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delle Membrane  
**Consiglio Nazionale delle Ricerche**

# SEMINAR DAY 2022

**The annual update of advances promoted at  
Institute on Membrane Technology,  
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## Book of Abstracts

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*Thanks to the Department of Computer Engineering, Modeling, Electronics and Systems Engineering (DIMES) of University of Calabria for the support in the organization.*



**DOI: 10.48263/ITM\_SEMINAR\_DAY\_2022**

# PROGRAM

8<sup>th</sup> February 2023

OPENING SESSION	
09:00 – 09:20	<b>Dr. Alberto Figoli, Director of CNR-ITM</b> ITM activity in 2022
<i>Moderator: Dr. Lidieta Giorno</i>	
09:20 – 09:50	<b>Twisted Monte-Carlo/CFD digital tool for predicting macromolecules fouling in ultrafiltration food processing</b> <i>Prof. Stefano Curcio</i>
<i>Moderator: Dr. Loredana De Bartolo</i>	
09:50 – 10:20	<b>Advanced materials and functional surfaces for reparative and regenerative medicine</b> <i>Prof. Diego Mantovani</i>
10:20 – 10:40	<b>Coffee Break</b>
<i>Moderators: Dr. Giorgio De Luca, Mr Antonio Condello</i>	
10:40 – 11:00	<b>The role of membranes in controlling supersaturation of antisolvent crystallization: Empirical and MD studies</b> <i>Ms Sara Chergaoui</i>
11:00 – 11:20	<b>Easy tool for prediction of separation performance</b> <i>Mr Ivan Mazza</i>
11:20 – 11:40	<b>Assessment of anisotropy and connectivity of microporous membranes by digital reconstruction of real 3D structures by computational fluid dynamics</b> <i>Prof. Alessio Caravella</i>
<i>Moderators: Dr. Adalgisa Tavolaro, Dr. Serena Regina</i>	
11:40 – 12:00	<b>Biofunctionalized membrane for fluorescence sensing of contaminants</b> <i>Mr Vittorio Sansone</i>
12:00 – 12:20	<b>Polymer-based TiO<sub>2</sub> membrane reactors for recalcitrant dye removal</b> <i>Mr Saurav Bhattacharyya</i>
12:20 – 12:40	<b>An innovative and scalable method of gelation ionotropic to produce chitosan nanoparticles by membrane process</b> <i>Dr. Beatrice Russo</i>
12:40 – 13:00	<b>Continuous production of zein nanoparticles by membrane nanoprecipitation</b> <i>Mr Antonio Condello</i>
13:00 – 14:30	<b>Lunch Buffet at the room “Sala Mostre-Centro Congressi”</b>
<i>Moderators: Dr. Adolfo Iulianelli, Ms Elisa Avruscio</i>	
14:30 – 14:50	<b>MOF-based mixed matrix membranes for propene/propane separation</b> <i>Ms Pegah Hajivand</i>
14:50 – 15:10	<b>Long-term performance of highly selective carbon hollow fiber membranes for biogas upgrading in the presence of H<sub>2</sub>S and water vapor</b> <i>Ms Elisa Avruscio</i>
15:10 – 15:30	<b>Mixed Matrix Membranes based on F<sub>4</sub>-UiO66(Ce)-MOF for CO<sub>2</sub> separation</b> <i>Dr. Carmen Rizzuto</i>

<b>15:30 – 15:50</b>	<b>Mixed matrix membranes for CO<sub>2</sub> separation based on imide/imine organic cages as fillers</b> <i>Dr. Mariagiulia Longo</i>
<i>Moderators: Mr Giuseppe Di Luca, Ms Maria Francesca Vigile</i>	
<b>15:50 – 16:10</b>	<b>Inorganic-based membranes for wastewater purification</b> <i>Dr. Hamdy Maamoun Abdel-Ghafar</i>
<b>16:10 – 16:30</b>	<b>Mg(Al)O mixed metal oxides (MMO) nanoparticles: application in the preparation of sustainable polymeric membranes</b> <i>Ms Hajar Jabkhiro</i>
<b>16:30 – 16:50</b>	<b>Preparation of non-woven supported Halar membranes and their application in membrane distillation</b> <i>Ms Xue Li</i>
<i>Moderators: Dr. Maria Concetta Carnevale, Dr. Mirko Frappa</i>	
<b>16:50 – 17:10</b>	<b>Salts recovery from mining tailings brines by membrane-assisted crystallization</b> <i>Dr. Elvira Pantuso</i>
<b>17:10 – 17:30</b>	<b>Composite membranes for photothermal sweeping gas membrane distillation</b> <i>Mr Giuseppe D'Andrea</i>
<b>17:30 – 17:50</b>	<b>MOFs-based mixed matrix membranes for efficient removal of heavy metals from water</b> <i>Dr. Marcello Monteleone</i>
<b>CLOSING REMARKS</b>	

# **ORAL PRESENTATIONS**

# TWISTED MONTE-CARLO/CFD DIGITAL TOOL FOR PREDICTING MACROMOLECULES FOULING IN ULTRAFILTRATION FOOD PROCESSING

Stefano Curcio, Prof.

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## Speaker Information

### Short biography



**Stefano Curcio** is Director of the Department of Computer Engineering, Modeling, Electronics and Systems and full Professor at the University of Calabria since 2018. Author of more than 75 papers published on international peer-reviewed scientific journals, ten book chapters, one patent and more than 120 presentations held in International Conferences and published in the Conference proceedings. Responsible for several research projects, visiting researcher at CERN (Geneve – CH). He has held scientific collaboration with several food industries, guest editor of special issues. Reviewer of research projects and different peer-reviewed scientific journals. Member of Editorial Board of *Journal of Bioprocessing & Biotechniques* and *BioMed Research International*.

## ADVANCED MATERIALS AND FUNCTIONAL SURFACES FOR REPARATIVE AND REGENERATIVE MEDICINE

Diego Mantovani, Prof.

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### Speaker Information

#### Short biography



Holder of the Canada Research Chair Tier I in Biomaterials and Bioengineering for the Innovation in Surgery (2012-2026), professor at the Department of Materials Engineering at Laval University, senior scientist at the Division of Regenerative Medicine of the Research Center of the CHU de Québec, Diego Mantovani is a recognised specialist in materials for health and medicine. He was Executive Co-Chair of the 10<sup>th</sup> World Biomaterials Congress 2016. He is advisor of three medical devices consortium in the Americas, Asia and Europe.

Over the last 50 years, biomaterials, prostheses and implants saved and prolonged the life of millions of humans around the globe. Today, nano-biotechnology, nanomaterials and surface modifications provide a new insight to the current problem of biomaterial complications, and even allows us to envisage strategies for the organ shortage. In this talk, creative strategies for addressing functional nanocoatings, new metals for tunable degradable metals for a new class of implants and mixing vascular cells and collagen-based materials for physiologically relevant models will be targeted with the overall aim to envisage today how far *innovation* can bring tomorrow solutions for reparative and regenerative medicine.

The overall take home message of this talk is aimed to show how nanocoatings, degradable metals and 3D pluri-culture of appropriate material/cell/environment represent the today bottleneck in reparative and regenerative medicine and which are few of the strategies that have to be investigated to push forward innovation in the field, for the benefit of patients and Humans.

# THE ROLE OF MEMBRANES IN CONTROLLING SUPERSATURATION OF ANTISOLVENT CRYSTALLIZATION: EMPIRICAL AND MD SIMULATION STUDIES

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## Abstract

Antisolvent crystallization is indispensable for the crystallization of heat-sensitive compounds from solutions. However, such crystallization happens instantly, and supersaturation is difficult to control, resulting in a non-uniform crystal morphology and size. Membrane-assisted antisolvent crystallization (MAAC) can control the mass transfer of the antisolvent into the solution and mixing, plus being a substrate for heterogeneous crystallization. This work investigates the optimum conditions to operate MAAC and attempts to deeper understand of different interactions between the membrane and the solute-solvent-antisolvent system through molecular dynamics (MD) simulations. Ongoing research on MAAC covered the use of Polyvinylidene fluoride (PVDF) and Polypropylene (PP) membranes for the crystallization of glycine in water, using ethanol as antisolvent (Fig. 1). Results demonstrated that an optimized operation of MAAC dictates a proper description of the mass transfer. The stability of the mass transfer coefficient is crucial to ensure no membrane wetting by the crystallizing solution and controlled transport of the antisolvent. Second, a specific combination of the operating condition, such as flow rate, antisolvent composition, temperature, or gravity resistance play key role in tailoring the induction time that correlates directly with crystal formation kinetics. Finally, fine tuning the properties of the membrane, such as its porosity, thickness, and hydrophobicity, is advantageous to control supersaturation further and assert a reproducible production of crystals with a narrow crystal size distribution (CSD) [1-3]. MD simulations of crystallization models of glycine-water and glycine-water-ethanol mixtures, built at supersaturation showed a difference in the organization of glycine molecules owing to the mutual diffusion behavior where the antisolvent diffuses faster into the solvent or vice versa (Fig. 2).

Membranes control of supersaturation and crystal properties has potential in intensifying crystallization processes necessary for different applications such as control of polymorphism, reaction purification, and crystal size control.

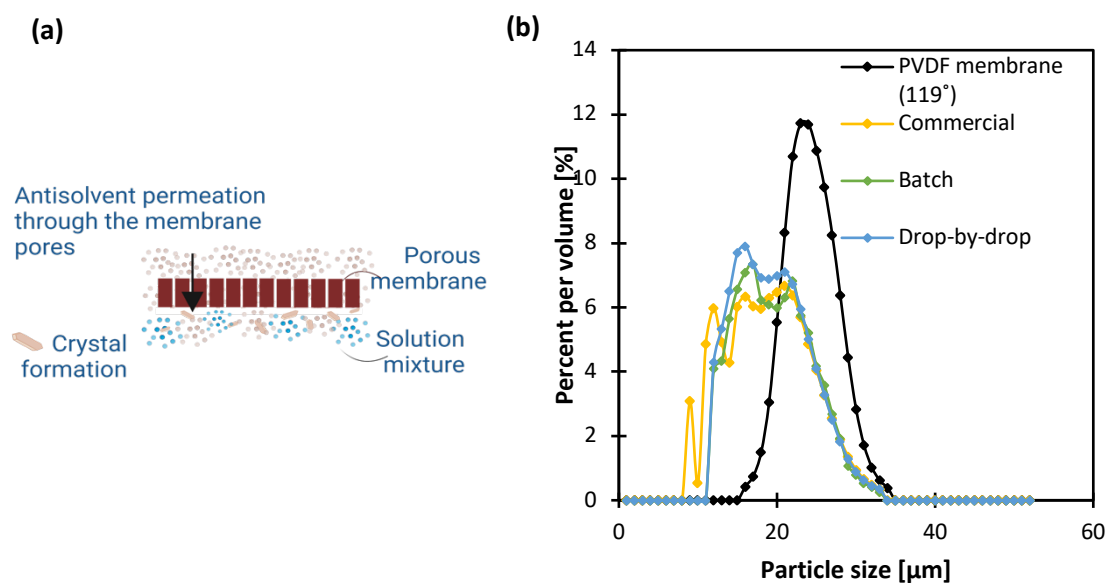


Figure 1. The controlled permeation of antisolvent through the porous hydrophobic membrane as illustrated in (a) results in a crystal size distribution much narrower than that obtained via batch or drop-by-drop crystallization (b).

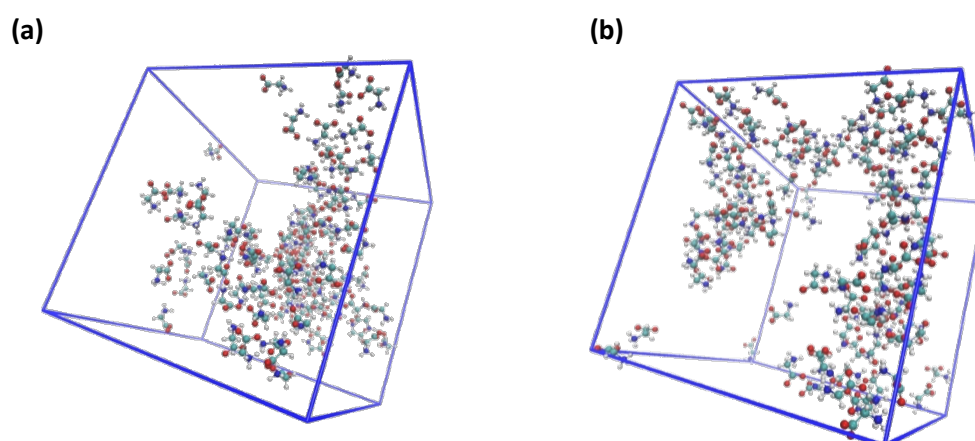


Figure 2. Glycine molecules arrangement after 300 ns in (a) water-glycine and (b) water-ethanol-glycine supersaturated solutions.

## References

- [1] S. Chergaoui, T. Leyssens, D. Debecker, P. Luis. (2022) Control of antisolvent mass transfer through porous membranes for the crystallization of organic compounds. (*Under preparation*)
- [2] S. Chergaoui, T. Leyssens, D. Debecker, P. Luis. (2022). Key parameters impacting the crystal formation in the antisolvent membrane-assisted crystallization. (*Under preparation*)
- [3] S. Chergaoui, T. Leyssens, D. Debecker, P. Luis. (2022) Pathways to control supersaturation of antisolvent crystallization via membrane properties. (*Under preparation*)

## Acknowledgements

This work has been funded by Actions de Recherche Concerté (ARC) under the project PURE- 20/25-108 - New approaches in Process Intensification: Towards combined PUrefication-REaction Membrane based processes.

# EASY TOOL FOR PREDICTION OF SEPARATION PERFORMANCE

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## Abstract

This paper proposes a tool for analyzing the performance of a membrane separator. The tool is based on mass balance and consists of 1D 1st order ordinary differential equations, which were solved using Wolfram-Mathematica. It gives various information such as permeate concentration of the permeating species as a function of the related recovery for any membrane length or area, concentration and pressure profiles of any species, permeating driving force, etc. The results provided various scenarios depending on the membrane properties (selectivity and permeance), operating conditions (feed/permeate pressures ratio), and permeation number (including feed flow rate, compositions and membrane area). As shown in figure 1, considering membranes with two different selectivities, respectively 20 and 40, we can compare the performance of membrane modules in terms of the permeate recovery and molar fraction of the more permeable specie. In fact, for a target recovery of 70% increasing the pressure ratio from 5 to 10, we can obtain higher values of permeate molar fraction from 0.76 to 0.84. Instead, with a target recovery of 70%, pressure ratio 10 and selectivity 40, we can obtain concentration values of the permeating species greater than 0.9. In addition, with increasing permeation number values from 0.5 to 1, gives higher permeate recovery values from 0.34 to 0.55. Therefore, with a less selective membrane, to obtain the desired specification, we have to increase the compression load, while with more selective membranes we can operate at lower pressure ratio; a higher-pressure ratio requires a greater energy and, hence, economic outlay. Furthermore, we can identify membrane properties (permeance, selectivity, area) and operating condition (pressure ratio) for meeting the desired system performance.

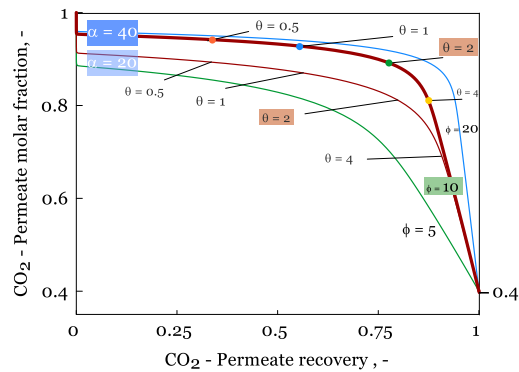


Figure 1. CO<sub>2</sub> permeate molar fraction vs CO<sub>2</sub> permeate recovery

## Acknowledgements

The project BIOVALUE “Advanced Membranes for biogas upgrading and high added value compounds recovery”, co-funded by Regione Calabria in the framework of M-Era.Net 2018 is gratefully acknowledged for funding this work.

# ASSESSMENT OF ANISOTROPY AND CONNECTIVITY OF MICROPOROUS MEMBRANES BY DIGITAL RECONSTRUCTION OF REAL 3D STRUCTURES BY COMPUTATIONAL FLUID DYNAMICS

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## Abstract

The progressive development of new porous materials with specific topological properties requires a precise characterization of the influence of system anisotropy. As pointed out in Kim et al. (1987), anisotropy is not an absolute properties of a material, but strictly depends on the specific transport phenomenon considered. For example, a material isotropic with respect to molecular diffusion could be – and in general is – anisotropic with respect to other transport phenomena.

In this work, an original and self-consistent systematic assessment of anisotropy and connectivity of 3D structures of real microporous membranes is presented. For this purpose, we introduce an *Average Effective Diffusivity Tensor*, whose components are evaluated by an appropriate set of computational fluid dynamic simulations in pure-diffusion conditions once reconstructed digital models of the desired real 3D structures. In particular, after a detailed explanation of the methodology and of the way to apply it systematically, we validate our approach by reproducing the values of tortuosity of an already well known isotropic structure, i.e., the face-centred cubic one (FCC). Afterwards, we analyse two artificial membrane structures of different orientations and two case-studies of digitally-reconstructed 3D real structures of zeolite membranes: the LTL zeolite and the CIT-5 one.

As main results, we show the ability of the presented approach in characterising precisely the distribution of the structural internal voids in terms of tortuosity and connectivity tensor, anisotropy factor and the here-called *preferential-direction factors*, introduced to quantify the preference of diffusional directions expressed in terms of percentage. Our methodology represents an original and relatively easy way for diffusional anisotropy assessment that can be effectively applied not only to existing materials of interest, but also to design novel materials – in form of membranes, catalysts and adsorbents – with desired characteristics in terms of internal void distribution and facilitated mass transport.

## References

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# BIOFUNCTIONALIZED MEMBRANE FOR FLUORESCENCE SENSING OF CONTAMINANTS

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## Abstract

The attention to safety and human health led to a continuous interest about the development of devices that allow monitoring in real-time and in a simple and effective way a specific substance. Biosensor is a device in which a biological molecule acts as a receptor and transducer to detect a specific analyte, converting a biological response into a measurable signal. The process of signal production during the interaction between the bioreceptor and analyte is called biorecognition. Biosensors are mainly classified as catalytic biosensors or non-catalytic biosensors. Catalytic biosensor principally includes enzymes, microorganisms, etc. and during the analyte-bioreceptor interaction, a new biological molecule is formed as a product of the reaction. In the non-catalytic biosensor, the analyte binds to the receptor irreversibly, but in this case, there is no reaction product. In these types of biosensors are involved antibodies, cell receptors, and nucleic acids. Some of the most studied devices in this period are enzyme-based biosensors that are based on enzyme-analyte interaction. The analyte recognition process is based on various mechanisms: measuring the formation of the product of enzymatic reaction and monitoring the enzymatic inhibition or alteration caused by analyte. Various biosensors can be produced on the base of enzyme specificity. However, the enzyme structure is extremely sensitive, so it is complicated to improve its sensitivity, stability, and adaptability, along with other important aspects, such as the increase of signal response time and reproducibility [1]. For these reasons, in the last period, the research is focusing on the introduction of polymeric membranes in biosensors design to mitigate these problems. The most important benefits of membranes integration are: greater surface area for higher enzymatic immobilization, higher stability, sensitivity and selectivity, faster response time, and lower detection limits [2]. The aim of this work is to develop an enzyme-based biosensor for the detection of pollutants in water, using the luciferin-luciferase system reproduced on a polymeric membrane. This system is still understudied, and it was reproduced on membrane only once [3] for the detection of ATP. Luciferase is an ATPase enzyme, that (at pH 7/8, in contact with oxygen, luciferin, phosphate ion and metallic ion) emits a fluorescent signal at a wavelength of 560 nm, directly proportional to the amount of ATP. The fluorescence emission is caused by the modification of the reaction product (oxiluciferin) [4]. The design and development of fluorescence-based membrane biosensors aims to benefit of this mechanism by tuning the properties of luciferase immobilization on polymeric nanostructured porous

membranes. The luciferase-loaded membrane will be tested in fresh and saline water spiked with pesticides and/or metallic ions to select the most selective and sensitive system.

## References

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## Acknowledgments

The authors thank the project CRIMAC (resources FSC 2014-2020, PNIR-IR) for the financial support.

# POLYMER-BASED TiO<sub>2</sub> MEMBRANE REACTORS FOR RECALCITRANT DYE REMOVAL

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## Abstract

Several industries discard polluted wastewater directly into the environment, which causes massive pollution [1]. Recalcitrant dyes in wastewater harm aquatic life. The high stability of these dyes causes long-term effects on the aquatic environment. Advanced oxidation processes provide an alternative method for pollutant degradation. However, the large-scale application of these processes is hindered by various drawbacks such as the formation of clusters during the reaction, and the TiO<sub>2</sub> nanoparticle recovery from the reaction medium for the re-use with a consequence increase of the cost of the process [2]. These limits can be overcome by using the Photocatalytic membrane reactors (PMRs). In this work polymeric-based photocatalytic membranes (loaded with TiO<sub>2</sub>) have been prepared membranes and tested for the removal of methyl orange considered a recalcitrant and carcinogenic dye. The influence of TiO<sub>2</sub> concentration and the methyl orange initial concentration on the catalytic process performance has been assessed. The membrane containing a TiO<sub>2</sub> concentration of 0.25 wt. % exhibited the best photocatalytic activity. Finally, the reusability of the membranes has been evaluated.

## References

- [1] L. Bai, Y Liu, A, Ding, N Ren, G. Li, H. Liang, *J. Chem. Eng.*, 358 . (2019) 1519–1528.  
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## Acknowledgments

This work has received funding from PRIMA Foundation under grant agreement no. Grant Agreement number: [2024] [TRUST]-Call 2020 Section 1 Water IA.

SEM-EDX analyses has been performed in the Centre of Microscopy and Microanalysis Lab.(CM2-LAB) of Progetto "Sistema Integrato di Laboratori per l'Ambiente – SILA\_2.0 - UNIVERSITA' DELLA CALABRIA".

# AN INNOVATIVE AND SCALABLE METHOD OF GELATION IONOTROPIC TO PRODUCE CHITOSAN NANOPARTICLES BY MEMBRANE PROCESS

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## Abstract

Ionotropic gelation (IG) is based on the capability of polyelectrolytes to crosslink in the presence of counter ions forming polymeric nanoparticles. The method is most frequently used for the preparation of chitosan nanoparticles (CS) and it has several advantages such as the use of aqueous solutions, the preparation of particles in the nanometric range of size, the control of particle size by the variation of parameters such as chitosan and TPP concentrations and the possibility to encapsulate a large variety of molecules. Although IG is well studied at laboratory scale its application at large scale is still under investigation.

In the present work, for the first time, a new scalable IG process by membrane technology was developed to produce chitosan nanoparticles using tripolyphosphate (TPP) as a cross-linking agent. For the purpose, the two phases, one containing chitosan and the other containing TPP were put in contact by using a tubular SPG hydrophobic membrane with a pore diameter of 1  $\mu\text{m}$ . TPP permeated through the membrane pores into the lumen side along which the chitosan solution flowed in continuous single-pass or recirculated operation mode.

The influence of formulation factors (concentration of chitosan and TPP solutions, pH of the chitosan solution, volume ratio) and process parameters (axial velocity, dispersed and continuous phase flow rate) on zeta potential, mean particle size and polydispersity index of chitosan nanoparticles was studied.

The membrane process allowed us to produce chitosan nanoparticles in the range of size between 170 and 300 nm and with a polydispersity index close to 0.2.

## Acknowledgements

The research work was carried out with the financial support of SAES Getters S.p.A. within the project "CAPME2- Preparation of capsules by membrane emulsification".

# CONTINUOUS PRODUCTION OF ZEIN NANOPARTICLES BY MEMBRANE NANOPRECIPITATION

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## Abstract

In this study, zein nanoparticles (ZNPs) were prepared by membrane nanoprecipitation as a simple method to produce in a continuous process stable ZNPs suspensions without the addition of stabilizing agents. A systematic study regarding the preparation of ZNPs by nanoprecipitation in a stirred tank (ST) system and membrane process (MN) will be illustrated. The investigation was pursued to account for the influence of the concentration of zein and solvent/non-solvent volumetric ratio on the size and size distribution of NPs. The Ouzo diagram was built to identify and compare the stable region where uniform ZNPs were obtained from both processes. ZNPs size distribution was analysed by Dynamic Light Scattering (DLS), the size and the shape of the ZNPs were monitored by Transmission Electron Microscopy (TEM) while the zein structure before and after the nanoprecipitation was characterized by Circular dichroism spectroscopy (CD). To the best of our knowledge, this is the first preparation of ZNPs in a continuous membrane nanoprecipitation process.

## References

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## Acknowledgements

Antonio Condello gratefully acknowledges the National Research Council of Italy (CNR) and BraccoImaging S.p.A. for financing the Industrial Doctorate fellowship within the Doctorate STFCM, University of Calabria.

# MOF-BASED MIXED MATRIX MEMBRANES FOR PROPENE/PROPANE SEPARATION

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## Abstract

The separation of olefins from their respective paraffins (e.g. ethene/ethane, propene/propane) is among the most energy-intensive industrial separation processes because of the massive scale and because of the high energy requirement for the traditionally used cryogenic distillation. Alternatives have been proposed, such as membrane separation with facilitated transport membranes, but the latter tend to have a low stability and lose their efficiency over time due to deactivation of the carrier [1]. In the present paper we will discuss the propene/propane separation using mixed matrix membranes based on metal organic framework (MOF) fillers from the MIL family and the ZIF family, dispersed in a suitable polymeric matrix, such as PIM-1, 6FDA-based polyimides or bio-inspired polymers. The membranes are prepared by the solution casting and solvent evaporation method. Single gas permeation measurements are carried out by the time-lag method in a fixed volume setup, yielding the pure propene and propane permeability and diffusivity, and the ideal selectivities. Light gases (He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>) are tested as well to obtain deeper insight into the gas transport mechanism of the membrane materials.

The propene/propane mixed gas permeation will be studied with an innovative permeation setup, based on the continuous online analysis of the permeate composition by a quadrupole residual gas analyser, with the unique possibility to determine the diffusion coefficients of the individual gases in the mixture from their permeation transient [2,3]. Argon is used both as the sweeping gas and as an internal standard for the determination of the permeate composition. The method is appropriately calibrated to account for the propene mass fragment formed upon ionization of propane, in addition to the original permeating propene from the mixture. The effect of the MOF type and concentration, the gas composition and the feed pressure on the separation performance of the investigated membranes will be discussed. The results will be described using the effective medium theory, and fitting the data with well-known models for binary systems, such as the Maxwell model and more sophisticated models.

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## **Acknowledgements**

Financial support from the Cariplo Foundation (Circular Economy for a sustainable future – 2019: MOCA project, grant 2019-2090) is gratefully acknowledged.

# LONG-TERM PERFORMANCE OF HIGHLY SELECTIVE CARBON HOLLOW FIBRE MEMBRANES FOR BIOGAS UPGRADING IN THE PRESENCE OF H<sub>2</sub>S AND WATER VAPOR

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## Abstract

Renewable sources are becoming today a suitable option to limit the use of fossil fuels. Among them, biogas is considered as one of the most mature energy sources that could guarantee a certain fraction of energy supply of the future. To be used, biogas needs to be treated and its upgrading to biomethane is up to know one of the most common way to use it. Membranes are a one of the technologies that are used for this purpose and their application on large scale is increasing rapidly.

The objective of this work is to study the performance of highly selective carbon hollow fibre membranes in the optic to be then used in biogas upgrading. Raw biogas is composed of different gases: CO<sub>2</sub> and CH<sub>4</sub> represent the majority of the fraction, while H<sub>2</sub>S, N<sub>2</sub> and water vapour coexist in traces. In literature, the use of carbon membranes results promising, due to their separation performance, pressure resistance and scalability. A key point to be focused on is the stability of the performance in presence of contaminants such as H<sub>2</sub>S and water vapour, always present in the real biogas streams.

In this work, the long-term performance, 183 days, of highly selective cellulose-based carbon hollow fibre membranes, for the first time in literature, were investigated, by keeping them under continuous exposure to a gas stream also containing H<sub>2</sub>S and/or water vapour [1]. First, the mass transport properties of the carbon membranes were evaluated with the single and mixed gases (CO<sub>2</sub> and CH<sub>4</sub>), in dry conditions. Subsequently, experimental measurements were performed by exposing the fibres to a gas mixture containing H<sub>2</sub>S in trace (up to 500 ppm) and water vapour (relative humidity 90%). Long-term tests showed that the addition of H<sub>2</sub>S and water vapour led to a permeability reduction of both CO<sub>2</sub> and CH<sub>4</sub> (figure 1), with a consequent selectivity increase, reaching a value above 200, compared to values obtained with dry mixed gas. Overall, the membranes showed high CO<sub>2</sub>/CH<sub>4</sub> selectivity with good H<sub>2</sub>S and water vapour tolerance, proving to be suitable candidates for biogas upgrading.

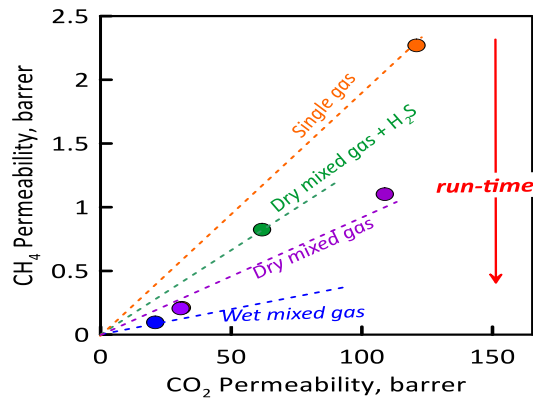


Figure 1. CH<sub>4</sub> permeability as a function of CO<sub>2</sub> permeability at different feeding conditions. Single gas (orange symbols), Dry mixed gas + H<sub>2</sub>S (green symbol), dry mixed gas (violet symbol), wet mixed gas (blues symbol).

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## Acknowledgements

The project BIOVALUE “Advanced Membranes for biogas upgrading and high added value compounds recovery”, co-funded by Regione Calabria in the framework of M-Era.Net 2018 is gratefully acknowledged for co-funding this work.

## MIXED MATRIX MEMBRANES BASED ON F4-UiO66(Ce)-MOF FOR CO<sub>2</sub> SEPARATION

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### Abstract

Mixed Matrix Membranes (MMMs) are considered innovative membrane materials in the field of gas separation and can be used for the CO<sub>2</sub> capture. These membranes offer the possibility to combine the permselectivity characteristics and processability exhibited by polymeric materials<sup>1,2</sup> with the excellent transport properties of inorganic fillers<sup>3</sup>. In this work, we considered the preparation of (Per)-fluorinated metal organic frameworks (F-MOFs) based mixed matrix membranes useful for the CO<sub>2</sub> recovery from flue gas and biogas. Three different polymers with different intrinsic characteristics, such as PIM-1, Hyflon®AD60x, and Pebax®1657 were combined with (Per)-fluorinated Ce-based MOF namely F4\_UiO66(Ce)<sup>5</sup>, obtaining F4\_UiO66(Ce)-PIM-1, F4\_UiO66(Ce)-Hyflon AD60x, and F4\_UiO66(Ce)-Pebax1657 as MMMs (Fig.1).

The pure gas permeability, diffusivity and solubility coefficients of these membranes were studied by the time-lag method, in order to compare the different behaviour of the same F-MOF in a rubbery, fluorinated and high free volume polymer.

Moreover, the gas transport properties of membrane samples of neat PIM-1 were studied after different conditioning treatments, namely: “as cast”, “after MeOH treatment”, and “after thermal treatment” in order to establish what is the best treatment to activate the membrane after its preparation. Similar studies on MMMs are in progress.

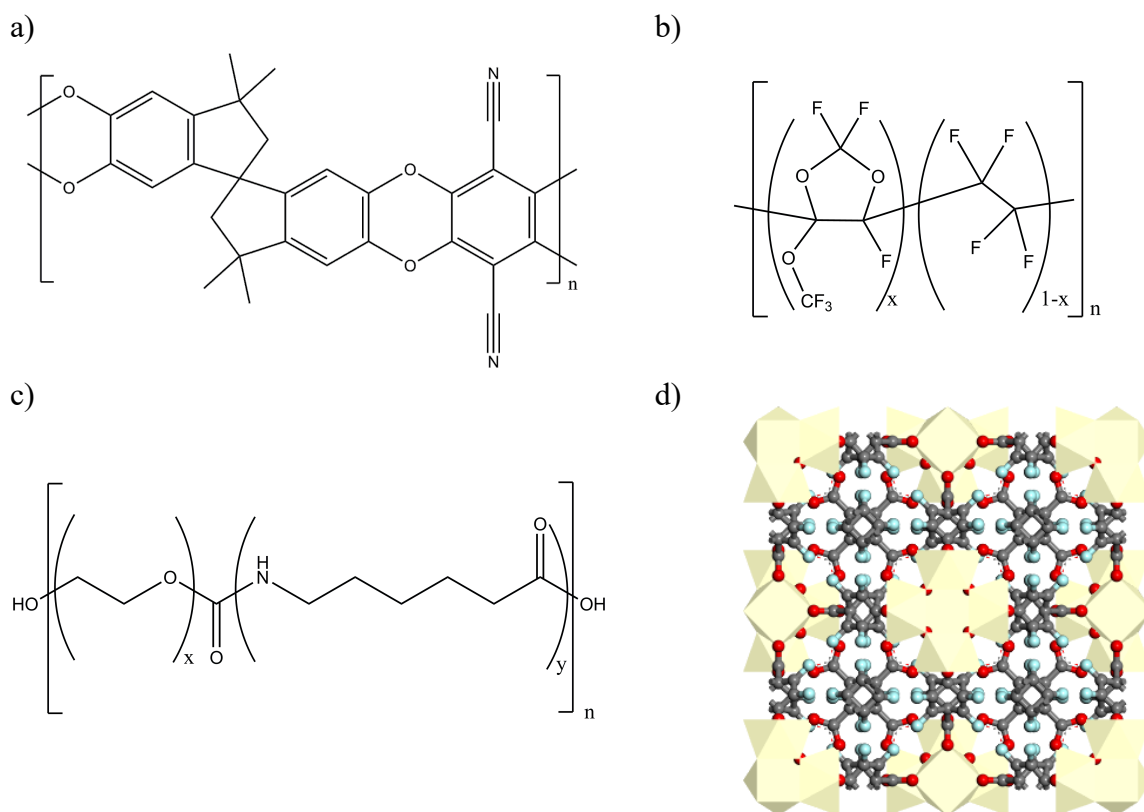


Figure 1. Chemical structure of a) PIM-1; b) Hyflon®AD60x, c) Pebax®1657, and d) Porous structure of F4\_UiO-66(Ce) MOF.

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## Acknowledgements

We gratefully acknowledge the Ministry for Universities and Research (MUR) for financial support under the program PRIN 2020 (project 2020P9K BKZ).

## MIXED MATRIX MEMBRANES FOR CO<sub>2</sub> SEPARATION BASED ON IMIDE/IMINE ORGANIC CAGES AS FILLERS

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### Abstract

The development of new membranes with improved separation performance represents an ongoing challenge in the gas separation field. A way to boost the performance of neat membranes is to incorporate intrinsically porous materials (IPMs) into the polymeric matrix, combining synergically the scalability and processability of polymers with the high gas separation performance of the filler. Organic cages represent a type of IPMs formed by single molecules with three-dimensional cavities and a well-defined pore structure in the solid state. One of their main advantages is that they are soluble in organic solvents and therefore more easily processed via solution-casting to yield mixed matrix membranes (MMMs).

In this work we describe a series of different polyimine cages and their corresponding MMMs in the solvent-processable poly(ether ether ketone) PEEK-WC [1] and in Matrimid<sup>®</sup>. Pure gas permeability measurements of the neat polymer and the MMMs are carried out to investigate the effect of the fillers on the gas transport parameters. The results showed that the use of imine based cages can tailor the gas transport properties of the pure polymer membrane, increasing either the permeability or the selectivity. In most cases, the increase in permeability is mainly due to the increase in diffusivity, while the enhanced permselectivity is mostly a result of an increase in the size-selectivity of the membrane, *i.e.* the cages favor the transport of the smaller gas molecules over that of the larger molecules. One of the synthesized cage molecules was found to be armphouse and allowed to form self-standing films. Comparison of the MMM permeability and selectivity with that of the pure cage and the pure polymer suggested that this cage acted as a plasticizer, rather than a porous filler in the polymeric matrix.

Further studies will focus on the comparison of pure gas permeability measurements and mixed gas permeation tests, in order to validate the potential of the most promising membranes for the separation of industrially relevant gas mixtures, such as CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub>.

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# INORGANIC BASED-MEMBRANES FOR WASTEWATER PURIFICATION

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## Abstract

Polymeric "organic" membranes dominated the market with respect to their inorganic counterpart due to their lower production cost, operation flexibility, and ease of preparation and scaling up. However, polymeric membranes have a short lifetime due to fouling problems and limited mechanical/thermal and chemical stability. On the other hand, ceramic membranes, a kind of inorganic membrane, can be easily back washed and cleaned with various cleaning agents and sterilized at high temperatures with no effect on their performance and lifetime, overcoming some of the most diffused drawbacks typical of polymeric materials. However, ceramic membranes were rarely used in wastewater purification due to their high fabrication and operating cost, and low membrane performance. In this work, we developed new hydroxyapatite-based membranes using ultra-long inorganic hydroxyapatite of one-dimensional size (1D) as a base of ceramic materials combined with two-dimensional (2D) graphene oxide (GO). Different ratios of GO were blended with ultra-long hydroxyapatite, and the membranes were fabricated via a simple vacuum-assisted filtration technique. The properties and performance of produced membranes were evaluated through different chemo-physical characterization techniques such as SEM, contact angle, and pure water permeability. The developed membranes can provide semi-flexibility with acceptable mechanical properties and superior hydrophobicity with an average contact angle of 146. The super hydrophobic character of the obtained membrane strongly recommended resisting organic fouling of such kinds of these membranes. There is no notable change in the contact angle values of the developed membranes, even with the blended ratios of GO. However, there is a notable improvement in the pure water permeability with GO.

## Acknowledgments

The work has been carried out within the CNR-ASRT (Egypt) 2022-2023 international Exchanges (project ID: 18775, project title: Flexible Ultrafiltration Inorganic Membrane Based on Ultra-long Hydroxyapatite for Wastewater).

# Mg(Al)O MIXED METAL OXIDES (MMO) NANOPARTICLES: APPLICATION IN THE PREPARATION OF SUSTAINABLE POLYMERIC MEMBRANES

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## Abstract

Nowadays, it has become essential to develop processes to effectively reduce water contamination since most toxins introduced into the aquatic environment are resistant to degradation. Among the several techniques under development, membrane technology offers many advantages such as high efficiency, low energy costs, and simplicity of usage [1]. Despite the undoubted importance of polymeric membranes in water and wastewater treatment, the major drawback is fouling. Mixed matrix membranes (MMM) can be an option for improving both the performance and antifouling capabilities. A typical challenge in membrane fabrication is finding non-toxic substitutes for traditionally used hazardous solvents. Mixed Metal Oxides (MMO), which are produced from Layered Double Hydroxides (LDH) precursors are one of the intriguing nanoparticles (NPs) that could be used in membrane modification. Thanks to their special characteristics, which include hydrophilic nature, intrinsic positive charge [2], minimal cytotoxicity, good thermal stability, large surface area, and low cost, these NPs are drawing increasing attention in environmental field. Following encouraging results as low-cost adsorbents in prior work [3], the grounds for testing Mg(Al)O as nanofillers were established. In this study, Mg(Al)O MMO NPs were prepared by pyrolyzing MgAl-LDH precursors in a single step. Then, homogenous dope solutions were obtained at 80°C using Rhodiasolv® PolarClean as a substitute green solvent. By non-solvent induced phase separation (NIPS) approach employing water as a coagulation bath, the membranes were fabricated. The effects of different NPs concentrations (0.1–1 wt%) and additives (PEG200, PVPK17, and PVPK90) were investigated. The morphology, porosity, thickness, pore size, contact angle, and pure water permeability of the prepared Mg(Al)O@PES membranes were all evaluated. Furthermore, using Acid Red 4 as a feed solution, rejection and antifouling capacity were examined. The ideal Mg(Al)O loading was found to be between 0.5 and 1 wt%.

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## Acknowledgements

The authors gratefully acknowledge financial support from the “Italian Ministry of Foreign Affairs and International Cooperation” (MAECI) within the framework of grants awarded to foreign citizens and Italian citizens living abroad for the academic year 2022-2023.

# PREPARATION OF NON-WOVEN SUPPORTED HALAR MEMBRANES AND THEIR APPLICATION IN MEMBRANE DISTILLATION

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## Abstract

In this work, new membranes for direct contact membrane distillation (DCMD) have been prepared, characterized and tested. In particular, cast-coating method was used for the fabrication of non-woven supported low melting point Ethylene-Chlorotrifluoroethylene (LMP ECTFE) (Halar<sup>®</sup>) flat sheet membranes. LMP ECTFE materials have been chosen because they have comparable chemical resistance and mechanical properties with standard Halar<sup>®</sup> but lower crystallinity, lower viscosity and lower melting point [1]. Two different non-woven supports in polypropylene (PP) were used (2 and 11  $\mu\text{m}$ ). Diethyl Adipate (DEA) was used as solvent. Membranes were prepared using various ECTFE concentrations (namely 3%, 5%, 7% and 10%). Diethylene Glycol (DEG) was used as coagulation bath and 2-propanol was used for washing the remained solvents [2]. The produced membranes were characterized by thickness, contact angle, SEM, porosity and pore size, and tested in DCMD experiments using pure water and 0.6 M NaCl solution as feed. Feed temperatures were set around 45-65 °C. Results show that the membranes with PP support of 2  $\mu\text{m}$  is more suitable as the support. Moreover, 5% ECTFE membranes present stable fluxes in DCMD operations (at around 6 LMH at 55°C), with salt rejections above 99.9%, indicating their good separation performance in membrane distillation process.

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## Acknowledgements

I would like to thank the Institute on Membrane Technology (CNR-ITM) and the University of Padova, Department of Chemical Science (UniPD-DISC) for jointly granting my PhD scholarship.

# SALTS RECOVERY FROM MINING TAILINGS BRINES BY MEMBRANE-ASSISTED CRYSTALLIZATION

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## Abstract

Brine discharge from process industries has a critical ecological impact if its disposal is not properly performed. The good news is that brine can be considered a resource to be exploited [1,2] since it contains valuable resources, such as magnesium, potassium and ammonium salts and their recovery is essential to decrease the environmental impact of the mining process while reducing production costs of these products at a commercial level. The aim of this work is the simultaneous recovery of valuable salts contained in brine from mining tailing waste streams and pure water using a membrane-assisted crystallization (MCr) approach [3]. MCr tests were conducted using both synthetic solutions simulating the real composition and real brine. The first part of the work included a theoretical study to estimate which salts and in which order can crystallize from the brine. This study provides a comparative analysis of two membrane crystallization configurations to treat the brine. In the first configuration the feed solution was kept at a constant high temperature, while in the second one the hypersaline feed stream passed first through an Intermediate Cooling System (ICS) and then back into the warm side to produce a gradient of temperature in the feed solution. A comparison study was carried out between the real and synthetic brine before and after a basic pretreatment with the aim of eliminating interfering ions at high concentration in solution. Results have shown that MCr process provides the possibility to separate different mineral salts from the waste stream playing on the feed composition and the operational parameters.

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## Acknowledgements

This work has received funding from the European Union's Horizon 2020 research and innovation programme within the INTELWATT project, under grant agreement n. 958454 (<http://www.intelwatt.eu/>).

# COMPOSITE MEMBRANES FOR PHOTOTHERMAL SWEEPING GAS MEMBRANE DISTILLATION

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## Abstract

One of the most challenging issues that governments, industries, and scientific community are facing in the last decades is the exponentially growth of world population, implicating an increasing of water and energy demand on global scale. In this scenario, Reverse Osmosis is the dominant technology in production of freshwater from seawater, allowing to decrease the water stress but, on the same time, showing many weaknesses like limited Recovery Factors, high energy demand and high environmental impact related to the back rejection of exhaust brine in seas and oceans [1]. On the other hand, Membrane Distillation (MD) is a thermally driven process that can be operated downstream to the Reverse Osmosis and that can provide a further water recovery in a logic of circular approach and Process Intensification. However, the high specific energy consumption caused by temperature polarization phenomena has hindered the feasibility of MD at large scale. Recent achievements about efficient photothermal nanomaterials have opened unprecedented perspectives for the implementation of self-heating membranes able to reverse the temperature polarization [2]. Nevertheless, photothermal materials still suffer from important limitations related to high fabrication cost. With respect to previous approaches based on the embodiment of the thermoplasmonic hot-spots into the membrane bulk; in this work composite photothermal membranes were prepared by concentrating the nano-heaters at membrane surface reducing the membrane cost [3]. Explicitly, the integration of Silver Nanoparticles (AgNPs) in a thin microporous hydrophobic layer supported by a non-woven tissue resulted in new photothermal composite membranes, capable to overcome the temperature polarization phenomenon [3]. These nanofillers, when irradiated by UV light behave as hotspots, promoted the Joule heating associated with plasmonic excitations in metal NPs, going to compensate the heat dissipation under the form of latent heat of vaporization [4]. Moreover, photothermal membranes were firstly employed in Sweep Gas Membrane Distillation and tested for the treatment of a synthetic seawater solution with a NaCl concentration of 0.5 M. These noble metal nanofillers, behaving as localized thermoplasmonic nano-heaters, promoted an efficient water vaporization and recovery, consisting formally in an increase of transmembrane flux under UV irradiation by about 10 folds when compared to unloaded PVDF membranes.

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# MOFS-BASED MIXED MATRIX MEMBRANES FOR EFFICIENT REMOVAL OF HEAVY METALS FROM WATER

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## Abstract

Water contamination by natural and anthropogenic pollutants is a major global issue owing to its adverse impact on human health. They constitute one of the most dangerous contaminants groups because of their persistent nature, toxicity, tendency to accumulate in organisms and undergo food chain amplification and more still, they are nondegradable [1]. The development of efficient and innovative methods with high specificity for the removal of these pollutants from aquatic matrices is an ever increasing-demand. Membrane processes are among the most efficient technologies applied in this field, but are not yet sufficiently selective to remove heavy metals down to sufficiently low levels for drinking water.

Incorporation of metal organic frameworks (MOFs) in membranes is a strategy to improve their efficiency, exploiting their high affinity for heavy metals [2].

In this work, novel biocompatible MOFs (bioMOFs), rationally designed to have a high affinity and high specificity, are embedded in porous membranes based on two different polymers: polyacrylonitrile (PAN) and Cellulose Acetate (CA). The employed filler materials consist of chiral 3D MOFs, with formula  $\{Ca^{II}Zn^{II}[(S,S)\text{-L}]_3(\text{OH})_2(\text{H}_2\text{O})\} \cdot 16\text{H}_2\text{O}$  (1), exhibiting functional channels decorated with  $-\text{CH}_2\text{SCH}_3$  (L = mecysmox) and  $-\text{CH}_2\text{CH}_2\text{SCH}_3$  (L = methox) thioalkyl chains derived from the residues of the natural amino acids L-Methylcysteine and L-methionine, respectively. Neat polymer membranes were prepared by nonsolvent-induced phase inversion (NIPS), optimizing the relevant parameters (e.g. polymer concentration, composition of the coagulation bath, additives, exposure to the air) in order to obtain membranes with the most suitable, sponge-like morphology. Mixed matrix membranes (MMMs) with various MOF loadings were prepared under the optimized conditions, and they were characterized in terms of morphology, hydrophobicity, water permeability. The metal retention was measured both in static and in dynamic mode, using water enriched with metal ions and/or other contaminants to simulate the real conditions of the purification process.

The results of this study provide new insight into the MMM/heavy metal interaction, and will pave the way towards the development of more efficient membranes for drinking water production.

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## Acknowledgements

This research received support from: Fondazione CARIPLO, programme “Economia Circolare: ricerca per un futuro sostenibile” 2019, Project code: 2019–2090, MOCA—Metal Organic frameworks and organic CAgEs for highly selective gas separation membranes and heavy metal capture devices.

# **PARTICIPANTS ABSTRACTS**

# MODELING OF THE GAS TRANSPORT IN POLYMER/IONIC LIQUIDS BASED NANOCOMPOSITE FILMS

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## Abstract

Ionic liquids (ILs) are organic salts with low melting points and tunable properties on the basis of their composition. The low resistance offered to the diffusion of gases and vapours as well as the possibility of specific interaction with polar molecules as CO<sub>2</sub> enable their use as additives to polymeric materials to prepare selective membranes for gas separation [1].

In this work, the modelling of nanocomposite membranes having a polymer matrix hosting Ionic Liquids as additives in the form of polymer inclusion membranes (PIMs) was carried out to gain insight into the structure.

The following models were considered, expressing the permeability measured in the nanocomposite membranes ( $P_{eff}$ ) as a function of the volume fraction ( $\phi$ ) and of the permeability of the composite constituent phases ( $P_d$ , permeability for the dispersed phase and  $P_c$ , permeability for the continuous phase):

$$\text{Maxwell [2]} \rightarrow P_{eff} = P_c \left[ \frac{P_d + 2P_c - 2\phi(P_c - P_d)}{P_d + 2P_c + \phi(P_c - P_d)} \right]$$

$$\text{Higuchi [3]} \rightarrow P_{eff} = P_c \left[ 1 + \frac{3\phi\beta}{1 - \phi\beta - K_H(1 - \phi)\beta^2} \right] \quad \text{where, } \beta = \frac{P_d - P_c}{P_d + 2P_c} \quad \text{and } K_H = 0.78$$

$$\text{Hennepe [4]} \rightarrow P_{eff} = P_c \left[ \frac{1}{1 - \phi^{1/3} + \frac{1.5\phi^{1/3}P_c}{P_c(1 - \phi) + 1.5P_d\phi}} \right]$$

In particular, the Maxwell model, initially developed for predicting electrical constants, is a reference for representing Mixed Matrix Membranes (MMMs) as heterogeneous systems with randomly distributed spherical fillers and that of Higuchi is derived from the Maxwell theory, while Hennepe's model implements a Resistance Model and was originally developed for MMMs based on rubbery polymers. The modeled data are those obtained in our previous work on membranes based on the PVDF-HFP copolymer encapsulating up to 60 wt% of [Bmim][BF<sub>4</sub>] or [Bmin][Tf<sub>2</sub>N] and showing excellent permeability gains [5].

The peculiarity of the experimental data can be predicted by the selected models considering the IL phase as the continuous one. Higuchi's model is the most interesting one as shown in Fig. 1 in reproducing the observed behavior on the whole explored concentration range of the ILs.

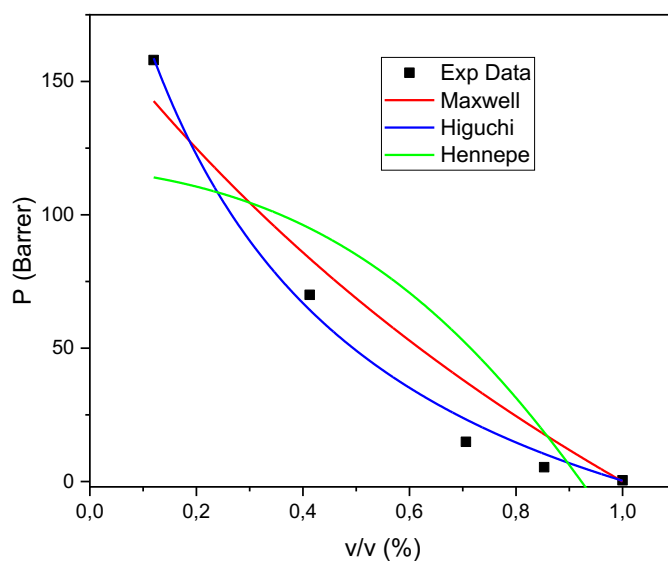


Figure 1. CO<sub>2</sub> permeability measured in MMMs of PVDF-HFP/[Bmim][BF<sub>4</sub>] at various polymer volume fraction and modelling predictions based on Maxwell, Higuchi and Hennepe models assuming the IL as continuous phase.

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## Acknowledgements

The project Prin2017 “MultiFunctional poLymer cOMposites based on grown matERials (MIFLOWER)” (grantnumber: 2017B7MMJ5\_001) from the Italian Ministry of Education University is kindly acknowledged.

# MULTISCALE MODELING OF THE TRANSPORT IN ANION EXCHANGE MEMBRANES

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## Abstract

The matter transport through ion-exchange membranes (IEMs) is basically characterized by their ion and water permeability. Currently, these properties are obtained through measurements or by means of fitting the transport equations against experimental data (semi-empirical fitting procedures), although these are not highly predictive.

*Ab-initio* multiscale modeling is a reliable solution to increase the predictions reliability in the field of electro membranes because it allows to evaluate macroscopic properties using appropriately molecular and nanoscale features of the IEM. Thus, through this theoretical framework, it would therefore be possible to obtain ion and water membrane permeability [1] without using experimental fitting, hence, avoiding ad-hoc measurements.

This contribution shows how water uptake ( $w_u$ ) and ion diffusivities can be obtained by combining suitably *ab-initio* calculations, molecular dynamics and macroscopic models [2]. It worth noting that equilibrium  $w_u$  and ionic diffusivities are properties necessary to evaluate in turn ion and water membrane permeabilities.

We developed an *ab-initio* and molecular dynamics protocol to predict the water uptake by considering a polysulfone, functionalized with tetramethylammonium, anion-exchange membrane compensated with chloride anions as case study. The procedure led to good agreement with reported experimental data in a wide range of ion-exchange capacities and improved the results obtained using a quantum-based approach, developed in our previous work [1]. The computed  $w_u$  were then used to evaluate counter-ion diffusivities through three different analytical models and it was found that a satisfactory agreement with experiments can be achieved. This confirms the potential of the current strategy to predict the permeabilities of IEMs without resorting to experimental data, thus paving the way towards a computationally driven design of new membranes.

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## Acknowledgements

This work is supported by the Joint Bilateral Agreement CNR/CONICET Programme 2021–2022 “multiscale modelling of nanostructured membrane-based separators for next generation lithium batteries”, prot.n.0027844-2021.

# FUNCTIONAL IONIC LIQUID CRYSTAL MEMBRANES BASED ON GALLIC ACID DERIVATIVES: A COMPUTATIONAL STUDY

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## Abstract

In this work we aim at investigating structural and dynamic features of Ionic Liquid Crystals' membranes (ILC membranes) for ion conduction and water desalination [1,2] using Molecular Dynamics (MD) simulations. We consider ammonium derivatives of gallic acid from the work of Ichikawa et Al. [1] These kinds of materials are very interesting for their ability to form different phases like bicontinuous cubic phase or hexagonal columnar phase which are employed, respectively, for lithium carrying systems in batteries or in ultrafiltration and nanofiltration of water solutions. The membranes formed by these materials are produced by polymerization of the elementary unit over a selected phase. These systems are highly organized with a hierarchy of structuring effects that take place in producing the final membrane's morphology. Small changes in the elementary units produce big effects of the phase behavior of such materials. For this reason, we have run MD simulations of the hexagonal and isotropic phase of some selected systems at several temperatures. We have calculated both structural properties such as Radial Distribution Functions and structure factors  $S(q)$  as well as diffusion coefficients. We have compared the results with experimental data from the literature. Fig. 1b and 1c show a sketch of the hexagonal packing of columnar aggregates (b) and a fully atomistic representation of hexagonal packed columns (c). These are new materials and the interest in them is increasing not only for the functions they carry out but also due to the fact that the mechanisms of self assembly, ions conduction and water desalination are not completely understood [3].

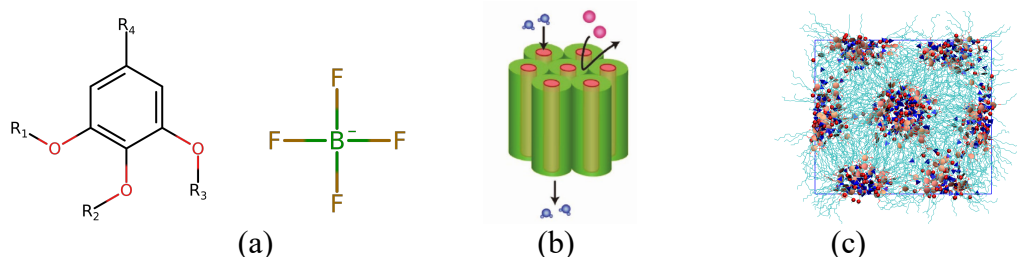


Figure 1. Starting from the left: constituents of the IL, columnar phase, hexagonal arrangement. Figure 1b is taken from the work in Ref. [2], Figure 1c is a snapshot of one of the simulations carried out in this research.

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# MOLECULAR SIMULATIONS OF (PER)-FLUORINATED MOFS-BASED MMMS FOR CO<sub>2</sub> CAPTURE

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## Abstract

In gas separation, membrane technology represents a growing field that is focalized on the research of new polymeric membranes able to overcome the well-known Robeson upper bound limit<sup>1,2</sup>. The Mixed Matrix Membranes have provided interesting gas separation performance consisting of fillers incorporated into a polymeric matrix (MMMs). Among inorganic fillers, special attention is focalized on nanoporous fillers such as Metal Organic Frameworks (MOFs). MOFs are innovative materials containing linking organic units bonded with inorganic metal complexes by coordination bonds<sup>3</sup>. Because of their interesting physical and chemical properties, these porous crystalline materials have been widely used in chemical processes, including gas separation<sup>4</sup>.

In this work, the atomistic simulations (Molecular Dynamics and Monte Carlo simulations) are applied as a powerful research tool that can provide a useful insight into the understanding of the gas separation of pure CO<sub>2</sub> in MOFs, the comparison of simulated adsorption isotherms to the experimental ones and, later the study of the compatibility between MOF and polymer at the interface in MMMs.

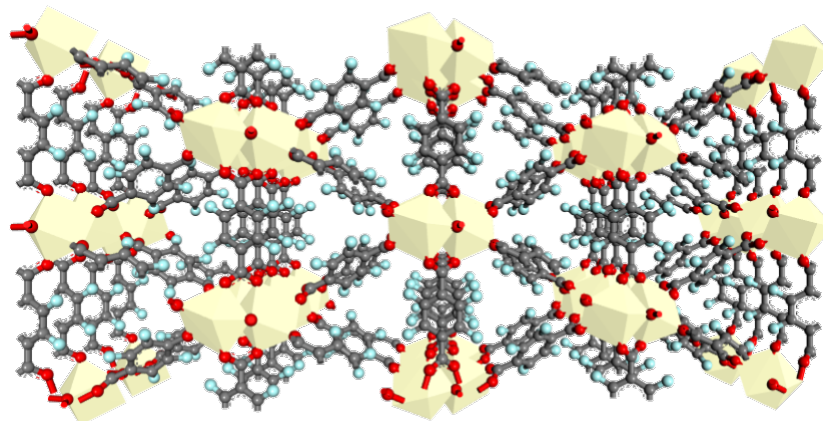


Figure 1. The (2×2×2) supercell structure of F4-MIL140A(Ce)-MOF.

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## Acknowledgements

We gratefully acknowledge the Ministry for Universities and Research (MUR) of for financial support under the program PRIN 2020 (project 2020P9KBKZ).

# BIOGAS UPGRADING USING A MEMBRANE SEPARATION PROCESS

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## Abstract

The purification of a wet gas stream having a typical biogas composition (i.e., about 60% of CH<sub>4</sub> and 40% of CO<sub>2</sub>) was investigated using a membrane process. The mass transport properties were evaluated by experimental measurements on a polyetherimide/polyimide membrane module under dry and wet conditions, analyzing also the effect exerted by the presence of H<sub>2</sub>S [1]. It was found that CO<sub>2</sub> permeance was reduced of almost 50% in mixture with CH<sub>4</sub> compared to the value as single gas, passing from about 11 to 6 nmol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> at 35°C. On the other hand, CH<sub>4</sub> permeance was slightly increased by the presence of CO<sub>2</sub>, which promoted its flux. This mutual interaction between the two species caused a significant drop of the CO<sub>2</sub>/CH<sub>4</sub> mixture selectivity compared to the single gas permeance ratio, whereas the presence of water vapor did not further affect the mixture selectivity. The experimental values of permeance and selectivity were used to simulate the purification of 1 Nm<sup>3</sup> h<sup>-1</sup> of a simplified biogas stream containing CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O. A typical three-stage configuration provided a good CH<sub>4</sub> purity of about 98%, with a recovery higher than 90%.

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# PERFORMANCE ANALYSIS AND MODELLING OF A CATALYTIC MEMBRANE REACTOR FOR H<sub>2</sub> PRODUCTION VIA AMMONIA DECOMPOSITION

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## Abstract

World energy demand today is met mainly by fossil fuels. The continuous increase in population on the one hand and the continuous decrease of fossil fuels on the other lead to paying more and more attention to alternative energies [1]. Hydrogen is increasingly emerging as the ideal partner for renewable energy sources such as solar and wind energy. However, it has a low energy density per unit volume, and consequently larger volumes of hydrogen need to be used and dislocate to meet the same energy demand than other fuels. Therefore, becomes interesting and more economically viable to produce hydrogen in situ, where it is required from liquid fuels, such as methanol [2], ammonia [3] and formic acid [4]. They could easily be transported over long distances, stored for a long time and subsequently decomposed to produce hydrogen when needed [5]. Among all possible candidates, ammonia is a particularly promising hydrogen carrier due to its high volumetric energy density, relatively low cost, and ease of liquefaction, storage, and transportation. However, its dominant role as liquid hydrogen carrier is conditioned by the technology then used for dehydrogenation. Ru-based catalyst is currently the most active metal in the decomposition of ammonia into nitrogen and hydrogen. However, in traditional operation, the dehydrogenation should be followed by a separation step for upgrading hydrogen to desired level of purity. The adoption of membrane reactors can intensify the process[6,7], allowing reaction and H<sub>2</sub> separation to be performed in only one unit also increasing the conversion at milder temperature [8]. Pd-based membranes stand out as the perfect candidates, exhibiting a considerable selectivity towards hydrogen [9]. In this work, we will analyse the performance of a catalytic membrane reactor for ammonia decomposition in comparison with a conventional reactor operated at the same conditions. Before the integration with a Ru-based commercial packed catalyst, the mass transport properties of the Pd-based membrane will be measured with single and mixed gasses at different compositions. The data from the reaction measurements will allow a multiscale modelling of the catalytic process under realistic conditions to be developed, starting from the reaction rates up to including the mass transport phenomena in the real device.

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# STUDY OF MEMBRANE NANOPRECIPITATION FOR PRODUCTION OF SOLID LIPID NANOPARTICLES

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## Abstract

Membrane nanoprecipitation (MN) is an emerging process that combines membrane technology with the nanoprecipitation method for particle manufacturing at the nanoscale. This membrane process is extremely attractive for the continuous development of nanoparticles at the industrial scale as it guarantees reproducibility and scalability [1, 2]. In this work, MN was explored for the first time for the production of solid lipid nanoparticles (SLNs) based on cocoa butter (CB) using a tubular SPG (Shirasu Porous Glass) membrane with a pore size of 1  $\mu\text{m}$ . Ethanol and water were used as solvent for CB and non-solvent, respectively. Different configurations of membrane nanoprecipitation were used to compartmentalize the two phases (solvent and non-solvent) in the membrane module. In particular, the formation of SLNs was performed in single-pass cross-flow mode in the lumen or shell side by permeation of the solvent containing CB into the non-solvent and *vice versa*. The effect of CB concentration, flux through membrane pores and volumetric ratio between solvent and non-solvent on particle size and polydispersity index (PDI) was investigated. The results demonstrated that MN is not affected by the flux through the membrane as well as by the process configuration and that the role of the membrane is to control the mixing of the solvent with the non-solvent. By tuning the CB concentration and solvent to non-solvent ratio, continuous production of uniform SLNs (PDI < 0.2) with particle size smaller than 300 nm was achieved under mild operating conditions.

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## Acknowledgements

The authors would like to thank POR Calabria FESR-FSE 2014/2020 for the financial support to the SmartMatter project in the M-ERA.NET Call 2019.

# IRON NANOPARTICLES PRODUCTION BY REACTION-BASED MEMBRANE NANOPRECIPITATION

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## Abstract

Iron nanoparticles were synthesized by coprecipitation of iron salts in alkaline medium by integrating membrane dispersion technology with reaction-based precipitation and non-solvent nanoprecipitation. The influence of chemical parameters (i.e. iron salts concentration, pH conditions) on the particle size distribution and structure was investigated. The produced iron nanoparticles were mixed with a dissolved polymer (chitosan) that was precipitated from the solution by supersaturation induced by the non-solvent onto the existing iron nanoparticles to obtain polymer-coated iron nanoparticles. The effect of polymer/iron nanoparticles relative concentration was studied to identify the most suitable conditions for achieving continuous polymer coating. This study aims to broaden the application of membrane nanoprecipitation as a competitive substitute method of conventional techniques used for nanoparticles production.

## Acknowledgements

The authors would like to thank POR Calabria FESR-FSE 2014/2020 for the financial support to the SmartMatter project in the M-ERA.NET Call 2019.

# DEVELOPMENT OF HYPERACTIVATED BIOHYBRID MEMBRANES FOR ORGANOPHOSPHATE PESTICIDES DEGRADATION

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## Abstract

The harmful effects of pesticides on humans and environment have led researchers to develop sustainable methods to inactivate them. The use of immobilized extremophilic enzymes seems very promising for the development of biocatalytic systems capable of degrading pesticides [1], but a deep understanding of the factors affecting the performance of the conjugated process and the development of strategies to further improve their catalytic properties are crucial. The aim of this study was to characterize the activity and stability of a thermophilic phosphotriesterase immobilized on polymeric membrane in the presence of cationic (CTAB) and anionic (SDS) surfactants to produce hyperactivated biocatalytic membranes for pesticide degradation and to understand the main mechanism that promotes activity enhancement. The effects of surfactant concentrations on enzyme activity, stability, secondary structure, aggregation, and kinetic parameters ( $K_M$ ,  $K_{cat}$ ,  $K_{cat}/K_M$ ) were investigated. The results showed that the activity of immobilized phosphotriesterase toward the pesticide paraoxon was greatly increased in the presence of SDS and CTAB (about 90% and 80%, respectively), because they can affect the performance of the biocatalytic membrane by inducing conformational changes in the secondary structure of the enzyme and in its aggregation state (CTAB) or by increasing the affinity of the enzyme for the substrate (SDS).

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## Acknowledgements

The authors acknowledge the Project SmartMatter, M-ERA.NET–Joint Call 2019-Project co-financed within the “Azione 1.1.4.-POR Calabria FESR 2014/2020”.

# Fe<sub>3</sub>O<sub>4</sub>@Au CORE/SHELL NANOPARTICLES FOR THE DEVELOPMENT OF BIOCATALYTIC MEMBRANE REACTOR AND COMPOSITE PLASMONIC MEMBRANES

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## Abstract

Over the past decade, interest in the fabrication of magnetic nanoparticles and their composites has increased due to their potential applications in areas such as medical imaging, drug delivery, therapy, catalysis, and sensors. In particular, magnetic nanoparticles gold coated with core-shell structure are attracting more and more attention due to their potential applications in separation and purification of biomolecules from matrices and biosensing due to the acquired plasmonic properties. In this work, gold-coated iron nanoparticles were prepared starting from commercially available iron nanoparticles (30nm). The gold layer was deposited by reducing gold salts with sodium borohydride. The prepared core-shell iron-gold nanoparticles have a very good distribution (PDI: 0.12, Fig. 1) and after synthesis they acquire plasmonic properties (Fig. 1), which are very important for biosensing. The gold-iron NPs were then biofunctionalized with phosphotriesterase for pesticide degradation. The goal is to develop a biosensor for pesticide detection and/or to develop a biocatalytic plasmonic membrane in which the prepared NPs are used to produce a composite membrane. Preliminary results showed that the phosphotriesterase was successfully immobilized and active after the immobilization procedure and that the plasmonic properties changed after the interaction of the enzyme with the substrate, so the developed system can be used for pesticide detection. The prepared biofunctionalized NPs are then used to develop a composite membrane for simultaneous hydrolysis and detection of organophosphate pesticides.

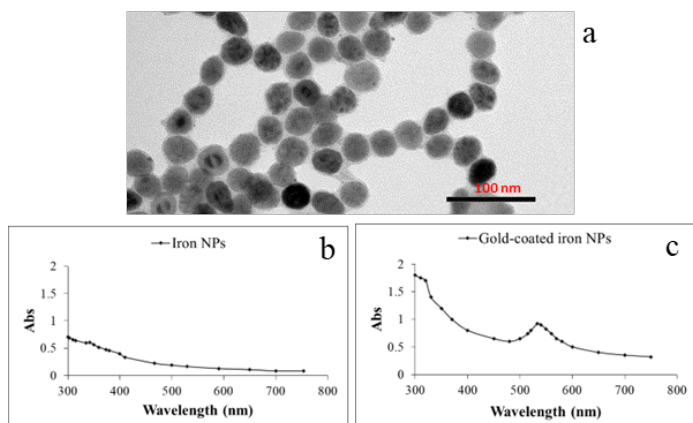


Figure 1. TEM images of gold coated iron nanoparticles (a); plasmonic signal measured before (b) and after (c) gold coating.

## Acknowledgements

The authors acknowledge the Project SmartMatter, M-ERA.NET–Joint Call 2019-Project co-financed within the “Azione 1.1.4.-POR Calabria FESR 2014/2020”.

# PDMS-AU NANOPARTICLES COMPOSITE MEMBRANES FOR BIOSENSORS DEVELOPMENT

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## Abstract

The incorporation of AuNPs into the PDMS matrix enables the development of localized biosensors by converting chemical or biomolecular information into a physically readable signal [1]. Generally, AuNPs-PDMS system is prepared by immersing a sheet of polymerized PDMS in an aqueous solution of chloroauric acid (HAuCl<sub>4</sub>), however, the insufficiency and non-uniform distribution of AuNPs in the PDMS matrix led to poor conductivity of PDMS [2,3].

In this work, the swelling properties of PDMS membranes in different solvents (ethanol and ethyl acetate) were exploited to improve the amount and the uniformity of AuNPs within the polymer matrix. The swollen polymer allows a higher permeation rate of the gold precursor into the film, thus improving the reduction reaction. In addition, the behaviour of the swelling solvents on the films obtained using different ratios of the two polymer components (base polymer and curing agent) and the effect of the AuNPs and the swelling step on the transport properties of AuNPs-PDMS membranes were evaluated. Results evidenced that the reaction without the use of swelling solvents prior to incubation in the aqueous solution of the gold precursor was much slower and the color of the final sample is lighter (after 24 hours), showing a smaller amount of Au nanoparticles. Instead, using swollen PDMS already after only 2 hours of incubation, highly colored samples are obtained. In addition, a larger amount of curing agent than the polymer base also increased the reduction rate of the gold precursor. The swelling of the polymer in ethyl acetate allowed the formation of a more uniform distribution of gold nanoparticles in the AuNP-PDMS composite. This result may be due to the higher swelling ratio of PDMS in ethyl acetate compared to ethanol (1.04 versus 1.18). The plasmonic signal of the prepared films was confirmed by UV-VIS measurements with an absorption peak at 536 nm.

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## Acknowledgements

The authors would like to thank POR Calabria FESR-FSE 2014/2020 for the financial support to the SmartMatter project in the ERA.NET Call 2019.

# BIOFUNCTIONALIZED MEMBRANE SYSTEM TO MODEL CANCER DISEASE FOR THERAPEUTIC SCREENING

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## Abstract

Cancer is the second most common cause of death worldwide. Unfortunately, the classical anti-cancer treatments, such as chemotherapy, radiotherapy and surgery, show various side effects, sometimes with low treatment efficiency. Therefore, in recent years, many new anticancer therapies have been developed to overcome these conditions. Furthermore, more accurate models of tumors are required for preclinical evaluation of new therapeutics. Recent advancements in the field of tissue engineering by means of membrane technology, led to the creation of membrane-based tools that provide reliable *in vitro* tissue/organ models [1-2]. In this study, a biofunctionalized membrane system that recapitulates cancer environment was developed as innovative tool for studying, for the first time, the anti-cancer effect of Plasma-Treated Water Solutions (PTWS). The efficacy of cold plasmas (CP) and PTWS in killing tumour cells is an emerging field of research [3] but needs suitable biomimetic environments for the *in vitro* validation. The membrane system consists of gas permeable fluorocarbon (FC) membranes, biofunctionalized with Poly-L-lysine (PLL) to mimic the extracellular matrix and to provide specific cues for modulating tissues growth. The selectivity, together with structural, physico-chemical and mechanical properties of PLL-FC membranes, which also ensure the adequate supply of oxygen, allow the realization of a suitable biomimetic interface for the growth of cancer cells. This system was employed as a reliable *in vitro* model of tumors, namely neuroblastoma, breast and colorectal cancers characterized by worst prognosis. Specific tumor cells were cultured within the biofunctionalized membrane platform and treated with different amounts of reactive oxygen and nitrogen species (RONS) delivered by PTWS, which were previously enriched with L-Tyrosine and exposed to different CP. PTWS displayed high cytotoxicity, anti-proliferative, pro-oxidant and pro-apoptotic effects through molecular mechanisms involving the intracellular ROS production and the activation of JNK and caspase-3, depending on PTWS's ROS/RNS ratios. The present study provides new membrane tools and approaches for the *in vitro* screening of anti-cancer treatments.

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# MEMBRANE DRUG LOADING AND RELEASE FOR SKIN TISSUE REGENERATION, REPAIR AND PROTECTION

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## Abstract

The development of biodegradable nano-structured membranes with specific functionalities and structural features able to provide adaptable biomimetic microenvironments for the control of the cell fate, represents one of the major challenges in skin tissue engineering [1-2]. Moreover, the membrane loading with a bioactive molecule constantly released in the time represents a further strategy to trigger or modulate biological processes needed for skin regeneration and repair. In this work, microporous membranes of chitosan loaded with a natural compound with therapeutic and healing properties were developed. 18- $\beta$ -Glycyrrhetic Acid (GA) is a natural derivative of licorice (Glycyrrhiza) extract, with a wide range of pharmacological activities, including anti-oxidant, anti-carcinogenic, anti-inflammatory, wound healing, and protective of aging- and UV-induced skin damages. The biomolecule was incorporated in the microporous structure of the chitosan membrane as a water-soluble inclusion complex with  $\beta$ -cyclodextrin ( $\beta$ -CD). Composite CHT membranes, with different ratio of  $\beta$ CD-GA inclusion complex, were realized by phase inversion process [3]. Membranes were characterized to evaluate structural, physico-chemical and biodegradation properties, and the GA incorporation and release were assessed in the time. Successively, the developed membranes were used for the formation of epidermal constructs by using human keratinocytes. The morphological behaviour, proliferation, metabolic functions, and the expression of specific cytokeratins involved in the keratinocytes differentiation, were expressed at different levels by cells cultured on native chitosan membrane, and on chitosan/ $\beta$ CD-GA composite membranes. Moreover, the protective effect of the GA was assessed after UV and oxidative stress damages induced in the developed epidermal membrane constructs, highlighting the pivotal protective role played by GA incorporated and released in the chitosan/ $\beta$ CD-GA membrane system. These achievements represent an attractive tissue engineering approach for the creation of membrane skin models that incorporate bioactive molecules useful in the tissue regeneration processes, and that could be used as a patch for topical drug delivery, wound healing and skin repair.

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## MEMBRANE TOPOGRAPHICAL CUES INFLUENCE CELL BEHAVIOUR: EVALUATION ON DIFFERENT CELL TYPES

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### Abstract

Topographical cues are highly sensed by living cells, therefore their presence on the membrane surface represents a useful modification which helps to study cell behavior in response to defined geometrical cues [1]. To this purpose lithographic molding technique was applied to introduce on the membrane surface microscale cues. This modification has the potential to enhance the overall membrane performance for biomedical applications. The introduction of the geometrical patterns was achieved by using different master molds made by UV mask lithography, which were used to prepare PLGA micropatterned membranes. For membrane preparation the phase inversion technique was used. In brief, PLGA (7.5% w/v) was dissolved in acetone and cast uniformly on PDMS master mold; they were dried at room temperature until complete solvent evaporation and then washed with distilled water. Beside the PLGA membranes in flat configuration [2], different PLGA membranes were prepared with the aim to offer to the cell different geometrical stimuli, thus evaluating 4 features of topography, namely channel, circular pillar, rectangular pillar and pits. The effects of the patterns were investigated on distinct kind of cells: neuronal cells, myoblasts and stem cells, evidencing peculiar cell behavior for the influence of the specific topographical stimulus sensed over the membrane surface. Confocal images of cells seeded on linear grooved membranes showed that this type of geometry enhanced an elongated cell morphology, guiding also cell orientation. Rectangular and circular pillars act instead as a discontinuous cue at cell-membrane interface, inducing a cell growth in several direction. The array of pits over the surface, highlighted also a precise cellular disposition; cells arranged within the interconnected membrane space between pits bypassing the microscale hole. All the results demonstrated that the geometrical elements over the membrane surface can precisely tune and control in a different way the cell behavior in terms of adhesion, migration and differentiation. The possibility to realize biomimetic membranes able to modulate cell response, helps to point out the mechanism of cell–microenvironment interactions providing new tools for the development of important technologies for advanced tissue engineering.

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# COMPREHENSIVE METABOLIC OVERVIEW OF CITRUS TACLE JUICE AND ITS MEMBRANE FRACTIONS BASED ON NMR AND UV-VIS SPECTROSCOPIC DATA COMBINED WITH PCA

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## Abstract

Tacle is a new triploid citrus hybrid developed in Sicily using traditional, strictly non-GMO techniques. Both its name and flavour recall the two parents' cultivars: the Tarocco orange (*C. sinensis* L. Osbeck) and the Monreal Clementine (*C. clementina* Hort. ex Tan.) [1]. Tacle gained increasing interest due to its antioxidant and biological properties [2]. This work is shaped on a metabolomic and lipidomic study of tacle juice using high-resolution Nuclear Magnetic Resonance (NMR) spectroscopy. Furthermore, the antioxidant capacity and the total content of flavonoids, polyphenols and  $\beta$ -carotene in the juice were investigated with UV-Visible spectroscopy. Ultrafiltration (UF) and nanofiltration (NF) membranes, in combination with diafiltration (DF), were employed to recover and purify bioactive compounds from the raw juice [3]. Retentate and permeate samples were analysed by NMR and UV-Vis spectroscopies. Using block-scaling pretreatment, a low-level data fusion was performed in the Principal Component Analysis (PCA), which allowed the evaluation of membrane processes' impact from a metabolomic perspective. In the PCA score plot of the studied UF/DF samples, PC1 described 59.9% data variation, while PC2 accounted for 33.5% of the total subset variance. UF/DF samples were separated into five clusters with no notable outliers, and the joint interpretation of the PCA score plot and loading plot showed that the UF process did not change the metabolic composition of the juice, contrary to the DF which led to a retentate stream purified in  $\beta$ -carotene. Moreover, in the PCA biplot of the studied NF samples, 91.6% of the total variance was explained by two principal components (PCs). NF fractions were positioned in different regions of the biplot with NF retentates in the same second quadrant, as being characterized by a close metabolite profile, mainly in terms of polyphenols, flavonoids, and TAA, thus confirming that, under the selected operating conditions, NF is suitable for enriching the clarified tacle juice in bioactive compounds.

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# MEMBRANE-BASED FRACTIONATION OF WHITE WINE LEES HYDROALCOHOLIC EXTRACTS

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## Abstract

Nowadays the recovery of water and bio-molecules from wine wastewaters and by-products has become a key topic in wine processing industry in agreement with industrial ecology and circular economy concepts. In this contest, research efforts are increasingly oriented to redesign the traditional industrial cycle closer to the concept of biorefinery, where losses are minimized and resources are used to the full, providing achievements in economic, environmental and social issues [1,2]. The main objective of this work was to investigate the recovery of wine-derived bioactive compounds from white wine lees through a combination of hydroalcoholic extraction and membrane-based operations, as a potential alternative for winery wastewater treatment and valorisation. Preliminary experiments were performed in order to identify the optimal conditions (solid-liquid ratio, extraction time and working temperature) for the extraction with ethanol-water mixtures. The hydroalcoholic extract was previously microfiltered in order to produce a clarified solution free of suspended solids and colloidal substances. Then, the clarified extract was fractionated with three different spiral-wound nanofiltration membranes with a molecular weight cut-off in the range of 200–1000 Da (TS40, XN45 and NP010, all from Microdyn-Nadir). Their performance was analysed in terms of productivity, fouling index and retention towards target compounds (polyphenols, flavonoids, sugars) and antioxidant activity. Among the selected membranes the TS40, with the lowest cut-off, exhibited higher rejections of phenolic compounds allowing to obtain concentrated fractions with a total polyphenol content up to 1.7 g GAE/L and permeate streams with negligible content of phenolics (Figure 1).

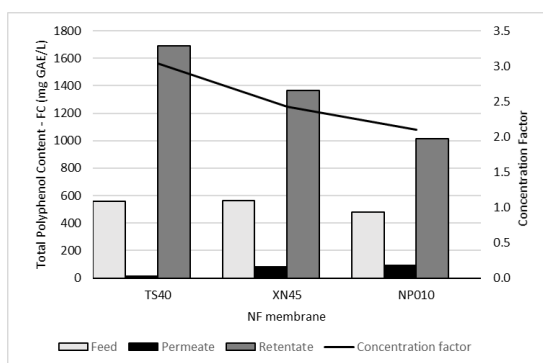


Figure 1. Total polyphenol content in permeate and retentate fractions from nanofiltration of clarified white lees extract with selected membranes.

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# HEALTH-PROMOTING PROPERTIES OF RED FRUIT JUICE CONCENTRATED BY NON-THERMAL MEMBRANE PROCESSES

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## Abstract

The consumption of red fruits is growing worldwide not only for their nutritive value, flavor, attractive taste, but also due to their well-known health-promoting properties (as dietary sources of bioactive compounds) showing a protective effect against many chronic diseases (cancer, heart disease, and type 2 diabetes). At the same time, among consumers, there is a growing demand, for safe and natural red fruit juices, produced with sustainable or ecological technologies capable to preserve the bioactive compounds (especially anthocyanins) susceptible to degradation at high temperature, exposure to oxygen and operations such as concentration [1]. In light of these trends, this work aims at investigating, for the first time, the non-thermal concentration of a blend of pomegranate, prickly pear and blood orange juices of Sicily origin for the production of a concentrated red juice with enhanced antioxidant capacity and potentially able to counteract obesity and type 2 diabetes [2]. The juice blend (65% blood orange, 25% pomegranate, 10% prickly pear) was clarified by microfiltration (MF), then pre-concentrated by nanofiltration (NF) up to 33 °Brix and finally concentrated up to 60 °Brix by osmotic distillation (OD). Experimental results showed that the content of bioactive compounds as well as the antioxidant activity of the original juice was very well-preserved in the concentrated juice independently of the concentration factor. The OD retentate at 60 °Brix showed an antioxidant activity of 11.5 mM of Trolox and a concentration of polyphenols, anthocyanins and flavonoids of 1363.92 mg GAE/L, 312.61 ppm and 400 ppm, respectively. It resulted also the most active sample against pancreatic lipase and  $\alpha$ -amylase inhibitory activity with IC<sub>50</sub> values of  $44.36 \pm 0.85$  and  $214.65 \pm 2.03$   $\mu$ g/mL, respectively. The concentrated blend, with enhanced health-promoting properties, offers interesting perspectives for developing phytochemical functional products (anti-cholesterol, antidiabetic, antiviral, antimicrobial, anti-inflammatory, antihypertensive products) and dietary supplements.

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# EFFECT OF GAS DIFFUSION LAYER TYPES ON THE PERFORMANCE OF PEM IN WATER ELECTROLYSIS

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## Abstract

In the next years the production of green Hydrogen as a form of energy carrier will play an important role for the energy transition [1]. In this contest the hydrogen produced with polymer electrolyte membranes (PEM) needs improvement in the energy efficiency to reduce cost and beginning competitive with grey/blue hydrogen [2]. This work presents a study on the influence of different gas diffusion layers, such as titanium, carbon cloth, carbon paper and graphite on the performance of proton exchange membrane in the water electrolysis. Different types of gas diffusion layers were used for Cathode and Anode sides during PEM electrolysis process at room temperature and atmospheric pressure. H<sub>2</sub> and O<sub>2</sub> production rate, electrical power, energy efficiency, Faradaic efficiency and polarization curves were determined for all experiments.

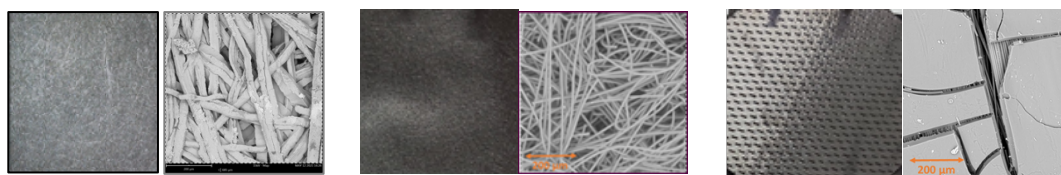


Figure 1. Different type of gas diffusion layer

The effects of different parameters such as clamping pressure and materials of the electrodes on polarization phenomena were studied. The PEM used is a catalyst coated membrane (Ir-Pt-Nafion™ 117 CCM). The type of GDL strongly influence the activation and ohmic polarization phenomena. The best results were found for Titanium-GDL on the anode side and Graphite-GDL on the cathode side. The maximum H<sub>2</sub> production was about 0.02 g min<sup>-1</sup> with a current density of 1.1 A cm<sup>-2</sup> and a current power about 280W.

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## Acknowledgements

The work leading to these results has received funding from the HPE - High Pressure Electrolysis project.

# NEEDLELESS ELECTROSPINNING SYSTEM FOR THE PREPARATION OF MORE SUSTAINABLE NANOFIBER-BASED MEMBRANES

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## Abstract

Thanks to nanometric fibers, nanofibrous-based membranes exhibit extraordinary characteristics (structural, chemical, and mechanical properties, high specific area, porosity and significant tensile strength) that make them valid candidates for several applications. Electrospinning is the most common procedure used in their manufacturing. A traditional electrospinning system is based on the application of a high electric potential between two electrodes of opposite polarities and connected to a needle (single, coaxial, or triaxial) and a collector. In this work, in order to overcome the low productivity of traditional needle electrospinning, a needleless electrospinning machine, commercialized as Nanospider™ (Elmarco, Czech Republic), was used [1]. In addition, the main focus of the work was to replace traditional toxic solvents used in membrane fabrication, like dimethylformamide (DMF) and dimethylacetamide (DMA), with greener alternatives [2]. However, the chemical-physical properties of the solvent used for polymer solubilization (e.g. viscosity, dielectric constant, polarity, evaporation rate) are pivotal and its replacement with a proper alternative is always challenging [2]. The use of green solvents, such as dimethyl sulfoxide (DMSO), has already started to be explored for the preparation of nanofiber-based membranes [3]. In this work, different attempts were carried out in order to study the electro-spinnability of polymeric solutions prepared using polyethersulfone (PES) and polyvinylidene fluoride (PVDF) as polymers which were solubilized in green or more sustainable solvents. The use of green solvents in combination with the innovative needle-free electrospinning machine can represent an important step forward in the preparation of nanofiber-based membranes.

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## Acknowledgement

The work has been carried out within the CNR-Royal Society (UK) 2022-2023 International Exchanges (IEC\R2\212100, project title: Sustainable manufacturing of membranes for water treatment and purification).

# NEW GENERATION OF POLYETHER SULFONE (PES) MEMBRANES PREPARED USING $\gamma$ -VALEROLACTONE (GVL) AS A GREEN SOLVENT VIA PHASE INVERSION TECHNIQUE

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## Abstract

Solvents are used in all chemical processes and affect safety, the environment, and the economy at large [1]. The membranes' manufacturing still requires the use of toxic solvents, as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMA) or N,N-dimethylformamide (DMF), and fossil-based polymers. The use of green solvents as substitutes for traditional solvents is the unavoidable trend of the future in phase inversion processes [2]. In this work,  $\gamma$ -Valerolactone (GVL) was chosen as an innovative renewable green solvent for the preparation of polyethersulfone (PES) membranes. GVL is a biodegradable, non-toxic chemical obtained from biomass. Membranes were prepared by coupling vapor-induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) techniques using polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) as pore-forming agents. The structure of the membranes was tailored by acting on the exposure time to humidity during VIPS process (from 0 to 5 min) and by varying the water coagulation bath composition during NIPS process (water and water/isopropanol). The thermodynamic aspects (i.e. solubility parameters, polymer-solvent distance and cloud point analysis) and kinetic parameter in terms of viscosity were well studied. The effect of the selected solvent on the morphology and performance of prepared membranes was investigated. It was possible, indeed, to produce membranes with finger-like and spherulitic structures. The membranes presented a pore size in the range of ultrafiltration (UF) and microfiltration (MF), from 0.05 to 0.4  $\mu\text{m}$ . The membranes showed a water permeability of up to 600  $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ , making them ideally suited for water filtration processes.

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## Acknowledgements

The authors extend their appreciation to the project ID VN21GR07 in the framework of the Agreement on Scientific and Technological Cooperation between the Government of the Italian Republic and the Government of the Socialist Republic of Vietnam (MAECI- Vietnam).

# HYDROLYZED POLYVINYL ALCOHOL IMMOBILIZED POLYETHERSULFONE MEMBRANE WITH GREEN SOLVENT FOR ENHANCEMENT OF THE HYDROPHILIC AND ANTIFOULING PROPERTIES

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## Abstract

Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv®PolarClean, Solvay Specialty Polymer) as an eco-friendly sustainable solvent was used to prepare the hydrolysis Polyvinyl Alcohol(PVA) immobilized Polyethersulfone(PES) ultrafiltration membrane. The membrane was formed by combining the non-solvent-induced and thermally induced phase separation techniques. At high temperature, PVA/PES polymers were blended in the presence of PolarClean (Green solvent) by adding dropwise water. Polyvinylpyrrolidone (PVP) was used as hydrophilic pore former agents. The PVA/PES blended membrane showed a considerably higher pure water flux and permeation compared to the pristine PES membrane. Water affinity improvement of the membrane surface was enhanced the surface hydrophilicity of the membrane. The properties of the blended membranes, such as morphology, mechanical properties, porosity, water permeability were investigated. Finally, lower MW and concentration of PVA could result in membranes with higher rejection and good fouling resistance, excellent pure water flux compared to the pristine PES membrane.

## Keywords

Hydrolysed PVA, Green solvent, Ultrafiltration membrane, Hydrophilicity, Antifouling

# PECTIN AND ALKALI LIGNIN USED AS NATURAL FUNCTIONAL MACROMOLECULES TO DEVELOP GREEN, STABLE AND PERFORMING MEMBRANES

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## Abstract

Aiming to develop membranes in a more sustainable way, pectin (PEC) and alkali lignin (AL) were used as crosslinking and hydrophilizing agents for polyvinyl alcohol (PVA) and polyvinylidene fluoride (PVDF) membranes, respectively. PVA is a synthetic polymer with good film forming ability and easy to biodegrade after disposal, but it has low stability in water. PVDF is a highly stable synthetic polymer, but it is a petrochemical derived material and its disposal remains an issue. Therefore, in the first case, the aim was to improve the stability in water of biopolymer-based membranes, in the latter case the aim was to reduce the amount of petrol derived synthetic polymer. The two natural macromolecules were selected on the basis of their functional groups considered suitable to carry out the chemical crosslinking and/or the blending reactions chosen as strategies to develop fully or partially biopolymer based-membranes.

PEC, with its carboxyl groups, successfully performed the esterification reaction on the hydroxyl functions of PVA. A highly water stable PVA/PEC crosslinked membrane, with an unprecedented mechanical strength, and with long-term stability of water vapor barrier properties has been developed by evaporation induced phase separation (EIPS) [1]. On the other hand, the hydrophobic/hydrophilic character of AL guaranteed a good interaction with the hydrophobic PVDF. Hydrophilic PVDF/AL membranes were prepared by non-solvent induced phase separation (NIPS). This strategy allowed to develop a membrane with a halved amount of PVDF, capable to fully separate oil droplets from a stable oil-in-water emulsion used as a model solution of oily wastewaters.

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## Acknowledgements

Authors acknowledge POR Calabria FESR-FSE 2014/2020 for the financial support to the SmartMatter project within the M-ERA.NET Call 2019.

# ENHANCED WATERPROOFING AND DURABILITY PERFORMANCE OF GRAPHENE OXIDE BITUMINOUS MEMBRANES

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## Abstract

Bituminous membranes are widely used to insulate the buildings. The primary role of the membrane is to prevent water from entering the structure, thus eliminating problems with mold and building damage. However, exposure to atmospheric agents, such as UV light and high temperatures, causes degradation phenomena in bituminous membranes. Several polymers have been used to improve the performance of bituminous membranes; however, several limitations have been found such as high cost and low resistance to aging. The advent of nanomaterials has opened the way for various interesting engineering solutions, allowing the production of materials with new properties and function. Despite the high costs, small amounts of nanomaterials have been shown to be enough to achieve desirable performance.

In this work small quantities of multilayer GO were used to produce high-performing bituminous membranes. Significant improvements were observed in terms of mechanical strength, chemical stability, and water vapor barrier. In conclusion, the bituminous membranes produced are stable for a long time in drastic conditions of temperature and UV radiation, mechanically resistant, with a high moisture barrier power. This has a significant economic and environmental impact, in fact the useful life of the doped bituminous membranes is much higher than the native one, this means a reduction in the use of raw materials and special waste production.

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## Acknowledgements

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# POLYMERIZABLE BICONTINUOUS MICROEMULSION EMPLOYED AS ANTI-FOULING COATING FOR PES AND PVDF MEMBRANES

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## Abstract

Processing steps necessary to convert fish and shellfish into exportable products produce a huge quantity of wastewater which needs to be treated. In this respect, due to the highest volume of seafood exported in the world, the Asian state of Vietnam necessitates a validate system to treat the produced wastewater such as membrane bioreactor (MBR), a combination of membrane technology with a biological process. However, one of the main drawbacks of this technology is related to membrane fouling and biofouling. Some of the approaches to limit these phenomena are oriented to the modification of membranes' surfaces in order to enhance their lifetimes and performances. Within the bilateral project MEMSEAFOOD, the surfaces of commercially available porous membranes were modified following the procedure described by Galiano et al. [1] with a polymerizable bicontinuous microemulsion (PBM) [1,2]. In particular, in this work, the PBM technique was applied to coat the surface of ultrafiltration polyvinylidene fluoride (PVDF) membranes. Pure water permeability, fouling tests (filtration with humic acid, 100 mg/L) and water permeability test after back-flushing were carried out on both coated and uncoated membranes and the results were also compared with previous tests carried out with polyethersulfone (PES) membranes used as a support. For surface modified PVDF and PES membranes, tests revealed a higher foulant rejection and better permeability after washing, thanks to their anti-fouling properties attributed to their improved hydrophilicity, nanostructured morphology, and low surface roughness.

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## Acknowledgements

This study was carried out within the project "Development Of An Innovative Ultrafiltration (UF) Membranes In Anaerobic Membranes Bioreactor (AnMBR) for Seafood Processing Wastewater Treatment" (project ID VN21GR07) in the framework of the Agreement on Scientific and Technological Cooperation between the Government of the Italian Republic and the Government of the Socialist Republic of Vietnam. The project is funded by the Italian Ministry of Foreign Affairs and International Cooperation (MAECI) and the Ministry of Science and Technology (Vietnam).

# TREATMENT OF SALTY SOLUTIONS WITH DIRECT CONTACT MEMBRANE DISTILLATION PROCESS

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## Abstract

When the reverse osmosis (RO) process is used to treat salty solutions, two streams are obtained: the brine, highly concentrated in salts, and the fresh water, depleted of salts. The first stream must be properly treated before being discharged into the sea, in order to avoid impacts on the marine environment. For this purpose, tests of Direct Contact Membrane Distillation (DCMD) are carried out in order to process simultaneously NaCl solutions with concentrations of around 70 g/L at the permeate side (to simulate RO brine) and of around 18 g/L at the feed side, with the aim to obtain, at both sides, streams with concentration of seawater (around 35 g/L). The experiments are realized with a lab setup (Fig.1) in which a polypropylene commercial membrane, with pore size of 0.2  $\mu\text{m}$ , thickness of 91  $\mu\text{m}$  and membrane area around 40  $\text{cm}^2$ , is sandwiched in a longitudinal flat module. The DCMD set-up is first used for tests in which deionized water is sent at both membrane sides, to have a reference for the performance of the system in ideal conditions. Then, the influence of the feed temperature (40-50-60°C) and flow rate on the permeate flux and feed/permeate conductivity is studied when the permeate flow rate and temperature are fixed at 42 L/h and 15°C, respectively.

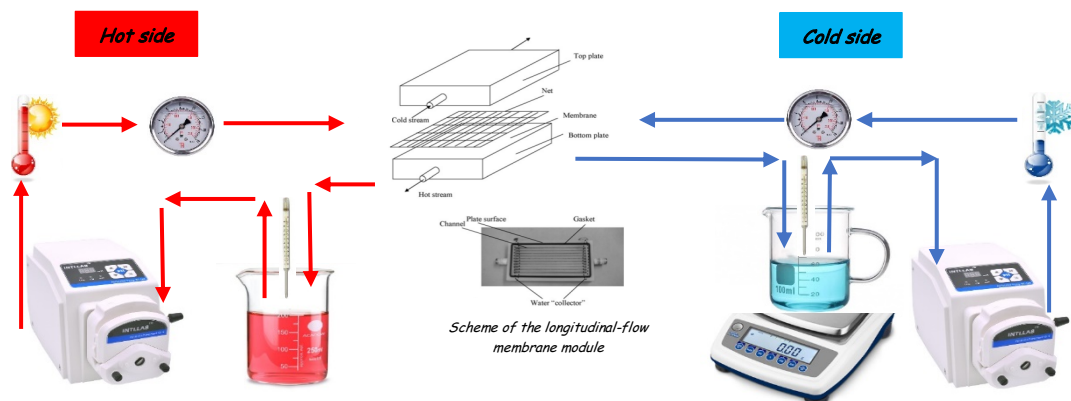


Figure 1. DCMD setup.

# EXFOLIATED BISMUTH TELLURIDE FLAKES FOR ENHANCING THE PERFORMANCE IN MD SYSTEM

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## Abstract

Water scarcity forces science to find the most environmentally friendly propulsion technology to provide abundant fresh water at low energy costs. Membrane distillation (MD) is a promising process for water desalination responding well to the criteria of environmentally sound management of natural resources, but it is not yet competitive on scale. New membranes also with different functionalizations are developed and proposed in order to improve the performance of the aforementioned membrane operation [1]. Here, a study on PVDF-based membranes functionalized with a highly exfoliated dichalcogenide compound ( $\text{Bi}_2\text{Te}_3$ ) is proposed in order to accelerate the performance in such processes [2]. For the preparation of the PVDF membranes a procedure based on the combination of liquid phase assisted exfoliation of the dispersant (WJM) and non-solvent phase inversion (NIPS) is used. Key insights were gained on the crucial role of this topological material confined in hydrophobic membranes dedicated to freshwater recovery from synthetic seawater.  $\text{Bi}_2\text{Te}_3$ -enabled membranes exhibit the ability to reduce mass transfer resistance while high resistance to heat loss is opposite, thus packing ultra-fast production and thermal efficiency into one device (Figure 1). The obtained results confirm the effectiveness of chalcogenides as frontier materials for the desalination of water of new conception through the innovative membrane distillation [2]. This work provides new insightful indication about the great potential of exfoliated few-layers materials in membrane engineering dedicated to water desalination.

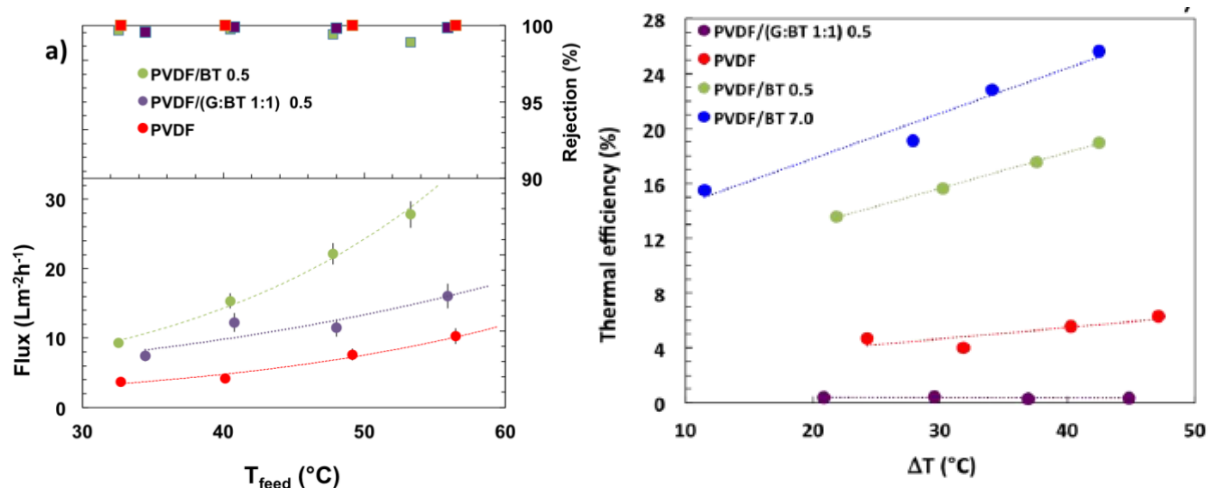


Figure 1. Flux and rejection values estimated at different  $\Delta T$  for PVDF, PVDF-(BT:G 0.5) (1:1) and PVDF-BT 0.5 membranes:  $T_{\text{feed}}$ , 32-55 °C ; Thermal efficiency estimated for all membranes within the overall range of temperature at flow rate of 100 mLmin<sup>-1</sup>.

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# FRESH WATER FROM PRODUCED WATER VIA MEMBRANE DISTILLATION

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## Abstract

Produced water (PW) is the water associated with hydrocarbons during the extraction of oil and gas from either conventional or unconventional resources. Proper treatment and management of produced water are necessary to avoid possible negative environmental impacts associated with its discharge. Moreover, the treatment of produced water can be beneficial in bridging the gap between demand and availability of freshwater in water scarcity regions where generally oil and gas reservoirs are located. Various physical, chemical, and biological methods and their combinations have been used to treat the produced water [1]. However, conventional treatment methods have certain limitations including the usage of toxic chemicals, high cost of treatment, large footprint, long retention times, and the creation of secondary pollution. Additionally, new stringent environmental regulations put emphasis on more effective treatments. Due to these reasons, recently membrane-based treatments have been tried widely for produced water treatment. Membrane distillation (MD) is an innovative membrane process with the capability to treat highly concentrated solutions and can be suitable to be used for produced water. In this direction, the performance of Polypropylene (PP) and Hyflon AD40H-based hollow fiber membranes was investigated in direct contact membrane distillation (DCMD) system for freshwater from produced water. A synthetic PW solution representing the characteristics and behavior of actual PW was prepared according to the literature [2]. Experimental studies showed a 50% increase in the permeate fluxes for both tested membranes when the feed temperature was increased from 50 to 70 °C. In addition, an excellent rejection factor, greater than 99% was observed in either type of membranes. These preliminary results indicate the good potential of PP and AD40H membranes for wastewater treatment applications.

Future steps include the study of minerals recovery from produced water and the preparation of thermoplasmonic membranes, able to minimize the temperature polarization phenomenon and, thus, improve the energy efficiency of the MD process [3].

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