Membrane Materials - Modification and Separation (M3-S) 3rd conference

“Applied polymers, nanomaterials, membranes, and composites”

27th – 30th May 2025

Programme Booklet

Edited by: Dagmara Bajer,
Anna Katafias, and Jolanta Kowalonek

Toruń 2025

Membrane Materials - Modification and Separation (M3-S) Conference

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Conference Venue

Faculty of Chemistry, NCU in Toruń
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Invited Lecturers

Suzana NUNES
King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
Molecular separation by pervaporation and nanofiltration with thin composite membranes

Frank BLOCKHUYS
Structural Chemistry Group, University of Antwerp, Antwerp, Belgium
Surface Modification of the Group 4 Metal Oxides: Structure, Properties and Applications of Phosphonic-Acid-Modified Titania

Athanasios CHATZITAKIS
Department of Chemistry, Centre of Materials Science and Nanotechnology, University of Oslo, Norway
Advanced catalysts for electrochemical energy conversion

CONFERENCE PROGRAMME

Academic Centre for Culture and Art “**Od Nowa**” - 37a, Gagarin Street, 87-100 Toruń, Poland

27th May 2025 (Tuesday)

8.00 – 10.00	**Registration of participants**
8.45 – 9.00	**Opening**
Session 1	**Chair persons: Wojciech Kujawski, Suzana Nunes**
9.00 – 9.20	SL01 – Short lecture **F. Lipnizki** *Challenges in Developing Industrial Membranes*
9.20 – 9.40	SL02 – Short lecture ***Young Researchers Competition*** **L. F. P. Carvalho*, H. K. Balakrishnan, H. A. Arafat, L. F. Dumée, K. Askar** *3D Printing Antifouling Properties into Nanoporous Membranes*
9.40 – 10.00	SL03 – Short lecture ***Young Researchers Competition*** **O.Al-Yafiee*, P. Kumari, G. N Karanikolos, Ch. Castel, E. Favre, L. F. Dumée** *Graphene Doped Membranes for Direct Air Capture (m-DAC) of* CO_2
10.00 – 10.20	SL04 – Short lecture **S. R Popuri*, K. C Mason, C. Wang, W. Kujawski** *Effect of Synthesized Multicarboxylic Copolymer on Chitosan and Cellulose Acetate Blend Membranes for Pervaporation and Microfiltration Applications*
10.20 – 10.40	SL05 – Short lecture ***Young Researchers Competition*** **S. Kroß*, M. Ulbricht** *Polymeric Fluorine-Free Ionomers and Their Complexes with Polyelectrolytes for Thin-Film Composite Nanofiltration Membranes*
10.40 – 11.15	**COFFEE BREAK**
Session 2	**Chair persons: Frank Lipnizki, Mathias Ulbricht**
11.15 – 12.00	PL1 – Plenary lecture **S. P. Nunes*, R. Esposito, B. Alhazmi, M. Abdulhamid, G. Szekely, A. Volkov, G. Ignacz, M. Di Vincenzo, M. Hedhili, L. Upadhyaya** *Molecular Separation by Pervaporation and Nanofiltration with Thin Composite Membranes*
12.00 – 12.30	KL01 – Keynote lecture **P. Luis** *An Overview of Different Membranes for Application in Pervaporation and Reactive Pervaporation*
12.30 – 12.50	SL06 – Short lecture ***Young Researchers Competition*** **I. Akshara*, L. Patricia** *Integrating Separation and Reaction in Pervaporation for Glycerol Carbonate Production*
12.50 – 14.00	**LUNCH**
Session 3	**Chair persons: Jolanta Kowalonek, Beata Malczewska**
14.00 – 14.30	KL02 – Keynote lecture **S. Vicini*, S. Pettineo, M. Alloisio, M. Castellano** *Biopolymeric Membranes and Gels for Advanced Applications*

14.30 – 14.50	SL07 – Short lecture **D. Bajer*, J. Kowalonek** *The Effect of UV Radiation on Starch-Rose Bengal Biocomposites*
14.50 – 15.10	SL08 – Short lecture **H. Nakatsuji*, M. Inoue, M. Liu, H. Nishihara** *Development of High-Strength Honeycomb Structural Polymer Composites*
15.10 – 15.40	**COFFEE BREAK**
Session 4	**Chair persons: Anna Siekierka, Takeharu Yoshii**
15.40 – 16.00	SL09 – Short lecture ***Young Researchers Competition*** **M. Zhai*, F. Moghadam, K. Li** *Facile orientation control of MOF-303 hollow fiber membranes by a dual-source seeding method*
16.00 – 16.20	SL10 – Short lecture **A. J. Tasiopoulos*, L. K. Komodiki, N. Panagiotou, H. Serier-Brault, F.García Moscoso, J. J. Romero-Guerrero, J. María Pedrosa** *Modulation of the Temperature and Gas Sensing Properties of New Metal–Organic Frameworks based on Hexanuclear Rare Earth Secondary Building Units through Single-Crystal-to-Single-Crystal Transformation Reactions*
16.20 – 16.40	SL11 – Short lecture ***Young Researchers Competition*** **B. Hao*, X. Yue, X. Li, Kang Li** *Polyamide Membrane with the Interlayer of Sulfonated COF for Artemisinin Concentration*
19.00 – 21.00	**GET-TOGETHER PARTY** (Copernican Integration Centre, 16 Olszewskiego, street) – KOI– dinner with bonfire)
	28th May 2025 (Wednesday)
Session 5	**Chair persons: Halyna Bubela, Jacek Nowaczyk**
8.30 – 9.00	**Registration of participants**
9.00 – 9.45	PL2 – Plenary lecture **F. Blockhuys** *Surface Modification of the Group 4 Metal Oxides: Structure, Properties and Applications of Phosphonic-Acid-Modified Titania*
9.45 – 10.15	KL03 – Keynote lecture **T. Yoshii** *Synthesis, Analysis and Catalytic Applications of 3D Graphene Materials*
10.15 – 10.35	SL12 – Short lecture ***Young Researchers Competition*** **Z. Li*, F. Moghadam, K. Li** *Graphdiyne Membrane for Molecular Separations*
10.35 – 11.10	**COFFEE BREAK**
Session 6	**Chair persons: Anna Ilnicka, Anna Szymczyk**
11.10 – 11.40	KL04 – Keynote lecture **M. Ulbricht*, Z. Gao, J. Leichtweis, L. Fischer, A. Wittmar** *Polymer-enabled Pathways to Carbon-containing or based Materials for Catalysis*
11.40 – 12.00	SL13 – Short lecture **K. Cieciuch*, Julia Kolodziejczyk, A. Hryniewicka, J. Breczko, M. E. Plonska-Brzezinska**

	Covalent Triazine Frameworks in Electrochemistry: Unlocking New Possibilities for Energy Storage
12.00 – 12.20	SL14 – Short lecture **A. Siekierka*, P. Ratajczak** *Imine-based ionic covalent organic frameworks for transition metal ions capturing via hybrid capacitive deionization*
12.20 – 12.40	SL15 – Short lecture ***Young Researchers Competition*** **J. Kolodziejczyk*, A. Hryniewicka, Marta E. Plonska-Brzezinska** *Composites Containing of Carbon Nano-Onions and S-Doped Covalent Triazine Frameworks: Synthesis and Physicochemical Properties*
12.40 – 14.00	**LUNCH**
Session 7	**Chair persons: Simonas Ramanavičius, Athanasios Chatzitakis**
14.00 – 14.20	SL16 – Short lecture ***Young Researchers Competition*** **J. Čížek*, V. Jandová, P. Stanovský, Š. Hovorka, F. Yalcinkaya, M. Kohout, P. Izák** *Enantioselective Membranes Prepared by Ionic Interactions between Ion Exchange Membranes and Charged Cyclodextrins*
14.20 – 14.40	SL17 – Short lecture ***Young Researchers Competition*** **D. Gardenö*, J. Wieczorek, T. Weber, M. Kaspereit, K. Friess** *A New Possible Application for 2D Carbon-Based Membranes in the Ultrafiltration Process*
14.40 – 15.00	SL18 – Short lecture ***Young Researchers Competition*** **A. Lizée*, P. Loulergue, A. Szymczyk** *Electrokinetic Measurements: A New Approach for Membrane Wetting Characterization*
15.00 – 15.40	**COFFEE BREAK**
15.40 – 16.00	SL19 – Short lecture ***Young Researchers Competition*** **E. Ansari*, R. K. Abu Al-Rub, K. Askar, L. F. Dumee** *Versatile Electrodes for Green Hydrogen Production – Achieving Energy Transition from Any Water Source*
15.60 – 16.20	SL20 – Short lecture ***Young Researchers Competition*** **J. Nieminen*, L. Soto-Salcido, M. Reza Moradi, A. Valassaari, A. Pihlajamäki, M. Mänttäri** *Reconditioning of End-of-Life Desalination Membranes with Polyelectrolyte Coatings: Advances in Optimization and Scale-up*
	29th May 2025 (Thursday)
Session 8	**Chair persons: Halyna Bubela, Anna Ilnicka**
9:00 – 9.45	PL3 – Plenary lecture **A.Chatzitakis** *Advanced Catalysts for Electrochemical Energy Conversion*
9.45 – 10.15	KL05 – Keynote lecture **A. Szymczyk*, N. Lotti, F. Miketa, D. Puglia** *Novel Furan-based Polyesters with Outstanding Barrier Properties for Green and Sustainable Packaging Applications*
10.15 – 10.35	SL21 – Short lecture **L. Rozhdestvenska*, K. Kudelko, O. Palchik, Y. Dzyazko** *Polymer Membranes Modified with Multicomponent Nanocomposite*
10.35 – 11.00	**COFFEE BREAK**

Session 9	**Chair persons: Frank Blockhuys, Dagmara Bajer**
11.00 – 11.20	SL22 – Short lecture *Young Researchers Competition* **G. Linkaite*, M. Adeel Tariq, R. Raiseliene, A. Kareiva, I. Grigoraviciute** *Production of Biphasic Calcium Phosphate Granules from Gypsum Using Static and Rotational Methods*
11.20 – 11.40	SL23 – Short lecture **L. Gabrielyan*, A. Harutyunyan, A. Aghajanyan, L. Gabrielyan, W. Kujawski** *Comparative Analysis of Antibacterial Properties of Silver Nanoparticles Synthesized Using "Green Biomass" of Phototrophic Organisms*
11.40 – 12.00	SL24 – Short lecture **S. Ramanavicius***, **S. Ali, K. Sobol, I. Navitski, G. Paulikaite, S. Zukauskas, A. Popov, O. Gogotsi, A. Ramanavicius, A. Ramanaviciene** *Synthesis of $Ti_3C_2T_x$ MXenes for Wastewater Treatment and Water Quality Monitoring*
12.00 – 12.20	SL25 – Short lecture *Young Researchers Competition* **R. Vevers*, A. Kulkarni, K. Schlenstedt, A. Seifert, J. Meier-Haack, L. Mezule** *Advanced Evaluation of Anti-Biofouling Potential of ZnO NP Doped Dual-Layer Photocatalytic Filtration Membranes*
12.20 – 12.40	SL26 – Short lecture **A. Katafias*, Y. Rao Pateda, O. Impert, E. Rakovsky, R. van Eldik** *Peroxidase Mimicking Activity of Nano-Size Ru(edta) Complex at the Solid-Liquid Interface*
12.40 – 13.00	SL27 – Short lecture *Young Researchers Competition* **M. Soriano*, K. Jafari, X. Zhang, D. Neagu** *Optimizing the Cobalt Content of Nanoparticle-Supported Catalysts for the Oxygen Evolution Reaction (OER)*
13.00 – 14.00	**LUNCH**
Session 10	**Chair persons: Anna Katafias, Lilit Gabrielyan**
14.00 – 14.20	SL28 – Short lecture *Young Researchers Competition* **T. Kokkinou, E.Mitrousi*, A.Chatzitakis, S.Sotiropoulos** *Amorphous Anodized Porous Titania as IrO2 Substrates for the Electrochemical Oxygen Evolution Reaction*
14.20 – 14.40	SL29 – Short lecture **A. Hubina* S. Rogalsky** *Design of Polymer Ionic Liquids for Electrochemical Applications Using Click Chemistry Tools*
14.40 – 15.00	SL30– Short lecture *Young Researchers Competition* **A. Volz*, L. Fischer, M. Ulbricht** *Porous contactor membranes for catalytic H2 gas release from aqueous chemical storages*
16.00 – 19.00	**Workshop for NAWA scholars** (NCU, Faculty of Chemistry, 7 Gagarina street)

30th May 2025 (Friday)
Conference venue: NCU, Faculty of Chemistry, 7 Gagarina Street

Session 11	**Chair persons: Patricia Luis Alconero, Joanna Kujawa**
9.00 – 9.20	SL31– Short lecture **H. Bubela*, V.Konovalova, J. Kujawa, W. Kujawski** *Magnetically Responsive PVDF Membranes: Enhanced Modification for Water Purification and Protein Separation*
9.20 – 9.40	SL32– Short lecture **J. Kujawa*, R. Alawawdeh, F. Abdelaal, S. Al. Gharabli, W. Jankowski, W.Kujawski**

	PVDF Membranes Reinforced with Rare-Earth Oxides for High-Performance Separation Applications
9.40 – 10.00	SL33– Short lecture **R. E. Khalifa*, F. Mesbah, D. El Gayar, H.Farag, M. S. Mohy-Eldin, Z. Spitalsky** *A Novel, Performant, and Low-Cost Branched Side-Chain Grafted Cellulose Acetate Proton Exchange Membrane for Direct Methanol Fuel Cells*
10.00 – 11.40	**Poster session + COFFEE**
11.40 – 12.20	**CLOSING**
12.30 – 13.30	**LUNCH**

ABSTRACTS

Authors are fully responsible for the content of the abstracts.
No technical or language corrections were made during editing.

PLENARY LECTURES

Molecular separation by pervaporation and nanofiltration with thin composite membranes

S. P. Nunes[1,*], R. Esposito[1], B. Alhazmi[1], M. Abdulhamid[2], G. Szekely[1], A. Volkov[1], G. Ignacz[1], M. Di Vincenzo[1], M. Hedhili[1], L. Upadhyaya[1]

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Keywords: Pervaporation, nanofiltration, polyimide, polyamides

Molecular separations are essential steps in the chemical and pharmaceutical industry. Our group has been developing and engineering thin film composite membranes as flat sheet and hollow fibers targeting the separation of azeotropic solvent mixtures using pervaporation and complex low molecular weight molecular mixtures using organic solvent nanofiltration. Recent results will be presented and discussed. Examples of approaches are based on hollow fiber dip-coating with hydrophilic thin polyimide carboxyl-functionalized layers [1] and interfacial polymerization macrocyclic amines [2]. The solvent separations systems investigated by pervaporation were azeotropic mixtures with high industrial relevance such as methanol/toluene, methanol/methyl tert-butyl ether and ethanol/cyclohehane. The systems investigated by nanofiltration were multicomponent mixtures of pharmaceutical ingredients.

Acknowledgements: The work was financially supported by KAUST

References

[1] Esposito et al., J. Membr. Sci., 713, 123390 (2025).

[2] Alhazmi et al., Nature Comm., 15, 7151 (2024).

PL2 - PLENARY LECTURE

Surface Modification of the Group 4 Metal Oxides: Structure, Properties and Applications of Phosphonic-Acid-Modified Titania

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Keywords: Titania, Adsorbates, Surface interactions, Spectroscopy, Density functional theory

Metal oxides such as titania (TiO_2) and zirconia (ZrO_2) are of great interest due to their high mechanical and chemical stability, and the fact that they can be prepared in a large variety of nano-morphologies, each with unique physisochemical properties. As a result, these materials have been implemented in a number of different applications such as (photo)catalysis, and separation and sorption processes. In many of these, the performance is governed by specific surface interactions, which are, however, limited by the oxides' native surface chemistry in terms of diversity and specificity. One way to overcome this is to graft organic groups at the surface, leading to a large variety of new surface interactions. Surface grafting provides the ability to specifically tailor the surface properties for increased control and selectivity, designed according to the requirements of a particular application.

Organosilylation remains a very common grafting method (in particular on silica) but it is not really applicable to metal oxides, given the limited hydrolytic stability of the resulting M–O–Si–R connection. Organophosphonic acids (PAs) are a superior alternative for the grafting of metal oxides, leading to more stable M–O–P–R connections. PA grafting can be performed in water and organic solvents and the modification can be easily controlled by adjusting the reaction conditions. Furthermore, this method leads to (sub)monolayer coverage and keeps part of the surface available, and the presence of the latter, in addition to the organic functional groups, gives rise to unique physicochemical properties and behaviour.

Initially, PAs containing hydrocarbon chains were used and the impact of the synthesis conditions on the surface properties has been described, in addition to the long-term stability of these hybrid materials. More interesting, though, with an extension of the applicability and versatility to metal sorption, heterogeneous (photo)catalysis, enzyme immobilization and nano-electronics in mind, are PAs containing heteroatoms in their functional group, *e.g.*, nitrogen atoms in aminoalkyl- and sulfur atoms in mercaptoalkylphosphonic acids (an example is given in Figure 1). Obviously, the success of such applications depends on the availability of the heteroatomic functional groups and, consequently, understanding what influences this has become of great importance.

The current paper provides an overview of all aspects of the work on surface-modified titania performed during the past decade at the University of Antwerp, not only from an application point of view but also detailing the considerable effort that has been made to understand the materials at the atomic level, based on the results of a variety of physico-chemical characterisation methods as well as spectroscopic, spectrometric and computational techniques. A glimpse of the first results of our work on the oxides of the heavier Group 4 congeners (Zr and Hf) is also given.

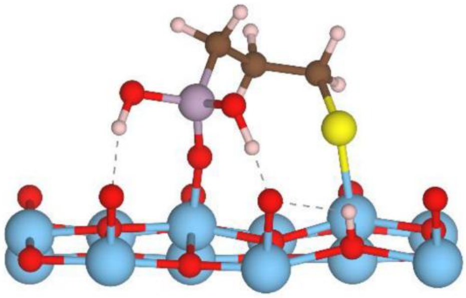

Figure 1. *Calculated geometry of monodentate-adsorbed (3-mercaptopropyl)phosphonic acid on anatase (101) with a dissociative S…Ti interaction.*

PL3 - PLENARY LECTURE

Advanced catalysts for electrochemical energy conversion

Athanasios Chatzitakis

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Catalysts form the backbone of our chemical industry with their applications ranging from catalyst in car exhausts, production of pharmaceuticals and therapeutics, for ammonia production to the production of hydrogen through water electrolysis. In several instances, catalysts face significant challenges in terms of efficiency, selectivity, stability, cost as well as sustainability. At UiO we are developing a technology platform with the main aim to address these challenges, but also provide catalyst materials with tunable catalytic functionalities through a base methodology. In this talk, a brief overview of such activities will be discussed.

KEYNOTE LECTURES

KL01 - KEYNOTE LECTURE

Biopolymeric Membranes and Gels for Advanced Applications

Silvia Vicini*, Simone Pettineo, Marina Alloisio, Maila Castellano
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Keywords: Electrospinning, Alginate, Agarose, Chitosan

In recent decades, natural polymers have garnered significant attention as potential substitutes for commonly used synthetic materials. Among these, polysaccharides have been extensively studied and employed due to their unique properties, such as non-toxicity, biodegradability, and biocompatibility.

Gels are widely present in everyday lives and are used in a broad range of applications, from food to the pharmaceutical and biomedical industries. Polysaccharides and in particular agar and gellan gels have gained prominence as cleaning tools in the conservation of Cultural Heritage, thanks to their versatility, low cost, and effectiveness. These gels can be easily applied to artwork and gently removed after an appropriate application time, allowing for better control of the cleaning process [1].

Recently electrospinning technique has emerged as an easy, fast and affordable approach for preparing nanofibrous membranes. This process involves applying a strong potential difference to create an electrically charged jet of polymer solution, leading to the formation of nano- or microfibers that are collected on a suitable surface. As a result, highly porous mats with a large specific surface area can be easily obtained. Nanofibrous mats have a wide range of applications. Their microstructure, which closely resembles the extracellular matrix, promotes human cell viability, making them ideal for biomedical applications. Additionally, these mats can be applied in fields such as artwork cleaning.

Polysaccharide-based membranes, made from alginate, agar, agarose, and chitosan, are prepared via electrospinning, using solutions and poly(ethylene oxide) as co-spinning agents [2]. Furthermore, polysaccharide-based nanocomposites are prepared with electrospinning. These nanofibrous mats possess antibacterial and antifungal properties, preventing biofilm formation and aiding disinfection, thanks to the incorporation of nanoparticles such as gold, silver, and zinc oxide, which are generated "in situ" through a bottom-up approach [3].

References

[1] Bertasa et al., Eur. Pol. J. 123 (2020) 109442

[2] A. Dodero et al., Carb. Polym. 235 (2020) 115976

[3] M. Castellano et al., J. Therm. Anal. Cal. 137 (2019) 767

Synthesis, Analysis and Catalytic Applications of 3D Graphene Materials

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Keywords: Graphene mesosponge, Temperature-programmed desorption, Ordered carbonaceous frameworks

Graphene is a remarkable two-dimensional carbon material composed of sp²-hybridized carbon atoms arranged in a hexagonal lattice. Known for its ultra-thin and lightweight nature, graphene exhibits exceptional properties such as high electrical conductivity, outstanding electron mobility, a large specific surface area, and superior thermal conductivity. In addition to the two-dimensional form, graphene-related nanostructures—such as zero-dimensional fullerenes and one-dimensional carbon nanotubes—exhibit distinct dimensional characteristics and functionalities. Recent progress in the design and synthesis of three-dimensional (3D) graphene-based architectures has opened new avenues for material innovation. One such material is the graphene mesosponge (GMS), synthesized via a templated chemical vapor deposition (CVD) process using thermally stable oxide nanoparticles such as Al_2O_3 and MgO as sacrificial hard templates [1]. Methane is employed as the carbon source, leading to the formation of one to two graphene layers on the template surfaces. After chemical removal of the templates, the resulting carbon mesosponge (CMS) features spherical mesopores. Subsequent high-temperature treatment at 1800 °C induces a graphene "zipping" reaction, which fuses the graphene fragments and significantly reduces edge-site density, ultimately yielding GMS. This process yields GMS, strongly reflecting the characteristic properties of graphene, such as high specific surface area, electrical conductivity, corrosion resistance, lightweight nature, and mechanical flexibility. It holds great potential for applications in various fields, including energy storage [2] and heat pumps [3]. Additionally, the presence of topological defects (e.g., 5- and 7-membered ring structures) was found to enhance catalytic activity, especially in Li–O_2 battery cathodes [4].

To evaluate these 3D graphene materials, we have established an ultra-high-temperature vacuum temperature-programmed desorption (TPD) technique [5, 6]. This method enables the quantification of edge sites and functional groups through the analysis of desorbed gases (e.g., H_2, CO, CO_2, H_2O) during controlled heating. From the desorption profiles, the number of edge sites can be estimated, allowing for the calculation of average graphene domain size. This approach revealed substantial domain growth and edge-site reduction during the transition from CMS to GMS. Furthermore, a recently developed TPD system capable of operating up to 2100 °C has enabled highly sensitive, qualitative and quantitative analysis of nitrogen species embedded in carbon frameworks, with detection sensitivity reaching down to the 10 ppm level [7, 8].

In parallel, 3D graphene-based porous carbons can also be synthesized via soft-template methods. A representative example is the development of ordered carbonaceous frameworks (OCFs), a novel class of carbon materials featuring three-dimensional structural order derived from the carbonization of metalloporphyrin crystals with polymerizable moieties [9-12]. Solid-state polymerization during heat treatment preserves the molecular-level structure of the precursor, resulting in graphene-based frameworks with regularly aligned single-atom metal sites. Due to their combination of high electrical conductivity, chemical/thermal stability, and atomic-level metal dispersion, OCFs serve as excellent platforms for electrocatalysis, including CO_2 reduction reactions.

References

[1] H. Nishihara *et al*., *Adv. Funct. Mater.*, **26**, 6418 (2016). [2] H. Nishihara *et al*., *Energy. Environ. Sci*., **12**, 1542 (2019). [3] H. Nishihara, *et al*., *Nat. Commun*., **10**, 2559 (2019). [4] W. Yu, T. Yoshii, H. Nishihara, *et al*., *Adv. Sci.*, **10**, 2300268 (2023). [5] K. Wakabayashi, T. Yoshii, H. Nishihara, *Carbon*, **210**, 118069 (2023). [6] T. Xia, T. Yoshii, H. Nishihara, *et al*., *Chem. Sci.*, **14**, 8448 (2023). [7] T. Yoshii, H. Nishihara, *et al*., *Chem*, **10**, 2450 (2024). [8] S. Shimizu, T. Yoshii, H. Nishihara, *et al*., *Chem. Sci.*, **15**, 10350 (2024). [9] H. Nishihara, *et al*., *Nat. Commun*., **8**, 109 (2017). [10] T. Yoshii, K. Chida, F. Tani, H. Nishihara, *Chem. Commun*., **58**, 3590 (2022). [11] K. Chida, T. Yoshii, H. Nishihara, *et al*., *Carbon*, **201**, 338 (2023). [12] K. Chida, T. Yoshii, H. Nishihara, *et al*., *Green Chem*., **25**, 8758 (2024).

Polymer-enabled Pathways to Carbon-containing or -based Materials for Catalysis

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Keywords: carbon materials; porous polymers; phase separation; electrocatalysis, photocatalysis

Catalysis is a key concept for the evolution of life and nowadays also essential for a wide range of industrial activities. The utilization of catalysts immobilized on suited solid supports, i.e. in the mode of heterogeneous catalysis, has several advantages, especially for processes that shall run continuously. Porous solid supports can be utilized to define and optimize the contact area between substrate and catalyst. Additional benefits can be expected from porous heterogeneous catalysts that can allow for flow-through of substrate because this can minimize mass transfer limitations for the catalytic conversion. In that context, the possibility to shape polymers, synthetic or biobased, into porous materials of the desired shape, flat-sheet or spherical particle, is of high interest. The extensive knowledge from the field of porous membrane fabrication via casting films of polymer solutions and subsequent controlled phase separation can be utilized for the preparation of porous catalytic materials. The focus of this presentation is on carbon materials as heterogeneous catalyst. One pathway is the straightforward fabrication of porous carbon-containing membranes for catalytic substrate conversion under flow-through conditions by using dope solutions containing the membrane polymer and the carbon material [2]. The other pathway the fabrication of porous particles by drop shaping *cum* phase separation in a coagulation bath from polymers that can subsequently be converted by controlled pyrolysis to carbon. The latter path is demonstrated for polyacrylonitrile [3] as well as from biopolymers or -materials such as spent coffee ground / chitosan or cellulose / chitosan mixtures [4,5]. Examples regarding material's functionality comprise photocatalysis in the context of advanced oxidation of micropollutants in water [2], or electrocatalysis, e.g. for the chemical utilization of carbon dioxide [3,4] or the production of hydrogen peroxide [5].

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Novel furan based polyesters with outstanding barrier properties for green and sustainable packaging applications

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Keywords: 2,4-furandicarboxylic acid, furan based polyesters, gas barrier properties, mechanical properties

The current objective of research especially in the field of food packaging is the prevention of environmental issues related to the production and use of plastic with the smart eco-design of biobased, single-component and easily recyclable or biodegradable polymers. 2,5-furandicarboxylic acid (FDCA) has appeared in recent years among the most relevant biobased chemical platforms to achieve this goal.

The extraordinary and versatile properties of biobased furan-based polyesters such as poly(alkylene furanoate)s [1-2] have been at the center of our attention within FURIOUS project, which aims to develop a sustainable polyesters having tuneable mechanical performance, to match the request of a flexible packaging resistant to gamma rays sterilization for biomedical sector and rigid packaging for electronics with high barrier properties to gases and humidity.

In our study, we focused on the eco-design of fully biobased polymers of FDCA, an emerging green building block, suitable for high-value packaging applications. It will be presented how by changing of the aliphatic diol in furan polyester or by copolymerization of with aliphatic polyesters [2-3], it is possible to tailor gas barrier properties and mechanical properties from rigid to flexible one and also ability to biodegradation.

Acknowledgements

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SHORT LECTURES

Challenges in developing industrial membranes

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Keywords: Membrane development, materials, fouling, cleaning

Most of the key membrane materials used in industry today were developed in the 1960s and 1970s. The dominant materials on the market include polysulfone, polyethersulfone, polyvinylidene fluoride (PVDF), and polyamide. These materials continue to be the backbone of membrane technologies, owing to their well-established performance, durability, and cost-effectiveness. However, despite significant advancements in membrane technology, the industry remains heavily reliant on these materials, primarily due to their proven track record in various applications.

The development of new industrial membranes presents several challenges beyond simply increasing flux and improving selectivity. One critical aspect is ensuring that membranes are compatible with standard cleaning methods, such as caustic and acid cleaning at elevated temperatures, which are commonly used in industrial settings. While these cleaning procedures are essential for maintaining membrane performance, they also contribute to a reduction in membrane lifespan, further complicating the development of more durable membranes.

Moreover, membrane stability is essential to ensure that the new membranes developed can be used effectively in standard module configurations, such as spiral wound and hollow fiber systems, which are widely employed in large-scale applications. Another important consideration is ensuring compliance with stringent industrial standards, such as FDA regulations (CFR Title 21) for applications in the food and pharmaceutical industries, or Regulation (EC) No 1935/2004 for materials and articles intended to come into contact with food. For drinking water applications, compliance with standards like NSF/ANSI 61 is critical to ensure safety and quality. However, apart from compliance, application knowledge is key. Understanding the specific requirements of different industrial processes and environments is crucial to tailoring membrane materials that can deliver the desired performance and longevity.

In addition to these established challenges, new issues are emerging, such as the sustainability of membrane materials and the solvents used in their production. In Europe, the REACH Regulation (EC) No 1907/2006 plays a key role in regulating and phasing out hazardous chemicals, including solvents used in membrane manufacturing. This regulation aims to minimize the environmental and health risks associated with chemicals, ensuring that membrane production evolves in a more sustainable direction.

The growing emphasis on sustainability is pushing the development of new, eco-friendly materials, alternative “green” solvents and new membrane production methods that can meet the performance demands of the industry while reducing their environmental impact. This shift is also influencing the need for innovations in membrane design, such as improving fouling resistance, enhancing the recyclability of membranes, and finding safer alternatives to toxic materials in membrane production.

This presentation aims to provide a deeper understanding of these challenges, offering insights into the key factors impacting the development of next-generation membranes and encourages close collaboration between membrane and membrane application developers.

Acknowledgements

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SL02 - SHORT LECTURE

3D printing antifouling properties into nanoporous membranes

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Keywords: 3D printing, Antifouling Properties, Digital Light Projection (DLP), Nanoporous Membranes, Patterned Membranes.

Nanoporous membranes are a pivotal technology in supporting the future growth of water purification, desalination, and wastewater treatment industries owing to their ability to selectively remove contaminants at the molecular level. However, they struggle with limited fouling resistance while trying to achieve high permeance [1]. Meanwhile, standard fabrication methods face challenges with homogeneity, waste production, and narrowing the pore size distribution at low costs which is essential to water applications [2]. In contrast, incorporating nanoporosity into 3D-printed materials through Digital Light Projection (DLP) is promising as it allows precise control over membrane structure with high geometry customization and minimal waste [3]. Within this context, we propose a novel strategy that relies on the advantages of UV-based additive manufacturing to design and produce nanoporous ultrafiltration polymeric membranes with organized porous micropatterns that promote not only antifouling properties but also increased flux and recovery due to increased shear stress and turbidity control. This approach enables the simultaneous production of the membrane and the pattern, increasing fabrication efficiency and further reducing waste generation. Furthermore, we showcase that the technique can be successfully applied to commercial bench-top 3D printers, contributing to lower production costs. The patterned membranes were tested in cross-flow filtration setups for Bovine Serum Albumin (BSA) fouling and rejection, as this technology is extremely valuable for downstream bioprocessing waste recovery. As such, this talk aims to discuss how the production of 3D-printed nanoporous patterned membranes represents a new step towards highly specialized membranes that achieve high separation efficiency while having an increased life span.

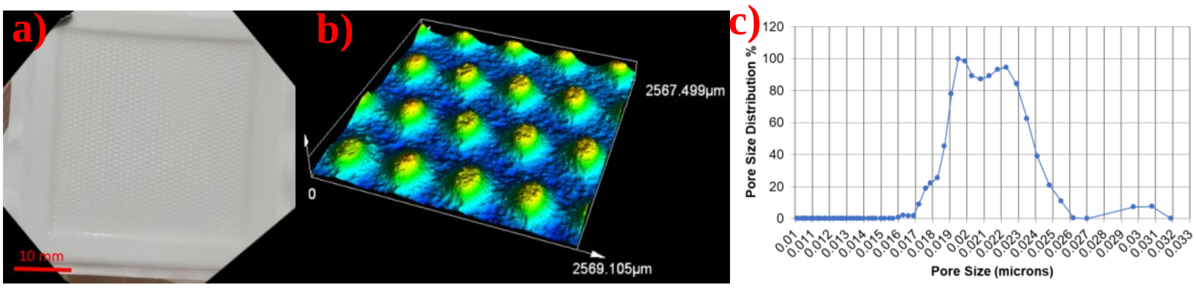

Figure 1. *3D printed patterned membrane (a), profilometry topography (b) shows off-set hill-like pattern design in detail and porometry (c) highlights nanoporosity of the material.*

Acknowledgements

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Graphene doped membranes for Direct Air Capture (m-DAC) of CO_2

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Keywords: m-DAC; Mixed Matrix Membranes; Graphene Oxide nanocomposites; Carbon capture.

The increasing concentration of carbon dioxide (CO_2) in the atmosphere is a significant driver of global warming and climate change, necessitating effective strategies to capture and reduce CO_2 emissions, even from dilute sources. This paper investigates advanced membrane-based technologies for capturing CO_2 from air. Traditional carbon capture methods, such as amine-based absorption, are effective but come with significant drawbacks, including high energy consumption, increased costs, and substantial water usage. Membrane gas separation offers a promising alternative due to its process simplicity, and lower energy demands [1]. Hence, this research explores the development of highly selective and permeable polymeric asymmetric membranes for capturing CO_2 from low concentration sources. The membranes were synthesized by forming Pebax -MH1657 films, which were incorporated with Graphene Oxide (GO) to improve permeability and selectivity, on a macroporous support made of poly(sulfone) (PSF) to provide the mechanical support necessary for the active layer to stand. Further amine functionalization to the GO was also investigated to study the impact of amine group attachment to the matrix in the performance, and two types of amines were used, Primary amine (NH_3) and Polyethylenimine (PEI). Chemical, physical, and morphological analysis to investigate the nature and compatibility of produced membranes to the desired application were done. As well as Pure gas and mixed gas (10% v/v CO_2 and 0.04% v/v CO_2 content in N_2) permeance tests were performed to study the performance of the membranes by obtaining the permeance and selectivity of the membranes at different loadings of GO in the matrix. The MMMs prepared in this research were able to achieve, under DAC condition, selectivity and permeability of 68 and 21.27 GPU with the A-GO MMM (0.3 wt.% loading), and 56and 16.9GPU with the PEI-GO MMM for the same loading. The findings demonstrate the potential of membrane technology in efficiently capturing CO_2 from dilute sources, paving the way for more sustainable and cost-effective solutions to mitigate climate change. The potential of membranes for m-DAC applications was assessed using a multi-stage membrane model implemented through the MEMSIC unit, integrated with CocoSimulator/PROSIM software. The analysis demonstrated that a high-purity CO_2 product ($\geq$ 50% v/v) could be achieved with a minimum of three stages arranged in series, yielding CO_2 recoveries within the range of 0.3 to 0.7.

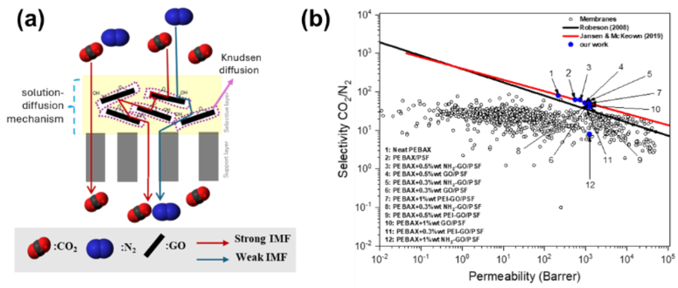

Figure 1: *(a) The GO-based MMMs structure and diffusion mechanisms, (b) Pure Gas permeation results: The ideal selectivity plotted against Permeability in Barrer; the white dots represent data from literature [2].*

Acknowledgements

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Effect of Synthesized Multicarboxylic Copolymer on Chitosan and Cellulose Acetate Blend Membranes for Pervaporation and Microfiltration Applications

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Keywords: Chitosan, Cellulose acetate, Poly(malic acid-citric acid), Pervaporation, Microfiltration

Abstract

A green copolymer, poly(malic acid–citric acid) (PMC), was synthesized through thermal condensation polymerization using DL-malic acid and citric acid as monomers. This multicarboxylic, hydrophilic PMC copolymer was incorporated into biopolymer matrices of cellulose acetate (CA) and chitosan (CS) to evaluate its impact on membrane performance for distillery wastewater treatment and organic/water separation applications.

For microfiltration membranes, PMC was added to a CA/CS (3:1) blend at varying concentrations (0.5, 1.0, and 1.5 ratios), and its effect on filtration performance was assessed. As PMC content increased in the CA/CS matrix, swelling decreased while membrane strength improved due to enhanced ionic interactions between CS and PMC. The average permeation flux of CA/CS/PMC (3:1:0.5), (3:1:1), and (3:1:1.5) membranes was 609, 523, and 464 $L \cdot m^{-2} \cdot h^{-1}$, respectively. TDS, conductivity, and salinity removal reached up to 80% with the CA/CS/PMC (3:1:1.5) membrane, making it the most effective for distillery wastewater treatment based on flux and water quality improvements.

The effect of PMC on CS membranes for organic/water separation via pervaporation was also investigated by varying the CS:PMC blending ratio (1:3, 1:1, and 3:1). Since both CS and PMC are hydrophilic, membranes were crosslinked with phosphoric acid to enhance stability and facilitate polyion complex formation between CS and PMC. The membranes' ability to break the azeotropic ethanol/water mixture was evaluated under different feed compositions. While the CS/PMC (1:3) membrane degraded easily, the CS (100%) and CS/PMC (3:1, 1:1) membranes demonstrated effective separation, achieving flux values of 96, 173, and 268 $g \cdot m^{-2} \cdot h^{-1}$ and selectivity values of 1221, 1214, and 1240, respectively. Moreover, the CS/PMC (1:1) membrane exhibited an increase in flux and a decrease in the separation factor as feed water concentration increased, suggesting that crosslinked membranes perform best when separating feed mixtures with lower water concentrations.

These findings highlight the potential of PMC-based membranes as eco-friendly, high-performance materials for wastewater treatment and pervaporation-based organic/water separation applications.

Polymeric fluorine-free ionomers and their complexes with polyelectrolytes for thin-film composite nanofiltration membranes

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Keywords: ionomer, polyelectrolyte complex, nanofiltration membrane

Selectivity in terms of ion and micropollutant rejection of nanofiltration (NF) membranes is a crucial factor for the performance in various applications, for example wastewater treatment. Membranes based on commercially available fluorine-free ionomers may extend the available selectivity spectrum and provide higher stability compared to conventional polyamide-based NF membranes [1].Herein, the fabrication of tunable and highly stable ionomer NF membranes by coating the negatively charged block copolymer Nexar (from Kraton) on polyacrylonitrile (PAN), with varied ultrafiltration (UF) characteristics is reported. The feasibility of post-treatment methods, e.g. thermal annealing, is also examined. In addition, in analogy to recent other work with Nafion as part of the selective layer [2], a polyelectrolyte complex (PEC) membrane is prepared by combining the fluorine-free Nexar layer with a polycationic polymer (e.g. polyethyleneimine, PEI) to further tune membrane separation performance. Prefunctionalization of the porous support membrane to introduce positively charged groups [3] was found to be critical for a defect-free and stable lamination with a film of the negatively charged ionomer and may also yield a kind of PEC membrane. A mixture of toluene and 1-propanol was identified as the solvent that results in superior morphology and performance compared to other solvents. Low Nexar film thickness was accomplished by dip coating at adapted conditions. Alternative casting methods, e.g. casting with a doctor blade, were also investigated. NF characterization of an exemplary new membrane (0.6 µm Nexar film thickness on aminated PAN support) revealed rejections for Na_2SO_4 of 90 %, for NaCl of 75 % as well as for PEG 600 of >99 %, and a pure water permeance of ~ 2.5 LMH/bar. Thermal annealing resulted in solute higher rejections at slightly reduced permeance. Investigation of the TFC membranes in wet state by AFM reveals characteristic features that can be related to nano-scale channel-in-matrix morphologies of the Nexar barrier film. To further improve overall performance, TFC membranes with thinner selective film (~0.1 µm) are currently fabricated. The PEC membrane obtained by coating the above mentioned exemplary Nexar TFC membrane with PEI yields higher permeances (> 3 LMH/bar) and higher rejections for all types of salts and neutral solutes. To further tune the PEC membrane perfomance, different types of PEI (low and high molecular weight, linear or branched) and other polycations are also investigated.

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Integrating Separation and Reaction in Pervaporation for Glycerol Carbonate Production

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Keywords: Reactive pervaporation, enzyme, transesterification, glycerol carbonate, lipase

Introduction. In recent years, green chemistry has been a niche study area in the development of industrial-scale biochemical synthesis and process intensification[1]. Glycerol carbonate is a non-toxic organic compound that serves as an intermediary in the manufacturing of batteries, surfactants, detergents, and medicinal products[2]. The process of producing glycerol carbonate, which includes transesterification of glycerol and dimethyl carbonate (DMC), has been chosen as a feasible conversion pathway since it principally produces methanol as a coproduct, which can be selectively separated from the mixture using pervaporation[2]. However, glycerol carbonate synthesis is not as environmentally safe as we think. There are two processes: the high-temperature reaction (70 – 80° C) is followed by a purification step, which compromises the process's greener character in terms of energy consumption, as an azeotrope methanol/DMC (approximately 30 wt% methanol azeotrope) is produced, resulting in an extremely energy intensive separation[3]. The separation portion, which involves pervaporation, has already been investigated with the construction of selective membranes using ZIF-8 fillers in chitosan polymer[3]. The ZIF-8/Chitosan membrane showed selectivity to methanol with a high separation factor and flux for separation of methanol from DMC. But the ZIF-8 is a zinc-centric MOF that forms a weak link with the carboxylic ligands often causing the crystals to disorient making the MOFs unstable[4]. Therefore, a different set of MOFs, which is zirconium-centric will be analyzed for methanol/DMC separation. The drop in temperature in the process can be addressed by adding enzymes that work at low temperatures (30 – 40° C)[5]. The goal is to integrate enzymes with methanol-selective membranes in a reactive pervaporation unit. This development will enable more efficient and regulated reactions, boosting the total production of glycerol carbonate and decreasing energy consumption.

Experimental/methodology. Lipases, enzymes that break down alcohol into ester, will be used to catalyze the reaction between glycerol and DMC, creating glycerol carbonate and methanol. Two separate lipases will be tested under various pH, temperature, enzyme, and reactant concentrations. The reaction kinetics will be determined by tracking the conversion of glycerol and DMC into glycerol carbonate using gas chromatography over time. The suitable lipase will then be used for further analysis.

Simultaneously, mixed matrix membranes (MMMs) with chitosan and different MOFs, will be synthesized. The MMMs will be prepared using different compositions of the MOF in chitosan. The characterization of the membrane will be done using a scanning electron microscope (SEM), X-ray diffraction (XRD), FT-IR, and solvent uptake. The membranes will then be used for the separation of methanol from DMC in the pervaporation unit, where the separation will be analyzed at different temperatures over time. The separated solution will be analyzed using gas chromatography. The results will be compared with the results obtained with the ZIF-8/Chitosan membrane.

Further, the selected enzyme will be used in combination with the membrane synthesized in the reactive pervaporation unit for the simultaneous production of glycerol carbonate and the separation of methanol from the reaction media. Combining enzyme catalysis with a methanol-selective membrane, this integrated approach will establish a system where reaction and separation occur concurrently, ensuring continuous glycerol carbonate production while eliminating the formation of azeotropes with methanol and DMC. Consequently, this streamlined process will eliminate the need for individual separation processes and in turn, reduce energy consumption and achieve green chemistry and sustainability goals.

Acknowledgements

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The effect of UV radiation on starch-Rose Bengal biocomposites

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Keywords: Starch, Chitosan, Rose Bengal, Intelligent packaging, Irradiation

Perishable food quality and shelf life (e.g., fresh fruit, vegetables, raw meat) may be a partially controlled by intelligent packaging. Protecting food from light plays a crucial role in packaging functions. The subject of the work was to obtain environmentally safe starch-chitosan films enriched with dialdehyde starch and Rose Bengal, limiting the direct 1O2 attacks, exhibiting UV-radiation absorption properties, and affecting the photo-stability of materials.

The mixtures of starch (S), starch-chitosan (SCh), and SCh crosslinked with dialdehyde starch (SChDs) and modified with Rose Bengal (RS, RSCh, RSChDS) were prepared by solution casting. Each composite was irradiated with a UV lamp at a wavelength of $\lambda = 254$ nm for 5 to 120 min. Spectroscopic studies (FTIR-ATR, XRD) allowed for the determination of the crystallinity degree, chemical structure, and interaction between blend components and the observation of the effect of UV irradiation.

The dye molecules' immobilization on biopolymers' backbones resulted in covalent binding as well as hydrogen and van der Waals interactions between the Rose Bengal-starch and chitosan chains. It may be due to the interaction of the Rose Bengal dianion with the amino groups of chitosan. As a result of UV–action, the process of dye decomposition dominates; however, it occurs with different intensities for different systems. Starch/chitosan/dialdehyde starch sample enriched with Rose Bengal was the most stable under UV irradiation. For RS composite, the photo-oxidation and photodegradation processes competed. However, the excessive exposure (to 2h) of the samples to UV light adversely affected the properties of the films and promoted their photodegradation. The blends RS and RSCh were characterized by similar thermal stability, which was not changed by irradiation.

Films differed in crystallinity degree of starch, which increased as follows: 16% for starch film, 19.6% for starch-chitosan (SCh) film, and 26,4% for SChDS film. The crystallinity degree of starch in composites containing Rose Bengal varied from 18.7% (RS), 19.9% (RSCh), and 13.9% (RSChDS). Similarly, the crystal structure of these samples turned out to be relatively stable towards UV radiation. UV-irradiation affected the new polymorphic transitions, recrystallization, and the formation of a new multicomponent crystal phase of chitosan and starch/DS chains and led to the conformational changes of starch.

The composites differed in strength, brittleness, and surface structure. Samples containing dyes were breakable. All the films had a rough surface. However, the presence of dye significantly reduced the values of the surface roughness parameters in most systems.

Due to their susceptibility to UV light, the examined composites can be used in the packaging industry, e.g., in food coatings or cosmetics, to protect them against UV radiation and microbial actions, which, in turn, contributes to sustainable food and agriculture developments.

Development of High-Strength Honeycomb Structural Polymer Composites

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Keywords: Honeycomb, Cellulose, Porous, Ice-template, Carbon

Honeycomb material is characterized by a structure in which polygonal pores are arranged in a uniform direction and extends through the entire material (Fig. 1a). Due to its high strength-to-weight ratio, excellent fluid permeability, and large surface area, honeycomb materials have potential applications in various fields, such as filtration. It has been reported that TEMPO-oxidized cellulose nanofibers (CNF) exhibit strong structural control in the fabrication of honeycomb materials using the unidirectional freezing (UDF) method[1]. However, honeycomb materials made from CNF generally have low mechanical strength, posing a challenge for practical applications in terms of durability. The strong structural control ability of CNF allows the honeycomb structure to be maintained even when various functional materials are added. Based on this property, we investigated the fabrication of honeycomb materials with enhanced mechanical strength by incorporating thermosetting resin.

In this study, we incorporated a phenolic resin into honeycomb materials and treated thermal cross-linking. A dispersion of phenolic resin was added to an aqueous dispersion of CNF and homogenized to prepare a mixed dispersion of CNF and phenolic resin. The prepared dispersion was poured into a polypropylene container, and after thoroughly removing bubbles, it was subjected to UDF by immersing it in liquid nitrogen at a rate of 100 mm h^{-1}. Subsequently, freeze-drying was performed to remove the ice.

It was found that a well-defined honeycomb structure could be formed even at a phenolic resin concentration up to three times that of CNF (Figure 1a). Although phenolic resin itself has limited dispersibility in water, CNF enables the high-concentration dispersion of phenolic resin and its incorporation into the honeycomb material by acting as a dispersant. In addition, no significant structural changes were observed in the honeycomb structure before and after thermal cross-linking at 150°C (Figure 1b), suggesting that the material could maintain adequate fluid permeability and mechanical strength per weight. In fact, the mechanical strength of the phenolic resin significantly improved after heat treatment, demonstrating that the combination of thermosetting resin and CNF is an effective strategy for fabricating robust honeycomb materials.

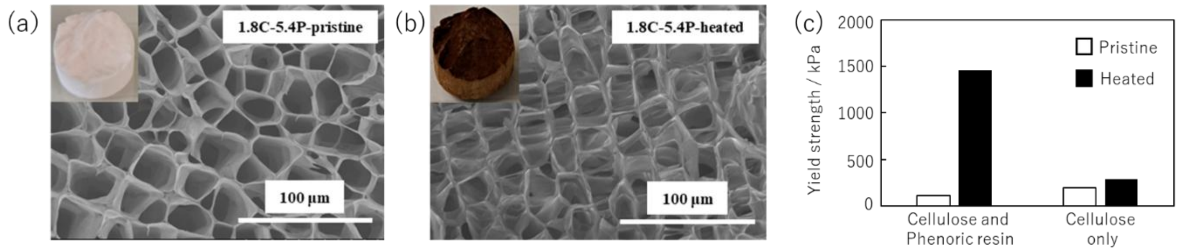

Figure 1. *Scanning electron microscopic images of Honeycomb materials composed of 1.8wt% Cellulose and 5.4wt% Phenolic resin (1.8C-5.4P) (a) before and (b) after heat treatment at 150℃ (c)Mechanical property of honeycomb materials composed of cellulose and phenolic resin and cellulose only.*

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Facile orientation control of MOF-303 hollow fiber membranes by a dual-source seeding method

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Keywords: MOF-303 membrane, Preferred crystallographic orientation, Dual seeding, Pervaporation Nanofiltration

Metal–organic frameworks (MOFs) are nanoporous crystalline materials with enormous potential for further development into a new class of high-performance membranes. However, the preparation of defect-free and water stable MOF membranes with high permselectivity and good structural integrity remains a challenge. Herein, we demonstrate a dual-source seeding (DS) approach to produce high-performance, water-stable MOF-303 membranes with hollow fiber (HF) geometry and preferentially tailored crystallographic orientation. By controlling the nucleation site density during secondary growth, MOF-303 membranes with a preferred crystallographic orientation (CPO) on the (011) plane were fabricated (Figure 1a)[1]. The MOF-303 membrane with CPO on (011) provides straight one-dimensional permeation channels with a superior water flux of 18 kgm^{-2} h^{-1} in pervaporative water/ethanol separation, which is higher than that of most of the reported zeolite membranes and 1–2 orders of magnitude greater than that of previously reported MOF membranes (Figure 1b). The straight water permeation channels also offer a promising water permeance of 15 Lm^{-2} h^{-1} bar^{-1} and a molecular weight cut-off (MWCO ≈ 269) for dye nanofiltration (Figure 1c). These results provide a concept for developing ultrapermeable MOF membranes with good selectivity and structural integrity for pervaporation and nanofiltration.

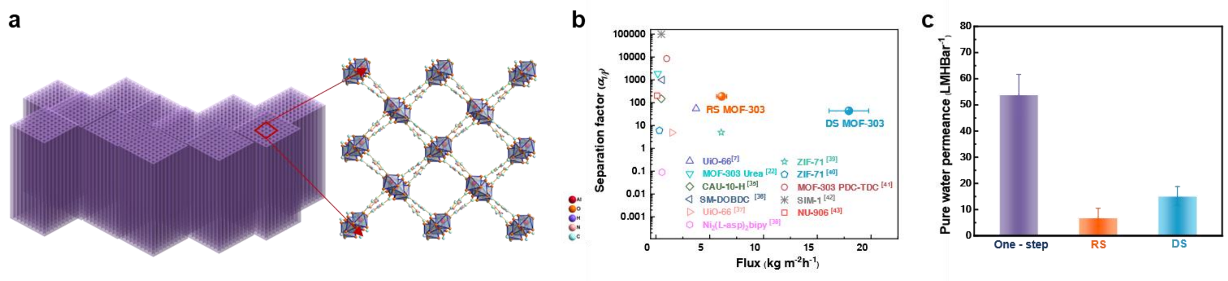

Figure 1. *a Schematic illustration of the DS membrane with vertical one-dimensional channels, b water/ethanol (5/95, wt%) separation performances of fabricated membranes compared to other MOF-based membranes and c Pure water permeance of MOF-303 membranes fabricated by different methods*

Acknowledgements

The authors gratefully acknowledge the financial support of this project by EPSRC in the United Kingdom (Grant no EP/R029180/1) and the Membrane Material Synthesis for High Selectivity (SynHiSel) project (Grant no EP/V047078/1).We also acknowledge the Barrer Center for the experimental support, and we appreciate the use of equipment for characterization in the analytical laboratory in the chemical engineering department and the electron microscopy center of Imperial College London.

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SL10 - SHORT LECTURE

Modulation of the Temperature and Gas Sensing Properties of New Metal–Organic Frameworks based on Hexanuclear Rare Earth Secondary Building Units through Single-Crystal-to-Single-Crystal Transformation Reactions

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Keywords: Metal Organic Frameworks, Crystal structures, Gas Sensing, Temperature Sensing, Single-Crystal-to-Single-Crystal Transformations

We shall discuss two families of trivalent rare earth (RE^{3+}) Metal-Organic Frameworks (MOFs)[1,2] based on a hexanuclear $(RE^{3+})_6$ SBU and their exchanged analogues. The first one involves 8-connected 2-D MOFs based on an angular dicarboxylic ligand 4,4'-(hydroxymethylene)dibenzoic acid (H_2BCPM), **UCY-17**(RE). A series of exchanged analogues **UCY-17**(Tb)/L produced from linker installation SCSC reactions of **UCY-17**(Tb) with selected dicarboxylic ligands shall also be discussed which resulted not only to the turn-on of the thermometric properties of these materials.[3] The second family of compounds with the general formula $\{((CH_3)_2NH_2)_2[Y_6(\mu_3\text{-}OH)_8(bpydc)_6]\}_n$ is based on the linear dicarboxylic ligand H_2bpydc= [2,2'-bipyridine]-5,5'-dicarboxylic acid. Its subsequent metalation with transition metal ions was achieved giving rise to a series of exchanged analogues with various metal ions. Gas sensing studies of the pristine and metalated compounds revealed a variety of different gas sensing capabilities. Thus, SCSC transformation reactions allowed not only the targeted modification of the structures of the two MOFs but also the modulation of their temperature and gas sensing properties.

Acknowledgements

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SL11 - SHORT LECTURE

Polyamide Membrane with the Interlayer of Sulfonated COF for Artemisinin Concentration

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Artemisinin, a vital anti-malarial pharmaceutical, is often extracted from artemisia annua using organic solvents, like ethanol or n-hexane [1]. Traditional concentration methods like evaporation can be energy-intensive, time-consuming, and lead to product degradation due to thermal instability [2]. Organic solvent nanofiltration (OSN) offers a more selective and energy-efficient alternative, preserving the bioactivity of artemisinin while recycling solvents and reducing environmental impact. Polyamide (PA) thin-film composite (TFC) membranes show great potential for this application due to their easy fabrication, high solvent stability and excellent separation performance. However, achieving a controllable interfacial polymerization (IP) of PA layer on microporous solvent-resistant support still remains a big challenge. To address this issue, we developed a facile method: A state-of-the-art single-phase synthesis was used to synthesize a DABA-TFP COF nanosheets dispersion with a high yield in a straightforward and effective manner. A sulfonated 2D covalent organic framework (COF) nanosheet-based interlayer was vacuum-assembled onto a microfiltration nylon 66 substrate under the aggregation effect of methanol. The obtained COF-H^+ interlayer can provide a dense and uniform surface and serve as a platform for IP, successfully preventing the PA intrusion when nylon is used directly as a substrate. After the post-treatment of COF-H^+ with either $NaHCO_3$ or NaOH, the as-formed COF-Na^+ interlayer mitigates the negative effects of H^+ on IP process, enabling the formation of a continuous, defect-free PA layer. The resulting PA-COF-Na^+ TFC membrane demonstrated excellent rejection performance for both charged and uncharged molecules, achieving 95.69% rejection for uncharged 2,4-Diphenyl-4-methyl-1-pentene (DMP), 95.73% rejection for positively charged Azure B, and 94% rejection for negatively charged 3, 5-dichloro-2-hydroxybenzenesulfonate (DHBS). Ethanol is generally used for artemisinin extraction due to its high extraction yield and safety [3]. In this research, the optimized TFC membrane can reject artemisinin from ethanol with a rejection of above 97% which is efficient for concentrating artemisinin in ethanol while simultaneously recycling the ethanol. This approach facilitates easier extraction of artemisinin from the concentrated solution, significantly reducing energy consumption and minimizing solvent waste.

Keywords: polyamide, interlayer, COF, organic solvent nanofiltration, artemisinin.

Acknowledgements

The authors gratefully acknowledge the donation from Mr Mark Richardson to the Department of Chemical Engineering, Imperial College London.

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Graphdiyne Membrane for Molecular Separations

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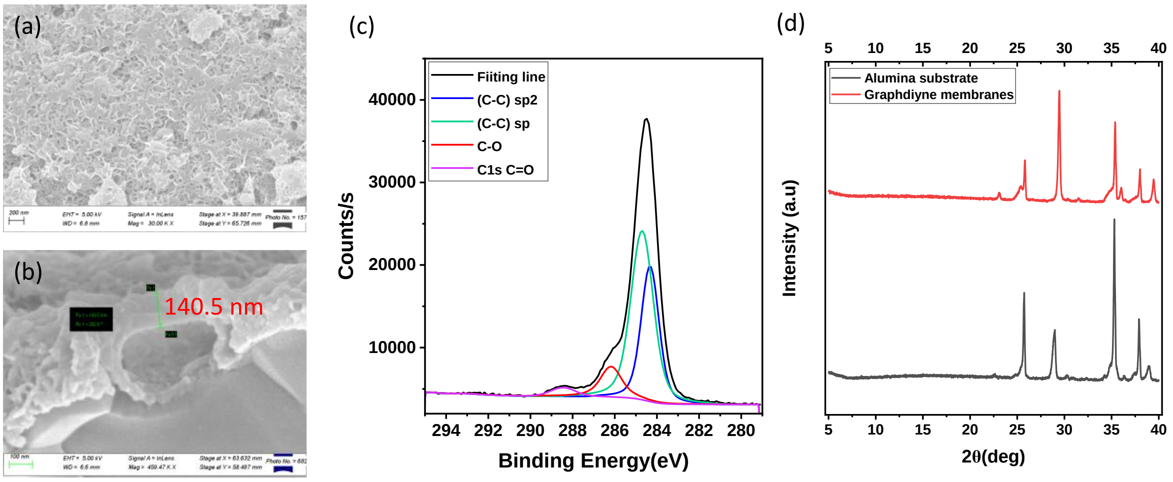
Keywords: Graphdiyne (GDY), interfacial cross-coupling polymerisation (ICP), two-dimensional (2D)

Graphdiyne (GDY), a novel two-dimensional (2D) carbon allotrope, has emerged as a promising candidate for next-generation membrane material. Its atomic-layer thickness, sub-nanometre intrinsic porosity, and hydrophobic nature enable ultrahigh gas and liquid permeance and excellent size-sieving capabilities [1]. However, the experimental investigations of GDY's practical application are severely limited by the scalability challenges of current fabrication techniques [2,3]. This project addresses these problems by employing direct interfacial cross-coupling polymerisation (ICP) for GDY synthesis, enabling cost-effective, scalable membrane production while maintaining structural integrity and performance.

The GDY membrane is prepared by direct ICP on the surface functionalised hollow fibre (HF), in which the GDY selective layer forms at the interface between the aqueous and organic solutions and simultaneously attaches to the HF substrate, resulting in a stable and robust GDY membrane. The membrane thickness is adjusted by controlling the synthesis time and GDY monomer concentration. The obtained membrane is characterised by XRD, XPS, SEM, etc. The performance of the membrane is evaluated by gas permeation and pervaporation.

The successful fabrication of the GDY membrane is confirmed by SEM, XPS, and XRD analyses, as shown in Fig. 1. SEM images (Fig. 1a and b) reveal that the vertically inclined nano-walls form a honeycomb-structured GDY 3D layer with full coverage. The dense 2D layer underneath has a thickness of approximately 140 nm. In the XPS C 1s spectrum (Fig. 1c), two main peaks are observed at 284.3 eV (sp² C=C) and 284.7 eV (sp C≡C) with a ratio of sp² C=C to sp C≡C being 0.64, close to the theoretical value for perfect GDY (0.5) [3]. The XRD pattern (Fig. 3d) shows a characteristic peak at 23°, corresponding to the (110) planes of GDY [3].



Acknowledgments

The authors gratefully acknowledge the financial support of this project by EPSRC in the United Kingdom (Grant no EP/R029180/1) and the Membrane Material Synthesis for High Selectivity (SynHiSel) project (Grant no EP/V047078/1).

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Covalent Triazine Frameworks in Electrochemistry: Unlocking New Possibilities for Energy Storage

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Keywords: covalent triazine framework, nanocomposite, energy storage, supercapacitor, carbon nano-onion

Covalent Triazine Frameworks (CTFs) are porous organic materials with the possibility of structural control at the molecular or atomic level. However, using CTFs as electrodes in energy storage devices is hampered by their low electrical conductivity and strong stacking effect between adjacent CTF sheets. We proposed a combination of a carbon nanostructure and spherical carbon nano-onions (CNOs) with CTFs to create nanocomposites for supercapacitors.

We designed CTFs with different pore diameters and their hybrids with CNOs in the pyrolysis at 600-800ºC.[1,2] High porosity (ca. 2000 m^2/g) of the CNO-CTFs, interconnections between micropores and mesopores preventing the walls of the pores from pulverizing while exhibiting an extremely high level of structural integrity, morphological heterogeneity resulting from the simultaneous presence of amorphous phases and crystalline zones that may result in higher structural stability and higher conductivity of the hybrid materials, a high percentage of the pyridinic-N, the pyrrolic-N and graphitic-N atoms, which are responsible for the pseudocapacitance in materials. The specific capacitance value of CNO-CTFs increased 2-2.5 times compared to the reference CTF value, reaching ca. 1000 F/g. With their unique characteristics, including high electrochemical capacitance, fast ion transport, and the possibility of structural optimization, nanocomposites containing CNO and CTF hold attractive properties for practical applications in electrochemistry.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Centre, Poland, grants #2017/25/B/ST5/01414 and #2019/35/B/ST5/00572 to M.E.P.-B.

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Imine-based ionic covalent organic frameworks for transition metal ions capturing via hybrid capacitive deionization

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Keywords: battery recycling, hybrid capacitive deionization, cobalt recovery, electrosorption

Ionic covalent organic frameworks (iCOFs) are highly ordered, porous crystalline polymers with charge-storage capabilities. Their unique reticular chemistry ensures high surface area, physicochemical stability, well-defined nanochannels, and favourable electrical properties. These characteristics position COFs as promising materials for energy storage, ion and gas adsorption, photocatalysis, electrocatalysis, sensing, and battery technologies. Advances in COF design focus on tailoring pore diameters, linkages, and nodal configurations via bottom-up, one-pot, and post-modification strategies to enhance performance.

COFs, traditionally considered inert in redox processes, can be customized with redox-active sites, making them highly suitable for capacitive deionization (CDI). They can be classified into electron acceptor (n-type), electron donor (p-type), and bipolar COFs. N-type COFs, which undergo reduction via cation insertion, exhibit n-type conductivity and rely on electron transport. Imide-functionalized COFs are particularly advantageous due to their electron-deficient π-systems, enabling efficient charge distribution and excellent redox reversibility.

This study presents the design of imide-functionalized n-type COFs optimized for the selective capture of transition metal ions (TMIs) from hydrometallurgical battery effluents under an external electric field. These COFs exhibit excellent conductivity, high cycle stability, and enhanced energy efficiency, setting a new standard for sustainable metal recovery.

Two synthesis methods were explored: solvothermal (120°C, 3 days) and microwave-assisted (30 W, 2 min). The frameworks were constructed using dihydro benzaldehyde (DHBA) and 5-chloro-7-iodo-8-hydroxyquinoline (HQ), with 2-methyl imidazolate (MIM) as both a linkage and an ion-exchange site.

Experimental results showed that iCOFs achieved the highest sorption capacity (SAC) for lithium and cobalt ions, with cobalt recovery increasing from ~20% to 52% via the solvothermal route. The Co/Li separation factor for iCOF-ST reached 2.5, compared to 1.1 for COF-ST, demonstrating the role of ion exchange functionalities in enhancing selectivity. The findings underscore the impact of synthesis methods on iCOF performance, offering new prospects for efficient and selective metal reclamation.

Acknowledgements

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SL15 - SHORT LECTURE

Composites Containing of Carbon Nano-Onions and S-Doped Covalent Triazine Frameworks: Synthesis and Physicochemical Properties

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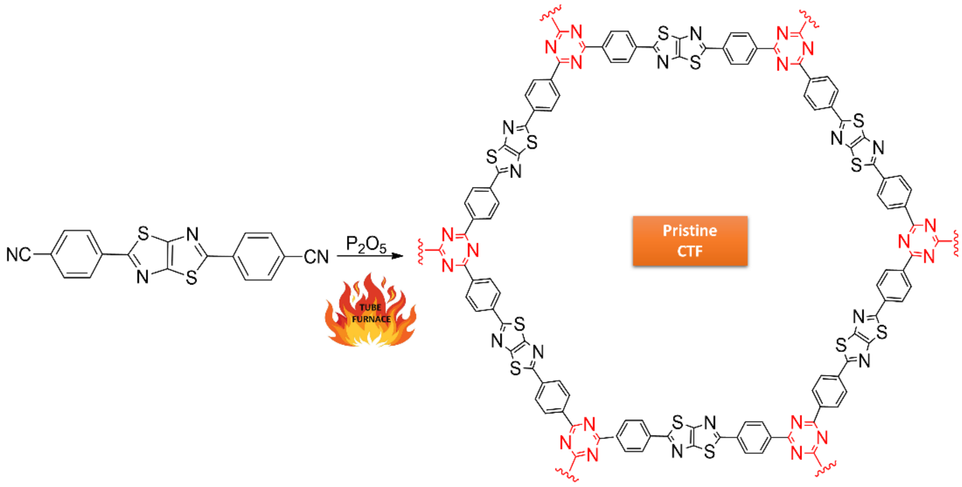
Keywords: carbon nano-onion, covalent framework, composite

The increasing demand for advanced energy storage materials drives the search for novel, safe, and efficient solutions. In particular, supercapacitor (SC) development relies on designing electrode materials with a high active surface area, appropriate porosity, and good electrical conductivity to enable effective charge storage.[1] In response to these challenges, we have developed nanocomposites based on covalent triazine frameworks (CTFs) combined additionally with carbon nanostructures such as carbon nano-onions (CNOs).[2,3]

We synthesized hybrid materials containing CTFs and CNOs doped with sulfur atoms. We selected the nitrile-functionalized heterocyclic compounds unit to form triazine rings to construct CTFs. The materials were synthesized using an ionothermal process at 700°C in the presence of P_2O_5. The covalent immobilization of triazine-based structures on spherical CNOs results in the organization of micro- and mesopores in a three-dimensional architecture. It was achieved by adding only 5% by weight of CNOs. At the molecular level, the forces that mainly influence the triazine structure organization are the surface chemistry of the CNOs and the experimental conditions used to prepare the composites.

The CNO-CTF was subjected to structural and textural characterization, including X-ray photoelectron spectroscopy, adsorption of nitrogen analysis, and transmission electron microscopy—incorporating sulfur-containing units into CTFs allowed for precise tuning of their structural properties. Additionally, introducing CNOs increased surface area and improved porosity, leading to well-developed hybrid structures. Our findings demonstrate that controlled pore engineering and chemical functionalization of CTFs enable the development of materials with tailored physicochemical properties, making them promising candidates for advanced applications in materials science, for example, next-generation energy storage devices.



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SL16 - SHORT LECTURE

Enantioselective membranes prepared by ionic interactions between ion exchange membranes and charged cyclodextrins

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Keywords: membrane, separation, enantioselective, chiral, selectivity

Enantiomers are optical isomers of (chiral) substances that are mirror images of each other. Although enantiomers have otherwise identical chemical structures, their reactions with other chiral substances, for example in human metabolism, can be stereoselective. The presence of the two isomers can then elicit quite different responses from the organism, which must be considered particularly during drug administration. However, many established, and newly developed chiral drugs on the market are only in the form of racemates (equimolar mixtures of the two enantiomers), as efficient separation of the enantiomers on an industrial scale remains a major challenge from a technological and economic point of view. The development of advanced enantioseparation methods is important not only to produce safer and more effective drugs, but also in terms of minimizing the environmental burden of metabolites of ineffective enantiomers. Although membrane processes are a potentially promising answer to this challenge, the preparation of special enantioseparation membranes is usually very complicated and expensive. This work demonstrates a simple method for the preparation of chiral membranes using strong ionic interactions between a charged chiral selector and an oppositely charged membrane[1,2]. A homogeneous anion-exchange membrane (TailorMem Hollex ADL 911 NR) was functionalized by dip-coating method with a polyionic chiral selector sulfobutylether-β-cyclodextrin (SBE-β-CD). The coverage of the membrane by the selector was 0.68 μmol.cm^{-2} or 130 μmol.g^{-1}, while the selector was found both on the surface and in the polymeric structure of the membrane. The separation properties of the modified membrane were verified in a diffusion cell with N-Boc-Tryptophan as a model analyte. The membrane exhibits sorption-selective properties due to the preferential formation of inclusion complexes between SBE-β-CD and N-Boc-L-tryptophan, with sorption decreasing with increasing proportion of organic phase (methanol) in the aqueous solvent. Lower feed concentration and low temperature of 8 °C favors the separation performance over time but slows down flux. Generally, the separation decreases over time due to saturation of the chiral selector, which can be subsequently regenerated in pure methanol to renew the membrane's selective capacity. It was confirmed that the modification is stable after both the experiment and the regeneration.

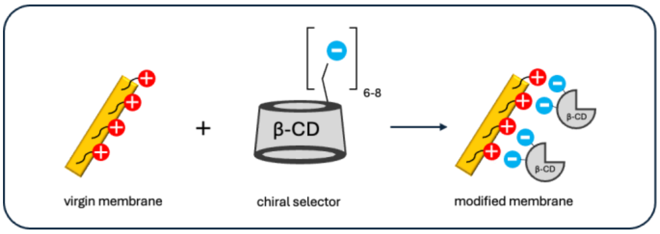

Figure 1. *Functionalization of anion exchange membrane with polyionic chiral selector*

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A New Possible Application for 2D Carbon-Based Membranes in the Ultrafiltration Process

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Keywords: Membrane, Ultrafiltration, Carbon-Based, 2D Materials, Graphene Oxide

Membrane separation processes are currently among the most rapidly expanding fields in chemical engineering due to their sustainability, effectiveness, and broad range of applications, significantly reducing energy costs. [1] However, the membranes employed in these processes are commercially available polymers that exhibit various disadvantages compared to inorganic membranes. In recent years, there have been numerous reports of the use of such materials for eliminating micro-pollutants from water, making them a promising candidate for industrial application.[2]

In this study, a novel application for two-dimensional carbon-based materials is presented and evaluated in comparison to traditional polymeric membranes for ultrafiltration (UF). These materials demonstrate significantly enhanced flux, augmented thermal and chemical stability, and a more sustainable synthesis process when compared to polymeric materials.

Polyethylene glycol (PEG) is a highly prevalent polymeric binder in diverse research domains. However, a critical challenge emerges in precisely controlling the molecular size, necessitating the development of a lab-scale UF module. This module utilizes membranes based on carbon nanotubes (CNTs) with a modified graphene oxide (GO) skin layer, which are employed to separate PEG molecules with molecular weight cut-offs ranging from 400 to 35,000. The characterization of the membranes involved a range of analytical methods, including ATR-FTIR, Raman, XRD, 3D-profiler, BET measurements, and TGA.

Initially, the membranes were assessed for their water flux, followed by a series of tests involving various mixtures of PEGs, exhibiting a notable rejection rate of 70% for higher molecular weight PEGs in some novel membranes. In comparison to conventional membranes, these novel membranes demonstrated higher flux performance.

A mathematical process model was formulated, encompassing a multi-step cascade membrane configuration that culminates in a final step via RP-HPLC. This prefiltration UF step, the separation efficiency of such operation could be increased or at least similar compared to a two column RP-HPLC setup.

Acknowledgements

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SL18 - SHORT LECTURE

Electrokinetic Measurements: A New Approach for Membrane Wetting Characterization

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For the first time, tangential electrokinetic measurements were used in this study to characterize wetting of hydrophobic membranes. The electrokinetic leakage phenomenon can parasite these measurements when conducted on porous samples [1]. This “parasitic” phenomenon provides additional information on the membrane porous layers [2, 3]. We show how the electrokinetic leakage phenomenon can provide critical information for hydrophobic membranes wetting monitoring. Two flat-sheet PVDF membranes with different pore diameter (0.22 µm and 0.45 µm) were used. Tangential streaming current and pore electrical resistance of the membrane samples were continuously monitored. During these electrokinetic measurements, membrane wetting was triggered by adding a non-ionic surfactant (Tween 20) in the measuring solution.

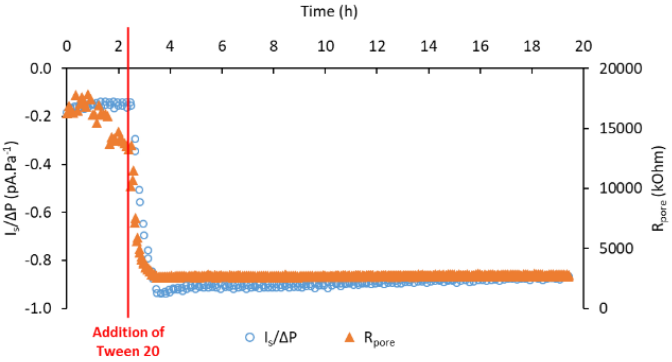

Figure 1: *Streaming current coefficient ($I_s/\Delta P$) and pore electrical resistance (R_{pore}) versus time; solution: 0.001 M KCl at pH 5.00 ± 0.05.*

Immediately after addition of the surfactant, streaming current coefficient and pore electrical resistance values drop: the streaming current coefficient is approximately multiplied by 4 while the pore electrical resistance is divided by 5 (Fig. 1). These variations are signatures of pores wetting with the electrolyte solution, allowing part of the streaming current to flow inside the porous layers (the so-called electrokinetic leakage phenomenon). In this study is demonstrated for the first time the usefulness of electrokinetic leakage for membrane wetting monitoring. This work paves the way for the development of a new class of on-line tools for early-stage wetting detection.

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Versatile Electrodes for Green Hydrogen Production – Achieving Energy Transition from Any Water Source

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Keywords: Green hydrogen, Additive manufacturing, 2D materials, Electrodes, Water splitting

Green hydrogen fuel production, based on water electrolysis powered by solar energy, requires very high-grade deionized water quality to avoid electrode degradation and process performance degradation over time. Given that approximately nine litres of deionized water is required per kg of hydrogen fuel produced [1], and that the global green hydrogen demand is expected to quadruple between 2022 and 2030, from 10 to ~40 Mt, it is clear that this green revolution will put extreme pressure on both existing infrastructures and global scarce freshwater resources [2]. As demand for green hydrogen increases, electrolysis will compete with sectors like agriculture and industries for scarce freshwater, emphasizing the need for electrodes that can sustainably and cost-effectively operate with a wider range of sources and lower grade water quality. Traditional commercial electrodes use noble metals such as platinum, which are costly due to their scarcity and high demand [3]. Carbon-based materials like graphene and carbon nanotubes present a viable solution due to their high electrical conductivity, large surface area, chemical stability, and affordability [4]. However, challenges remain in enhancing their electrochemical efficiency for water splitting. This study explores an innovative approach to electrode fabrication that leverages the properties of 2D materials and additive manufacturing [5]. The complex porous geometries of the electrodes not only increase the surface area but also aids in faster bubble detachment, enhancing the overall efficiency. The durable and versatile nanostructured electrodes will be used for water splitting with multiple waste and sea water grades to mitigate the impact of water impurities on the electrolysis efficiency and long-term process stability to significantly reduce the water footprint and costs associated with hydrogen production via electrolysis, thus accelerating the journey towards a sustainable future.

Acknowledgements

Support by the Research & Innovation Center for Graphene and 2D Materials (RIC-2D) of Khalifa University is gratefully acknowledged.

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SL20 - SHORT LECTURE

Reconditioning of End-of-Life desalination membranes with polyelectrolyte coatings: Advances in optimization and scale-up

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Keywords: Desalination membranes, End-of-Life membranes, oxidation, polyelectrolyte coatings, recycling

Up to 2 million RO spiral wound (SW) elements might be discarded at desalination plants in 2025.[1,2] Reuse methods for the End-of-Life (EoL) elements have been studied, much of them based on oxidative removal of fouled polyamide top-layer. Often a successive modification, such as polyelectrolyte coating, is needed to make the membrane sufficiently tight. Such treatments are generally cheap, can be performed in water and can be tailored to needs. Here, our latest findings on EoL membrane reconditioning front are shown. Our approach comprises alkaline cleaning, oxidative treatment and polyelectrolyte coatings. Each step can be optimized and leveraged on in pursuit of highly permeable and selective membranes.

Firstly, soaking the EoL membranes for 16 hours in alkaline cleaner causes reversible swelling of the membrane. Successive rapid coating with PDADMAC (poly(diallyldimethylammonium chloride)) will result in a membrane that has a higher pure water permeance (PWP) and higher retentions compared to a membrane that is given time to contract between the alkaline treatment and coating.[3] Secondly, the extent of oxidation has similarly clear influence on the performance of the coated membrane. While an underoxidized membrane will not get to benefit the high permeance of an open substrate, an overoxidized membrane might adsorb coatings inside pores causing unnecessary hydraulic resistance. Optimization of this is very case-specific, but in one of our studies, EoL membranes oxidized to around 20–30 L/m^{2}hbar PWP resulted most optimal coated membrane performance[4]. Lastly, reconditioning treatment was upscaled into an SW configuration to show applicability of the method. Differences were minimal between the lab-scale flat-sheet membrane (280 Da MWCO, 19 L/m^{2}hbar PWP) and similarly treated SW element (320 Da MWCO and 17 L/m^{2}hbar PWP).[5] Furthermore, the reconditioned membranes often outperform even commercial NF membranes, in terms of model substance filtrations.

Encouraging steps are made towards recycling massive amounts of EoL membrane elements, currently considered near worthless plastic waste. While reducing the amount of waste, such recycling procedures could potentially help with prominent water treatment issues by allowing for second-hand market of the used elements. Cheap reconditioned membranes could reduce the costs of water purification processes, whether they be related to drinking water production, wastewater treatment or even water reclamation.

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Polymer Membranes modified with Multicomponent Nanocomposite

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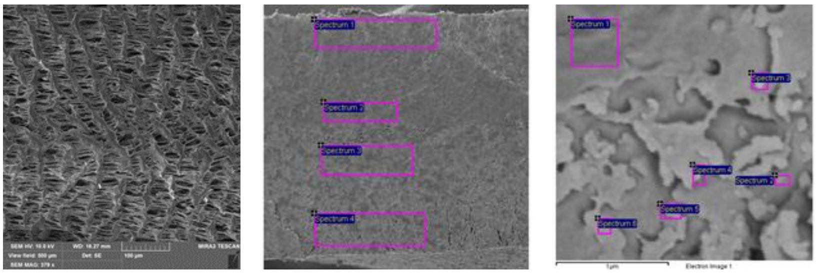
Keywords: ultrafiltration, e-PTFE membrane, zirconium phosphate, Silver nanoparticles, Carbon Nano Dots

A new approach to modifying expanded macroporous polytetrafluoroethylene (e-PTFE) tubular membranes with a multicomponent nanocomposite is presented in this study. The modifier consists of hydrated zirconium phosphate (HZP), PTFE polymer, silver nanoparticles (AgNP) and carbon nanodots (CND). It has been incorporated into e-PTFE tubular filters to improve selectivity, mechanical and antimicrobial properties. Modification of the e-PTFE tube separators involve a sol-gel process followed by the addition of an antibacterial components to provide disinfection capabilities. Characterization of the nanocomposite included FTIR, TEM, DLS and UV-VIS spectroscopy, contact angle and zeta potential measurements. The surface area and pore structure of the membranes were studied using low-temperature nitrogen sorption-desorption methods and SEM. It is shown the functional properties of the composite tubular membrane depend on the amount of the modifier. In addition, the introduction of an inorganic ion exchanger result in the transformation of a microfiltration e-PTFE membrane into an ultrafiltration one with a cutoff of 14-30 kDa due to the formation of a secondary porous structure (Fig.1a,b). Synthesis conditions allow to control the composition of the modifier (the content of the inorganic component can reach 50%). SEM analysis of the membrane surface revealed the Ag content up to 2.2 atomic % (Fig. 1c). The mechanical and structural properties of the PTFE matrix, including hardness, flexibility, and permeability, were significantly improved by the proposed approach. The selectivity of the membrane to globular proteins was reached to 96%, and the resistance to fouling was 2-4 times higher than that of the pristine polymer filter. The obtained membranes restore permeate flux by 50% without chemical cleaning, and protein substances are deposited mainly on the outer surface. They form a dynamic layer that can be easily removed from the membrane surface by reverse filtration.



a b c

Figure 1. *SEM images cross section of pristine e–PTFE (a), cross section (b) and surface (c) of composite membrane with multicomponent modifier.*

The hydrophilic nature of the inorganic ion exchanger and CND, coupled with the antibacterial properties of the silver nanoparticles and CND, result in fouling decreasing. This functionalization approach make the composite e-PTFE membranes highly suitable for the treatment of biological solutions and water disinfection.

Acknowledgements

The work was performed within a framework of the program 0122U001235 entitled “Development of membranes modified with composites based on polymers with inorganic hydrophilizing and antibacterial additions”. The program was supported by the National Academy of Science of Ukraine.

Production of Biphasic Calcium Phosphate Granules from Gypsum Using Static and Rotational Methods

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Keywords: biphasic calcium phosphates, carbonate hydroxyapatite, magnesium whitlockite, implants

The growing need for bone implants, fueled by an aging population, is spurring research into synthetic alternatives that replicate the composition of human bone. This bone structure features calcium phosphate (CP) nanocrystals, primarily nonstoichiometric hydroxyapatite and magnesium whitlockite (Mg-WH), integrated within a collagen matrix [1], [2]. Recent studies have shown that while various CP's can be used independently for implantation purposes, their composites exhibit a superior biological response compared to traditional single-phase calcium phosphate-based materials [3]. CP composite materials maintain the osteoinductive, osteoconductive, and biodegradable properties typical of monophasic CP, while also providing the benefit of adjustable biodegradability and mechanical properties through modification of the ratios of their individual CP phases [4].

In this study biphasic calcium phosphate (BCP) granules composed of Mg-WH and carbonate hydroxyapatite were developed to closely mimic the natural composition of bone, aiming to enhance biocompatibility and performance in implant applications. BCP granules were synthesized from an environmentally benign gypsum precursor at low temperatures through dissolution-precipitation reactions conducted under static and rotating conditions. different synthesis dynamics, i.e. static or rotational, have been used to investigate how this affects the phase composition of the synthesis product as well as the product structure and morphology. A range of analytical techniques, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and inductively coupled plasma optical emission spectrometry (ICP-OES), were employed to analyze the composition of the synthesized materials. Additionally, scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) methods were utilized to characterize the surface properties of the granules.

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Comparative Analysis of Antibacterial Properties of Silver Nanoparticles Synthesized Using “Green Biomass” of Phototrophic Organisms

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Keywords: Silver nanoparticles; “Green synthesis”; Phototrophic organisms; Antibacterial activity

Nanoparticles (NPs) are considered a promising alternative for targeting drug-resistant bacterial strains [1,2]. The “green synthesis” method for producing NPs is environmentally friendly, as it uses natural resources as reducing and stabilizing agents. Among various types of NPs, silver nanoparticles (Ag-NPs) are particularly effective in combating microbial drug resistance and are increasingly being used in biomedicine and biotechnology [1-3].

This study presents a comparative analysis of the antibacterial properties of Ag-NPs synthesized using the “green biomass” of various phototrophic organisms, including cyanobacterium *Arthrospira platensis*, green alga *Parachlorella kessleri*, and medicinal plants *Moringa oleifera*, *Artemisia annua*, and *Stevia rebaudiana*. These phototrophs are widely used in biotechnology, biomedicine, pharmaceuticals, and the food industry due to their rich content of biologically active compounds. The biosynthesis of Ag-NPs was performed under daylight illumination using the “green biomass” and an aqueous solution of $AgNO_3$ [3].

Ag-NPs synthesized using the biomass of all phototrophs displayed notable antibacterial activity against conditionally pathogenic Gram-positive and Gram-negative bacteria (*Enterococcus hirae, Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhimurium, Escherichia coli*) by inhibiting growth rate and colony formation. Ag-NPs synthesized using the biomass of cyanobacterium *A. platensis* and green alga *P. kessleri* had a spherical shape and demonstrated bactericidal effects at low concentrations (5-10 µg/mL). Ag-NPs derived from the leaf extracts of *M. oleifera* and *S. rebaudiana* showed a more pronounced antibacterial effect at a lower concentration (10 µg/mL) against *E. coli*, while higher concentrations (25-50 µg/mL) were required to affect *E. hirae* and *S. aureus*. In contrast, Ag-NPs synthesized from the leaf extract of *A. annua* only demonstrated antibacterial effects against these bacteria at higher concentrations (100 µg/mL). Moreover, Ag-NPs synthesized from the “green biomass” of phototrophs seem to be more effective against Gram-negative bacteria than Gram-positive bacteria. This behavior of biogenic Ag-NPs is due to the difference in the structure of cell walls of Gram-positive and Gram-negative bacteria and their interactions with biogenic NPs. The findings highlight the potential of natural “green” resources in nanobiotechnology.

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Synthesis of $Ti_3C_2T_x$ MXenes for Wastewater Treatment and Water Quality Monitoring

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Keywords: MXenes, Adsorbent, Raman spectroscopy

According to the World Health Organization, an estimated 2 billion people globally use a contaminated drinking water source, leading to severe diseases such as cholera, diarrhoea, and dysentery. There is a high demand for highly efficient water quality monitoring and wastewater treatment methods [1].

MXenes is a family of two-dimensional (2D) nanomaterials, first discovered in 2011 at Drexel University. Materials belonging to a family of MXenes have a general structure of $M_{n+1}X_nT_x$, where M is a transition metal, X is C and/or N, and T_x is the surface functional group, consisting of transitional metal carbides, nitrides, and carbonitrides [2]. MXenes find applications in various fields, including wastewater treatment, electrochemical and optical sensors, and electronics [3-5].

In this study, $Ti_3C_2T_x$ MXenes in both multi-layered and delaminated forms were synthesized from Ti_3AlC_2 MAX phase precursor. Synthesis products were characterized by XRD, SEM, Raman spectroscopy, and FTIR to prove the quality. $Ti_3C_2T_x$ MXenes were tested as an adsorbent material for various pollutants and showed promising results in water quality monitoring and wastewater treatment.

Acknowledgements: This project received funding from the Research Council of Lithuania (LMTLT), agreement No S-MIP-24-14.

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Advanced evaluation of anti-biofouling potential of ZnO NP doped dual-layer photocatalytic filtration membranes

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Keywords: biofouling, extracellular polymeric substances, mixed matrix membranes, photocatalysis, zinc oxide

Membrane modifications for biofouling mitigation have been researched for decades. In our previous study ZnO-doped membranes showed excellent antibacterial properties for reduction of cultivable *Escherichia coli* counts. However, it was determined that microorganisms indigenous to tap water proliferated, therefore it was speculated that bacteria could have entered so called viable but nonculturable state (VBNC) which would cause false colony reduction with the cultivation [1]. Therefore, in this study additional advanced microbiological testing method was used to confirm the inactivation of *E. coli* cells after the contact with the photocatalytic membranes and compare to cultivation results. Additionally, biofilm reduction was confirmed by evaluating extracellular polymeric substance (EPS) production by *Pseudomonas aeruginosa*, which is often found in membrane systems [2].

Dual-layer flat sheet mixed matrix membranes were prepared using co-casting approach. For surface layer modification multiple concentrations of ZnO nanoparticles (NPs, GetNanoMaterials, France) were mixed into casting solutions. Membranes were characterized with scanning electron microscopy (SEM), filtration, fouling and molecular weight cut-off (MWCO) via dextran filtration. Surface antibacterial properties were evaluated via cultivation of *E. coli* as a test organism. Cell viability was evaluated using microscopy method of counting 5-cyano-2,3-ditolyltetrazolium chloride (CTC) treated metabolically active cells. *P. aeruginosa* biofilm formation reduction was determined by staining extracellular polymeric substance (EPS) protein structure. Protein quantification was done using microplate reader and visual confirmation of reduced EPS with fluorescence microscopy. During microbiological tests, membranes were irradiated using 50W visible light source to trigger the photocatalytic activity.

SEM analysis revealed an asymmetric structure with NPs distributed in a surface layer. Filtration and fouling tests showed on average a 20% flux decrease in reference to pure PES membrane. Modification with solely ZnO did not reduce the fouling within a dextran filtration test. MWCO of all the membranes remained in the range of 19-41 kDa. All membranes exhibited excellent antimicrobial properties by inactivating more than 99.9% of *E. coli* and reaching 99.999% reduction after 24-hour irradiation. Yet, viability tests revealed that only approximately a half of the cells were truly killed, suggesting that the rest only lost their cultivability. In samples with the lowest NP concentration, which showed >99.9% *E. coli* CFU reduction, no difference in bacterial cell death was found compared to the reference membrane. However, reduced EPS was produced by *P. aeruginosa* within 24 hours at higher NP concentrations. The reduction was confirmed visually via microscopy where no extracellular structures were found on ZnO membrane.

This study highlights the need for more advanced microbiological testing methods for membranes. It was demonstrated that despite excellent antibacterial activity determined via cultivation, the results might be false since bacterial cells can lose their ability to form colonies on agar plates yet being still alive.

Acknowledgements

The study was carried out within the ERA-NET project "Earth abundant Ca-Fe-oxide-based materials with tailored antimicrobial functionalities for diverse applications on surfaces, in water and membranes (CaFeOx)" and financially supported by Project No. 5.2.1.1.i.0/2/24/I/CFLA/003 (Grant No. RTU-ZG-2024/1-0003).

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SL26 - SHORT LECTURE

Peroxidase Mimicking Activity of Nano-Size Ru(edta) Complex at the Solid-Liquid Interface

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Keywords: Ru(edta) nanoparticles, peroxidase activity, methylene blue degradation, solid-liquid interface

The surface coordination chemistry of transition metal complexes has become an intense interest. Although research in this direction is still in its early stages, there is information available in the literature on the potential applications of submicron scale complexes in various fields, such as catalysis [1-3], nanomedicine [4,5] and biosensors.[6] The attention is mainly focused on several intriguing aspects of surface coordination chemistry, including ligand binding on the surface of metal nanocrystals, electronic structure, and chemical transformations at the interface.[7,8] However, the synthesis of submicron-scale metal complexes and their chemical transformations (ligand substitution, redox reactions) at the solid-liquid interface is still *terra incognita*. The only report on the ligand substitution in a nanocomplex suspended in an incoming ligand solution can be found in [9]. In this work, the first example of a colloidal coordination compound of ruthenium, [Ru(edta)], that mimics peroxidase activity in the catalytic oxidative degradation of methylene blue (MB) at the solid-liquid interface, is described.

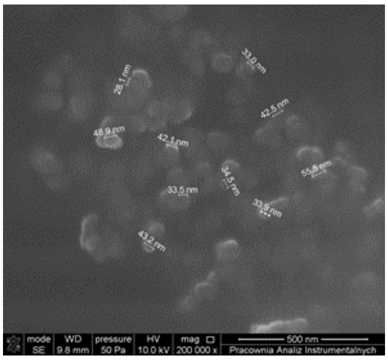

Figure 1. *SEM image of nanoparticles of [Ru(edta)]obtained from the anti-solvent method*

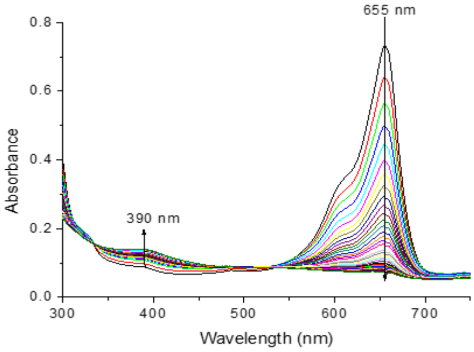

Figure 2. *UV-vis spectral changes pertinent to the H_2O_2 degradation of MB with colloidal [Ru(edta)]. $[H_2O_2]$ = 5 mM, T = 15 °C. Overall time 140 s*

Acknowledgements

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Optimizing the Cobalt Content of Nanoparticle-Supported Catalysts for the Oxygen Evolution Reaction (OER)

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Keywords: Sustainability, Catalysis, Perovskites, Nanoparticles, Electrochemistry,

An established hydrogen economy is central to many global net-zero strategies and at the center of this is the increasing demand to grow production power. An efficient and sustainable solution lies within designing catalysts from earth-abundant materials to combat the sluggish kinetics of the oxygen evolution reaction (OER) which impacts the overpotential required for electrolysis and subsequently the efficiency of these systems.

Perovskite oxides with a simple cubic structure of ABO_3 have gained traction for this purpose due to their inherent high electrical and catalytic activity as well as tunable composition. The cations occupying the lattice are traditionally comprised of larger alkaline earth metals at the A-site and much smaller transition metals on the B-site which are the source of catalytic activity. Exsolution is employed as a technique to mobilize these ions and encourage their migration and socketing to the surface as circular nanoparticles increasing the electrochemically active surface area of the material.

Doping these structures with cobalt are found to perform better in electrochemical testing and exhibit superior OER activity compared to other dopants. Despite these technical advantages, this material suffers heavily from negative environmental and social implications where this investigation compares two Co-doped perovskite oxide families with the compositions of STFC (Sr, Ti, Fe, Co) and BSCF (Ba, Sr, Co, Fe). The results establish a minimal dosing threshold to exploit the superior performance of this metal whilst maintaining sustainability considerations.

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SL28 - SHORT LECTURE

Amorphous Anodized Porous Titania as IrO_2 Substrates for the Electrochemical Oxygen Evolution Reaction

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Keywords: OER, IrO_x catalysts, anodized TiO_2, Galvanic replacement

In this study, amorphous and crystalline anodized porous TiO_2 were investigated as a substrate for Ir catalysts. To compensate for their low conductivity, Ni was electrodeposited onto the substrate, which also acted as a sacrificial layer for the galvanic deposition of iridium from an Ir(IV) chloro-complex solution. The thus deposited Ir was then converted into stable 3D oxides through electrochemical anodization [1]. The substrates were prepared via anodization of a Ti foil in a glycerol-based solution (10% wt. H_2O, 0.5% wt. NH_4F) for a short time (15 min), and either used as-prepared (amorphous; a-TiO_2) or annealed at 500°C for 2 hours to obtain anatase-structured TiO_2 (crystalline; c-TiO_2). A uniformly distributed IrO_x film was observed when a-TiO_2 were used as a substrate, with Ir nanoparticles around 250 nm in size and an Ir atomic ratio of 6.9:1 (**Figure 1a**). In contrast, very small amounts of Ni and Ir were detected in the case of c-TiO_2. This could be due to the fact that Ni electrodeposition on c-TiO_2 occurred mainly on the surface of the substrate [2], and during electrochemical anodization, the remaining nickel after galvanic replacement was electrochemically dissolved, thereby leading to the co-dissolution of Ir as well. This conclusion is consistent with the surface electrochemistry of the catalysts (**Figure 1b**), where, at positive potentials (0.6-1.2 V_{SCE}), peaks attributed to IrO_x are observed only for a-TiO_2. Finally, the electrocatalytic activity of IrO_xNi/a-TiO_2 for the OER surpassed that of c-TiO_2 ($\eta = 248$ mV @ 10 $mA.cm^{-2}$, 2.57 $A.g_{Ir}^{-1}$ @ $\eta = 300$ mV), and their performance is comparable to or even better than similar catalysts reported in the literature [3].

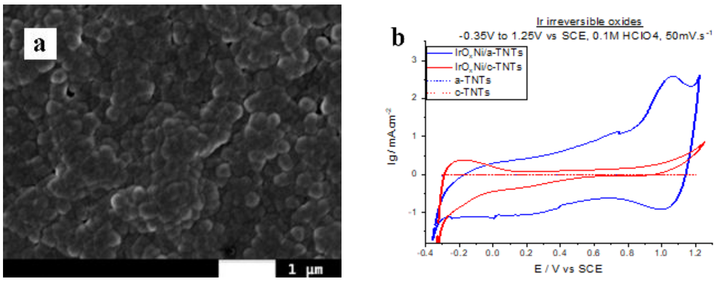

Figure 1. *a) SEM micrograph of the* IrO_xNi*/a-TNTs catalyst, b) Cyclic voltammetry of the samples in 0.1 M* $HClO_4$ *with a scan rate of 50* $mV.s^{-1}$.

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Design of Polymer Ionic Liquids for Electrochemical Applications Using Click Chemistry Tools

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Keywords: polyionic liquids, polytriazole, click chemistry, ionic conductivity

The development of polymer ionic liquids (PILs) has gained increasing attention due to their unique combination of ionic liquid properties and polymeric stability, making them ideal candidates for various electrochemical applications [1,2]. PILs offer high ionic conductivity, excellent chemical and thermal stability, and tunable physicochemical characteristics, which make them suitable for applications such as fuel cells, batteries, supercapacitors, and electrochromic devices. Click chemistry, particularly the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC), provides a modular and highly efficient approach to synthesizing PILs with 1,2,3-triazolium-based backbones [3,4,5]. This synthetic strategy enables the development of polyelectrolytes with controlled architectures, facilitating the fine-tuning of ionic conductivity and mechanical properties.

This research aims to develop backbone cationic PILs with enhanced ionic conductivity following the synthetic route comprising CuAAC dialkyne-diazide polyaddition followed by quaternization (Figure 1).

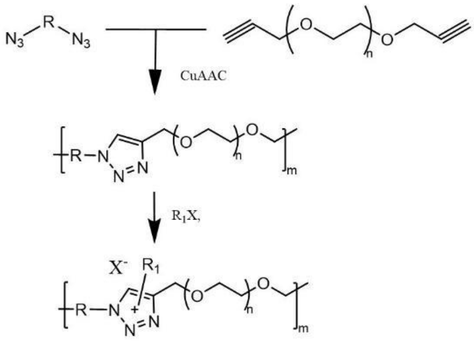

Figure 1. *Scheme of polytriazolium backbone PILs synthesis*

The series of PILs were synthesized with aromatic sulfone or ether fragments in the backbone attached to triethylene glycole fragments *via* triazole links. As quaternizing agents alkyl halides of different length were applied. Chemical structure of all synthesized PILs as well as degree of quaternization was determined by NMR. GPC results revealed that CuAAC polyaddition allowed to achieve the molecular weights of the polytriazoles up to 20 000 g/mol. Thermal properties of synthesized polytriazoles and politriazolium PILs were investigated by were determined by TGA and all the samples showed no weight loss under 200°C.

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Porous contactor membranes for catalytic H_2 gas release from aqueous chemical storages

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Keywords: membrane contactor, catalyst, hydrogen storage

As a clean and renewable energy carrier, hydrogen can play a lead role for a more sustainable future, but storage and transportation remain challenging. Liquid aqueous chemical storages are a promising approach but lack efficient on-demand hydrogen gas release methods. In this project, we investigate a novel approach, which utilises a catalytic membrane contactor for the H_2 gas release from aqueous ammonia borane.

Based on a method established in an earlier study[1], we fabricated catalytically active porous polymer-based multi-composite membranes by film casting cum non-solvent induced phase separation of the matrix polymer polyethersulfone, incorporating Ni or Pd nanoparticles as catalyst and carbon particles or a cationic ionomer as additives to alter the pore properties. We explored different strategies for incorporating catalysts, including mixing commercially available catalyst particles or in-situ nanoparticle synthesis within the casting solution.

By this approach we obtained several membranes, with differing properties such as cross-section morphology, pore size, hydrophobicity, and catalytic activity. These were then further investigated in batch experiments [2] and both cross-flow and flow-through setups, allowing correlation of process performance with membrane properties and evaluating the overall potential of the approach.

Additionally, the gained insights aim to facilitate the tailored synthesis of capillary membranes as a potential for more flexible design and process intensification. Beyond ammonia borane, we also apply this membrane concept to hydrogen release from formic acid, representing a crucial step toward a more economic and fully recyclable hydrogen storage system.

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Magnetically Responsive PVDF Membranes: Enhanced Modification for Water Purification and Protein Separation

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Keywords: PVDF membrane, membrane modification; iron (II, III) nanoparticles; magnetically active membranes

This study focuses on the modification of polyvinylidene fluoride (PVDF) membranes to improve their transport parameters, antifouling properties, and magnetic responsiveness. The efficiency of the modification process was evaluated for both commercial and self-fabricated membranes, confirming its broad applicability. The modification involves the incorporation of iron (II, III) oxide (Fe_3O_4) nanoparticles into the membrane matrix and onto the membrane surface using polyethyleneimine (PEI) as a polymer spacer (Fig.1). Structural and morphological characterization using FTIR, SEM, AFM, water contact angle measurements, and zeta potential analysis confirmed the successful integration of Fe_3O_4 nanoparticles.

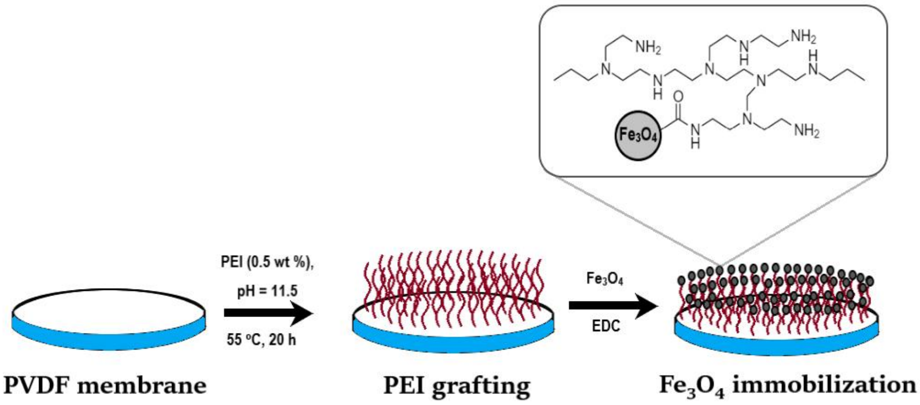

Figure 1. *Illustrative representation of the surface modification process of PVDF membranes [1].*

The first part of the research [1] aimed to develop a method for modifying the surface of commercial PVDF ultrafiltration membranes (MWCO 150 kDa) with Fe_3O_4 nanoparticles to create hydrophilic and magnetoactive membranes capable of reactive removal of foulants over long-term operation. The hydrodynamic water flux increased from 45 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for pristine PVDF to 72 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ for PVDF with immobilized Fe_3O_4 nanoparticles. Additionally, the magnetoactive membranes minimized lysozyme accumulation at pH 12, achieving only 5.3% rejection. These membranes show promise for protein fractionation due to the movement of Fe_3O_4 nanoparticles in a magnetic field, which prevents protein accumulation on the membrane surface, thereby improving separation and fractionation efficiency. Moreover, the magnetic responsiveness of the membranes enhanced mass transport coefficients, reducing fouling and concentration polarization effects.

The next phase of the research [2] investigated modified self-fabricated PVDF membranes in polyelectrolyte-enhanced ultrafiltration using polyacrylic acid (PAA) to form Fe^{2+}-PAA coordination complexes. The efficiency of iron (II) removal was examined for three types of self-fabricated PVDF membranes: pristine PVDF, PVDF/Fe_3O_4 blend membranes, and PVDF/Fe_3O_4 blend membranes with additional surface immobilization of Fe_3O_4 nanoparticles. These modified membranes exhibited a hydrodynamic permeability coefficient of 17.1 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, approximately 2.5 times higher than pristine PVDF membranes. Rejection rates of Fe^{2+}-PAA complexes reached 97.1% and 99.4% at pH 8, reducing Fe^{2+} concentration in permeate from 20 ppm to 0.08 ppm and 0.11 ppm for PAA concentrations of 0.5 wt% and 0.3 wt%, respectively. These results comply with WHO (0.3 ppm) and EU (0.2 ppm) water quality standards.

These findings highlight the effectiveness of magnetoactive PVDF/Fe_3O_4 membranes in water purification and biotechnological applications. The improved permeability, rejection efficiency, and antifouling properties, along with the ability to manipulate membrane function using an external magnetic field, make these membranes highly promising for advanced filtration technologies.

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SL32 - SHORT LECTURE

PVDF Membranes Reinforced with Rare-Earth Oxides for High-Performance Separation Applications

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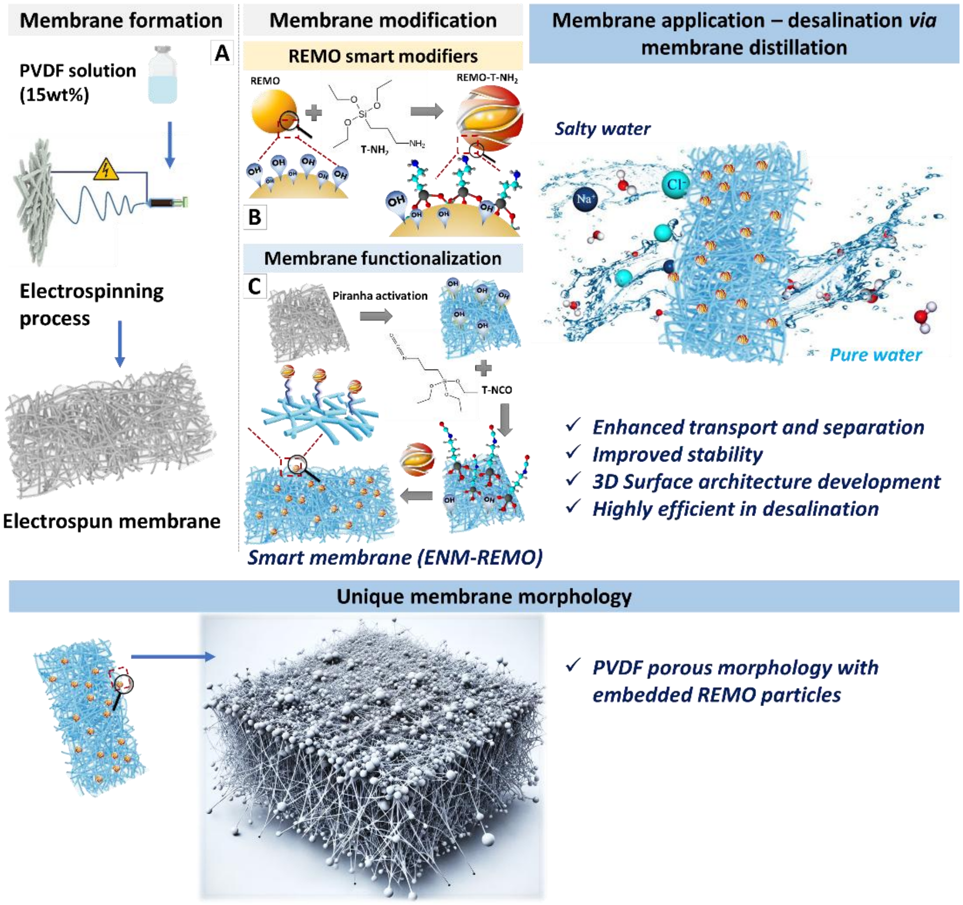
Keywords: Electrospinning, Nanofibrous PVDF membrane, Air-gap membrane distillation, Rare earth metal oxides, Hansen solubility parameters, Pearson's hard–soft acid–base theory

In the studies presented, a new class of separation materials designed for membrane distillation was developed and systematically analyzed. Using poly(vinylidene fluoride) (PVDF) electrospun membranes as a starting point, hybrid organic-inorganic materials were created to improve performance and material features. These materials demonstrated high hydrophobicity, with superhydrophobic characteristics at the micro-scale due to fractal-like structures on the inorganic surface. Rare-earth metal oxides (REMO) were introduced as innovative smart modifiers, being covalently bonded to the functionalized membrane surface for the first time. Three types of REMO were selected to assess their influence on membrane performance in air-gap membrane distillation (AGMD) for desalination. The following rare earth metal oxide nanoparticles (Pr_6O_{11}, Sm_2O_3, and Ho_2O_3) with intrinsic hydrophobicity were applied. The chemical bonding through sufficiently long linkers created a flexible, active surface structure that enhanced transport and separation. Dynamic goniometric studies assessed the membranes' wetting stability. Particularly significant was the membrane enhanced with Ho_2O_3 particles, which demonstrated high flux and salt rejection rates of 14.41 ± 1.35 kg $m^{-2}h^{-1}$ and >99.5%, respectively. The membrane's stability and affinity were further evaluated using Hansen Solubility Parameters and Pearson's hard–soft acid–base (HSAB) theory. The potential of these hybrid membranes extends beyond desalination, as their surface properties can be tailored using various silane linkers, enabling oleophobicity or oleophilicity for applications such as wastewater treatment or oil/water separation.



A Novel, Performant, and Low-Cost Branched Side-Chain Grafted Cellulose Acetate Proton Exchange Membrane for Direct Methanol Fuel Cells

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Keywords: Cation exchange membrane; Cellulose acetate; Nafion; Grafting; Proton conductivity.

Novel cellulose acetate-based cation exchange membranes (CEM) have been successfully synthesized via grafting with poly (2- acrylamide-2-methylpropane sulfonic acid-*co*- methyl methacrylate) as a possible renewable alternative proton exchange membrane (PEM) to Nafion. FTIR, TGA, SEM, and AFM characterize the CEMs with different copolymer compositions. The grafting of side-chain groups was adjusted to maximize the physicochemical features of the fabricated membranes. The results show that the grafted membranes exhibit a higher ion exchange capacity of 3.4 mg. g^{-1} obtained at a high degree of grafting of 40% corresponding to 9:6 P(AMPS-co-MMA) composition. Furthermore, the optimized membrane exhibits significantly improved mechanical properties (21.45 N), enhanced oxidative stability, moderate water, and methanol uptake, as well as decreased methanol permeability (8.071×10-8 $cm^2.s^{-1}$) and adequate ionic conductivity (6.44×10^{-3} S/cm) when compared to both pristine cellulose acetate and Nafion membranes. The increased ionic conductivity, selectivity, and overall membrane performance suggest that the fabricated membranes are promising candidates for use as PEM in direct methanol fuel cell applications.

Acknowledgements: We acknowledge the financial support of this work by the EU through the Recovery and Resilience Plan of the Slovak Republic within the framework of project no. “09I03-03-V04-00237”.

POSTERS

Hansen Solubility Parameters (HSP): A Path to More Efficient Pervaporation

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Keywords: Pervaporation, Hansen solubility parameters, solvent-polymer affinity

In this study, we investigate the pervaporation performance of two organic solvents–ethyl acetate and dimethyl carbonate–using a lab-fabricated polydimethylsiloxane (PDMS) membrane cast onto a PVDF porous membrane via the doctor-blade method (2 mm blade gap) under controlled crosslinking conditions. Our objective is to correlate membrane flux behavior with Hansen Solubility Parameters (HSPs). By examining the dispersion (δd), polar (δp), and hydrogen-bonding (δh) components for each solvent and calculating the Hansen distance (Δ), we demonstrate that lower Δ values indicate stronger membrane-solvent compatibility, leading to higher solvent flux. Conversely, larger Δ values suggest weaker interactions and reduced permeation. This finding is consistent with other studies, such as those conducted by Knozowska et al. [1] and Li et al. [2]. Notably, ethyl acetate–which has a smaller Δ with PDMS–exhibits a higher flux than dimethyl carbonate. These results highlight the direct impact of HSP-related compatibility on pervaporation efficiency. Moreover, they underscore the utility of HSP analysis as a predictive tool, not only for expediting membrane selection and design in organic solvent separations, but also for enabling process intensification in industrial settings, such as solvent recovery and purification.

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Membrane-Assisted Separation and Valorisation of Fusel Oil for the Production of High-Value Chemicals

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Keywords: Fusel Oil, Membrane Separation, Pervaporation, Valorisation, Biorefineries

Fusel oil is a complex by-product formed during the fermentation and distillation stages of bioethanol production, typically composed of higher alcohols such as isoamyl alcohol, isobutanol, and n-propanol, along with minor compounds like aldehydes, esters, and pyrazines [1]. Its chemical composition depends on the feedstock type (e.g., corn, molasses, barley), fermentation parameters (amino acid content, temperature, yeast type), and separation conditions [2]. While generally considered a low-value waste due to its unpleasant odor, variable composition, and high water content, fusel oil represents an unexploited source of valuable chemicals for various industries [1, 2].

The main objective of this study is to develop efficient separation and fractionation strategies to recover and valorise key components of fusel oil for use in high-value applications. Specifically, the study focuses on overcoming current technical barriers related to its water content and azeotropic behaviour, which hinder the purification and application of its alcohol constituents.

Water in fusel oil, typically ranging from 5–20% of content, forms azeotropes with alcohols, complicating their separation by distillation [3]. To address this, membrane-based technologies, especially pervaporation, are being investigated for their ability to selectively remove water and facilitate downstream processing [4]. Once dehydrated, fusel oil can be subjected to fractional distillation to isolate target alcohols such as isoamyl alcohol, isobutanol, and isopropanol [2]. These alcohols are then suitable for esterification reactions, yielding high-value compounds such as isoamyl acetate, isoamyl butyrate, and isoamyl oleate, which have applications in flavourings, fragrances, biolubricants, and green solvents [2].

To maximize efficiency and sustainability, hybrid membrane–distillation systems are suggested, offering energy savings (up to 85%), enhanced separation performance, and improved process modularity [4]. Moreover, such systems may be integrated with chemical reactors to enhance conversion rates by selectively removing by-products such as water during equilibrium-limited reactions like esterification [4].

In addition to major alcohols, fusel oil contains bioactive minor components, pyrazines, which possess antimicrobial properties and may be valorised as functional agents in pharmaceutical or agricultural formulations [5]. Although their separation is more complex, their presence adds further value to the fusel oil's potential.

In conclusion, this study aims to establish a systematic and scalable approach for the separation, fractionation, and valorisation of fusel oil. Through advanced process integration involving membrane dehydration and fractional distillation, the project envisions transforming fusel oil from a challenging by-product into a sustainable source of ingredients for the pharmaceutical, cosmetic, chemical, and automotive sectors.

Acknowledgements

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P03 – POSTER

Optimisation of Polyacrylonitrile Hollow Fiber Membrane for CO_2 Separation from Flue Gases

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Keywords: Polyacrylonitrile; Hollow Fiber Membrane; Synthesis Parameter Optimization; Flue Gas; CO_2/N_2 Selectivity.

CO_2 separation has been recognized as a potential approach to address the impacts of climate change resulting from greenhouse gas emissions. Efficient separation technologies are required to effectively remove CO_2 from flue gases, enabling their widespread adoption. Membrane-based gas separation technology is much more compact, energy-efficient, and economical than other conventional technologies [1]. In particular, polymeric membranes in hollow fiber configuration, though under development, are one of the next-generation, widely considered, promising technologies for CO_2 separation from flue gases produced by fossil fuel combustion [2]. However, the separation performance of polymeric hollow fiber membranes is still limited due to the inverse correlation between flux and selectivity. The factors that generally affect the membrane material, structure, transmembrane pressure, and thickness of the membranes. Therefore, this work aims to prepare a scalable and high-performing polyacrylonitrile hollow fiber membrane via optimized synthesis parameters for efficient CO_2 separation from flue gases. The scanning electron microscopy analysis reveals a difference in morphology with the variation in the synthesis parameter of the prepared membranes. Also, the characterisation results indicated that all the membranes had finger-like structures in their cross-section, exhibiting a thermal stability upto 300 °C. The membranes underwent testing through pure gas experiments. The resulting membranes exhibited high CO_2 permeability (91,166 Barrer), and good CO_2/N_2 selectivity (~4.4) based on the findings the position of the membrane in relation to the Robeson Upper Bound is illustrated in the schematic below. Thus, this study provides insights and guidelines to fabricate highly permeable membranes in the industry for CO_2 capture, N_2 enrichment, and flue gas treatment.

Acknowledgements

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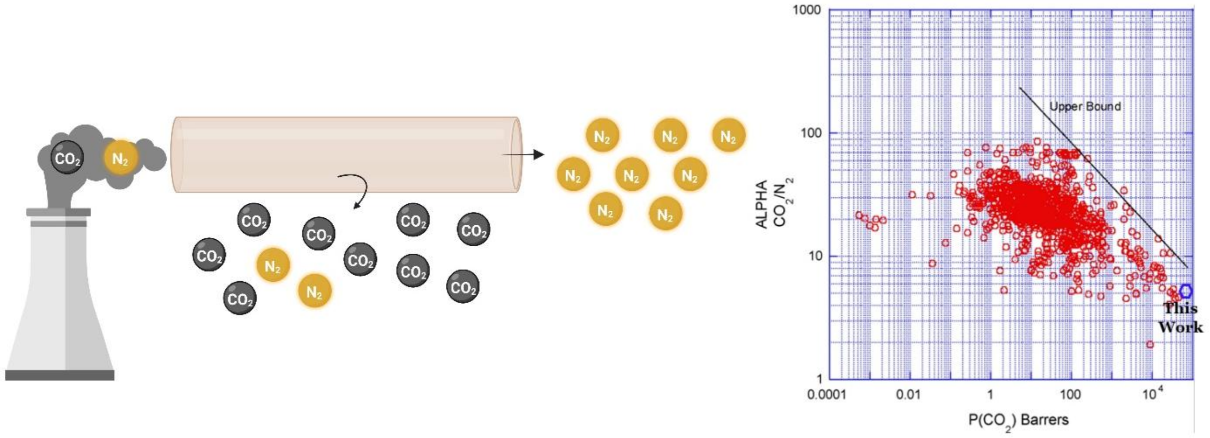

Schematic: *Illustration of CO_2 removal from flue gas using optimized PAN hollow fiber membrane and its position the updated Robeson Upper bound plot.*

Research on the chitosan/polysulfone composite's separation characteristics to improve removal of natural organic materials and mitigate fouling

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Numerous studies have been conducted on modified PSf membranes, encompassing both material and surface alterations. In this study, chitosan powder was used ranging from 0 to 2 wt.% to create composite polysulfone (PSF) ultrafiltration membranes. A thorough analysis of these membranes was conducted, which included evaluations of their morphology, hydrophilicity, porosity, average pore size, pure water flux, and organics separation. ATR-IR analysis verified that polysulfone and chitosan were properly blended in PSf–CS membranes. Scanning electron microscopy (SEM) was used to examine the membranes' surface and cross-sectional morphology. A number of qualities, including hydrophilicity, were enhanced by the addition of chitosan. The hydrophilicity of the PSf–CS membrane was higher than that of a PSf ultrafiltration membrane. Additionally, chitosan-based membranes had the maximum flow in the water flux test. The organics rejection was unaffected by this improvement. Furthermore, the addition of chitosan had a noteworthy impact.

Fabrication Of PVDF Membranes Using Cyrene™ Greener, Biodegradable Solvent For Saltwater Treatment By Membrane Distillation And Membrane Crystallization

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Keywords: P(VDF-HFP) membranes, Cyrene™ bio-degrable solvent, non-solvent induced phase separation, membrane distillation (MD), membrane crystallization (MCr).

The study aims to address the significant challenges in fabrication of polymeric membrane, i.e., use of toxic solvents. In this work a greener, bio-degradable solvent Cyrene™, is used for the fabrication of Poly(vinylidene fluoride-hexafluoropropylene) PVDF-HFP flat sheet membranes and its application in membrane distillation/crystallization. The membranes were prepared via phase inversion method. The influence of the additive polyethylene glycol PEG (200) and of the co-solvent triethyl phosphate (TEP) on membrane morphology and properties was investigated. The effect of different coagulation baths (only water and ethanol and water (1:1)) was also studied. Five different membranes were prepared which were further classified as M1, M2, M3, M4 and M5. The prepared membranes were well characterized through pore size, contact angle, porosity, thickness, mechanical test and scanning electron microscopy. The results showed asymmetric structure with the formation of macrovoids along the cross-section like in terms of morphology for membrane produced with ethanol and water (1:1) as coagulation bath. The pore size of the membranes was in the microfiltration range (0.09 µm - 0.42 µm), the porosity lied between 80 to 86 % and thickness ranged from 78.5 µm to 106.4 µm. M5 membrane (mean pore size around 0.2 µm, 84.4 % porosity and 106.2 ± 2.2 µm thickness) was tested in a DCMD and MCr lab set-up with different concentrations of brine solution (0.6 M, 1.1 M, and 5.3 M). In all tests, rejection rates higher than 99% were obtained. Moreover, NaCl crystals of uniform shape were also achieved after 300 minutes of membrane crystallization tests carried out on the 5.3 M NaCl solution at 42.1 °C of temperature.

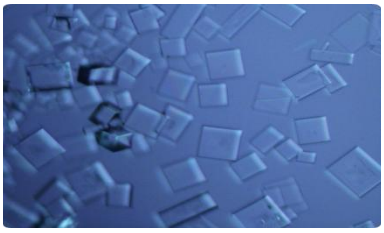

Figure 1. *Image of NaCl crystals achieved at 300 mins in the test of membrane crystallization (MCr).*

Acknowledgements

The authors thank the project "Tech4You—Technologies for climate change adaptation and quality of life improvement"—National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.5, funded from the European Union–NextGenerationEU, Identity code: ECS 00000009, CUP B83C22003980006imes

Real-Time Characterization of Sodium Bicarbonate Crystallization in PVDF Membrane Modules Using FBRM.

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Keywords: Osmotic Membrane Distillation Crystallization, Sodium Bicarbonate, FBRM, Real Time Monitoring.

Introduction: Sodium bicarbonate ($NaHCO_3$) crystallization is pivotal in various industrial processes, including water treatment and resource recovery[1]. Osmotic Membrane Distillation Crystallization (OMDC) has emerged as an innovative technique that leverages osmotic gradients to induce supersaturation, facilitating controlled crystallization.[2][3]While traditional crystallization methods have been extensively studied, real-time monitoring within membrane modules remains underexplored.[4], [5] This study introduces the direct insertion of a Focused Beam Reflectance Measurement (FBRM) probe into the membrane module, enabling in situ monitoring of crystal size distribution (CSD) and growth kinetics. This novel approach aims to enhance our understanding of the effects of feed concentration and flow rate on $NaHCO_3$ crystallization within an OMDC system.

Experimental Methodology: Commercial polyvinylidene fluoride (PVDF) flat-sheet membranes were utilized in the OMDC setup. A sodium bicarbonate feed solution, with concentrations ranging from 10 to 96 g/L, and a sodium chloride (NaCl) osmotic solution concentration 200 g/L were employed to drive water transport across the membrane, inducing supersaturation and subsequent crystallization. The system operated at feed flow rates between 100 and 700 mL/min to assess their impact on crystallization behavior while the osmotic side constant at 400ml/min. For the first time, an FBRM probe was directly inserted into the membrane module, facilitating real-time monitoring of CSD dynamics and providing insights into nucleation, growth, and agglomeration phenomena. The integration of the FBRM probe allowed continuous observation of crystallization processes within the membrane module. Data indicated that higher flow rates enhanced shear forces, leading to the formation of smaller, more uniform crystals.

Conversely, increased feed concentrations elevated supersaturation levels, promoting rapid nucleation and the growth of larger crystals. These findings underscore the critical influence of hydrodynamic conditions and supersaturation on crystal morphology and size distribution, aligning with previous studies on membrane crystallization processes. This study successfully demonstrated the feasibility of using an FBRM probe for in situ monitoring of $NaHCO_3$ crystallization within an OMDC system. The findings highlight the significant roles of feed concentration and flow rate in determining crystal characteristics, offering valuable insights for optimizing membrane-based crystallization processes in industrial applications

Acknowledgements

I would like to acknowledge that the project has been funded by the French Community of Belgium

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Bionics inspired modified PVDF membranes for hypersaline water treatment

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Keywords:

Membrane Distillation (MD) is a thermally-driven separation process that offers significant potential for addressing the global challenge of hypersaline wastewater treatment. Unlike conventional desalination techniques, MD relies on a hydrophobic, microporous membrane that permits the selective transport of water vapor while rejecting non-volatile solutes, such as salts. The driving force for separation is the vapor pressure gradient, induced by a temperature difference between the heated saline feed and the cooled permeate side. While MD is particularly promising for treating complex waste streams—including reverse osmosis (RO) brines, oil and gas produced waters, and geothermal effluents—it faces substantial challenges when applied to hypersaline feeds with salt concentrations exceeding 70,000 mg/L.

Key technical hurdles in hypersaline MD include reduced vapor flux due to lowered water activity, membrane wetting exacerbated by surfactants and high osmotic pressure, and scaling caused by the crystallization of salts such as calcium sulfate and sodium chloride. These phenomena significantly impair membrane performance, energy efficiency, and long-term operational stability.

To address these challenges, we present the development and application of bionics-inspired polyvinylidene fluoride (PVDF) membranes functionalized with rare earth metal oxides (Nd_2O_3 and Gd_2O_3) and REMO-type smart modifiers. Inspired by gecko skin morphology, the engineered membranes exhibit a tuned 3D surface architecture, increased wetting resistance, improved surface charge characteristics, and optimized pore structures. These features enhance both water vapor transport and salt rejection, offering superior performance in hypersaline conditions.

The functionalization process involved membrane activation via piranha treatment followed by chemical grafting with REMO-NH_2 and REMO-NCO modifiers. The structural and chemical modifications were confirmed through FTIR spectroscopy and morphological analyses. Performance testing revealed a marked improvement in average pore size (PVDF: 0.407 µm; PVDF-Nd_2O_3: 0.258 µm; PVDF-Gd_2O_3: 0.362 µm), reduced wetting, and enhanced water flux and stability during Dead Sea water distillation.

The advanced membranes demonstrate significant potential for integration into Zero Liquid Discharge (ZLD) systems, facilitating both freshwater recovery and mineral extraction. Moreover, their compatibility with solar-assisted MD makes them suitable for decentralized and sustainable water treatment applications in arid and off-grid regions.

This study highlights the efficacy of bioinspired material design in overcoming critical barriers in hypersaline MD and supports the broader implementation of advanced membrane technologies for sustainable water management.

Structure and properties of carboxymethylcellulose films with resveratrol and berberine

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Keywords: Carboxymethylcellulose (CMC), berberine, resveratrol, scanning electron microscopy (SEM), ATR-FTIR spectroscopy

The aim of this study was to develop carboxymethylcellulose (CMC) films incorporating active substances such as resveratrol and/or berberine. These films are intended for use as active packaging for food storage, particularly for fruits and vegetables. Unlike synthetic packaging, which is non-biodegradable and contributes to landfill waste, CMC is a polymer that decomposes in the environment after use. Additionally, biopolymer films can be functionalized with natural active compounds to impart antioxidant and antibacterial properties, thereby preventing or significantly delaying food spoilage and extending shelf life.

In this study, glycerol-plasticized CMC films containing berberine, resveratrol, or both were prepared, with active compound concentrations of 1% (w/w) and 5% (w/w). The structure of the films was analyzed using ATR-FTIR spectroscopy, UV-VIS spectrophotometry, and SEM. Various properties, including mechanical properties, thickness, moisture content, water vapor transmission rate (WVTR), and antioxidant properties, were investigated.

The infrared spectra of the CMC films containing resveratrol and berberine were similar to that of the plasticized CMC film, indicating no significant interactions between the film components. The functionalized films exhibited excellent UV-blocking properties. SEM images revealed distinct structural differences among the films. Additionally, the polymer film with a higher resveratrol content demonstrated reduced moisture content and water vapor transmission rate (WVTR). The incorporation of berberine imparted antibacterial properties to the films, while resveratrol contributed to their antioxidant characteristics.

Acknowledgements

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Towards Sustainable Meat Packaging Using Chitosan-Based Emulsions

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Keywords: edible packaging, chitosan, sutainable packaging, emulsion based films.

Recent trends advocate for replacing plastic packaging with alternative materials to reduce environmental impact. However, grooving number of studies, such as [1] has revealed that commonly used plastic packaging, generally exhibits lower environmental impact compared to alternatives like paper, glass, or aluminum [2]. These findings suggest that while non-plastic materials offer certain advantages the environmental implications of replacing plastic packaging are complex and context dependent. Therefore, a nuanced approach, considering specific applications and materials characteristics, is essential for making sustainable packaging decisions.

The primary problem we aimed to address is investigation of biobased polymers as a waste free packaging solution. Active packaging and edible biopolymer packaging are two examples of the alternative solutions being considered in light of the drawbacks of biomaterial packaging [3]. There are a lot of materials that can't be utilized as the foundation for edible packaging due to legal limits and system regulations. In reality, these substances fall under a class of molecules that includes polysaccharides, proteins, lipids, and waxes.

In present work, we looked into the properties of edible packaging for poultry meat made of a emulsion based formulation with an aqueous chitosan solution as a continuous phase and edible plant oil as lipophilic disperse phase. Given its known antibacterial activity and reasonable gas barrier properties, chitosan has natural potential as a food packaging material [4]. Furthermore, it doesn't have any harmful effects on the body and breaks down naturally. Neat chitosan films are fragile and rigid, and they do not efficiently prevent moisture penetration. To address this disadvantage we propose to incorporation of two phase system comprising a hydrophilic chitosan matrix and hydrophobic oil inclusion. We found that adding a dispersed oil phase to chitosan-based films improved their mechanical properties. Additionally, we anticipate that adding oil phase microdroplets to chitosan films would change their mechanical characteristics and enable the addition of active substances that are water insoluble. This innovation may expand the use of chitosan-based films in edible packaging, particularly in the realm of active packaging. In the assigned study, we looked at the basic mechanical characteristics and storage capabilities of films made from solutions with various compositions.

Acknowledgements (Heading: Times New Roman, 10 pt., bold, centered)

The work was financially supported by Project 4101.00000081 Emerging Field (Applied polymers, nanomaterials, membranes, and composites)

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PDMS as absorber film to enhance ATR-IR detection of organic micropollutants in aqueous media

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Keywords: PDMS, organic micropollutant, absorption, ATR-IR,

This work within the EU project IBAIA aims at the detection of organic micropollutants in aqueous media using an ATR-IR-based sensor system. For this purpose, a hydrophobic coating of the ATR crystal is developed to enrich the pollutants for a more sensitive analysis and to minimize water uptake and its impact on IR signals.

Polydimethylsiloxane (PDMS) is a widely used transparent elastomer with thermal and chemical resistance that is also easy to process [1-3]. Due to its intrinsic hydrophobicity, PDMS has antifouling properties, making it an excellent polymer for applications in freshwater or marine environments [4]. PDMS has already been used to absorb the pollutants benzene, toluene and xylene from water with subsequent UV-Vis analysis [5].

Based on this, different types of thin PDMS films are adapted to be suited also for more polar micropollutnats such as pharmaceuticals, and optimized for high absorption and subsequent complete desorption to enable long-term continuous measurements.

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Study of Exfoliated Graphite-Polypyrrole Composites and Their Use in Electrochemical Sensors for Dopamine Detection

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Keywords: Exfoliated graphite, polypyrrole, structural analysis, electrochemical sensors, dopamine.

Graphene and graphene-related materials are characterized by high surface area, chemical stability, and capacity to immobilize various biomolecules; therefore, they are promising candidates for designing electrochemical sensors with high sensitivity and selectivity [1]. Owing to dopamine's (DA) significant role in the human body, there has been substantial focus on creating graphene-based electrochemical sensors for DA detection. DA neurotransmitter is responsible for human emotional responses and control of muscle movements. Deviations from the optimal concentration of DA can cause a wide range of disorders, including schizophrenia, Parkinson's disease, and heart failure [2,3]. Thus, the development of sensitive platforms for DA detection has become an important issue in clinical diagnosis.

This research aimed to study and develop electrochemical sensors based on exfoliated graphite-polypyrrole (GPPy) composites for DA detection. For this purpose, three graphite precursors with grain sizes of <50 µm, ≥149 – ≤840 µm, and 2000 µm were intercalated with sulfuric acid and heat-treated at a temperature of 800 °C to acquire exfoliated graphite (EG). During the wet-synthesis procedure, EG was further modified with polypyrrole (PPy). The obtained GPPy samples were characterized using SEM, XPS, and Raman spectroscopy and were tested as active electrode materials for detecting DA.

XPS and Raman analyses confirmed the successful functionalization of EG with PPy. The medium-sized grain sample (GPPy_2) showed the highest nitrogen content (5.12 at.%) with 15.16% graphitic-N, enhancing electrocatalytic activity. Raman spectra revealed D, G, and 2D bands alongside additional PPy peaks. The bands at 930 $\mathrm{cm^{-1}}$ and 980 $\mathrm{cm^{-1}}$ indicate the oxidation state of the polymer. The presence of both bipolaron and benzoic states suggests that the PPy is in a conductive polaronic state. The relative intensity of these bands increases in this order GPPy_3 > GPPy_2 > GPPy_1, indicating that a composite made with larger graphite particles has the highest amount of bipolaron units. Electrochemical investigations revealed that the GPPy_2/GCE sensor demonstrated the most promising parameters, including high sensitivity (2468 $\mu\mathrm{A\ mM^{-1}\ cm^{-2}}$) and a low limit of detection value of 34 nM for the DA. The introduction of these innovative synthetic modifications offers the prospect of creating advanced materials based on graphene, which could be utilized across a wide range of sectors.

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The influence of modification of layered double hydroxides on their adsorption capacity towards Cr(VI) ions

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Keywords: chromium(VI), sorption, layered double hydroxide, LDH

Chromium compounds are of great industrial importance, because they are widely used in the production of steel, textiles, artificial fertilizers, as well as in galvanization processes and the electronics industry [1]. As a result of extensive human activity, the environment is polluted with chromium compounds, in particular Cr(VI) salts, which are highly toxic and have proven carcinogenic properties [2]. These pollutants are among the most hazardous, because they spread relatively easily through aquatic systems [3]. Therefore, in order to reduce the environmental burden of Cr(VI) compounds, new methods of their removal from industrial wastewater and contaminated groundwater are being sought.

In this study, the sorption of chromate(VI) ions on six different layered double hydroxides was investigated. Two basic materials Mg_2Al and Mg_3Al and their derivatives modified with Cu^{2+} and Zn^{2+} or Fe^{3+} ions were obtained by the co-precipitation method. The next step was to replace carbonate ions with chloride ions in the interlayer space. The materials obtained in this way, both in CO_3^{2-} and Cl^- form, were used as adsorbents of CrO_4^{2-} from aqueous solutions. Adsorption isotherms and kinetics studies were conducted. Sorption capacities of the synthesized LDHs were determined and the effect of solution pH on the sorption process was investigated.

The prepared adsorbents were characterized by powder X-ray diffraction (XRD) using a Rigaku MiniFlex II diffractometer. Fourier transform infrared spectroscopy (FTIR) was performed using an Alpha spectrometer (Bruker, Inc.). Thermal analyses of obtained materials were made applying the TG and DSC methods using the SETSYS 16/18 analyzer (Setaram). The absorption measurements were performed on a JASCO V-660 UV-Vis spectrophotometer. The concentration of Cr(VI) ions in solutions before and after the sorption process was determined by the colorimetric method based on 1,5-diphenylcarbazide dye.

The adsorption process of chromate(VI) anions was successfully carried out on all synthesized materials. Generally, higher sorption parameters were obtained for layered double hydroxides in chloride form, compared to carbonate one, while the best adsorption capacity of CrO_4^{2-} ions was demonstrated by LDHs containing Cu^{2+} and Zn^{2+} ions in their structure. A non-monotonic course of the sorption process over time was observed, which may be caused by the sorption of various complexes of the considered anions with the surface of the sorbents.

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CDI process with covalent organic frameworks as cathode for metal ions recovery

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Keywords: Covalent Organic Frameworks (COFs); CDI; metal ions recovery.

Covalent Organic Frameworks (COFs) represent an innovative class of crystalline and porous materials which could be used for metals recovery, from spent batteries [1]. The primary objective of this experiment was to study prospects of metal ions separation with electrodes fabricated from COF. The COF materials were synthesized via a solvothermal method, employing seven different amines, each paired with corresponding ketones, aldehydes, and carboxylic acids. The obtained products underwent material characterization, including solubility assessments in water and 0.1M HCl, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, electrochemical impedance spectroscopy (EIS), porosity analysis, and X-ray diffraction (XRD).Afterward capacitive deionization (CDI) process was performed. The setup was constructed with anode made of comprised activated carbon and cathodes fabricated from selected COF. The working solution contained metal ions such as Co, Ni, Mn, and Li, which are common components of batteries. The experiment was conducted under varying voltages and initial solution concentrations to evaluate the sorption capabilities of the COF material. The COF was synthesized through a solvothermal reaction using p-phenylenediamine (PDA) and Isophthalaldehyde (IPA) in a molar ratio of 1:1.25. The reaction was carried out for 4 hours at 70°C in an air atmosphere. During the procedure, ions were adsorbed onto the COF-based electrode for 10 minutes, followed by desorption into deionized water for 5 minutes. Solution samples were analyzed using atomic absorption spectroscopy (AAS) to quantify the concentrations of sorbed ions. The CDI processes using cathodes made from COF materials achieved the expected metal ion sorption objectives. In the CV mode (CV=2V), the selectivity factor (β) reached values of βNi/Co = 2,70 , βNi/Li = 0,31 and βNi/Mn =2,33. Synthesized PDA-IPA COF material is a promising cathode material for the recovery of nickel metal ions from battery effluent spent.

Acknowledgements

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P14 – POSTER

Pt and Pt-Ni Catalysts Supported on Ti as HER Cathodes in Alkaline Media

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Keywords: AWE, HER, Pt-based catalysts, Galvanic replacement/deposition

Alkaline water electrolysis (AWE) is a mature technology for hydrogen production, but the slow hydrogen evolution reaction (HER) kinetics in basic media may still benefit from Pt-based electrocatalysts. Because of its high cost, a significant reduction in Pt mass loading is necessary for large-scale applications, in combination with non-noble active metals (e.g. Ni) and the use of stable substrates, such as Titanium [1]. This study focuses on novel Pt and Pt-Ni catalysts prepared via galvanic deposition or replacement, respectively, on Ti foil to be used as HER cathodes in alkaline media. The Pt/Ti electrodes were prepared by reduction-deposition of Pt from a 1 mM K_2PtCl_6 solution at 65°C for 15 minutes on freshly etched titanium [2], while the Pt/Ni/Ti electrodes were produced by Ni-mediated galvanic replacement on electrodeposited Ni films (q_{Ni}=293 mC.cm^{-2}) [3]. The Pt/Ti electrodes were characterized in their as-prepared state or after annealing at 500°C for 3 h, whereas the Pt/Ni/Ti electrodes were characterized as-prepared or after electrochemical anodization. SEM micrographs of the Pt/Ti electrodes reveal highly dispersed Pt particles forming nano-scale cauliflower-like structures before annealing (**Figure 1a**), which transform into dendritic structures with oblong sticks after annealing (**Figure 1b**). In contrast, the Pt/Ni/Ti electrode exhibits a continuous film with a nodular structure and high Pt coverage, typical of electrodes prepared by this method (**Figure 1c**). EDS analysis indicates a Pt:Ni ratio of 28:72 (w/w). The intrinsic electrocatalytic activity for HER i.e. the current per electroactive Pt area, j_{ea}, (**Figure 1d**) shows that annealing significantly enhances the performance of Pt/Ti electrodes, likely due to increased crystallinity, surface area, and synergism of the oxidized Ti support. However, the Pt/Ni/Ti electrodes, benefiting from higher Pt coverage and the synergistic effect of Ni oxides, exhibit superior performance, with the anodized Pt/Ni/Ti electrode achieving the highest current densities (at a given overpotential). The Pt/Ti (not annealed) and Pt/Ni/Ti (anodized) electrodes showed good stability for 4 h, with an overpotential of $\eta \leq 200$mV @ -50 mA.cm^{-2} and $\eta \leq 50$ mV @ -10 mA.cm^{-2}, respectively.

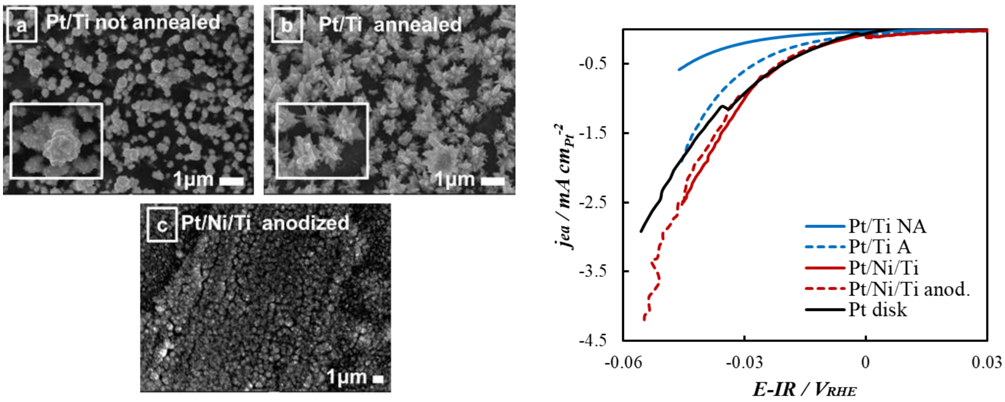

Figure 1. *SEM micrographs of a) Pt/Ti not annealed, b) Pt/Ti annealed, c) Pt/Ni/Ti anodized and d)* j_{ea} *vs. E-IR graph obtained at 5 mV.s*$^{-1}$ *in 0.1 M KOH*

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P15 – POSTER

Effect of Graphene on the Electrochemical Efficiency of BiMeVOx Catalysts for Hydrogen Production from Water Splitting

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Keywords: waste coffee grounds; bifunctional electrocatalyst; water splitting; oxygen evolution reaction; hydrogen evolution reaction

Increasing attention is being paid to the production of green hydrogen, seen as the fuel of the future and offering a sustainable solution for the energy transition. Sustainable methods of generating green energy focus on photocatalysis, electrocatalysis, or photoelectrocatalysis. These methods represent pathways towards achieving pollution-free green hydrogen production via water splitting in the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). For HER and OER to proceed effectively, catalysts are essential. So far, platinum-based (Pt) materials have been known to efficiently catalyze water splitting for HER, while iridium (Ir) or ruthenium (Ru) have been utilized for OER. However, due to their high cost and limited availability, researchers strive to replace these elements with more cost-effective and abundant alternatives.

In our studies, we synthesized BiMeVOx compounds obtained by our proposed method [1]. In the next step of our study included an examination of the effect graphene addition had on the catalytic activity of the obtained materials [2]. Pristine $BiVO_4$/C and metal-doped $BiMeVO_4$/C were characterized using transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The synthesized materials have been subjected to electrochemical tests in oxygen and hydrogen evolution reactions, and their stability in these processes was determined.

The preparation of heterogenous nanostructures of $BiVO_4$/C and BiMeVOx/C materials containing highly conductive carbon was successful. Electrochemical water splitting results revealed enhanced activity of BiMoVOx/C and BiCoVOx/C versus that for pristine $BiVO_4$/C. Addition of graphene and molybdenum into the $BiVO_4$ in sample BiMoVOx/C increased activity in the hydrogen evolution reaction, with an overpotential and Tafel slope at 432 mV and 76 mV dec ^{1}, respectively. In the case of the oxygen evolution reaction, the addition of cobalt and graphene in sample BiCoVOx/C drastically improved catalytic performance, with the Tafel slope a 100 mV dec ^{1}, a lower value than that for commercial IrO_2 (100 mV dec ^{1}). The improved catalytic efficiencies are attributed to enhanced conductivity and metal-doping (Mo or Co). The approach taken here was not standard. As we described in our paper [1], BiMeVOx are good photocatalysts; however, the use of graphene in these materials creates good electrocatalysts [2].

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Perovskite oxide-based catalysts for electrochemical water electrolysis

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Keywords: Perovskite oxides; Sol-gel method; Water electrolysis; Electrocatalysts; Energy conversion

Climate change is forcing society to rethink its approach to sourcing materials for energy storage and conversion. In this context, water electrolysis powered by renewable energy, which enables the production of green hydrogen, plays a crucial role in the transition to sustainable energy sources. Consequently, researchers are striving to develop efficient catalysts capable of effectively facilitating the oxygen evolution and hydrogen evolution reactions (OER and HER). Perovskite oxides represent a promising alternative due to their compositional versatility, exceptional catalytic activity and high stability in energy conversion systems, like water electrolysis. In particular, an anode catalyst based on $SrTiO_3$ combines high catalytic activity with reduced cost due to the possibility of utilizing limited content of selected metals (Ni, Co, Fe, Ir, Ru) in the perovskite structure that are known for their high electrochemical activity [1, 2].

In this study, perovskite oxide-based materials were synthesized using the sol-gel method, a versatile and cost-effective technique that allows precise control over composition, morphology, and phase purity. The sol-gel process enables the formation of homogeneous gels at relatively low temperatures, facilitating the preparation of nanostructured materials with a high surface area, which is beneficial for electrocatalytic applications. The synthesized materials were subjected to structural and morphological characterization using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm phase purity and microstructural properties. To thoroughly investigate the catalytic properties of the obtained materials in the oxygen evolution reaction (OER), a series of electrochemical tests were conducted in a 1M KOH solution. The experiments included polarization curve measurements using cyclic voltammetry (CV) and linear sweep voltammetry (LSV), as well as the determination of the overpotential required to achieve a specific current density.

Preliminary studies indicate that the modification of the material significantly improves its catalytic properties. The proposed approach not only promotes an increase in electrochemical activity, but also aligns with a sustainable development strategy. Additionally, its application can contribute to the development of more sustainable technologies in the field of electrocatalysis, reducing both production costs and negative environmental impacts.

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Application of Chemometric Methods for Selecting a Hydrogen Bond Acceptor (HBA) as a Carrier Component for Metal Ions Transport through Polymer Inclusion Membranes

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Keywords: chemometric methods, polymer inclusion membranes, deep eutectic solvents as carriers, metal ions transport

Deep eutectic solvents (DESs) are formed by the combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), allowing for tunable properties such as viscosity, conductivity, and melting point, which can be adjusted based on the composition. This flexibility makes DESs appropriate for various applications, including solvent extraction, liquid membranes, and polymer inclusion membranes (PIMs). Tri n-octyl phosphine oxide (TOPO) is a well-known HBA applied in the formation of DESs, due to its ability to form effective interactions with different HBDs, including carboxylic acids and alcohols [1-3]. This study applied α-benzoin oxime (Cuprone) as a novel HBD, setting it apart from typical acid-based HBDs.

Chemometric methods, specifically hierarchical cluster analysis (HCA) and principal component analysis (PCA), were used to explore and optimize the constituents of deep eutectic solvents (DESs). These methods facilitate the selection of appropriate hydrogen bond donors (HBDs) by analyzing the relationships and similarities among various molecular descriptors (values calculated from the substance structure) associated with a set of compounds.

Chemometric analysis indicated that Cuprone has distinct physicochemical properties compared to conventional carboxylic acids typically used as HBDs. Cuprone was found to exhibit a unique profile, making it a promising candidate for use in DES formulations. The DES composed of TOPO and Cuprone in a 2:1 molar ratio was successfully synthesized. The resulting DES was characterized by its low melting point, high viscosity, and thermal stability, demonstrating potential as an effective solvent for metal ion transport.

The transport properties of this new TOPO-Cuprone DES were investigated in PIMs for the selective transport of Zn(II), Cd(II), Pb(II), and Cu(II) ions from chloride media. PIMs are a relatively new type of membrane, commonly prepared from a solution containing a polymer, carrier, and plasticizer using the solvent evaporation technique. In this research, membranes were composed of cellulose triacetate (CTA) as a polymer (19.1 wt. %), o-nitrophenyl octyl ether (NPOE) as a plasticizer (31.9 wt.%), and TOPO:Cuprone (2:1) as a carrier (49.0 wt. %). The effectiveness of the new DES was compared with PIM systems utilizing TOPO: benzoic acid, TOPO: dodecanoic acid, and pure TOPO as carriers.

The experimental results indicated that transport selectivity order of Zn(II) > Cd(II) > Pb(II) ≫ Cu(II) is attributed to the presence of TOPO in the DES. The maximum fluxes of transported ions were $2.47\times10_{10}$, $1.81\times10_{10}$, $1.61\times10_{11}$, and $2.41\times10_{13}$ mol/cm_2s for Zn(II), Cd(II), Pb(II), and Cu(II), respectively. Furthermore, PIM systems incorporating a plasticizer exhibited high operational stability during long-term experiments exceeding 500 hours. The results demonstrate the potential of Cuprone as an effective HBD in DESs for PIM applications, offering a promising possibility for selective metal ion separation. Chemometric methods proved valuable in predicting and describing DES constituent properties, leading to the successful development of a novel DES with enhanced transport capabilities.

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P18 – POSTER

Structural Properties of Cellulose Acetate Membranes Modified with Graphene Oxide Nanoparticles

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Keywords: cellulose acetate, graphene oxide, composite membranes

Membranes prepared from cellulose acetate (CellAc) are still of interest owing to their good mechanical properties, resistance to degradation and relatively simple fabrication methods. Moreover, CellAc can be applied for separation of environmental water samples [1]. Thanks to above mentioned features cellulose acetate membranes can be effectively applied in various separations, such as nanofiltration (NF) or forward osmosis (FO). It is worth to mention that properties of CellAc membranes can be altered by an addition of different modifying particles, such as graphene oxide (GO). The aim of the present study was the preparation and modification of cellulose acetate based membranes by the addition of GO into the membrane matrix. Additionally, the structural and surface properties of the prepared materials have been performed.

Cellulose acetate based membranes for forward osmosis (FO) were prepared by a phase inversion method using water as non-solvent [2]. Casting solutions were prepared by mixing defined volumes of solvents (dioxane, acetone, methyl alcohol) with given amounts of maleic acid and cellulose acetate. Subsequently, graphene oxide (GO) nanoparticles in the range of 0.1-0.5 wt.% with respect to polymer, were added to the solution. In the next step, the polymer-solvents solutions were mixed, sonicated and used for casting of membrane film applying automatic casting knife. Structural and surface properties of the obtained materials were determined using scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle (CA) and thermogravimetric (TG) methods.

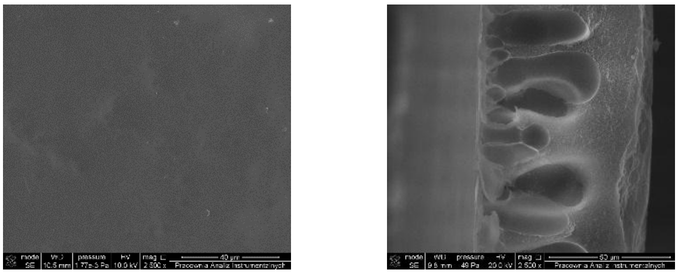

Figure 1. *SEM images of CellAc_GO_0.5wt.% membrane: skin layer (left), cross section (right).*

Obtained membranes possessed porous structure with a nonporous, dense skin layer (**Figure 1**). It was found that an addition of graphene oxide slightly affected roughness of the obtained materials (increase in surface roughness - R_q values from 4.2 nm in case of CellAc_GO_0.1wt.% membrane to 6.1 nm for CellAc_GO_0.5wt.%). Moreover, incorporation of GO into the membrane structure resulted in slight improvement of hydrophilic properties of the obtained materials (decrease of water contact angle value from 74±2° for native CellAc to 71±2° for CellAc_GO_0.5wt.% membrane).

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P19 – POSTER

Novel enhancers based on functionalized MIL-53(Al) for improved dimethyl carbonate/methanol pervaporative separation

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Keywords: Dimethyl carbonate; Organic-organic Pervaporation (ORGPV); MOF; water influence in ORGPV

Dimethyl carbonate (DMC) is considered as an alternative, green solvent characterized by low toxicity and good biodegradable properties. During the production of DMC, excess methanol is used, and dimethyl carbonate creates the binary azeotrope with unreacted methanol. There are several, various method which has been used for the separation of an azeotropic mixture of dimethyl carbonate/methanol. Membrane separation techniques especially pervaporation appear to be alternatives to the traditional separation methods.

In this work hydrophobic, heterogeneous PDMS based membranes with MIL-53(Al) and analogues of MIL-53(Al) (NH_2-MIL-53(Al) and $NHOCOCF_3$-MIL-53(Al)) were fabricated for enhanced removal of DMC from azeotropic DMC/MeOH mixture. Hydrophobic $NHOCOCF_3$-MIL-53(Al) was obtained during the post-synthesis modification of NH_2-MIL-53(Al) with trifluoroacetic anhydrate (TFA). Moreover, the influence of the presence of water in the separated mixture on the efficiency of pervaporation was investigated.

The physicochemical properties of prepared MOFs and membranes were determined by applying advance analytical methods. FTIR-ATR analysis of $NHOCOCF_3$-MIL-53(Al) powder confirmed the successful modification. The characteristic peaks of NH_2-MIL-53(Al) and TFA were detected. Obtained MOF particles are highly crystalline, and the NH_2-MIL-53(Al) structure is well retained after modification. SEM analysis proves the formation of the dense membrane. TGA analysis showed that membranes are thermally stable up to 250°C. Pervaporation results were analyzed implementing separation factor and thickness normalized Pervaporation Separation Index. Pervaporation experiments showed that the optimum amount of particles in the PDMS matrix is equal to 5 wt%. The best separation efficiency was found for the PDMS/$NHOCOCOCF_3$-MIL-53(Al) 5 wt%. Modified PDMS membranes possess better separation properties compared with pristine one. Results revealed that the incorporation of 5 wt% of NHOCOCF3-MIL-53(Al) caused an increase of β from 3.1 to 3.7, a significant value for organic-organic PV.

Essential part of the work was to analyze impact of the presence of water in the feed on overall membrane effectiveness. It was observed that in the case of traces amount of water in the feed solution, water was preferentially transported from the feed to the permeate side. However, the transport of water through membranes was partially suppressed when water content in the feed was over 0.7 wt%.

Rare-earth metal oxide-based modifiers for membrane distillation

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Keywords: Rare earth metal oxide, Air gap membrane distillation, Polyvinylidene fluoride (PVDF), Covalent modification, Desalination process.

This study employed a multi-stage modification of a Polyvinylidene fluoride (PVDF) membrane, initiating with a piranha solution activation, followed by silanization and modification using rare earth metal oxide (Gd_2O_3, Nd_2O_3) by a covalent bond. The modifications were validated using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The membrane's potential to alleviate the global water crisis was demonstrated through its evaluation using air gap membrane distillation with NaCl solutions of varying concentrations, including 0.5 M and 3 M. Despite the challenges of high flux and salt rejection, the modified membrane successfully achieved a flux of 7.3 kg m^{-2} h^{-1}, and 99.9% salt rejection. Analysis revealed that the modified membranes exhibited the highest wettability resistance among the tested membranes, including pristine, activated, and silanized membranes.

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Enhancing PVDF Membrane Performance for Hydrophilic and Hydrophobic Surface Modifications

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Keywords: Bovine Serum Albumin (BSA), Microfiltration, PVDF membrane, Rare earth metals oxide (REMO), Surface membrane modification.

Polyvinylidene fluoride (PVDF) membranes were functionalized with hydrophobic and hydrophilic functionalities for potential microfiltration use. Rare-earth metal oxides (REMO), including Gadolinium (Gd) and Neodymium (Nd), were grafted onto a hydrophobic membrane, enhancing the membrane roughness and contact angle of water over 80°, with improved wetting resistance and outstanding flux performance. In hydrophilic functionalization, L-histidine was chemically grafted onto PVDF, minimizing the possibility of protein fouling and improving water permeation. These materials were used to enhance the surface structure, which was evaluated through XRD and FTIR. Using FTIR, observed–OH, -C=N, and –NH, and using the XRD patterns, changes were observed in the structure of the membrane, with reduced crystallinity, indicating increased amorphous regions favorable for water transport. Filtration experiments were conducted with a bovine serum albumin (BSA) model foulant at a range of transmembrane pressures (2 to 4 bar) in a pressure-resistant stirred cell. Hydrophilic membranes gave higher flux and were easier to clean. After washing, they recovered most of their performance up to 90%. Hydrophobic membranes had lower flux but showed better stability and recovered about 60% after cleaning. Hydrophilic membranes of this kind exhibited high rejections of BSA and stable flux, especially at low pressure, by improved surface wettability and reduced protein adsorption. On the other hand, increased protein adsorption and fouling resistance at elevated pressures were experienced for the hydrophobic membranes. The results validated that the surface modifications optimize the performance of PVDF membranes according to the requirements of the application, with a universal platform of pressure-dependent protein separation and fouling protection.

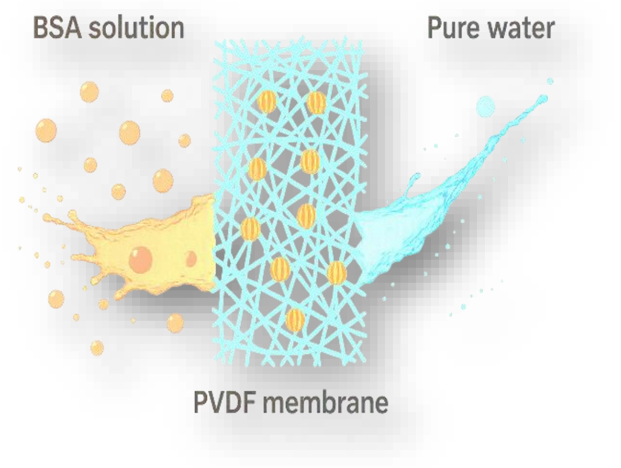

Figure 1: *BSA Separation with Modified PVDF membrane*

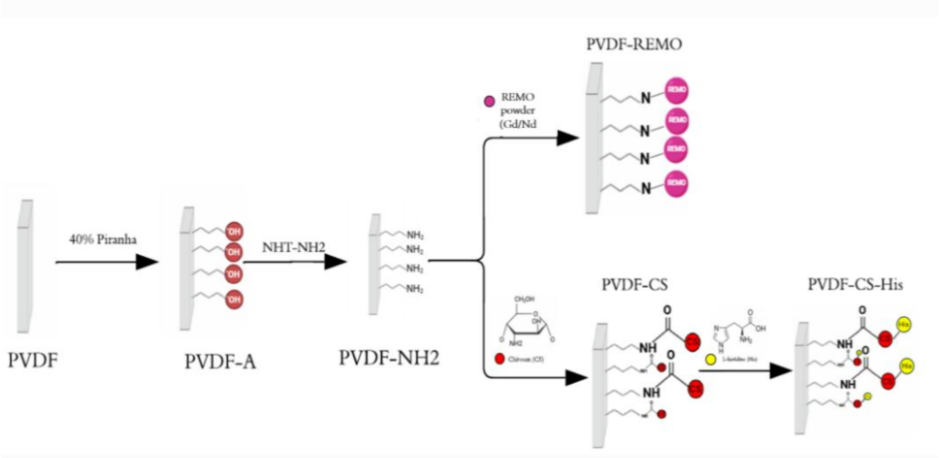

Figure 2: *PVDF Membrane Surface Modification Steps*

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Design of Polymer and Hybrid Particles via Membrane Nanoprecipitation for the Development of Pervaporation Nanocomposite Membranes

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Keywords: membrane nanoprecipitation, composite particles, nanocomposite membranes, pervaporation

Nano- and sub-micrometric particles (NPs and SMPs), in particular polymer-based ones, exhibit remarkable and tunable properties that differ significantly from those of their bulk materials. The processing routes play a key role in determining their crucial characteristics, including size and distribution. One widely studied method for their bottom-up synthesis is nanoprecipitation, recognized as a simple and energy-efficient strategy. The principal mechanism involves the dropwise addition of a polymer solution into a miscible non-solvent that cannot dissolve the solute: the solvent-non solvent diffusion reduces the solvent quality, leading particle formation through precipitation.

Despite its benefits, scaling up this technique remains challenging. Membrane nanoprecipitation (MN) is counted among the high throughput processes, and it is considered a highly promising approach to address this main limitation. This is made possible precisely by a porous membrane, which serves as an efficient contactor between the two phases, thereby promoting optimal mixing and yielding a continuous particles production with uniform dimensions and low polydispersity [1].

This technique has been explored mainly to engineer hydrophobic and amphiphilic NPs and SMPs, and more recently, hydrophilic ones. However, beyond pristine polymer-based ones, MN could be employed to design hybrid SMPs in which the inorganic core is coated by a thin organic layer. Integrating inorganic compounds into polymers allows for improving functionality of both, offering enhanced structural properties and increased colloidal stability.

Polymer and, above all, hybrid NPs and SMPs can find application into the development of next generation materials. They could be included in polymeric matrices to prepare nanocomposite membranes for various applications in which it is useful integrate the selective transport pathways of inorganic fillers with the processability of polymers. Pervaporation nanocomposite membranes have attracted significant interest for azeotropic mixture separations due to their superior permeability-selectivity trade-offs and enhanced thermal and mechanical stability [2],[3].

This work offers an overview of the principles of nanoprecipitation and highlights the advantages of membrane-based processes for producing pristine polymer particles. Particular attention is given to the application of membrane nanoprecipitation in the synthesis of polymer-coated zeolites particles. The study also outlines future perspectives aimed at advancing the development of hydrophilic nanocomposite membranes for high-performance ethanol dehydration via pervaporation.

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