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The annual update of advances promoted at
Institute on Membrane Technology,
National Research Council

December 17th - 18th, 2019
Sala Stampa in Aula Magna, UNICAL, Rende (CS), Italy

PROGRAM

Local Organizing Committee
G. CHIAPPETTA
R. DE LUCA
R. JERACE
A. STAFFA
V. TORRELLI

17 December

09:00 - 09:30	Arrival
09:30 - 09:50	Opening Session & ITM report 2019 <i>Alberto FIGOLI</i>
	Chairman L. DE BARTOLO
09:50 - 10:25	Membrane Engineering today and tomorrow <i>Enrico DRIOLI</i>
10:25 - 11:00	Bio-functionalized membranes: a strategy to boost enabling technologies <i>Lidietta GIORNO</i>
11:00 - 11:30	Coffee break
	Chairman C. CONIDI
11:30 - 11:50	Valorization of olive leaves by bioproduction and formulation of high-added value compounds <i>Fabio BAZZARELLI</i>
11:50 - 12:10	Bioremediation of organophosphates in a real matrix <i>Giuseppe VITOLA</i>
	Chairman A. BRUNETTI
12:10 - 12:30	Mutual interaction in mixed gas permeation through zeolite membranes <i>Pasquale ZITO</i>
12:30 - 12:50	SSZ-13 zeolite membranes for CO₂/CH₄ separation <i>Aydani AZAM</i>
12:50 - 13:10	Pd-Cu/Al₂O₃ and Graphene Oxide/TiO₂-Boehmit/Al₂O₃ membranes for hydrogen separation/purification <i>Adolfo IULIANELLI</i>
13:10 - 14:40	Lunch together at Mensa
	Chairman E. FONTANANOVA
14:40 - 15:00	Sugar-Based Dimethyl Isosorbide as a New Green Solvent in Membrane Preparation <i>Francesco GALIANO</i>
15:00 - 15:20	Unprecedented porous Matrimid®5218 membrane preparation <i>Francesca RUSSO</i>
15:20 - 15:40	Development of Stable Biopolymeric Membranes by Crosslinking with Bio-Derived Compound <i>Serena REGINA</i>
	Chairman F. BAZZARELLI
15:40 - 16:00	Ultrapermearable benzotriptycene-based PIMs that redefine the upper bounds for CO₂ separations <i>Alessio FUOCO</i>
16:00 - 16:20	Efficient Gas Separation and Transport Mechanism in Rare Hemilabile Metal-Organic Framework <i>Rosaria BRUNO</i>
16:20 - 16:40	Glassy vs rubbery polymers: effect on the gas transport in CuNi-MOF based mixed matrix membranes <i>Elisa ESPOSITO</i>
16:40 - 17:30	Christmas aperitif

18 December

	Chairman F. MACEDONIO
09:30 - 09:50	Sustainable Production of Customized Polymeric Membranes and their Use in the Purification of an Anticancer Monoclonal Antibody <i>Gianluca DI PROFIO</i>
09:50 - 10:10	Graphene assisted Membrane Crystallization technology: A combined experimental-computational approach <i>Maria Luisa PERROTTA</i>
	Chairman A. CRISCUOLI
10:10 - 10:30	Waste gaseous streams treatment and reuse by membrane condenser <i>Francesca MACEDONIO</i>
10:30 - 10:50	Fluorolink®perfluoropolyether (PFPE) compounds: an easy way in order to prepare tailored hydrophobic/hydrophilic membranes for water treatment <i>Claudia URSINO</i>
10:50 - 11:20	Coffee break
	Chairman P. BERNARDO
11:20 - 11:40	Hydrogen generation by steam reforming of a synthetic biogas mixture in a Pd-Au membrane reactor packed with a Rh(1%)-MgAl₂O₄/Al₂O₃ catalyst <i>Matteo MANISCO</i>
11:40 - 12:00	Dimethylether production in a catalytic membrane reactor <i>Adele BRUNETTI</i>
12:00 - 12:30	<i>CLOSING REMARKS</i>
13:00 - 14:30	Lunch together at Mensa

Membrane Engineering today and tomorrow

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Abstract

Our modern Society has to solve and overcome various severe problems for maintaining and increasing the quality of our life, from the global water stress to raw material depletion, from energy production to CO₂ capture and environmental pollution.

Process intensification in process engineering, new advanced smart materials, molecular engineering are all discipline which might contribute to find solutions. Membrane engineering is one of the disciplines most involved in the technological innovations necessary to face the problems characterizing the world today and in future. Membrane operations contribute to solve these problems, and the potentialities of membrane operations have been widely recognized in the last few years. The design and development of innovative membrane-based integrated processes continue to increase, providing critical support for the future improvement of sustainable industrial growth.

The growing interest for new materials and, specifically, for inorganic materials with new interesting properties such as the graphene family, the 2D chalcogenides are receiving strategic interest for new membrane preparation. The specific characteristics of these materials in terms of thermal conductivity (very high or in some other case very low), the plasmonic phenomena inducing interesting surface properties, and the mixed matrix membranes filled with them are examples of new areas of immediate research to be addressed. These new membranes might be of particular importance for appropriate design of membrane and module for innovative new membrane assisted unit operations, such as membrane distillation, membrane crystallizer, membrane condenser, etc.

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Bio-functionalized membranes: a strategy to boost enabling technologies

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Biomolecules and their hierarchical organization in supramolecular systems bear unparalleled efficiency in terms of transport, selectivity, recognition, sensing, catalytic, camouflage, healing, cleaning properties. These are pivotal for breakthrough processes needed in all strategic areas enabling sustainable development and inclusive society.

The bio-functionalization of artificial membranes lies in this framework.

Bio-functionalized membranes can be obtained by attaching i) a biomolecule/biocomponent, ii) a biomimic molecule/component, or iii) a bioinspired molecule/component to a membrane matrix. The different paths will lead to so called biohybrid, biomimic, bioinspired systems, respectively. Even though these terms are often used as synonymous, they respond to a substantially different approach. The uniqueness of bionic membranes will be also underlined. Examples of the various cases will be presented. Besides the molecule/component availability, the choice on the type of approach may strongly depend on the type of application, which dictates the needed properties. Membranes made of synthetic or natural polymers or a mixture of them, in flat-sheet, capillary or capsule geometry, were used.

The lecture will also focus on strategies explored to bear advanced functions to manmade membranes via functionalization using biomolecules and applications of the biohybrid membranes where the authors have most contributed, such as biocatalytic membranes, biosensors, drug delivery.

Despite the abundance of studies in the literature referred to biomacromolecules (such as enzymes, antibodies) immobilization [1-3], fundamental understanding on how to predict and govern biomacromolecule loading, keeping the native bio-function and increasing its stability as well as how to avoid biomacromolecule deactivation during membrane cleaning and maintenance is still not fulfilled.

General observations at macroscopic level indicated that the amount of immobilized biomacromolecule and its distribution within the membrane support play a crucial role. Spherical nano-architectures favour optimal spatial orientation preventing deactivation by crowding phenomena. Immobilized biomacromolecules characteristics and their aggregation at the membrane and pore surface are strongly affected by their bulk properties. Spacers size and shape influence the biomacromolecule functional properties; a balance of interactions between biomacromolecule and spacer/surface is necessary to guarantee enough molecular flexibility while reaching a certain rigidity to maintain high selectivity and stability, respectively. Physical-

chemical parameters at microenvironment level (including surface energy and water activity) and mass transport strongly influence the overall performance.

The behaviour of the bio-functionalized membranes as a function of major parameters will be discussed. A brief hint on strategies to reversibly immobilize biomacromolecules on membranes, in order to remove them during membrane cleaning will be also presented.

Conclusions will outline drivers and brakes of the bio-functionalized membranes as well as future research directions to promote forefront achievements.

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Acknowledgements

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Valorization of olive leaves by bioproduction and formulation of high added-value compounds

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Abstract

The olive leaves represent a rich source of biophenols with pharmaceutical and nutraceutical activities. This biomass is a renewable material from which important phytotherapeutics such as oleuropein, rutin, and verbascoside can be extracted. The development of environmentally friendly strategies for the valorization of biomass is of crucial importance in view of a circular economy. In this work, the bioconversion of oleuropein to produce oleuropein aglycone (OA) and its encapsulation in particles was investigated by an integrated membrane process. The biocatalytic membrane reactor (BMR) has been studied for the production of oleuropein aglycone using oleuropein contained in olive leaves extract [1]. Subsequently, oleuropein aglycone was encapsulated in structured particles by membrane emulsification. Two different configurations of integrated membrane processes were studied. In the first one, a BMR unit was combined with two membrane emulsification (ME) units (one for extraction of oleuropein aglycone using a green solvent and one for its formulation) obtaining the encapsulation of oleuropein aglycone in solid lipid particles. Instead in the other configuration, BMR was combined with one ME unit and OA-loaded poly(vinyl alcohol) (PVA) particles were produced. The noncommercially available oleuropein aglycone was produced in the BMR with immobilized β -glucosidase with a conversion of 40% at each passage of the substrate through the system. Regarding the production of particles loaded with biophenols, uniform particles with high encapsulation efficiency up to 98% were produced under mild operating conditions.

References

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Acknowledgments

The authors acknowledge for the financial support the project PON01_01545, *Olio piÙ*, within the framework PON Ricerca e Competitivita 2007–2013.

Bioremediation of organophosphates in a real matrix

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Abstract

Organophosphates (OPs) are among the most concerning substance for human health, due to their hazardous nature and their applications as pesticides and chemical weapons. Therefore, efficient and environmentally sustainable methods for their detection and inactivation are highly needed. OPs bioremediation by isolated enzymes is an appealing strategy because can provide advantages such as high specificity, efficiency and low energy consumption. On the other hand enzymes can suffer of low stability. The use of intrinsically stable enzymes such as extremophiles and their immobilization on suitable supports can both ensure high stability and activity. The aim of the present work was the study of a biocatalytic membrane reactor (BMR) able to operate OPs degradation in a real matrix. The waste waters coming from the manufacturing of olive oil (olive mill waste waters, OMWWs) added with a model pesticide (paraoxon) were selected as real matrix and as feed for the BMR. The BMR was developed immobilizing covalently, on functionalized regenerated cellulose (RC) membrane, the extremophile *Solfolobus solfataricus* (named Sso-3M), an enzyme able to hydrolyze OPs with high efficiency. By using the optimal immobilized enzyme amount [1] and optimizing the residence time it was possible to manage high paraoxon degradation (about 70%) during the first reaction cycle. A constant degradation of 25% for the subsequent reaction cycles, within a period of two months was obtained. Although a severe conversion decrease was observed, these results are interesting considering that OMWWs are a very stressing environment and the BMR is significantly more stable than the free enzyme, which completely loses its activity in a few weeks (in aqueous paraoxon solution).

Kinetic characterization of the enzyme in batch demonstrated that the lower performance of the biocatalyst towards the pesticide in OMWW respect to the one contained in water is due to a competitive inhibition given by the biophenols present in the real matrix.

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Acknowledgements

The authors gratefully acknowledge for the financial support the project PON01_01585 “Innovative products for monitoring and detoxification/decontamination of nerve agents and explosives in the environment and/or for handling of emergency” (BIODEFENSOR) within the framework PON Ricerca e Competitività 2007–2013.

Mutual interaction in mixed gas permeation through zeolite membranes

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Abstract

The gas permeation through zeolite membranes is strongly affected by the mixture concentration and the operating conditions used. In this work, we experimentally investigated the separation performance of a DDR membrane for separation of CO₂ from H₂ and N₂ in the temperature range 25-75°C and up to 700 kPa [1]. Single gas measurements showed that CO₂ is the most permeable species, followed by H₂ and N₂. In mixture, the preferential adsorption of CO₂ significantly hinders the permeation of weakly adsorbed species. At the same time, CO₂ is itself influenced by the presence of H₂ and N₂, increasing its permeation when the composition of the other species is higher. The difference between single and mixed gas permeation is emphasized by the low temperature, reflecting in a high selectivity in this region (Figure 1). The highest CO₂ selectivity values are 28 and 17 in presence of N₂ and H₂, respectively, whereas the CO₂ permeance exceeds 1.5 times the single gas value (i.e., 18 nmol m⁻² Pa⁻¹ s⁻¹) for a CO₂:H₂ mixture = 40:60. We found that diffusion of CO₂ is promoted more by H₂ than by N₂. Similarly, the hindering effect exerted by CO₂ is more important on H₂ than on N₂. These behaviors are confirmed in other zeolite membranes [2].

The choice of appropriate operating conditions makes DD3R particularly suitable for CO₂ separation. The permeance variations with the mixture composition reflected directly on selectivity, which can be five times higher than that in single gas in presence of H₂.

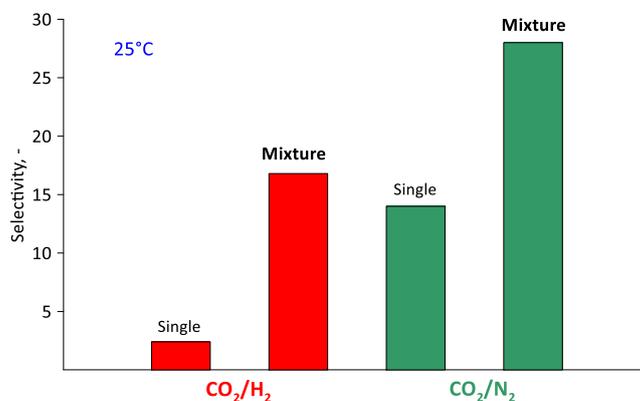


Figure 1. CO₂/H₂ and CO₂/N₂ selectivity values through a DD3R membrane in single component and mixture containing 40% of CO₂ [1].

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Acknowledgements

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SSZ-13 zeolite membranes for CO₂/CH₄ separation

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Abstract

Natural gas, the greater source of methane on the earth, contains some pollutants such as carbon dioxide (1 – 50%), carbon monoxide (0-2 %) and hydrogen sulfide (1-15%) that need to be removed before its final injection in pipelines [1]. Carbon dioxide is an acid gas, which is highly corrosive and can damage pipelines and equipment in the presence of water. In addition, CO₂ reduces the calorific power of natural gas and also causes crystallization in the liquefaction phase [2].

The main traditional processes that can be adopted for CO₂ removal include absorption (physical and chemical), adsorption and cryogenic separation [3]. Today, the rapid growth of membrane technology make it a good candidate also for this application, owing to its various advantages over conventional separation technologies, such as environmental compatibility, intensive process, economic efficiency, low energy consumption [4].

Polymeric membranes are widely used in the industry because of their low cost and ease of manufacture, but they have disadvantages such as low resistance to chemical and thermal conditions and trade-off limitations [4]. Zeolite membranes often exhibit high permeability and high selectivity due to their crystalline structure and high resistance to chemical and thermal conditions, thus making them a good alternative to polymeric membranes in gas separation processes. Therefore, the attempt to fabricate a suitable zeolite membrane for carbon dioxide separation from methane is of particular importance.

In this work, we used SSZ-13 zeolite membrane for CO₂/CH₄ separation. SSZ-13 zeolite (Standard oil Synthetic Zeolite-13) is an aluminosilicate, which has a Si/Al ratio that, depending on the synthesis condition, can vary from 2.5 to 175 [5]. Here, SSZ-13 membranes were synthesized by secondary growth method on the outer surface of α -alumina support, by means of the dynamic rub coating for the seeding of the support. The good intergrowth behaviors among the crystals displayed a smooth surface and a uniform crystal with diamond shape structure. Permporometry analysis showed the most size distribution of the defects were between 1 to 2 nm confirming SSZ-13 membrane as a proper zeolite membrane for separation of CO₂/CH₄ and CO₂/N₂ mixtures.

The performance of the membranes were evaluated for separation of CO₂ from N₂ and CH₄. Single gas measurements carried out as reference at 30°C showed a CO₂ permeance of 226 nmol m⁻² s⁻¹Pa⁻¹ and an ideal selectivity of CO₂/CH₄ and CO₂/N₂ of 67 and 10 respectively.

References

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Acknowledgements

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Pd-Cu/Al₂O₃ and Graphene Oxide/TiO₂-Boehmit/Al₂O₃ membranes for hydrogen separation/purification

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Abstract

The growing interest about hydrogen as a green energy carrier is involving a particular attention towards inorganic hydrogen permeable membranes, useful for its separation and purification due to their behaviors of hydrogen perm-selectivity, constituting a valid alternative to the conventional operations [1]. Till now, palladium results to be the dominant membrane material at relatively high temperature because it shows full hydrogen perm-selectivity over the other gases. In the last years, composite Pd-based membranes attracted more interest over the unsupported ones because they show better mechanical resistance, higher hydrogen permeability and are constituted of a reduced Pd content [2]. In this work, a Pd₇₀-Cu₃₀/Al₂O₃ membrane (Figure 1a) was experimentally studied for hydrogen separation/purification. It was prepared by metal vapor synthesis, depositing the metals (Pd and Cu) in their active form from solvent-stabilized bimetallic nanoparticles (solvated metal atoms) on the inner surface of the alumina support. The experimental campaign was performed between 300 °C and 470 °C by varying the feed pressure from 150 to 250 kPa. At 400 °C and 50 kPa of transmembrane pressure, the reference H₂/N₂ perm-selectivity of the Pd₇₀-Cu₃₀/Al₂O₃ membrane was around 1800, remaining stable for around 1000 h under operation (Figure 2), while an excellent H₂/CO₂ selectivity around 6500 was reached at the same operating conditions, particularly important in the viewpoint of the membrane application in pre-combustion capture.

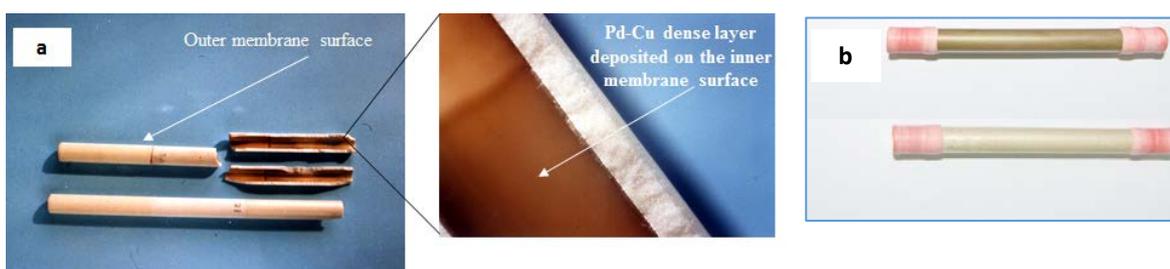


Figure 1. Pictures of: a) Pd₇₀-Cu₃₀/Al₂O₃ membrane; b) GO/TiO₂-Boehmit/Al₂O₃ membrane samples

Meanwhile, low cost and low temperature operations are imposing to investigate on membrane solutions alternative to palladium. Among them, special interest is gaining the development and utilization of 2D-materials such as phosphorene, MoS₂, ZIF-7 and graphene, particularly because they are able to overcome the trade-off between permeability and selectivity, generally observable using traditional polymeric membranes [3,4]. In this work, the preparation and experimental characterization of two nanocomposite graphene oxide (GO) membrane samples are shown. The GO membranes are obtained by using the vacuum deep coating method, depositing the GO solutions as single layers on a TiO₂-Boehmit modified Al₂O₃ substrate (Figure 1b).

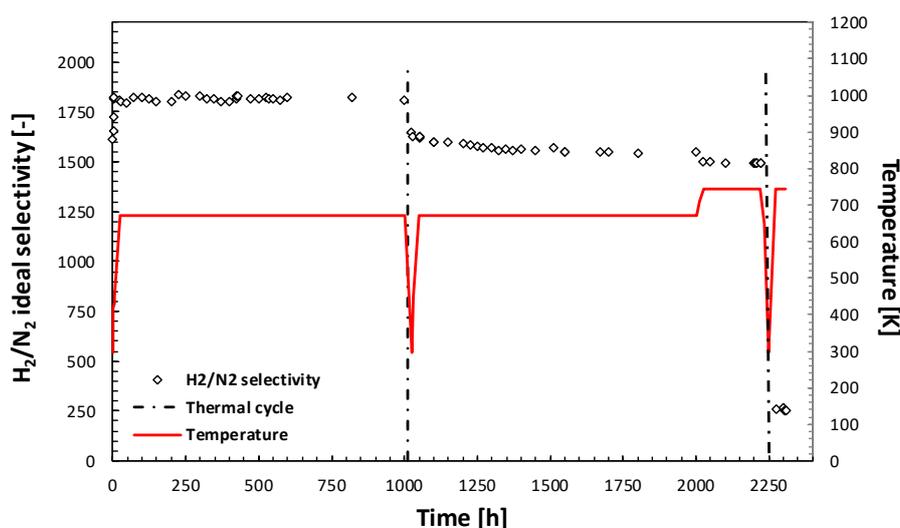


Figure 2. H₂/N₂ perm-selectivity of the Pd-Cu/Al₂O₃ membrane vs time and different operating temperature at $\Delta p = 50$ kPa.

Temperature and pressure variations were evaluated to reach the best performance in terms of H₂ permeance, and H₂/N₂ and H₂/CO₂ ideal selectivities. One of the best results of this work was reached using GO membrane sample 1, which showed at room temperature H₂ permeance $\sim 0.3 \cdot 10^{-6}$ mol·m²/s·Pa and H₂/CO₂ equal to 26.

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Sugar-based dimethyl isosorbide as a new green solvent in membranes preparation

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Abstract

Membrane operations are recognized as green and eco-friendly technologies able to perform separation and purification processes with a low energy requirement and without the use of chemical additives. However, when the membrane process is considered in its whole, the way the membranes are produced is not sustainable and green at all. The fabrication of polymeric membranes, in fact, requires the use of solvents which are toxic for humans and harmful for the environment [1, 2]. In this work, we investigated, for the first time, the use of dimethyl isosorbide (DMI) as a new sugar-based solvent, for the preparation of polyethersulfone (PES) and poly(vinylidene fluoride) (PVDF) membranes [3] (Figure 1). DMI is a green low-toxic solvent derived from D-sorbitol mainly applied in the pharmaceutical and cosmetic sectors.

A predictive investigation on the possibility of using DMI as a solvent for both polymers was carried out by evaluating thermodynamic (Hansen and Hildebrand solubility parameters, relative energy difference) and kinetic (viscosity) studies. Polymeric membranes were then prepared by coupling vapour induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) techniques. The different exposure time to humid environment allowed to tune membranes pore size without the need of any pore forming additive. Prepared membranes were fully characterised in terms of morphology, mechanical resistance, contact angle, pore size, porosity and water permeability. The membranes exhibited a tuneable pore size in the range of micro and ultrafiltration and a spongy and finger-like morphology (depending on the preparation conditions). The membranes obtained with DMI displayed also a good mechanical resistance and properties, like water permeability, comparable to the membranes prepared with traditional solvents.

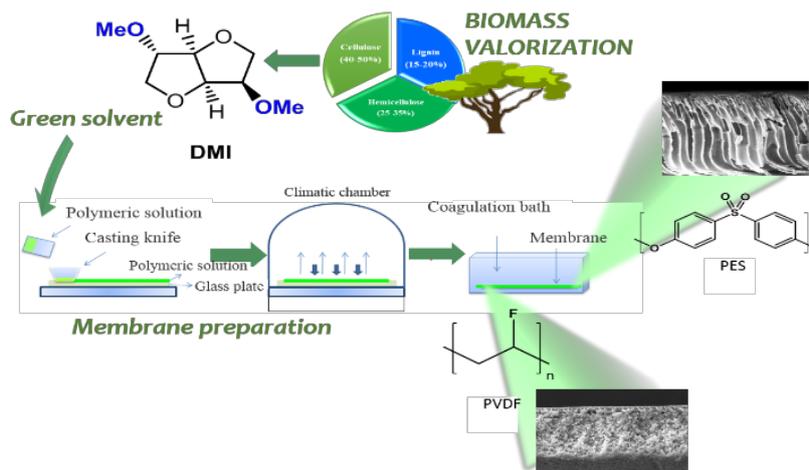


Figure 1. Preparation of PVDF and PES membranes with the green solvent DMI

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Unprecedented porous Matrimid®5218 membrane preparation

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Abstract

The aim of the work was the use of an unconventional green solvent for the sustainable preparation of polymeric membranes with a new morphology according to the Green Chemistry principles and pursuing the systemic approach of the circular economy. For the first time, porous Matrimid® 5218 membranes were prepared by employing a combination of vapour induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) technique. [1] Matrimid® 5218 is one of the most commercially thermoplastic polymers used in gas separation for its properties such as high chemical resistance, good thermal stability and good processability. [2] N-methyl-2-pyrrolidone (NMP) and Rhodiasolv® Polarclean were used as a traditional and new green solvent, respectively, for the preparation of Matrimid® membranes. Rhodiasolv® Polarclean solvent, in fact, completely fulfils the V principle of Green Chemistry: “*The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.*” The properties of the solvent include biodegradability, high boiling point, total solubility in water, high solvency capacity, low carbon footprint and low risks for human health. [3] In this study, ternary phase diagrams with both solvents (NMP and Rhodiasolv® Polarclean) were preliminary carried out. Different exposure time to humidity (0, 2.5 and 5 minutes) and the effect of polymer concentration (8, 10 and 12 wt.%) on membrane morphology and properties were evaluated. The resulting membranes were fully characterized in terms of morphology, shrinkage propensity, thickness, porosity, mechanical properties, pore size, contact angle and water permeability. All the prepared membranes showed a porous architecture with a predominance of a sponge-like structure (for the membranes prepared with Rhodiasolv® Polarclean) and a macrovoid structure (for the membrane prepared with NMP) as showed in Figure 1. The membrane pore size was in the range of 0.05- 0.73 µm making the prepared membranes suitable in water and wastewater treatment applications.

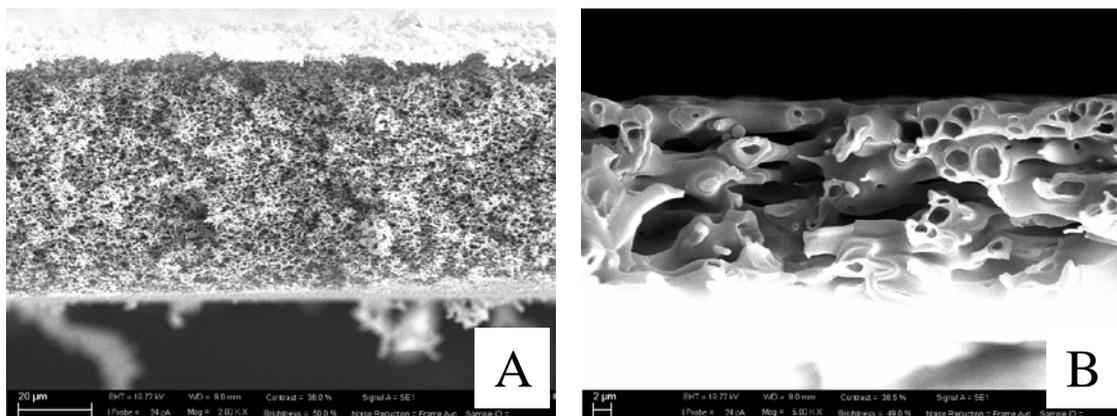


Figure 1. Sem images of Matrimid5218® membranes prepared using A) Rhodiasolv® Polarclean and B) NMP.

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Development of Stable Biopolymeric Membranes by Crosslinking with Bio-Derived Compound

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Abstract

In order to reduce the use of non-renewable resources and to minimize the environmental pollution caused by fossil-fuel-derived materials, biopolymers such as cellulose, starch, chitosan, polyvinyl alcohol (PVA), polylactic acid, and others represent a growing and promising area for membrane manufacturing. They combine high technical potential with the concept of eco-sustainability, both in terms of natural raw materials and their recovery/disposal at the end of their life [1]. Nevertheless, their application is hindered by the poor stability in aqueous environments necessary in many fields. Crosslinking is recognized as a strategy to improve the properties of biomaterials, but most crosslinking agents (such as glutaraldehyde) cause unwanted changes in the functionality of biopolymers or are hazardous [2]. In this work, a bio-derived compound (BDC), with antiradical and antibacterial activity, was employed for the first time as crosslinking agent, in order to improve the stability and the mechanical properties of PVA-based membranes. The crosslinking was carried out with different PVA/BDC ratios to produce membranes by using a conventional solution casting technique. The produced membranes were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Static Water Contact Angle (SCA). Besides, the crosslinking degree was also measured to confirm the formation of covalent ester bonds. Properties such as swelling degree, stability to high-temperature and to acid-basic solutions, antiradical and antibacterial activity and biodegradation level were determined. All these properties were compared with those obtained from PVA membranes crosslinked with citric acid (PVA/CA) [3]. The successful of crosslinking reaction (crosslinking degree of 65%) was confirmed by FTIR spectra pointing out the presence of absorption bands of the ester group and by TGA curves in which the temperature *onset* decreased. Besides, results demonstrated that the membrane prepared with appropriate ratio showed good performance in terms of water uptake degree, stability to acid and basic solutions, resistance to high temperature and antiradical activity. Furthermore, the PVA/BDC membrane degradation was rather limited even under soil burial conditions. In fact, after 20 days, they lost about 4% wt, whilst PVA/CA lost about 30% wt and PVA membranes were totally decomposed.

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Ultrapерmeable benzotriptycene-based PIMs that redefine the upper bounds for CO₂ separations

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Abstract

Polymers of Intrinsic Microporosity (PIMs) combine the desirable processability of polymers, with a significant degree of microporosity generated from the inefficient packing of their rigid and contorted macromolecular structures. They are attracting attention for a number of industrial gas separation applications, such as oxygen or nitrogen separation from air (i.e. separation O₂/N₂) or natural gas treatment and biogas upgrading (i.e. separation CO₂/CH₄). However, a further enhancement of the polymer transport properties is desirable to be cost effective in comparison with the traditional separation technology, currently applied for CO₂ capture or removal.

In this work, we report a series of benzotriptycene-based PIMs showing outstanding CO₂/CH₄ and CO₂/N₂ permselectivity properties [1], due to the inefficient packing of their polymeric chains which results in large interconnected pores that enhance gas permeability. These benzotriptycene-based PIMs demonstrate ultrapерmeability ($P_{CO_2} > 20000$ Barrer) and interesting selectivity, and their combination allows the introduction of a new upper bound to define the current state-of-the-art for CO₂ membrane separation processes (Figure 1).

Their gas transport properties will be discussed in terms of permeability, diffusivity and solubility on freshly methanol-treated and aged samples. The effect of the temperature on the transport properties will be also discussed. Particular attention will be paid to the relative contribution of diffusivity coefficients with the analysis of the size-selectivity in terms of entropic and energetic selectivity [2], and as a function of the effective diameter of the penetrant gas [3]. The latter analysis demonstrates that the diffusivity of light gases through PIMs shows that smaller H₂ and He gas molecules have a transport mechanism that is similar to that of porous materials, whereas larger gas molecules, CH₄, N₂, O₂ and CO₂, show activated transport similar to that of conventional dense polymers. A typical and defining feature of PIMs, which differentiates their properties from other high free volume

polymers, glassy polymers and rubbers, is the change in slope of the plot of the diffusion coefficient as a function of the gas diameter, with a stronger size-selective trend for the larger gas molecules than for He and H₂.

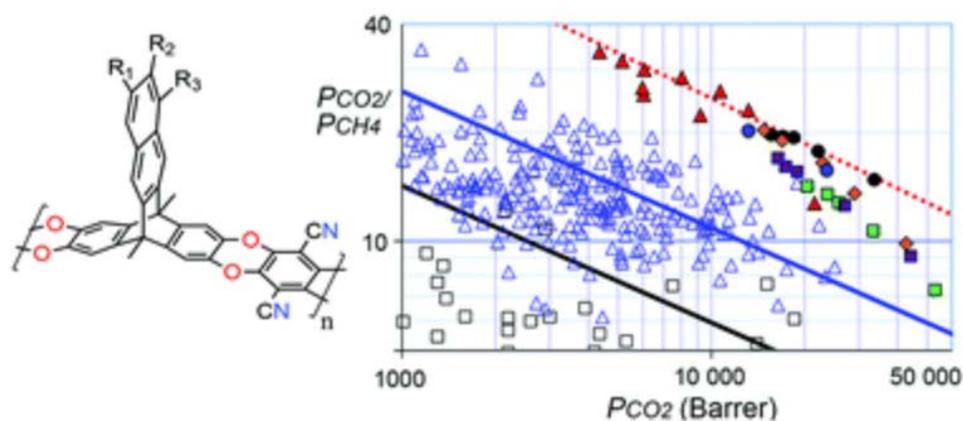


Figure 1. Molecular structure of the ultrapermeable PIMs and their gas permeability data on the Robeson plot for the CO₂/CH₄ gas pair, including the proposed upper bound.

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Efficient Gas Separation and Transport Mechanism in Rare Hemilabile Metal-Organic Framework

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Understand/visualize the established interactions between gases and adsorbents is mandatory to implement better performant materials in adsorption/separation processes. Herein we describe the synthesis and extensive characterization of a novel hemilabile and very robust chiral metal-organic framework (MOF) derived from a natural amino acid, following our rational approach, *L*-histidine, featuring an unprecedented (for MOFs) **qtz-e**-type topology (**1**). It exhibits a reversible breathing behavior, based on the hemilability of carboxylate groups from *L*-histidine. *In-situ* powder and single crystal X-ray diffraction, using synchrotron radiation, allowed to unveil the crystal structures of 4 different host-guest adsorbates (Ar, N₂, CO₂ and C₃H₆@**1**), the rationalization of the breathing motion and unravel the mechanisms governing the adsorption of these gases. This information has been transferred to implement efficient separations of mixtures of industrial and environmental relevance such as CO₂/CH₄ separation from natural gas or from biogas, CO₂/N₂ separation from flue gas, or olefin/paraffin separation in the petrochemical industry, using **1** in packed columns as the stationary phase and dispersed MOFs into the rubbery polymer Pebax®.

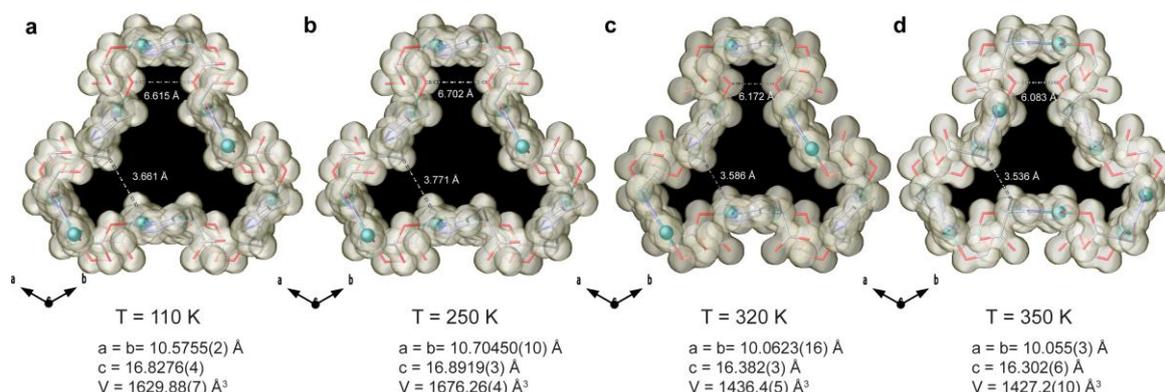


Figure 1. View of one single channel of **1** for temperatures: 110 K (a), 250 K (b), 320 K (c) and 350 K (d).

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Glassy vs rubbery polymers: effect on the gas transport in CuNi-MOF based mixed matrix membranes

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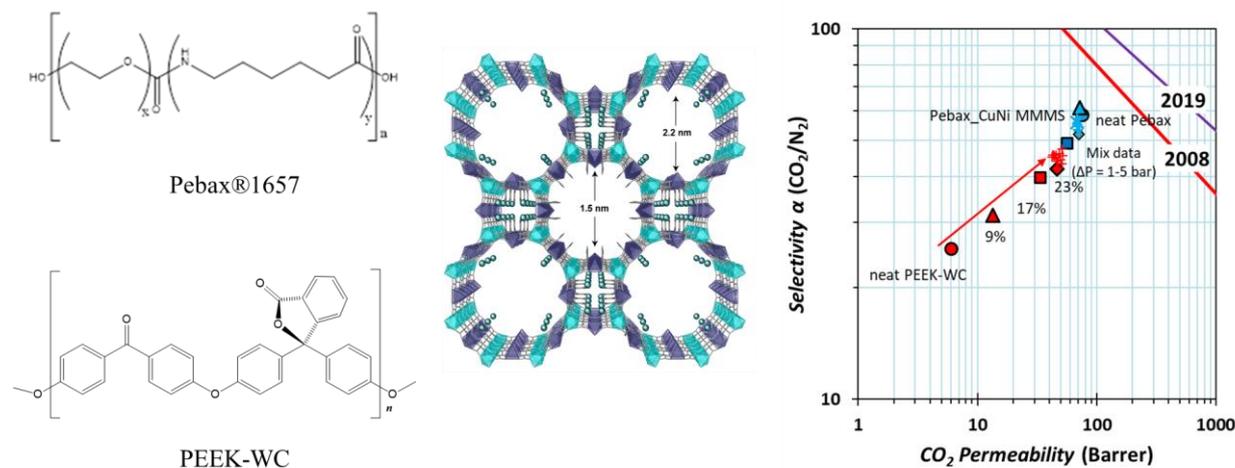
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Abstract

Mixed matrix membranes (MMMs) are seen as promising candidates to overcome the fundamental limit of polymeric membranes, known as the so-called Robeson upper bound¹⁻³, which defines the best compromise between permeability and selectivity of neat polymeric membranes. To overcome this limit, the permeability of the filler particles in the MMM must be carefully matched with that of the polymer matrix. The present work shows that it is not sufficient to match only the permeability of the polymer and the dispersed phase, but that one should consider also the individual contributions of the diffusivity and the solubility of the gas of interest, in both components. Here we compare the performance of two different MMMs, containing the metal organic framework CuNi-MOF⁴ in the rubbery Pebax®1657 and in the glassy poly(ether ether ketone) with cardo moiety, PEEKWC. Permeability, diffusion and solubility coefficients and their corresponding ideal selectivities were determined for the gases He, H₂, O₂, N₂, CH₄ and CO₂ on the “as-cast” samples. Mixed gas permeation tests were performed on a representative sample to investigate the actual separation performance with industrially relevant gas mixtures. The detailed analysis on the gas transport properties of the two set of MMMs highlights the different effect that the same CuNi-MOF can have when it is embedded in a rubbery or a glassy polymer.



Chemical structure for Pebax®1657, PEEK-WC and CuNi-MOF. Robeson's plot for CO₂/CH₄ showing the pure and mixed gas data of Pebax1657/CuNi and PEEK-WC/CuNi with increasing MOF loading (direction of arrow).

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Sustainable Production of Customized Polymeric Membranes and their Use in the Purification of an Anticancer Monoclonal Antibody

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Abstract

Antibodies are natural component that help the immune system to identify foreign substances by binding to and marking them as foreign. Each antibody is tailored to a specific kind of pathogen, which it recognises through a feature that is characteristic of this particular troublemaker. Monoclonal antibodies (mAbs) are produced by recombinant DNA technology by copies of a single cell. They can precisely target some proteins only found on specific cells and flag for the immune system to attack without harming healthy cells. This directed method has made it possible to fight cardiovascular and infectious diseases, inflammatory and autoimmune disorders, and cancer, with fewer side effects. As such, mAbs currently represent one of the greatest therapeutic/diagnostic modalities in modern medicine.

Extracting mAbs from the growth medium and purifying them to the high levels required by biopharmaceutical standards involves several labour-intensive steps and expensive materials, which cause a bottleneck in the production and impact goods and facility costs. Current challenges in chromatography-based downstream purification of mAbs include 1) cost of resin inventory, especially protein A; 2) the production of huge amount of chromatography dilute and 3) large footprint. Furthermore, continuous operation is possible but it is complex and with discontinuous elution.

In this work, engineered functionalized membranes have been used for the first time in membrane-assisted crystallization [1] as innovative downstream stage for the extraction and purification of full-length monoclonal antibody Anti-CD20 directly from the medium in which it is grown. Customized polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), polyvinylidene fluoride (PVDF) and PVDF/PVDF-HFP blend membranes have been manufactured by a sustainable method based on a combination of vapour-induced and liquid-induced phase separation (VIPS and LIPS) stages, in which DMSO is employed as non-hazardous solvent in place of substances of very high concern, without using any chemical additive as pore forming [2]. Symmetric porous membranes, with customized rough surface topography and hydrophobicity according to a biomimetic behavior as that of lotus leaves surfaces, have been synthesized through an environmental friendly fabrication process. The resulting membranes are characterized by a high porosity with well-interconnected pores, making them suitable for membrane-assisted crystallization [3].

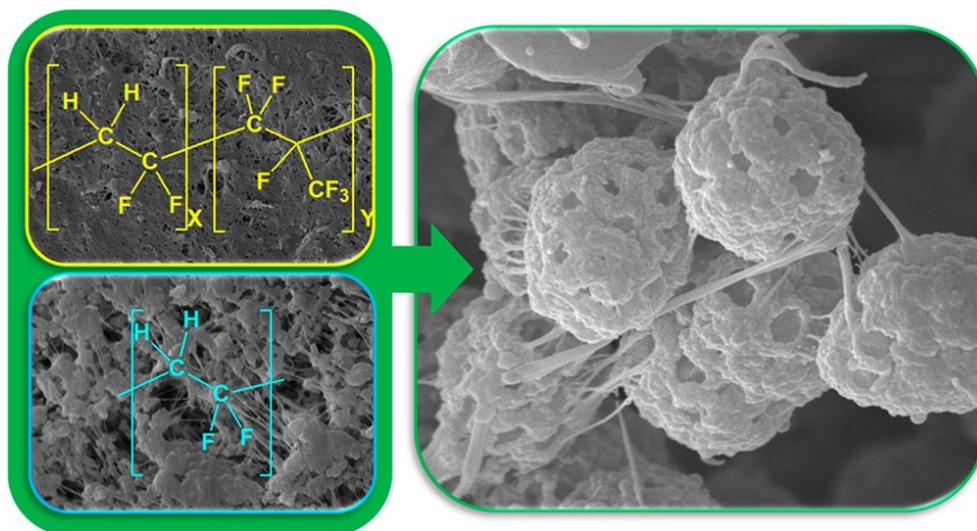


Figure 1. High magnification SEM image of the hierarchical substructure of the blend membranes, showing a typical morphology with microprotrusions

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Graphene assisted Membrane Crystallization technology: A combined experimental- computational approach

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Abstract

The aim of this study [1] was the design and the development of innovative membranes through confinement of graphene platelets in Polyvinylidene fluoride (PVDF) membranes matrix, in order to evaluate the establishing of fruitful interactions for assisting Membrane Crystallization (MCr) process. The understanding of selected material effects was further assessed by using Molecular Dynamics (Figure 1a and 1b), for a better comprehension of each phenomenon at molecular level. Graphene (G) as nanofiller in PVDF polymeric membranes, was used at different concentration with respect to pristine PVDF. From the experimental point of view, the results achieved showed reduced induction time followed by very quick growth rate for crystals formation [2]. Furthermore, better values of CV [%] were reached with graphene-PVDF based membranes (Figure 1a'' and 1b''), with respect to pristine PVDF, leading to a more homogenous crystals shape and size distribution. The computational approach confirmed that, graphene polymeric surfaces speeded up crystal nucleation, in comparison with the pristine PVDF (Figure 1a' and 1b'), with nucleation times from 0.45 to 0.9 ns, in full agreement with the trend obtained with the MCr experiments [3]. This confirmed the experimental results, bringing to a reciprocal validation and useful correlations between MD and the experimental analysis.

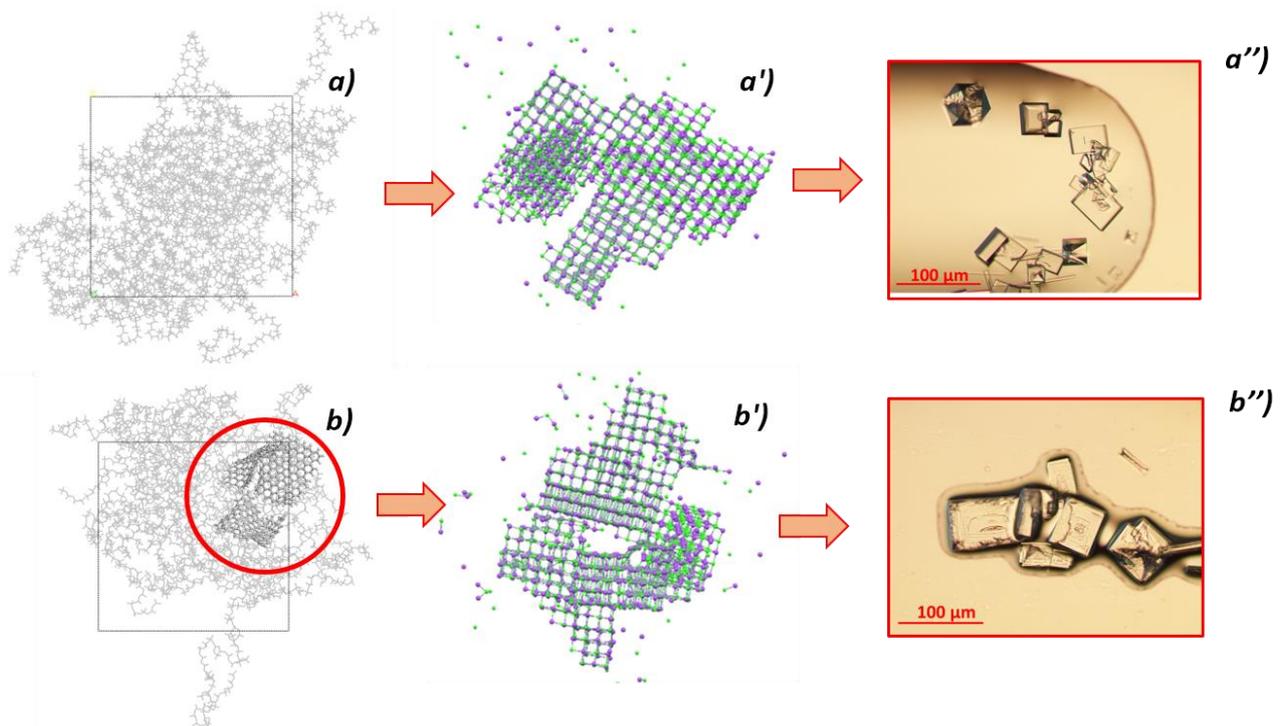


Figure Front view of models produced of a) pristine PVDF and b) PVDF with Graphene; final crystals achieved from simulations for a') pristine PVDF and b') PVDF with Graphene; final crystals achieved from MCr experiments with a'') PVDF membrane and b'') PVDF with Graphene membrane.

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Waste gaseous streams treatment and reuse by membrane condenser

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Abstract

In the last decades an international awareness increased for minimizing potable water scarcity. One area that received a considerable amount of attention is the problem of industrial wastewater treatment and reuse. In industrial processes, the recycling and reusing of process streams and, in particular, of water, is necessary for minimizing fresh water requirements. For example, in power plants the two main sources of emissions are from the stack and the cooling towers. Streams emitting from a stack become saturated in the desulfurization step, and the streams from cooling towers are typically river or seawater evaporated to cool the steam cycle stream. If the evaporated water can be effectively recovered, it can represent a real new source of high-quality water, to be utilized both at industrial (as make-up water) and at human level (as drinkable water). A technology currently investigated for water recovery from waste gaseous stream is membrane-assisted condenser (MCo). The latter exploits the hydrophobic nature of microporous membranes to promote water vapor condensation and recovery. In details, the waste gaseous stream (e.g., the plume of the cooling tower) at a certain temperature and, in most of the cases, water saturated, is fed to the membrane condenser kept at equal or lower temperature. Once this stream is brought into contact with the retentate side of a microporous membrane, its hydrophobic nature prevents the penetration of the water droplets into the pores letting pass the dehydrated gases through the membrane. Therefore, the liquid water is recovered at the retentate side, whereas the other gases at the permeate side of the membrane unit.

A simulation study of the process has been developed for predicting the membrane-based process performance. A lab scale plant was realized to verify the results achieved by the simulation analysis. As humidified waste gases, streams simulating the plume of cooling tower were selected [1].

The simulation allowed predicting the process performance. In particular, it was found that the recovery of water can be increased with the grow of ΔT (temperature difference between the plume and the gas before entering the membrane module), RH_{plume} (relative humidity of the plume) and Q/A (ratio between feed flow rate and membrane area). The experimental results showed good agreement with the simulation ones. Experiments proved that considering a plume at 25°C and utilizing $Q/A = 1.2$ m/h, water recovery ranges from 36.24% ($\Delta T = 5.84^\circ\text{C}$ and $RH = 104.9\%$) to more than 55%

($\Delta T \approx 10^\circ\text{C}$, $T_{\text{plume}} \approx 25^\circ\text{C}$ and $\text{RH} > 140\%$). Moreover, experimental tests performed considering the presence of NH_3 in the fed gaseous stream revealed that the contaminants concentration increase with the growing temperature difference between fed plume and membrane module due to the dependence of gases solubility on temperature.

Finally, membrane condenser was utilized for microparticles removal from gaseous streams [2]. Experimental tests showed that microparticles did not affect membrane condenser performance, neither in terms of water recovery nor in term of fouling, at least in the performed experiments. Moreover, the carried-out tests revealed also that the complete retention of particles can be achieved only through the proper choice of the membrane, with pore size lower than particles diameter.

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Flurolink®perfluoropolyether (PFPE) compounds: an easy way in order to prepare tailored hydrophobic/hydrophilic membranes for water treatment

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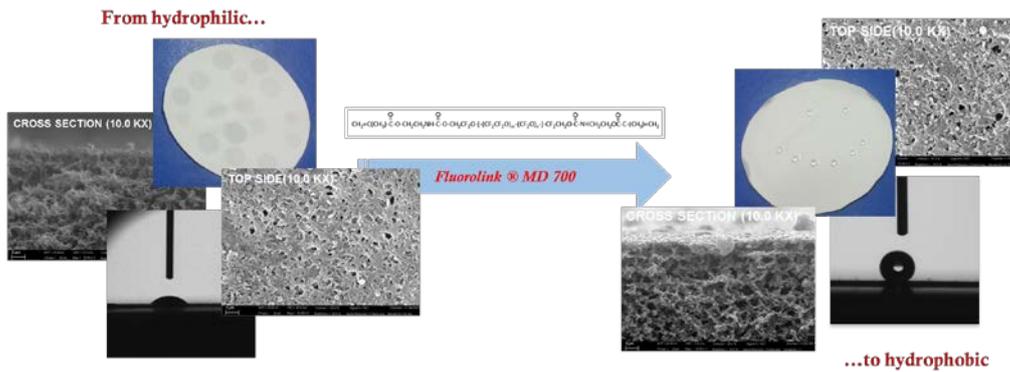
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Abstract

As it is known, several methods were reported in literature in order to produce tailored membranes by surface modification. Hydrophilization and hydrophobization membrane surface modification is the most common treatment, usually via solution coating or polymerization reaction [1]. Recently, Solvay Specialty Polymers developed novel surface modifiers of the family of perfluoropolyether (PFPE) compounds UV-curable, named Flurolink®. Using few amount of these monomers and hydrophilic cheaper membranes as supported material, hydrophobic/hydrophilic and oleophobic coated membranes can be easily prepared [2]. In this work Fluorolink® MD700 PFPE UV cross-linkable, was used as surface modifier on two different hydrophilic commercial membranes. Polyamide (PA) and polyethersulfone (PES) membranes at three different pore size (0.1, 0.22 and 0.45 μm) were treated via dip-coating and in situ polymerization, using only 5wt.% of oligomer concentration. The obtained coated membranes were initially studied in terms of influence of starting material on water/oil repellence and subsequently were characterized in terms of morphology (SEM and AFM), porosity and pore size, water liquid entry pressure (LEPw) and mechanical tests. Coating stability during time was evaluated using salty solution NaCl 0.6 M, typical feed in desalination treatment and chemicals cleaning agents (KMnO₄ 0.1 wt.%, Hypochlorite NaClO pH 4.25, HCl pH 2.5, NaOH pH 11.5). The best membrane was tested in DCMD configuration, using deionized water and salty solution 0.6M (NaCl), as feed, obtaining an highest value of permeate flux until 22 kg/m²h and a final salt rejections of about 99.95% after 158h of test [3].



Schematic procedure of Fluorolink®MD700 coated membranes preparation and characterization

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Hydrogen generation by steam reforming of a synthetic biogas mixture in a Pd-Au membrane reactor packed with a Rh(1%)-MgAl₂O₄/Al₂O₃ catalyst

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Abstract

Today, the application of the principles of Process Intensification Strategy is gradually leading to a revolution of the conventional hydrogen energy production processes and, among a number of alternative technologies, membrane engineering is playing a crucial role in the substitution of traditional devices used in the process engineering with membrane-based units [1]. According to the requests of the Circular Economy [2] and in the framework of the so-called Hydrogen Economy [3], the hydrogen generation coming from derived of biomass as renewable sources may play an interesting role as a valid option to the fossil fuels exploitation [4]. In this work, the production of hydrogen via reforming reactions of a synthetic biogas mixture carried out in a Pd-Au/Al₂O₃ membrane reactor (MR), Figure 1, packed with a not commercial Rh(1%)-MgAl₂O₄/Al₂O₃ catalyst, is proposed.



Figure 1. Picture of the supported Pd-Au/ α -Al₂O₃ membrane

Particular attention is paid toward the investigation of the negative effects on the H₂ permeation membrane performance of H₂S present in typical H₂-rich gas mixture, simulating possible biogas reformed streams in the MR reaction side, Figure 2. Furthermore, synthetic biogas streams (with and

without H₂S) were fed to the MR for generating H₂ and for analyzing how the presence of H₂S affects the MR reaction performance in terms of methane conversion and hydrogen recovery.

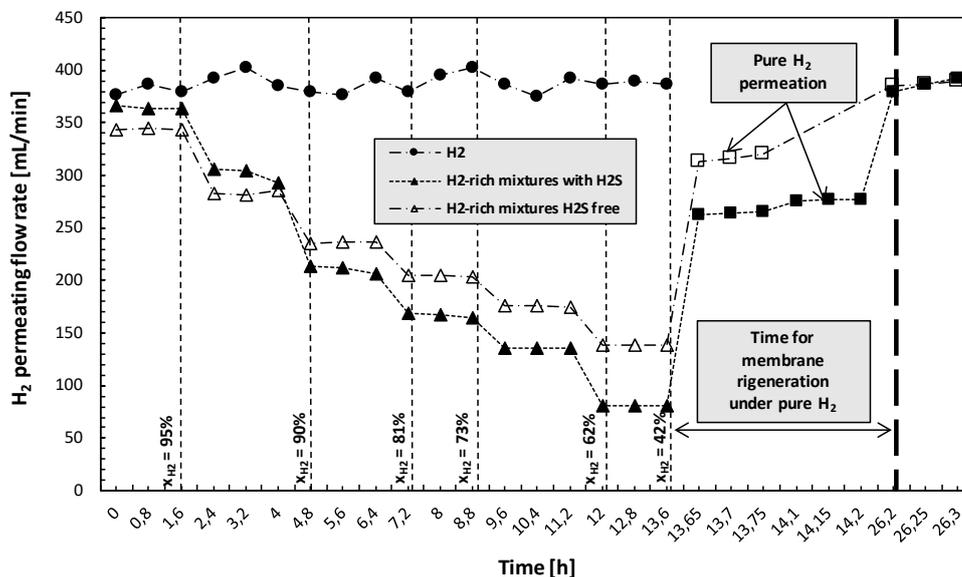


Figure 1. Hydrogen permeating flow rate as single gas and as component in H₂-rich gaseous mixtures (with and without H₂S) using a supported Pd-Au/Al₂O₃ membrane at 673 K and 100 kPa of transmembrane hydrogen partial pressure difference.

After the H₂ permeation and reaction tests, a post mortem analysis was performed on the Pd-Au/Al₂O₃ membrane and the Rh-based catalyst as well. Finally, a comparison with a commercial selfsupported Pd-Ag MR is also proposed in order to highlight the difference between two different Pd-based membrane systems.

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Dimethylether production in a catalytic membrane reactor

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Abstract

Dimethyl ether (DME) has drawn increasing attention as a promising and clean alternative to diesel fuel, owing to its high cetane number, low auto-ignition temperature, and low emission of pollutants. So far, DME can be produced via methanol dehydration over solid acid catalysts and via CO₂ conversion in a two-step process with methanol as an intermediate. The methanol dehydration is regarded as the most mature route and is widely used in the chemical industries, by using different solid acid catalysts such as γ -Al₂O₃ and acidic zeolites (H-ZSM-5, H-Y, H-ZSM-22) [i]. Despite the importance of the acid catalyst, studies were primarily carried out over γ -Al₂O₃, exhibiting a high selectivity in the temperature range 200–300°C [ii]. However, the presence of water, reaction product, significantly deactivates the catalyst, owing to the blocking of the active sites by its molecules. In this concern, zeolites (mainly MFI) were also investigated as alternative to γ -Al₂O₃ revealing a better stability to water presence and good conversion and selectivity. Nevertheless, in the temperature range of direct synthesis (260–300°C), the acid catalyst may start to promote other reactions, converting the methanol to a range of different hydrocarbons, such as poly-methylbenzenes, which basically constitute coke [iii]. On the light of this considerations, it is still a considerable challenge to develop new strategies to simultaneously enhance the conversion and selectivity of methanol dehydration to DME. Catalytic membrane reactors are recognized as a promising solution for several processes and in various cases they are used as contactors for optimizing the contact among reactants and catalyst.

In this work, we used a catalytic membrane reactor as a contactor for the DME production from MeOH dehydration [4]. We considered two different membranes having the same zeolitic layer

(MFI), but a different support (TiO_2 and $\gamma\text{-Al}_2\text{O}_3$), aiming at investigating also the eventual effect of the support on MeOH conversion and DME selectivity. Significant relevance was devoted to the analysis of the performance as a function of the temperature (120-280°C), feed pressure (120-300 kPa), spanning a wide range of WHSV (1-13.3 $\text{g}_{\text{MeOH}} \text{g}_{\text{Catalyst}}^{-1} \text{h}^{-1}$) and feed composition (20-100% $_{\text{mol}}$ MeOH). Reaction measurements revealed an effect of the membrane support, since MFI- Al_2O_3 MR exhibited always greater conversion than MFI- TiO_2 one. This can be attributed to an additional catalytic effect induced by the Al_2O_3 , which further enhances the DME production. In addition, both MRs showed 100% DME selectivity, exceeding the performance of the traditional reactor.

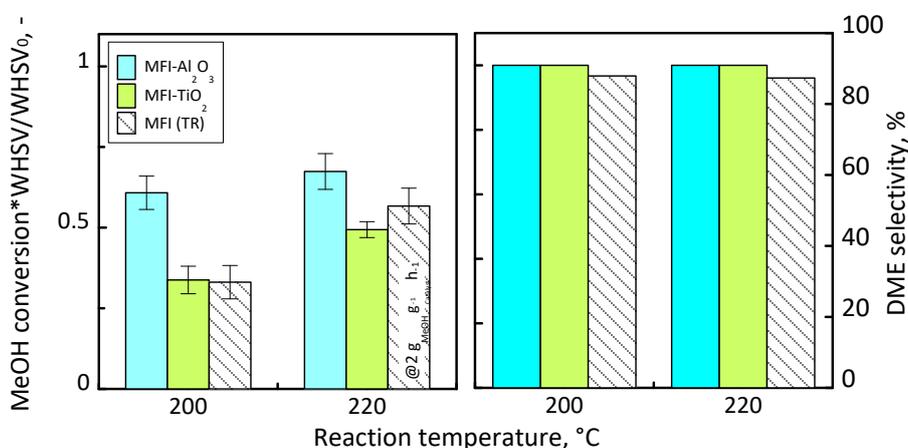


Figure 1 – MeOH conversion and DME selectivity at 200 and 220°C for MFI- Al_2O_3 and MFI- TiO_2 membrane reactors. Feed pressure=120 kPa; $\text{WHSV}^0 = 2 \text{ g}_{\text{MeOH}} \text{g}_{\text{Catalyst}}^{-1} \text{h}^{-1}$

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