(g)} + \mathrm{C(s)}$. CMS is widely accepted to be structure-sensitive over metal surfaces, requiring the use of nanoparticles, stabilized on a ceramic support, to catalyse the reaction [1]. Although hydrogen is seen as the main product of this reaction, the formation of highly graphitic carbon materials would add commercial value to the process, allowing for greater competitiveness and industrialization potential. In this sense, films of Ni/Al_2O_3-SiO_2 (commercial catalyst) were deposited by screen printing on glass substrates and tested in a planar slab reactor, operating at 550 °C and room pressure. During the methane splitting reaction, catalytic loads between 1.63-2.12 $\mathrm{mg_{cat}{\cdot}cm^{-2}}$ were assessed, and the carbon produced was analyzed by Raman (Figure 1). By deconvoluting the spectra obtained, it was observed that the I_D/I_G ratio increases with the catalytic load of the sample, indicating that the carbon generated becomes more amorphous at higher catalyst loadings. This effect has been assigned to stereochemical factors since there is less space for the carbon to grow under higher catalyst loadings, and consequently, growth occurs in a more disordered way. In addition, it was observed that the ratio I_{2D}/I_G was directly related to the catalyst load, with I_{2D}/I_G increasing with the load. Higher I_{2D}/I_G values are related to carbon nanotubes with fewer layers, indicating that with limited space to grow, carbon allotropes nucleate fewer graphite sheets [2]. An additional cyclic regeneration test, through periodical interfacial hydrogenation steps with hydrogen, was also carried out [3]. It was observed that beyond the interface catalyst/carbon, bulk carbon becomes more amorphous after contact with the hydrogen.

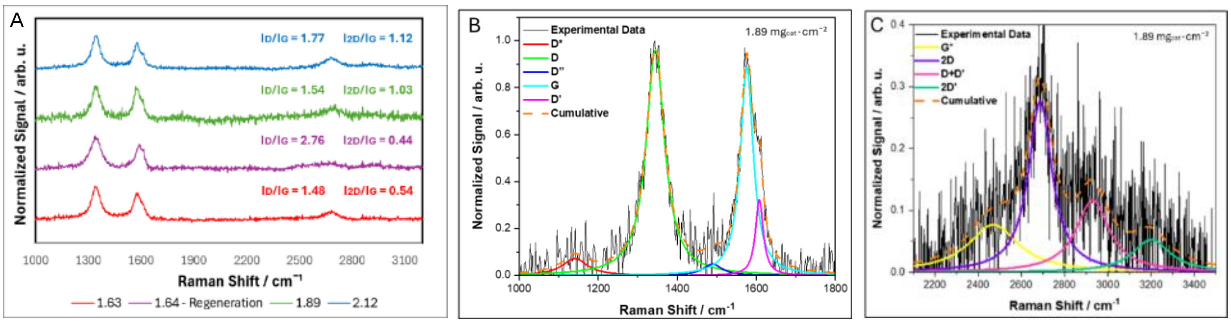

Figure 4 – Raman spectrum of the carbon produced during CMS at 550 °C and 1 bar: A – spectrum for different catalytic loadings; B and C – peak deconvolution for the carbon generated by the 1.89 $\mathrm{mg_{cat}{\cdot}cm^{-2}}$ catalytic film.

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References

[1] I. Gonzalez et al., J Phys Chem, vol. 116, no. 40, pp. 21577-21587, 2012/10/11 2012.
[2] A. Reina et al., Nano Lett, vol. 9, no. 1, pp. 30-35, 2009/01/14 2009.
[3] L. Alves, V. Pereira, et al., Renew Sustain Energy Rev, vol. 137, p. 110465, 2021/03/01.

Comparing the thermoelectric properties of polypropylene composites melt-processed with Pyrograf® III carbon nanofibers

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This work compares the electrical conductivity σ (T) and Seebeck coefficient S (T) of melt-processed polypropylene (PP) composites filled with 5 wt. % of two Pyrograf® III carbon nanofibers (PR 19 LHT XT and PR 24 LHT XT). Despite both carbon nanofiber (CNF) grades show similar σ (T) and S (T) dependencies, whereby interestingly S (T) has negative values, the S (T) of their derivative PP/CNF19 and PP/CNF24 polymer composites are not analogous. Thus, while the S (T) of PR 19 LHT XT CNFs governs the S (T) of its corresponding PP/CNF19 polymer composite, this does not happen for the PP/CNF24 polymer composite, which its S (T) differs from the S (T) observed for PR 24 LHT XT CNFs. To understand this, the σ (T) and S (T) of all them have been analysed with the help of theoretical models to aim to understand the role of these commercial CNFs on the transport properties of the conducting polymer composites produced from them [1-4].

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References

[1] Paleo AJ, Vieira EMF, Wan K, Bondarchuk O, Cerqueira MF, Goncalves LM, et al., Carbon, 150 (2019) 408-16.
[2] Paleo AJ, Krause B, Cerqueira MF, Melle-Franco M, Pötschke P, Rocha AM, Polymer Journal, 53(10) (2021) 1145-52.
[3] Paleo AJ, Krause B, Cerqueira MF, Muñoz E, Pötschke P, Rocha AM, Polymers, 14(2) (2022) 269.
[4] Paleo AJ, Krause B, Mendes AR, Tavares CJ, Cerqueira MF, Muñoz E, et al., Journal of Composites Science, 7(4) (2023) 173.

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III REUNIÃO DO GRUPO DO CARBONO

LIVRO DE RESUMOS

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