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Monoclonal Antibodies Purification by Membrane-Assisted Crystallization – the AMECRYS FET-OPEN Project

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Abstract

In the biopharmaceutical industry, downstream processing (DSP) of therapeutics are primarily based on labor-intensive and expansive chromatographic methods, which cause a bottleneck in the production and impact goods and facility costs.

Monoclonal antibodies (mAbs) are biological drugs that 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, like COVID-19, 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.

mAbs are produced by recombinant DNA technology, by copies of a single cell. They are extracted from the growth medium, and purified to the high levels required by biopharmaceutical standards, by chromatography-based methods. However, chromatographic DSP platforms include several challenges: 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. Therefore, alternative procedures to replace chromatographic operations are currently subject to extensive research.

In this work, engineered functionalized membranes have been developed and used in osmotic membrane crystallization (MCr) [1] as innovative DSP stage for the extraction and purification of full-length monoclonal antibody Anti-CD20 from the medium in which it is expressed. Customized membranes have been manufactured by a sustainable method, based on a combination of vapor-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 (Figure 1) and hydrophobicity according to a biomimetic behavior as that of lotus leaves surfaces, have been synthetized through an environmental friendly fabrication process, by using polyvinylidene fluoride (PVDF) and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), as single polymer and as blend of different composition. The resulting membranes are characterized by a high porosity with well-interconnected pores, making them suitable for membrane-assisted crystallization [2,3].

Blend as well as polymer membranes were functionalized, characterized and tested in MCr, thus highlighting the positive outcomes of the selected strategy in terms of surface/interface and transport properties. Trans-membrane flux is effectively enhanced by increasing the osmotic solution concentration and/or the feeding rate, as a result of the increase of the osmotic pressure gradient between the two solutions contacted by the hydrophobic membrane. However, critical values have

been determined for both parameters, which have to be set within a certain range to preserve both membrane rejection and concentration factors. The appropriate operative configuration of the osmotic MCr unit allowed for controlled water removal at suitable flow rates, while the membranes ensured high rejection values over a wide range of working conditions. Most important, Anti-CD20 mAb has been successfully recovered from clarified fermentation broth at high level of purity and with suitable yield with the membrane-assisted crystallization process developed in this work.

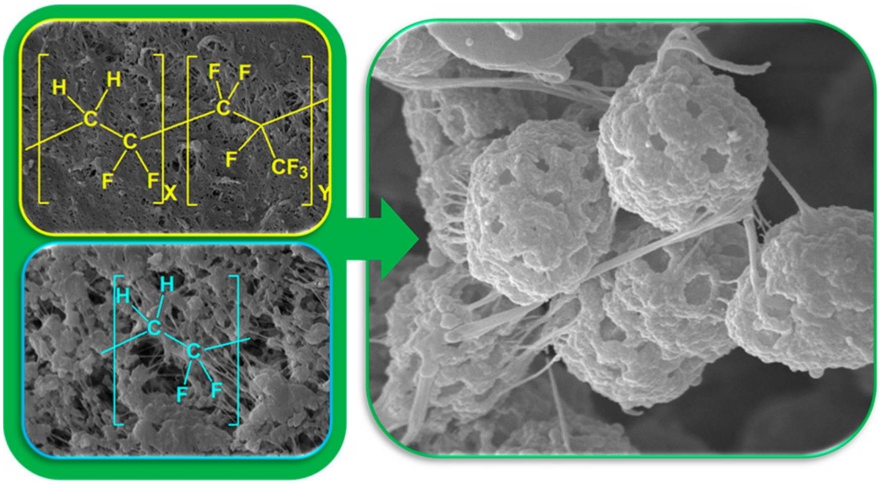

Figure 1. High magnification SEM image of the hierarchical substructure of the blend membranes, showing a typical morphology with microprotrusions

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A combination of eco-friendly extraction techniques and membrane operations for the recovery of bioactive compounds from wine by-products

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Abstract

Winemaking generates huge quantities of waste streams represented by leaves, stems, pomaces (including grape skins and seeds) and lees. Conventional treatments of winery wastes are increasingly expensive, requiring significant amounts of effort, resources and energy for a safe discharge into the environment. Among wastes, grape pomaces and wine lees constitute a valuable source of phenolic compounds (flavonoids, tannins and benzoic acids derivatives) which are biomolecules of both technological and nutraceutical interest, acting as antioxidants in biological matrices through the inhibition of lipid peroxide radicals and reactive oxygen species [1].

In agreement with industrial ecology concepts, like cradle-to-cradle and circular economy, the need to recycle, reuse and recover valuable chemicals from waste and wastewaters has become a major topic in wine processing industry [2,3].

In this work, the combination of eco-friendly extraction techniques with membrane-based operations has been implemented in two different case studies in order to develop a sustainable process for the extraction and separation of phenolic compounds from wine by-products. In the first approach, a microwave/hydro-alcoholic extraction, followed by the clarification and fractionation of the hydro-alcoholic extract, was studied for the recovery of phenolic compounds from red wine lees. Specifically, commercial polymeric membranes with a molecular weight cut-off in the range 150-1,000 Da were tested to fractionate the hydro-alcoholic extract clarified by microfiltration.

The second case study was focused on the recovery of phenolic compounds from red grape pomace through a combination of ultrasound-assisted enzymatic extraction and membrane fractionation with cellulose acetate laboratory-made nanofiltration membranes.

In both cases the performance of selected membranes was evaluated in terms of productivity, fouling index and selectivity towards target compounds. Typical rejections of nanofiltration membranes to different compounds of the grape pomace extract are illustrated in Figure 1.

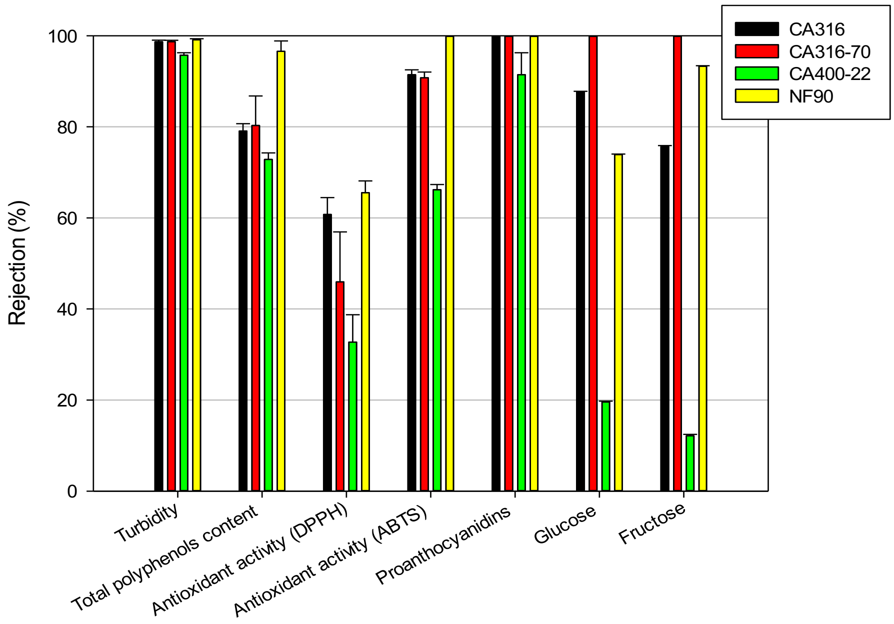

Figure 1. Rejections of NF membranes to specific compounds of grape pomace extract (CA316, CA316-70, CA400-22, cellulose acetate NF laboratory-made NF membrane; NF90, commercial polyamide NF membrane)

The investigated processes represent an option of sustainability for the winery industries since the obtained fractions could be used as high value-added products due to their antiradical properties.

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A membrane-based tool for natural molecule screening: study of daidzein neuroprotective effect.

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Abstract

Innovative investigational insights on new and effective therapeutics to treat neurological disorders, and correlated pathological events, require the use of reliable in vitro platform in which the in vivo structure complexity of neuronal tissue is recapitulated and maintained.

Membrane-based tools have a great potential as in vitro screening platforms thanks to the possibility to create a cell-friendly interface; indeed, the polymeric membranes act as a biomimetic matrices able to boost cell attachment and the formation of intercellular contacts [1]. The building up of a realistic biomimetic platform allows to use membrane system for a breakthrough analisys of the pathogenic mechanisms at the basis of the fatty acids/diet neuroinflammation, and also for the screening of bio-molecules to evaluate their pharmacological potential.

On the basis of this consideration, a PLGA membrane system was set up to drive the in vitro reconstruction of GnRH hypothalamic tissue analogue. The membrane tool served as model system to test daidzein's ability to stop and reverse the imbalanced neuroinflammatory responses caused by high fat diet. Within the membrane system were recapitulated the pathological features of the obesity-related neuroinflammation in order to highlight daidzein potential in controlling high-fat diet-induced hypothalamic inflammation. The investigation evidenced that daidzein is able to neutralize palmitate-induced neurotoxicity by reversing the neuroinflammatory cascade. Indeed, daidzein exerted a wide neuroprotection preventing cell death and inhibiting the proinflammatory processes, oxidative stress and apoptosis. Daidzein cotreatment enabled also the cell to restore and maintain a proper cell morphology and the expression of specific hypothalamic receptors [2].

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Development of Chitosan Membranes Loaded with 18-β-Glycyrrhetic Acid for Skin Regeneration and Repair

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The development of biodegradable nano-structured membranes that provide physical support, mechanical stimuli and biochemical cues able to modulate the cell fate, represents a major challenge for the creation of skin tissues. Flat nanoporous chitosan (CHT) membranes were developed and tested as promising biomaterials for skin reconstruction, since they allow the formation of specific epidermal strata and complete dermal/epidermal constructs [1, 2]. A further strategy is represented by the membrane loading with a bioactive molecule constantly released in the time that facilitate the biological processes needed for skin reconstruction and repair.

In this work, microporous membranes of chitosan loaded with a natural compound with therapeutic and healing properties were developed. 18-β-Glycyrrhetic Acid (GA) is a natural derivative of Licorice (*Glycyrrhiza*) extract, with a wide range of pharmacological activities, including anti-allergic, anti-oxidant, anti-carcinogenic, anti-inflammatory, immune-modulatory, 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 β-cyclodextrin (β-CD). Cyclodextrins are recognized as promising pharmaceutical excipients in several formulation and biomaterials for controlled drug delivery and release of hydrophobic molecules, and as versatile cues to study cellular behaviour [3].

Composite CHT membranes, with different ratio of βCD-GA inclusion complex, were realized by phase inversion process. 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 that were maintained for 21 days of culture. 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/βCD-GA composite membranes highlighting the pivotal role played by GA. These results represent a starting point for the development of new membranes that incorporate bioactive molecules useful in the tissue regeneration processes of the epidermis, and that could be used as a patch for topical drug delivery, wound healing and skin repair.

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Towards the preparation of fully biobased membranes

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Abstract

The transition towards a sustainable economy, imperative for facing the current global problems, passes through the replacement of traditional petroleum based and hazardous materials with new chemicals which can be obtained from renewable, recyclable and biodegradable resources. The use of new sustainable materials, such as biopolymers and green solvents, meets the requirements of the Process Intensification Strategy [1] and Green Chemistry Design [2-3]. Membrane technology is widely recognized as one of the Best Available Technologies in the field of separation and filtration also thanks to their low environmental impact. However, the preparation of polymeric membranes is, most of the times, still based on the use of toxic solvents and fossil derived polymers.

Aim of this work, was to fabricate fully biobased sustainable membranes employing poly(hydroxybutyrate-co-hydroxyvalerate) (PHBhv) as a biopolymer and Cyrene^{TM} as a green solvent [4]. Membranes have been prepared by coupling induced phase separation (NIPS) technique with evaporation (EIPS) technique. Polyvinylpyrrolidone (PVP K17 and K30), poly (ethylene glycol) (PEG) at different molecular weight (200 and 600 g/mol) and epoxidized broccoli oil (EBO), a valorized co-product from the synthesis of a food active ingredient, have been investigated as additives for tuning membrane properties. Membranes have been prepared by varying different parameters including polymer concentration, additives concentration and evaporation time before coagulation. Obtained membranes were characterized in term of morphology, pore size, porosity, contact angle, mechanical properties, FT-IR spectroscopy, water permeability and biodegradability. Membranes with different morphologies and pore sizes have been, thus obtained, on the basis of the selected operating conditions and dope solution composition. PHBhv membranes, with a dense structure, have been finally tested in pervaporation for the separation of the azeotropic mixture methanol/methyl-*tert*-butyl-ether.

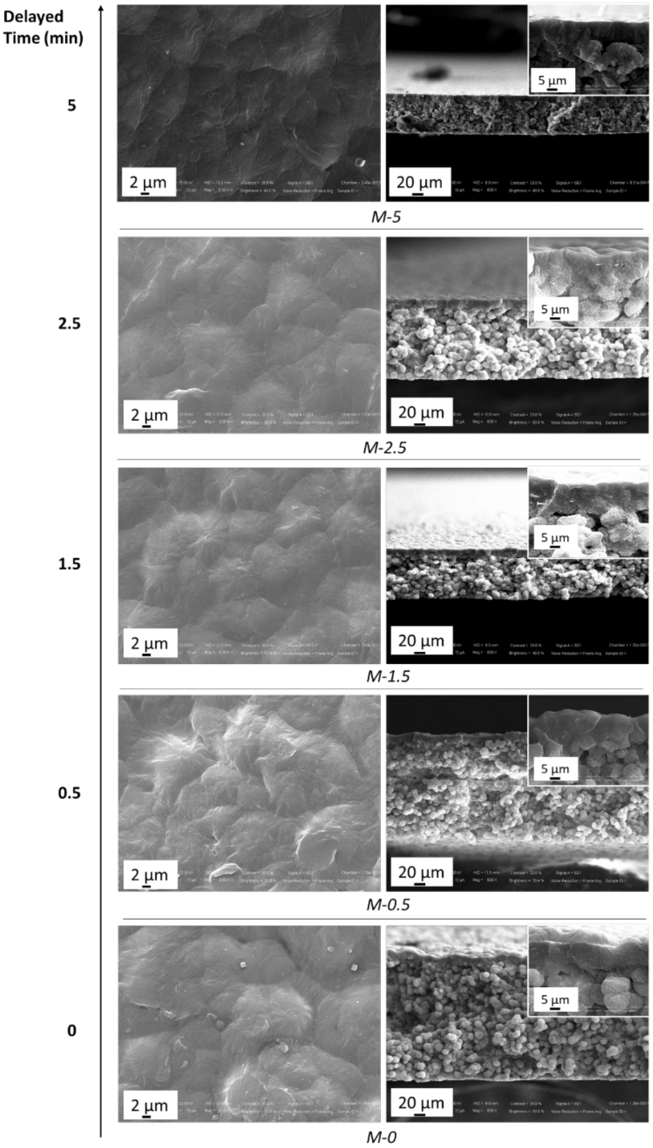

Figure 1. SEM pictures (surface and cross-section) of PHBhv membranes prepared at different evaporation times

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Use of pectin as crosslinking agent and functional additive in membrane preparation

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Abstract

Employing natural materials derived from renewable waste biomass for membrane preparation is in line with the strategy of circular, sustainable and responsible economy. To follow this green route, pectin (PEC), a heteropolysaccharide abundant in agri-food industry wastes, was used for the first time in this work both as crosslinking agent and functional additive. Polyvinyl alcohol (PVA), a synthetic biodegradable polymer, was selected as a model biopolymer to prepare crosslinked membranes.

The crosslinked PVA/PEC membranes were prepared by Evaporation-Induced Phase Separation technique. The influence of PEC/PVA mass ratio and crosslinking reaction time of the casting solution on the membrane stability was investigated. Results demonstrated that PVA/PEC (1:1) membranes prepared with casting solution crosslinked for 5 h (crosslinking degree 86±2%) had superior stability in water (tested up to 100 °C) compared to membranes prepared with PVA/PEC (1:1) blend and much higher stability compared to membranes prepared with PVA alone. The crosslinking did not reduce the water vapor permeability of the PVA/PEC (1:1) compared to the PVA membranes [1]. The presence of PEC made the developed membrane active against free radicals (maximum scavenging effect after 30 min) and capable of inhibiting the growth of the tested bacterial strains both on solid and liquid culture (after 24h of contact between bacteria suspension and PVA/PEC 1:1 membrane, the bacteria concentration decreased from 10^7 to 10 CFU/mL).

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Biohybrid membrane for organophosphate degradation in real aqueous streams: unveiling the mechanism causing lower catalytic activity in vegetative water

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Abstract

Considering the increasing threats for human health due to the presence of hazardous compounds such as pesticides polluting various aqueous environments and mediums, the need of effective strategies to decontaminate water is more and more stringent. For this purpose, the use of enzymes immobilized on membranes is a promising technology since it permits process intensification and specific contaminant degradation in streams containing other molecules to preserve. This study proposes the use of a biocatalytic membrane for specific degradation of an organophosphate pesticide (paraoxon-ethyl) contained in two different real aqueous matrices, i.e. surface-water and vegetative water coming from olive milling. With this aim, a thermophilic phosphotriesterase on functionalized regenerated cellulose membrane was covalently immobilized [1]. The biohybrid membrane (Fig. 1), assembled in a biocatalytic membrane reactor (BMR) allowed pesticide degradation in both streams, beside to stabilize the enzyme and to enable their efficient use in a continuous process. In particular, a paraoxon-ethyl degradation of 83% and 65% was obtained when surface water or vegetative water were used as contaminated feed, respectively. Moreover, the half-life time of the immobilized enzyme increased compared to the one of the free enzyme used in both surface water (more than three-fold) and vegetative water (more than four-fold). The kinetic characterization of the phosphotriesterase revealed that its low performance towards paraoxon-ethyl contained in vegetative water was due to a competitive inhibition given by the biophenols. In order to enhance phosphotriesterase activity in presence of inhibitors, amphiphilic molecules were used. Among the tested surfactants, the ionic ones, i.e. sodium dodecyl sulphate and cetyltrimethylammonium bromide, showed the capability to improve enzyme activity (1.6 and 3.3 times, respectively). The degradation capacity in both surface water and vegetative water as well as the improved enzyme stability make the BMR promising for environmental bioremediation and decontamination of matrices which contain high added value compounds, such as biophenols, without determining modification of their composition.

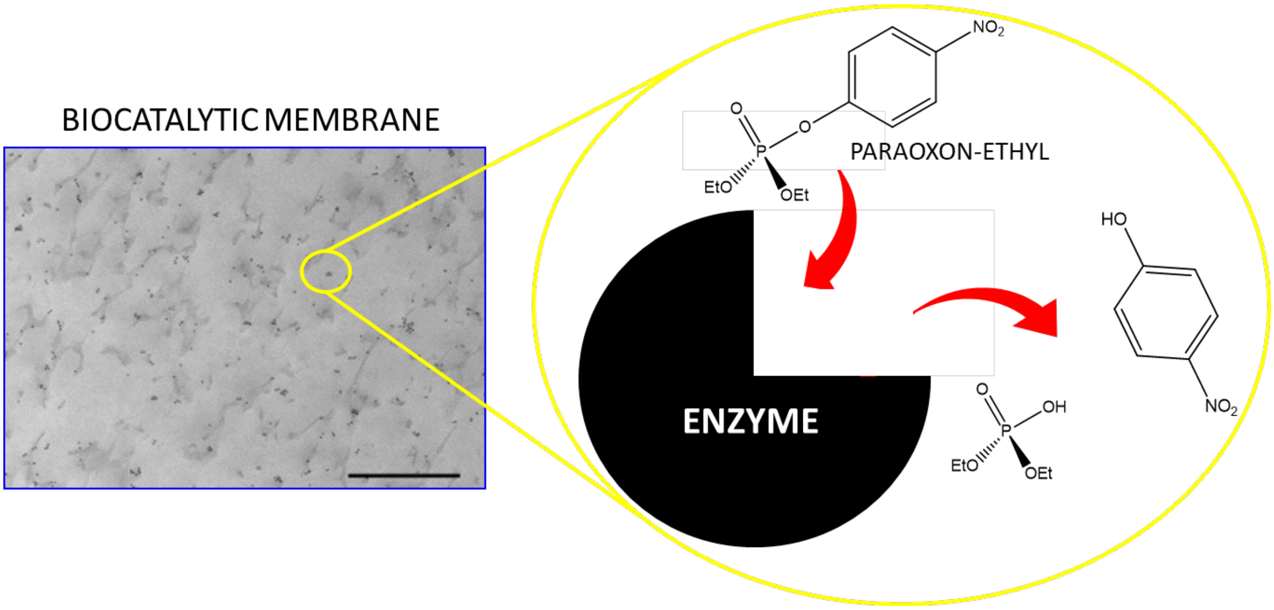

Fig. 1. TEM image of immunolabelled biocatalytic membrane (cross section), black spots indicate phosphotriesterase enzyme immobilized on the membrane. The magnification shows the paraoxon-ethyl degradation scheme.

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Biohybrid membranes and their perspective in boosting efficient and precise processes

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Abstract

Artificial membranes bearing biological components and functions constitute a class of highly performing membranes. Among the large variety of components that can be used to impart biological functions to synthetic membranes, macromolecules such as proteins, are the most popular. For example, enzymes, antibodies, protein channels are used to impart biocatalytic, affinity recognition, ion selective properties, respectively. To maintain the unpaired functional properties of the bio-macromolecules within the synthetic membranes, physical-chemical as well as structural and morphological properties of the material at nanoscale play an important role. For example, besides, pH, temperature, ionic strength, water activity, interfacial tension, etc., spherical geometry of the nanostructure seems to favor stability of conformational and functional properties. To maximize the biological function, fluid dynamics and transport mechanisms are also important. It is worth to mention, for example, that biological systems operate under laminar flow and diffusion transport (as far as passive transport is concerned). Furthermore, the flow direction through biological asymmetric basal membranes occurs from mesoporous to microporous structure (which is the opposite compared to synthetic asymmetric membranes, where, in order to limit fouling, the transport occurs in the direction from thin selective layer to porous support layer).

Thanks to the extremely high selective and precise functional properties of biological components, biohybrid membranes are gaining attention in other fields than biomedical and biotechnological traditional ones. They are being exploited in water desalination, energy and chemicals production, environmental remediation. The transition from a depleting to a sustainable production system, the search for processes that eliminate the use of hazardous chemicals and have low carbon and water footprint, the need for low or no waste production, are all drivers for novel biohydrid membrane-based operations.

Acknowledgements

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Extending the application field of electrokinetic characterizations in membrane science

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The zeta potential of membranes can be inferred from electrokinetic methods such as streaming potential and streaming current. Since these techniques permit to consider the compensation of the surface charge by the ions within the electrical double layer on the liquid side of the interface, they are particularly useful when investigating problems of practical relevance. Assessing the zeta potential of membranes is particularly attractive to provide insight into the charge formation process of membrane surfaces but also to investigate surface functionalization, fouling, ageing... From the experimental point of view, the easiest way to perform the electrokinetic characterization of membranes is to implement transversal (i.e. through-pore) measurements. However, the multilayer structure of many membranes makes the determination of the skin layer properties quite tricky. In order to overcome this issue, tangential measurements (streaming potential or streaming current) based on the application of a pressure gradient along the membrane skin layer have been developed and have become the most widely used method for determining the zeta potential of membranes.

However, complications have been pointed out when such tangential electrokinetic measurements are applied to membranes for which a part of the experimental signal is likely to pass through the membrane matrix (and not only on the external surface of the skin layer) [1]. This parasitic contribution to the experimental signal, referred to as electrokinetic leakage [2], has been largely overlooked in the literature although it may lead to a relatively inaccurate determination of the zeta potential or even to misleading conclusions about the surface properties of membranes. However, relevant information on the membrane matrix can extracted from electrokinetic leakage since the membrane is crossed by this parasitic phenomenon. Thus, we will show that electrokinetic leakage can be used as a probe for investigating various phenomena occurring inside the membrane matrix, paying special attention to fouling and ageing issues.

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Computer simulations of ionic fluids: structure, dynamics and NMR properties

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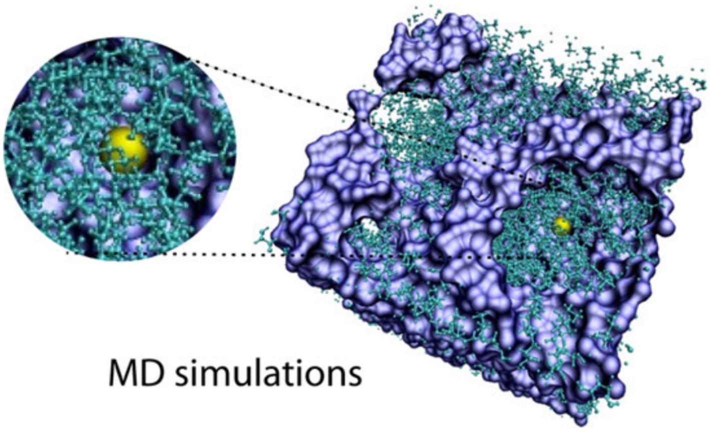
Abstract

Ionic Liquids (ILs) and Ionic Liquid Crystals (ILCs) are fluid phases made of ions. Typical systems are composed of bulky organic cations, with low symmetry and a distributed charge, and organic or inorganic anions, for example 1-alkyl-3-methylimidazolium, pyridinium or bipyridinium cations paired with halides, hexafluorophosphate and bistriflimide. Depending on the length of the alkyl chain(s), a liquid-crystalline phase can be formed, in addition to the isotropic liquid phase, resulting in a ILC system almost invariably of smectic type, that is layered.

In this presentation we will show some recent results concerning the prediction of the NMR properties of pure ionic liquids and xenon dissolved therein as a probe. The first example [1,2], will highlight the power of DFT for non-covalent systems provided that some strong and specific interaction exist between cation and anion. On the other hand, when weak interactions are dominant it is necessary to resort to a molecular dynamics simulation in order to take into account the time dependence of the structural arrangement of the ions. This case will be discussed presenting the results of the structural [3] and dynamic [4] properties of xenon dissolved in two different ionic liquid systems, imidazolium chlorides and imidazolium hexafluorophosphate. These methods have been reviewed recently [5].

We will finish our presentation by highlighting future developments and applications of the computational protocols to membrane systems.



Xenon atom (yellow) confined within the alkyl domains (cyan) of the ionic liquid 1-decyl-3-methylimidazolium chloride (anion and cationic head in violet)

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A multiscale procedure for modelling OH$^-$ transport in anion exchange membrane at different hydration levels

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Cutting-edge technologies rely on cost-effective high-performance materials. In the framework of Ion Exchange Membrane (IEMs) processes, this implies tuneable membrane features that lead to predictable structure-property correlations, such as controllable ion selectivity and appropriate ion diffusion. In the last years, these issues have been approached by our group through a full-atom multiscale computational methodology. This methodology, applied to a polysulfone-tetramethylammonium (PSU-TMA) anion exchange membrane (AEM) counter-balanced with hydroxide anion (OH$^-$) [1], is herein synthetically illustrated and schematized in Figure 1. The membrane hydration number (λ), defined as the number of water molecules per TMA fixed charge group, is computed through Density Functional Theory calculations (DFT) by developing a simple yet efficient hydration algorithm. The computed λ is then used as starting point to calculate the expected water uptake (WU) of the membrane, by considering a polymer chain with variating Ion Exchange Capacity (IEC), finding good agreement with the experimental WU. Subsequently, λ, as obtained from the quantum calculations and validated with respect to the WU, is used to perform classic Molecular Dynamics simulations (MD) on a larger scale. The atomic partial charges, used in the MD force field, are parameterized by additional DFT calculations. Then, PSU-TMA polymer chains showing different IEC, are randomly assembled from constitutive hydrated monomers, after which equilibration of the hydrated membrane by a suitable simulated annealing protocol is carried out. The MD simulations allowed to study the ion-clustering micro-structure details such as the percolation degree and to get an intuitive dynamic picture of the hydrophilic-hydrophobic separation by means of 2D density maps. Moreover, the proposed multiscale method aims to study the OH$^-$ transport inside the different membranes, which is performed by means of two methods: (i) time-ensemble average Mean Square Displacement analysis, as derived from MD simulations, and (ii) by the Mackie-Meares analytical model; for the later, the required water volume fraction of the membrane is also calculated from the membrane models. The computed diffusion coefficients as a function of the membrane hydration are in fair agreement with experimental data coming from hydroxide conductivity measurements. The versatility of the multiscale model, mainly due to the drastic minimization of adjustable or empirical parameters, allows an easy transferability to study similar systems where ions hydration in complex matrices are involved; this work is in progress.

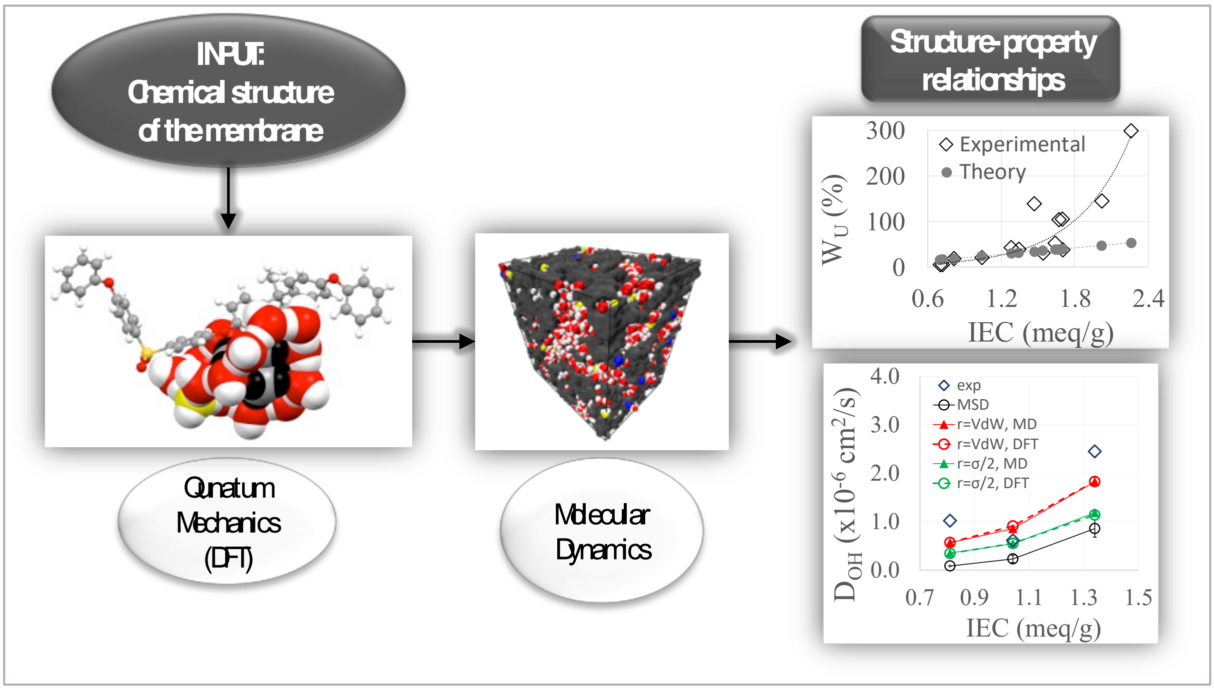

Figure 1. Schematic workflow of the proposed multiscale methodology.

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Advances in Hydrogel Nanoparticles production by membrane nanoprecipitation

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Abstract

In the early 1990s, membrane technology has been introduced for the production of emulsion droplets with tuned size and uniform distribution. In the so-called membrane emulsification process, two immiscible phases are separated by the membrane and a high interfacial tension exists between the membrane surface and the droplet-forming phase. More recently, an innovative method for the production of polymeric nanoparticles (NPs) by combining membrane contactors with the well-known nanoprecipitation process has been introduced. In this case, two miscible phases are separated by the membrane and meet each other at the pore exit where the mixing of the polymer solution (i.e., acetone) with the non-solvent phase (i.e., water) occurs. The emerging study of nanoprecipitation in combination with membrane contactors (membrane nanoprecipitation) has opened a new window on the application of membrane science in the production of NPs. The challenges in this field are: 1) to achieve a fine control of the mixing processes in order to tune with good accuracy, the size and physicochemical properties of the NPs; 2) to design new processes to reach large-scale production with high reproducibility.

In this work, the powerful of membrane nanoprecipitation for the production of hydrogel NPs will be demonstrated. Hydrogel NPs have attracted considerable attention as promising drug carriers for therapeutic applications. They are currently produced starting from emulsion templates (also produced by membrane emulsification) while the use of nanoprecipitation for hydrogels is still limited and the application of membrane nanoprecipitation has never been reported. The production of Polyvinyl Alcohol (PVA) NPs by using water and an alcohol (ethanol and methanol) as solvent and non-solvent, respectively will presented as case study. The influence of parameters related to formulation composition (i.e. solvent, polymer concentration, phases ratio, non-solvent) and operative conditions (shear stress, flux) to develop a scalable formulation method by using membrane nanoprecipitation has been investigated.

Novel Polymers of Intrinsic Microporosity

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Abstract

Polymers of Intrinsic Microporosity (PIMs) are attracting attention as suitable materials for the preparation of gas separation membranes, since they combine the desirable processability with high permeability. The latter is due to their rigid and contorted macromolecular chains that inhibit inefficient packing and generate their microporous structures. In this paper, we discuss the effect of different monomeric units on the gas transport properties of PIMs, e.g. increasing steric hindrance of the rotational centers, the use of a Tetraoxidethianthrene instead of the traditional tetrafluoro-terephthalonitrile, or the use of benzotriptycene units. 2D-shaped benzotriptycene-based PIMs have recently been used to redefine the Robeson's Upper Bounds for the CO_2/N_2 and CO_2/CH_4 gas pairs [1], and their properties have now been matched by spiro-center based PIMs. We will focus on novel 3D ultrapermeable PIMs, discussing their permeability properties when exposed to single gas or mixture. A detailed analysis of their transport properties as a function of the temperature will give a deep insight into the diffusion process of the gases in these novel materials.

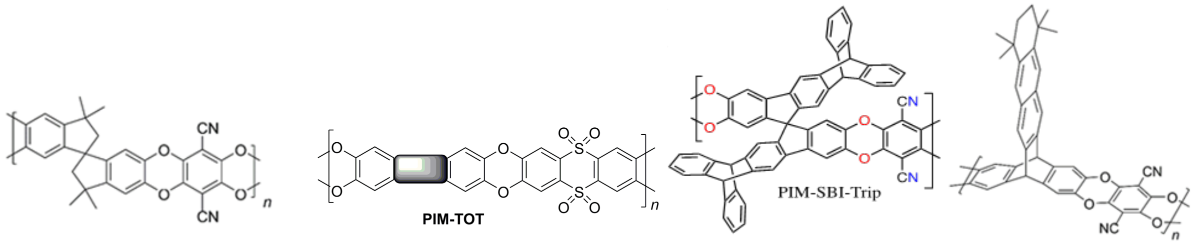

Fig.1 Molecular structures of different PIMs discussed in this work.

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Promoting/slowing effect of permanent gases on CO_2 permeation through zeolite membranes

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Abstract

Permeation of several mixtures containing CO_2 and permanent gases (i.e., H_2, N_2 and CH_4) through a SAPO-34 membrane was investigated. A model considering gas translation and surface diffusion was used for prediction of permeance and selectivity in mixture [1]. The analysis of various CO_2-containing mixtures revealed a mutual interaction among carbon dioxide and permanent gases [2]. In particular, as expected, CO_2 always hinders permanent gases, reducing their permeation in mixture compared to the pure gas. Differently, CO_2 can be itself promoted or slowed depending on which species is present in the mixture. Specifically, its flux and permeance resulted higher than the single gas values in presence of H_2 and lower if mixed with CH_4 (Figure 1). These promoting and slowing effects are due to the Maxwell-Stefan binary diffusivity, which controls the mixture permeation by surface diffusion [2]. In particular, the binary CO_2:H_2 diffusivity increases compared to the pure CO_2 value owing to the effect of the faster H_2. On the other hand, CH_4 slows down the carbon dioxide permeation, since its diffusivity is much lower than that of the pure CO_2. These effects are balanced in case of a ternary equimolar mixture (Figure 1); thus, CO_2 flux and permeance assume again the single gas values. Nitrogen does not promote or slow the carbon dioxide permeation, since the two species have a similar diffusivity.

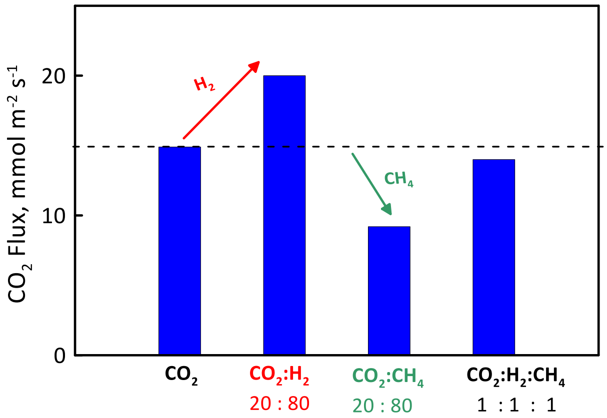

Figure 1. CO_2 molar flux of various mixtures compared to the single gas value at 24°C for a fixed ΔP_{CO2} of 1.4 bar.

Hindering, promoting and slowing are responsible for the increment of mixture selectivity compared to the ideal one, obtained as the single gas permeance ratio. These effects make zeolite membranes very selective towards CO_2 and, thus, good candidates for purification of streams of industrial interest.

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Performance of PVDF-based membranes functionalized with high-exfoliated Graphene flakes for enhanced and efficient Membrane Distillation and membrane Crystallization

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Abstract

Most of membrane transport processes are isothermal and their driving forces are transmembrane hydrostatic pressures, concentrations, electrical or chemical potentials. Membrane distillation (MD) and Membrane Crystallization are non-isothermal processes that actually still needs to be developed for treating saline and hyper saline solutions such as seawater or reverse osmosis (RO) brine [1,2]. These operations exploits the hydrophobic nature of the membrane to reject, theoretically, 100% of all non-volatiles components contained in the aqueous solution. Considered the increasingly demand of fresh and reusable water, our intent is to identify new materials to increase the production and the efficiency with eco-sustainable membrane operations. In literature are present some of these materials used in membrane processes, such as Bi_2Se_3 and Graphene that allows to increase the crystallization of NaCl, leading to a higher uniformity of the crystal size[3,4]. Graphene receives great interest for its additional functionalities to the host material. It is two-dimensional (2D), single carbon atom composed of sp2 arranged in a honey comb structure, used in various research fields including water treatment and purification processes. Graphene is particularly attractive for MD application due to its hydrophobic nature, selective sorption of water vapours, and anti-fouling properties[5]. The incorporation of graphene provides additional properties to the composite membrane such as added roughness and hydrophobicity that leads to robust and highly efficient MD membrane. In the present work, the Graphene flakes for the preparation of the membranes, were exfoliated with Wet Jet Mill technique according to the procedure described in the previous work[6]. The membranes functionalized with Graphene flakes have been prepared via NIPS, characterized and tested in membrane distillation and membrane crystallization. Moreover, we discuss experiments carried out under different operating condition.

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Membrane microgravity humidity separator

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The separation of water vapour from gaseous streams by membranes is a recent operation, which is attracting significant attention in these last years for many applications (plume of cooling tower, flue gas dehydration etc.). Very recently, Thales Alenia Space and CNR-ITM started a collaboration in the framework of the ESA MELiSSA PFPU (Precursor of Food Production Unit) project aiming at using membrane humidity separators for space applications within a plant growth facility for microgravity applications.

In the extensive research activity at CNR-ITM on this membrane operation, hydrophobic porous membranes are utilized for condensing water vapour contained in gaseous streams, allowing the permanent gas permeation through the membrane, while keeping on the membrane surface (feed side) the drops of the liquid phase, even the small ones. The hydrophobic nature of the polymeric membranes not only avoids water droplets dragging, but also promotes vapours condensation exploiting the principle of dropwise condensation where, when condensation takes place on a surface that is not wet by the condensate, water beads up into droplets and rolls off the surface.

The typical pore dimension of the membranes used is of 0.1-0.2 micrometers, well above the kinetic diameter of any gas present in the feed; therefore, the membrane cannot have any selective separating function among the various gases as well as it will not be able to retain the water vapor that has not been condensed.

In this collaboration, a devoted device was designed and built for operating in steady state in microgravity. In a typical application, the membrane unit is vertical oriented and the condensed water is usually collected on the bottom of the condenser since the drops fall down. Specific solutions are being investigated to promote water harvesting for different orientation of the membrane humidity separator. The appropriate design of the membrane module together with the suitable choice of membrane type and related configuration (i.e. hollow fiber) are indeed crucial aspects that have been considered to make this technology successful.

Here, we will present some results measured with the designed separation unit as function of the main variable affecting the separation process.

Membrane condenser for ammonia removal from gaseous streams

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Abstract

Ammonia is a harmful pollutant that is commonly produced in livestock facilities from the breakdown of animal waste, from integrated coal gasification combined cycle power generation systems and from many other sources, such as landfills for waste disposal, crematory, chemical and manufacturing industries [1] and wastewater treatment plants, etc. [2,3]. As gas, ammonia is colour-less, toxic, reactive, corrosive and with a very sharp odour. Emission of NH_3 without appropriate treatment is causing frequent complaints from neighbouring communities. Breathing levels of 50–100 ppm ammonia in air, can give rise to eye, throat and nose irritation. To control malodour and protect the health of people working on animal farms and in the industries that use ammonia in their processes, waste gases containing ammonia are required to be treated in an efficient and viable process. Another aspect to be considered is that ammonia dissolves easily in water. In water, most of the ammonia changes to ammonium, which is not a gas and does not smell. Ammonia and ammonium can change back and forth in water. Strategies for reducing ammonia include preventing ammonia formation and volatilization. Other conventional methods for NH3 removal from gas streams include absorption (wet scrubbing), adsorption and incineration (either thermal or catalytic), and biological techniques. Nevertheless, all these methods may have technical and/or economic limitations in removing NH3 from gas streams.

To overcome these deficiencies. objective of the present work is to consider membrane condenser (MCo) technology in order remove ammonia from waste gaseous streams [4,5,6,7]. Moreover, different MCo configurations were analyzed with the aim to determine the one more energetically efficient. In configuration 1, the feed is cooled via cooling water before entering the membrane module; in configuration 2, a cold sweeping gas cools the plume stream directly inside the membrane module; in configuration 3, the feed is first partially cooled via an external medium and then a sweeping gas is used for the final cooling of the stream. Therefore, configuration 3 is a combination of configuration number 1 and 2. Moreover, when a cold sweeping gas is utilized, the ratio between its flow rate and the feed flow rate is defined as the sweeping factor (I).

The achieved results shoved that the removal efficiency of membrane condenser increases with the growing cooling of the feed, and with the rising of I. Even if the higher ammonia removal was achieved with configuration number 3, the best compromise between energy consumption and ammonia removal was found in configuration number 2.

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Catalytic Zeolite Membrane Reactors

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Abstract

Catalytic membrane reactors represent a promising solution in different industrial fields including biotechnology, pharmaceutical sector, petrochemical, chemical plants, energy and environmental applications [1]. Zeolite membranes for their well defined pore size, high thermal and chemical stability can be used as membrane reactors.

Carbon monoxide selective oxidation (SelOx) is the most cost effective method for the purification of H_2–rich gas streams, reducing CO to the desired level (e.g., less than 10 ppm for PEM fuel cells) without excessive hydrogen consumption. Catalytic Pt–loaded zeolite membranes were prepared and used for performing the CO SelOx from hydrogen rich streams [2-3]. An effective CO removal from 10,000 ppm down to 10–50 ppm was achieved [2-3].

The isomerization of catalytic linear alkanes to branched alkanes is an important industrial reaction owing to the increasing demand for iso alkanes used as a substitute for octane boosters instead of aromatic and oxygenate compounds that are subjected to severe environmental limitations [4]. In isomerization reactions, a mixture of di-branched, mono-branched, and linear molecules is produced; consequently, the conversion is limited by the thermo- dynamic equilibrium. Pt-ZSM5 supported membrane was prepared and used for the isomerization of n-pentane (n C5) [5]. The catalytic tests showed the possibility to perform the nC5 isomerization [5].

These results indicate that supported zeolite membranes could still be interesting candidates for intensified industrial processes in the future.

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Gas separation using zeolite membranes

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Gas separation is a crucial step in industrial processes, allowing the recovery of purified components from multicomponent feed streams. Zeolite membranes are a promising alternative to the traditional separation techniques (e.g., cryogenic distillation, absorption), moving in the direction to design more sustainable processes (low energy consumption and no use of solvents).

In this work, permeation of CO_2, H_2, N_2, CH_4 and CO through various membranes (i.e., NaY, DD3R and 4A) was investigated under dry and wet conditions by means of a mass transport model paring surface and gas translation diffusion able to predict permeance and selectivity [1-2].

Among the main results achieved, CO_2/H_2 and CO_2/N_2 selectivity values were estimated to be higher than 30 in NaY at 303 K, when an equimolar mixture was fed. At a moderate temperature, the strong CO_2 adsorption hinders the permeation of the weakly adsorbing species (e.g., H_2), making the material very selective. This hindering effect is more evident in wet condition through a 4A membrane, where the adsorbed water vapour drastically reduces permeance of the other species. Therefore, a net increment of selectivity was found with respect to that in single gas, being about 45 times in case of H_2O/H_2, (from 5 to 225). Concerning H_2O/CH_4 and H_2O/CO, this increment was about 30 and 9 times, respectively.

Hence, operating at a low temperature allows exploiting the preferential CO_2/H_2O adsorption and the consequent hindering effect on the weakly adsorbed species, which makes membrane selective. Zeolite membranes are good candidates for gas separation within an appropriate range of operating conditions, allowing the purification of CO_2 and water vapor from multicomponent mixtures.

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Enhanced gas permeation properties in polymer materials via Ionic Liquids incorporation

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Abstract

New trends in the development of advanced polymeric membranes include the identification and incorporation of selected additives within the polymeric matrix. In this respect, Ionic Liquids (ILs) are particularly interesting to be used as additives by virtue of their properties such as high chemical and thermal stability, low volatility, affinity for specific gases and capability to affect membrane morphology. The research activity, illustrated in this contribution, was carried out in collaboration with the Institute of Polymers, Composites and Biomaterials (IPCB-CNR), Catania [1]. Self-standing films were prepared by solution casting and solvent evaporation, incorporating selected imidazolium ILs within a PVDF copolymer (poly(vinylidenefluoride-co-hexafluoropropylene)), a low permeable material for the transport of gas species. The chosen ILs differ for the anion type, while their concentration in the membranes was in the range 0-60 wt.%. The characterization of the membranes was carried out by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR), in order to investigate their morphology, thermal properties, thermal stability and spectral properties.

The gas permeation tests demonstrated the absence of defects in the blend membranes, even at the highest IL concentration. SEM evidenced a spherulitic structure, while FT-IR proved the conversion of the polymer matrix from a predominantly apolar α-phase to polar crystalline phases for PVDF. DSC and TGA analyses showed a heterogeneous structure for the polymer blends. TGA indicated that the onset of degradation is reduced for the blends, with no evidence of complexation between polymer and the ILs. On the other hand, DSC evidenced the plasticization exerted by the ILs on the polymer matrix. These investigations support the observed significant enhancement of gas

permeability (up to three order of magnitude at the highest ionic liquid loading). In addition, the ideal CO_2/N_2 selectivity was significantly enhanced upon the addition of the BF_4^- based IL to the polymer. A modelling study on gas permeability was performed to interpret the experimental data. Finally, the investigated gas transport properties were correlated to the anion chemistry and to the specific polymer/IL interactions [1].

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Acknowledgements

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The contribution of solubility and diffusivity in the gas separation performance of mixed matrix membranes based on CuNi-MOFs: Glassy vs. Rubbery polymers

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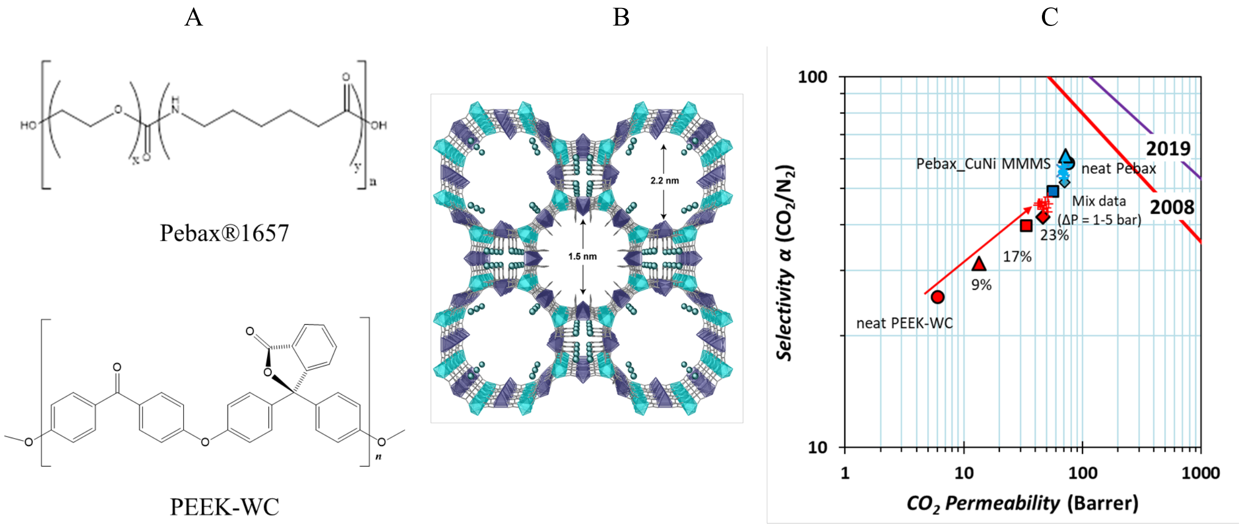
Abstract

Mixed matrix membranes (MMMs) are seen as promising candidates to overcome the fundamental limit, known as the so-called Robeson upper bound[1-3], 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-MOF (Fig 1B) in the rubbery poly(ether-amide) multiblock copolymer, Pebax®1657 and in the glassy poly(ether ether ketone) with cardo moiety, PEEKWC (Fig. 1A). Permeability, diffusion and solubility coefficients and their corresponding ideal selectivities were determined for the gases He, H_2, O_2, N_2, CH_4 and CO_2 on the "as-cast" samples in a fixed volume setup by the so-called time lag method. Mixed gas permeation tests were performed on a representative sample to investigate the actual separation performance with industrially relevant gas mixtures CO_2/N_2 and CO_2/CH_4. The detailed analysis on the gas transport properties of the two set of MMMs highlights the radically different effect that the same CuNi-MOF can have when it is embedded in a rubbery or a glassy polymer. In the rubbery Pebax®, the MOF provides a large additional volume for absorption of the gas, which yields a strong increase in solubility with an apparent decrease in diffusion coefficient, but has minor effect on the permeability and permselectivity. Instead, in the glassy PEEKWC, the MOF offers a pathway for faster diffusion and effectively increases the permeability of the gases at least five-fold, and doubles the CO_2/N_2 selectivity at a filler content of 25 wt%. This simultaneous increase in permeability and selectivity moves the data towards the 2008 upper bound for the CO_2/N_2 gas pair (Fig. 1C), close to the data for the Pebax®-based MMMs, which are hardly affected by the MOF



Pebax®1657

PEEK-WC

Figure 1. A) Chemical structure for Pebax®1657, PEEK-WC and B) CuNi-MOF. C) Robeson's plot for CO_2/CH_4 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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Acknowledgements

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Polylactic acid-based membranes for CO_2 separation

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Abstract

Today, there is a growing attention toward the adoption of green membrane materials based on biopolymers, which represents a starting point to exploit raw feedstocks in the viewpoint of a carbon footprint [1,2]. In particular, biogas represents a renewable source, from which bio-methane could be extracted separating CO_2 and other byproducts to constitute a viable and green alternative to the exploitation of natural gas. Biogas is known to be constituted of various compounds: CH_4 (40-70 vol%), CO_2 (30-60 vol%) and trace amount of NH_3, H_2O and H_2S.

The aim of this work focuses on the preparation and characterization of polylactic acid (PLA) dense membranes *via* solvent evaporation technique to be used in gas separation and, particularly, for CO_2/CH_4 separation. The selected membranes are based on 10wt% of biopolymer concentration and the membrane thickness results to be ~ 30 μm. The preliminary results showed interesting performance at room temperature in terms of CO_2 permeability (> 10 Barrer) and CO_2/CH_4 ideal selectivity (~ 220), well above the related Robeson's upper bound, Figure 1.

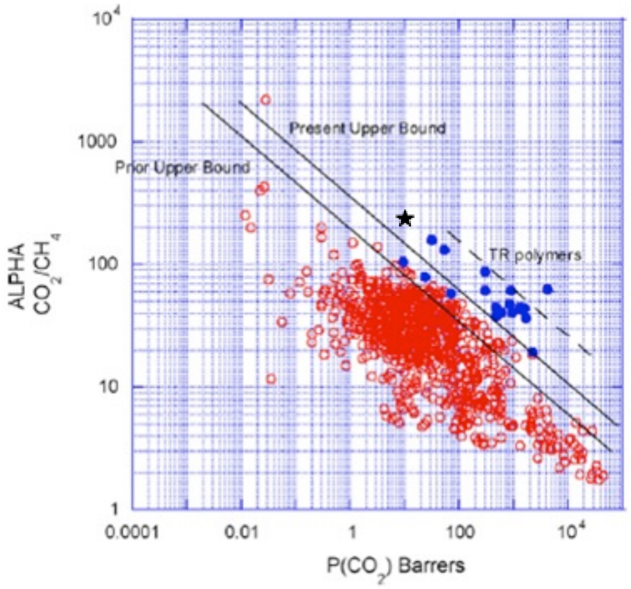

Figure 1. Polylactic acid based membrane performance (★) in the Robeson CO_2/CH_4 selectivity-CO_2 permeability upper bound.

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Effect of humidity on the mixed gas permeation of the highly fluorinated polymer of intrinsic microporosity PIM-2

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Abstract

The exploration of novel materials for use in gas separation membranes requires a precise understanding of their properties and performance under realistic operation conditions. The most common method used to study the transport properties of novel membrane materials is the so-called time lag method, which measures the pressure increase in a previously evacuated fixed permeate volume after exposure of the membrane to a gas. This method is limited to dry single gases, whereas real processes deal with mixtures that often have minor components, such as trace amounts of solvents or humidity. In this work, we use an advanced mixed gas separation instrument with a versatile quadrupole mass-spectrometric analyser [1] to study the composition of the gas streams during the permeation of dry and humidified model mixture of biogas. The membrane used in this work is made of PIM-2 (Fig. 1A), a partially fluorinated linear copolymer synthesized from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane and decafluorobiphenyl [2].

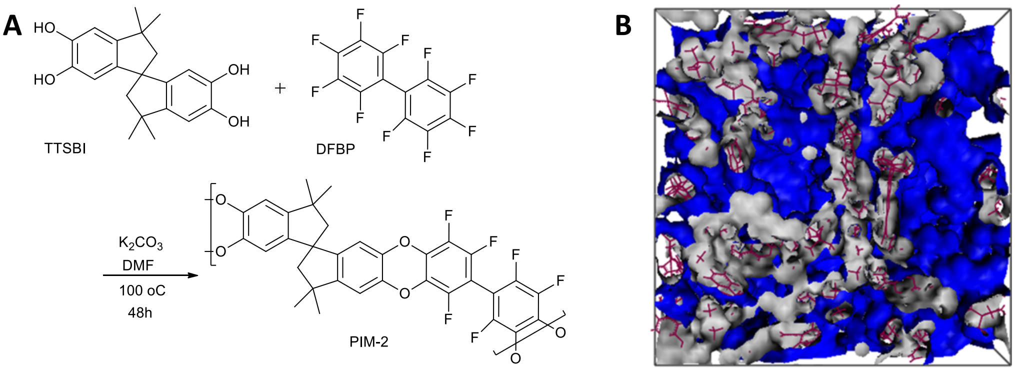

Figure 1. A) Reaction scheme and structure of PIM-2. B) Molecular model showing the isosurface (blue = outside, grey = facing polymer) of the polymer packing.

The experimental work is supported by molecular modelling studies of the polymer (Fig. 1B), demonstrating a high fractional free volume (34%) and an elevated surface area (642 m^2 g^{-1}). AFM force spectroscopy measurements reveal a high Young's modulus, > 2 GPa for the fresh sample, which further increases up to ca. 6 GPa upon aging and thermal conditioning. This suggests a high size-selectivity of the polymer, in favour of separations such as CO_2/CH_4, where size-selectivity and solubility selectivity synergistically favour the permeation of CO_2 over that of CH_4. Extensive studies were performed to verify the effect of humidity on the gas transport of a synthetic biogas mixture, containing 35 vol% of CO_2 and 65 vol% of CH_4 (Fig. 2). The results show only marginal differences between the dry and the wet gas streams, even at very low flow rates, where polarization phenomena might have been be expected. This remarkably small effect of humidity on the membrane performance is likely due to the high fluorine content and the consequently low water vapour solubility in the polymer, as confirmed by gravimetric sorption measurements [2]. It suggests the potential use of PIM-2 in separations where other materials suffer the presence of humidity.

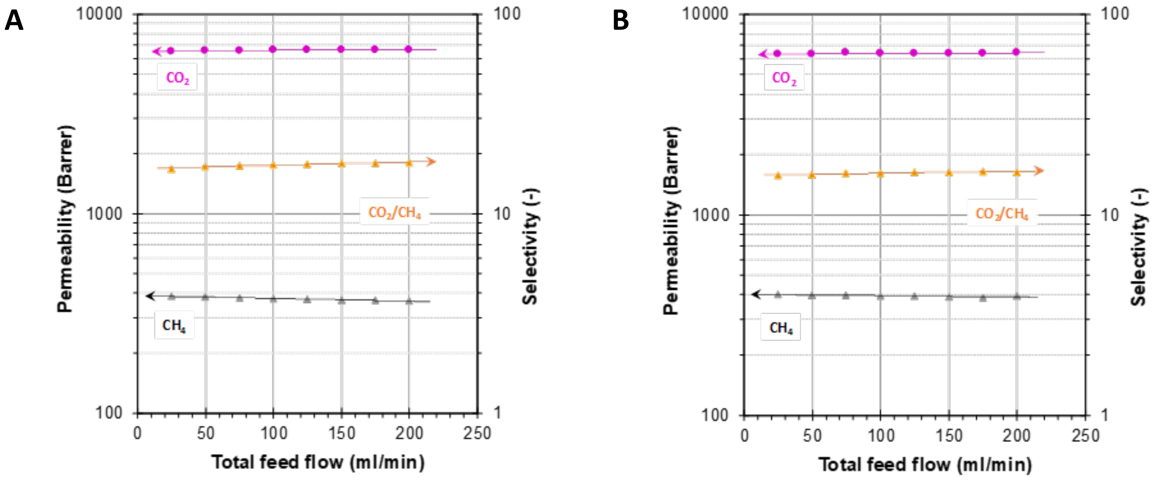

Figure 2. Mixed gas permeation test of an aged PIM-2 sample using a CO_2/CH_4 (35/65 vol%) mixture at 2 bar(a) as a function of the total feed flow rate in dry (A) and wet conditions (B). [2]

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Mechanical stiffness of PIMs copolymer with the archetypal PIM-1

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Abstract

High performing membranes must couple superior gas transport properties to high mechanical stability at the operational conditions, because membranes are subjected to high pressures in several applications. Thus, the analysis of the mechanical properties is essential prior their exploitation in the fabrication of industrial modules. Traditionally these properties are investigated by tensile tests but in a previous paper we have demonstrated that the force spectroscopy is a suitable alternative in the determination of Young's elastic modulus. [1] It was also shown that mechanical properties of PIMs strongly change upon aging and that they correlate well with transport of gases. [2] In this work, the mechanical properties of copolymer composed by the archetypal PIM-1, Figure 1, and the PIM-SBI-Trip are assessed considering the different ratio between monomers and the effect of physical aging. [3]

PIM-1

Figure 1. Chemical structures of PIM-1.

The Young's moduli of the PIM-SBI-Trip films and the reference PIM-1 were investigated by AFM force spectroscopy measurements. Each sample was measured in total at least 60 times in three different areas of the membrane sample and the data were statistically analysed to obtain the frequency distribution of Young's modulus displayed in Figure 2. The three distributions are referred to the archetypal PIM-1, to PIM-SBI-Trip homopolymer and to its copolymer with PIM-1, i.e. PIM-SBI-Trip/PIM-1. All polymers are tested after methanol treatments. The average Young's modulus increases with increasing PIM-SBI-Trip amount. It was about 2.00 GPa and 1.79 GPa for the freshly methanol treated PIM-SBI-Trip and its copolymer, respectively and about 1.2 GPa for pure PIM-1. The modulus of the copolymer PIM-SBI-Trip/PIM-1 falls between those of the homopolymers PIM-

1 and PIM-SBI-Trip. Both polymers based on SBI-Trip are not as stiff as the very rigid PIM-BTrip, [2] but much stiffer than PIM-1. [4]

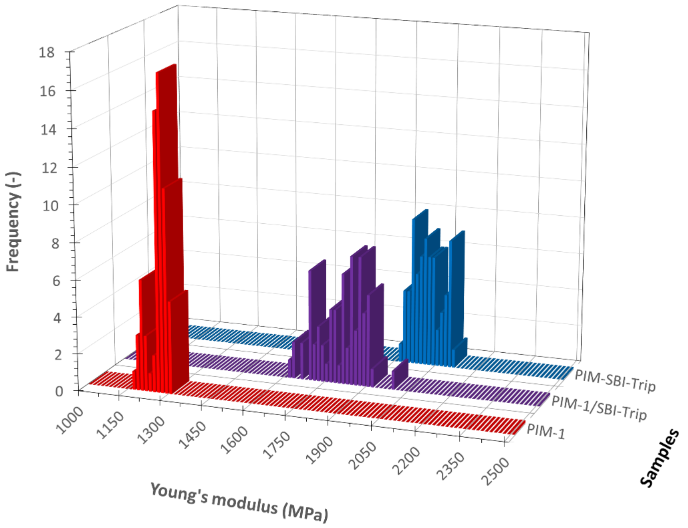

Figure 2. Distribution of the local Young's modulus for a total of ca 60 individual force spectroscopy measurements on PIM-1, PIM-SBI-Trip and PIM-1/PIM-SBI-Trip copolymer.

Studies of the transport properties and of aging of these polymers are currently in progress.

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Biological evaluation of olive mill wastewater polyphenol-enriched in concentrated fractions by membrane operations: comparison of direct and sequential processes

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Abstract

The valorisation of olive mill wastewaters (OMWs) is a challenging opportunity for the green, sustainable, and competitive development of olive oil industry [1]. In this view, the combination of conventional and innovative membrane operations represent an useful approach for the recovery of phenolic compounds of OMWs contributing to the sustainability of olive waste sector, reducing its environmental impact and promoting the development of innovative formulations of interest for pharmaceutical, nutraceutical and cosmeceutical applications [2,3].

The present study evaluated, for the first time, sequential and direct membrane-based processes such as nanofiltration (NF), reverse osmosis (RO) and membrane distillation (MD) to produce concentrated polyphenol-enriched fractions that have been analysed for their chemical profile as well as for their antioxidant and hypoglycaemic activities.

OMWs were at first pre-treated by microfiltration (MF), in order to remove suspended solids, and then concentrated directly by membrane distillation (MD) or submitted to a combination of NF/RO or NF/MD in a sequential design. The performance of direct and sequential operation modes were compared in terms of productivity (permeate fluxes) and efficiency in the concentration of compounds of interest and in the preserving the biologically activity of concentrated fractions. Experimental results showed that, at the same volume reduction factor, MD retentates exhibited the highest content of hydroxytyrosol, tyrosol, oleuropein, coumaric acid and caffeic acid. In particular, a content of hydroxytyrosol of 1.9 mg/L, about five times higher than the MF feed, was found. On the other hand, sequential MD retentate, showed the most ABTS and DPPH radicals scavenging activity with IC50 values of 0.9 μg/mL and 6.25 μg/mL, respectively. Moreover, the same fraction inhibited α-amylase and α-glucosidase with IC50 values of 41 and 32 μg/mL, respectively. In terms of productivity, direct and sequential MD process showed higher initial and steady state permeate fluxes in comparison with sequential RO.

The whole results indicate that MD can be applied successfully to concentrate microfiltered OMWs or MF/NF pre-treated OMWs in order to obtain polyphenol-enriched fractions effecting in scavenging radicals and protecting lipid-oxidations and in inhibiting key enzymes such as lipase, α-amylase, and

α-glucosidase, useful therapeutic targets for the development of functional products for obesity and diabetes type 2 prevention.

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Deep eutectic solvents (DESs)- a New Era in Membranes Preparation

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Abstract

In the last few decades, the concept of ''Green Chemistry'', ''Green Engineering'' and ''Circular Economy'' are often used to describe the development of new technologies and products that have la lower environmental impact and are based on renewable resources. Membrane Science can be identified as a "Green Technology" that offers a lot of advantages such as low cost, energy recovery, possibility of integration with conventional technologies, safety and flexible scaling up [1]. At the same time, the use of well-known toxic solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) for the membrane preparation represents a severe problem for both human health and environment. Recently, new alternative solvents attracted a great interest in accordance to the fifth principle of "Green Chemistry" stating that "the use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used" [2]. In this work, for the first time, deep eutectic solvents (DES) were explored as novel alternative solvents for the preparation of membranes thanks to their favourable green properties, such as low flammability, low or absent toxicity, high recycle and reuse capability, chemical and thermal stability, non-flammability, high dissolution ability [3].The research focuses on the possibility of using DESs for solubilizing the most used polymers such as polyvinylidene fluoride (PVDF, Solef® 6012, Solvay Specialty Polymer, Italy), polyethersulfone (PES, Solvay Specialty Polymer, Italy) and polyacrylonitrile (PAN) for the development of porous membranes via non solvent induced phase inversion (NIPS). The effect of the selected DES solvents on the morphology and performance of prepared membranes was investigated. The results confirm the possibility to obtain membranes for microfiltration (MF) and ultrafiltration (UF) applications.

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Imprinted membranes in valuable separation processes

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Abstract

Contemporary to the development of membrane technology and to the rapid industrial growth in the field of separations, also more and more selective materials for achieving sustainable processes in terms of resource recovery and recycle, health safety, reduction of operating costs and environment protection are requested. In this perspective, the born of imprinted membranes containing the memory of the compound to be recovered give the opportunity of developing valuable separation processes that requires high specificity [1, 2]. These smart membranes are capable of recognizing specific molecules or ions of interest from a mixture containing other compounds or structural analogues. Up to date imprinted membranes for application in many sectors have been produced [1, 2]. Some examples of imprinted membranes successfully developed at CNR-ITM are enantiomeric separations [2], organic solvent nanofiltration [1], removal of pesticides from water [3], specific recognition of bioactive compounds [4]. Recently we also prepared flat-sheet hybrid imprinted membranes able of specifically recognize the drug theophylline in organic environment [5]. This drug is used in the treatment of chronic obstructive pulmonary disease, asthma and chronic bronchospasm. Theophylline- imprinted membrane working in eco-friendly water phase and in hollow-fibres configuration are under development.

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Preparation of photocatalytic PVDF/Nano-TiO2 hollow fibers for wastewater treatment

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Abstract

Wastewater treatment represents one of the major goals of this century. The research of a better water quality alongside a greater awareness of the environment health leads to the development of new technologies in order to satisfy these new needs. In this scenario, membrane purification processes represent one of the most advanced and versatile technologies for wastewater treatment. As it is known, membrane processes include several advantages such as a lower energy consumption, the process can take place at low temperature, also are reliable, sustainable, and cost-effective alternatives to traditional filtration procedures. However, a disadvantage is represented by the fouling and, especially, biofouling, that leads to a decline of the permeate flux during time. For these reasons, in recent years the attention towards self-cleaning membranes, a synergistic combination of photocatalysis and membrane filtration. These membranes represent the solution for reducing the fouling via degradation of organic product and increase the membrane permeability. Titanium dioxide (TiO2) is one of the most used photocatalysts thanks to its good photocatalytic activity, high stability, low environmental impact, and low cost [1]. In this direction, Polyvinylidene fluoride (PVDF) was selected as polymer for making hollow-fibers (HFs) loaded with inorganic TiO2 nanoparticles (NPs) in order to increased hydrophilicity, stability and catalytic activity under UV-A irradiation. PVDF HFs were prepared via non-solvent induced phase separation (NIPS) technique. Polarclean® was used as eco-friendly sustainable solvent [2]. 0.5 wt.% of TiO2 NPs was dispersed in the dope solution, according to literature for reducing the particle agglomeration and improving their distribution [3]. After a preliminary study on the type of PVDF grade, PVDF 6012 (Mw ~680) was selected and the HFs were prepared by varying polymer concentration (17-18-19 wt.%) and bore fluid composition. The morphology of the produced HFs was analyzed by scanning electron microscopy (SEM) and light scattering was employed to monitor the inter-dispersion of TiO2 in the HFs surface and matrix. The results images show that the produced HFs presents a spongy structure with macrovoids. The presences of Titanium is visible on the HFs surface (Figure 1). The produced HFs were further characterized in terms of pore size diameters and thickness, porosity, mechanical properties, and pure water permeability (PWP) both in inside-out and outside-in configuration. The best HFs presented a

pore size ranging from 0.17 to 0.19 µm with a PWP of 230 L/m2 h bar. The long-term stability under UV-A irradiation, and photo-catalytic activity experiments are in progress.

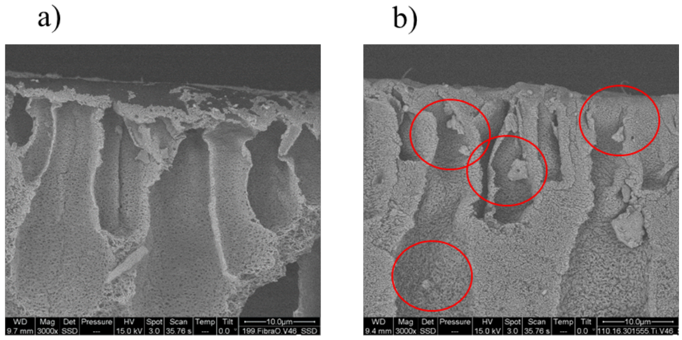

Figure 1. Example of SEM and Light Scattering of the PVDF hollow-fibers with *b)* and without *a)* the TiO_2 NPs

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Graphene Oxide Composite Membranes for water treatment

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Abstract

Graphene oxide (GO) membranes are outstanding candidates for water treatment thanks to the fast water permeation through two-dimensional nanocapillaries, combined with size and electrostatic ion exclusion mechanisms [1]. However, their use for aqueous separations processes is limited due to swelling phenomena, which reduce both the selectivity and mechanical stability of GO laminates.

In the framework of the project IDEA [2] researchers from ITM-CNR are actively working on the design and development of high performing "green" GO membranes. Moreover, modelling studies are in progress with the aim to investigate graphene GO-polymer and GO-water interfaces interactions at the atomic and molecular scales (Figure 1).

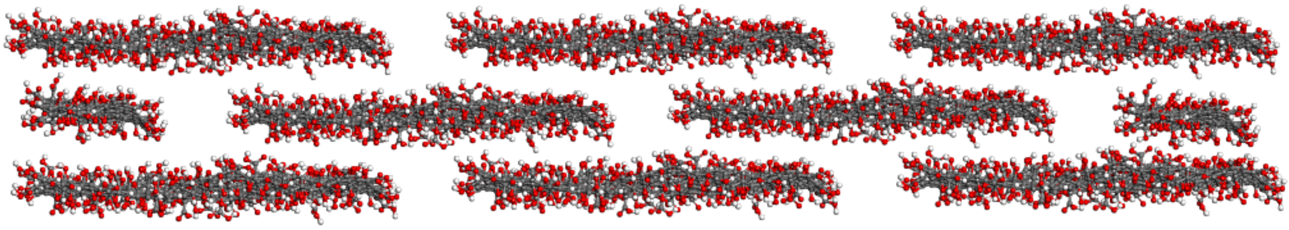

Figure 1. Model of GO laminate unit

Our results validate an easily scalable method with a low environmental impact to produce GO supported on functionalized polymeric support exhibiting an excellent stability in water and saline

solutions [3]. The experimental results highlight the key role of support chemistry, surface charge and topography to obtain composite membranes free from swelling or delamination issues. The composite GO membranes developed represent a further step ahead toward the large-scale application of GO-based membranes in separation processes.

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Acknowledgements

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IDEA project: Theoretical investigations on Graphene oxide systems

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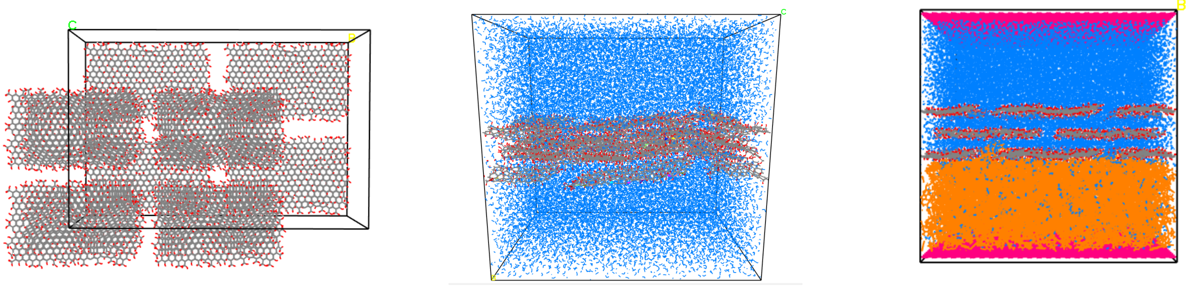
Abstract

The portion of potable water could be inadequate for half world population in the next 10 years because of climate changes, overpopulation, and poor management of water supply networks. The project IDEA [1] aims to use Graphene Oxide (GO) membranes to perform water desalination of marine water to supply freshwater shortage. GO is an adequate candidate for water separation because it leads to complete salts elimination with good permeability performances [2]. In order to use GO membranes on a large scale, GO must be supported to reach adequate processability and prevent it from flacking apart. A branch of the IDEA project addresses the GO system stability via Molecular Dynamics (MD). Here we present a step-by-step building process of a GO system by MD.

We have built a model with staked GO sheets growing the system from a single sheet of GO (916 atoms) to a system of 12 GO sheets both in void (Figure 1a) and in water (Figure 1b). We also designed our first system of supported GO in water (Figure 1c).

We present some initial results obtained from ongoing data-production dynamics addressing the stability of GO in water and the adhesion of GO to a polymeric substrate.



(a) (b) (c)

Figure 1 (a) GO system in void (10992 atoms, TOP view), (b) GO system in water (74634 atoms, SIDE view) and (c) Supported GO in water (105579 atoms, SIDE view).

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Preliminary computational studies of membranes probed by ^{129}Xe NMR

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Abstract

Satisfying the demand for an increasing computational power became easy, thanks to the computer industry which fulfils the needs of the Information Age, in which we still live. Performing simple simulations are, nowadays, tasks that everyone could attempt just with an ordinary personal computer. However, doing simulation isn't just pressing buttons of black boxes. Computational chemists' expertise relies on evaluating numbers, thus answering the question: "How good are the numbers that have been calculated?" **[1]** could be sometimes tricky, because this implies knowing how the black box is made and what are the mechanisms working inside it.

This work focuses on Mixed Matrix Membranes (MMM) with ionic mesogens (ILC) employed as fillers. It aims to bridge the experimental knowledge **[2]** with the computational counterpart. Nevertheless, such complex systems aren't straightforwardly modelled: the overall properties depend on a sum of contributions. ILC' structure and morphology are investigated experimentally using Xenon-129 Nuclear Magnetic Resonance (NMR) spectroscopy **[2]**. In these materials, Xe atoms reside in the lipophilic moiety, often constituted by a long alkyl chain. To model and calculate accurately ^{129}Xe NMR properties for such □ateriali s compulsory to rightly model, first, ^{129}Xe NMR spectra in simple alkanes, whose experimental data exist in literature **[3,4]**, and discern which contributions have more weight and thus, have to be treated more carefully.

The first steps in this work are: choosing a suitable Force Field (FF) for modelling alkanes, in molecular dynamics simulation, and selecting an appropriate level of theory for quantum mechanical DFT calculations which generates NMR spectra. AMBER-94 **[5]** FF and L-OPLS-AA **[6]** are used in Molecular Dynamics (MD) simulations. The latter better represents the conformational space explored by alkanes and it better reproduces the transition temperatures from solid to liquid of these substances. For the NMR calculations relativistic corrections should be included; QZ4P basis is employed in modelling Xe, while three different bases (DZP, DZ, SZ) are evaluated in modelling C and H atoms. ^{129}XeNMR spectra are, also, exploited in the morphological and structural determination of inorganic membranes made of certain Zeolites **[7]**. In this case, Xe loading, and thus

its concentration, create clusters of Xe in zeolite's cavity. This evidence is not deeply understood and the reasons that rule these systems are not fully clear up to now.

The sub-microscopic lens of simulation could improve our knowledge of this issue and gives insights on mechanisms working inside these systems.

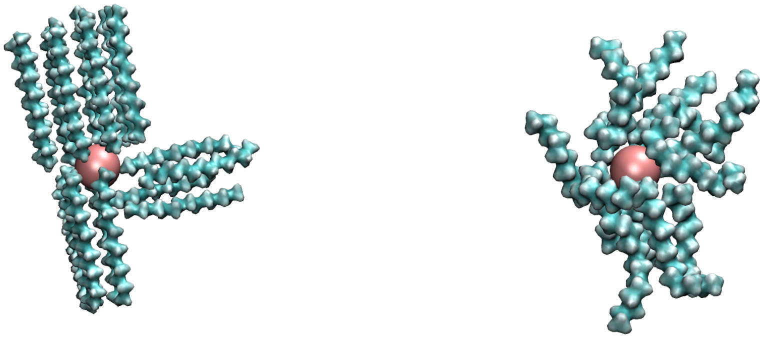

Figure 1. Clusters of n-tetradecane, blue, around Xe atom, pink. The different FF produces, in the same condition, two distinct phases: on the left, a crystalline phase is generated from MD simulations using AMBER-94 **[5]** parameters, on the right, a liquid phase is produced using L-OPLS-AA parameters **[6]**

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Crystallization behavior of NaCl on PVDF polymorphs

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Abstract

Membrane-assisted crystallization (MCr), is a new unit operation for the separation and/or promotion of solid pure crystals where microporous hydrophobic membranes are used not as selective barriers but to promote the water vapor transfer between phases inducing supersaturation in solution. MCr aiming to induce supersaturation in a solution, has been successfully tested in the crystallization of ionic salts, low molecular organic acids, and proteins [1]. Although some experimental studies probed the early stage of crystals formation [2], molecular modelling helped to investigate the mechanism of nucleation and crystals growth [3]. Poly(vinylidene fluoride) (PVDF) is one of the most utilized polymers because of its excellent combination of properties and processability and has been used in wide plethora of applications in membrane technology including membrane crystallization. PVDF has different polymorphs, that can be obtained depending on the membrane preparation technique and solvent used [4], and this property is important in membrane technology, because different phases might significantly affect the final membrane properties and performances, e.g. on membrane fouling and membrane wetting. A clear correlation between the dominating crystalline phases in PVDF and the performance in membrane contactor applications, and in particular in membrane crystallization is still missing and necessary. Here we will present a detailed computational analysis [5] of the crystal nucleation and growth of sodium chloride in contact with hydrophobic polymer surfaces at a supersaturated concentration of salt. Amorphous, α and β PVDF surfaces were studied. Results

specified the crystals (as cluster) size distributions, the size of critical nuclei, and the nucleation rate. The amorphous PVDF lead to the formation of smaller but more regular clusters in reference to the other samples; α PVDF produced much more inhomogeneous and of small dimensions crystals; β PVDF produces crystals of larger dimensions than α PVDF.

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Membrane Technology: a key platform for the implementation of the blue economy

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Abstract

The socioeconomic and industrial development and the population growth have put a strain on the water-energy nexus. Seawater Reverse Osmosis (SWRO) has gained more attention as the technological answer to water shortage by ensuring the production of freshwater from seawater, brackish and saline groundwater. However, the desalination process still presents serious drawbacks: *i*) recovery factor limited to ca. 50% by osmotic pressure and concentration polarization phenomena and *ii*) specific energy consumption (SEC) of 2.5–4.0 kWh m^{-3}, much higher than the theoretical minimum value of 1.07 kWh m^{-3}. Moreover, the produced hypersaline by-product from SWRO plants (brine) is directly discharged into the sea with detrimental effects on the marine and costal ecosystems.

Absolutely, desalination industry requires innovate solutions to drive the transition towards a sustainable Blue Growth by implementing the approaches of the Zero Liquid Discharge and Circular Economy. In order to achieve this demanding goal, a technological platform has been built on two main pillars: 1) Next-generation functional membrane materials for hypersaline brine treatment; 2) Blue energy generation by harvesting mixing energy of seawater/hypersaline brine.

In this scenario, Membrane Distillation (MD) has emerged as a hybrid thermal-membrane technology able to intensify the desalination process hitting water recovery factor above 80%. However, the main barriers to its commercial breakthrough on a large-scale application are the high SEC of the process and the heat loss associated to the thermal polarization [1,2].

Recently, the advent of thermoplasmonics opened up unprecedented horizons in MD by revolutionizing the concept of heat harvesting [3]. In fact, thermoplasmonics nanoparticles (NPs) act as nano-antenna for an *in-situ* light-to-heat energy conversion thanks to the optically resonant plasmonic excitations [3]. Interestingly, the embodiment of silver nanoparticles (Ag NPs) provided to polyvinylidene fluoride (PVDF) membrane an outstanding light absorption in the UV region exploitable for photothermal applications. Measurements with the IR-camera revealed an improvement of the membrane temperature to 41°C upon the exposure to the UV light thanks to an efficient light-to-heat conversion. Utilization of the self-heating membranes allows an enhancement

of the driving force resulting superior performance of SGMD process. Concisely, the flux of the photothermal membrane made of PVDF load with Ag hot-spots improved one order of magnitude under the UV radiation reaching a value of 8.6 kg m^{-2} h^{-1}

The protraction of the SGMD process ensured a water recovery factor of ca. 87% generating a hypersaline brine as by-product (4M NaCl) exploited for the Salinity Gradient Power production via Reverse Electrodialysis (SGP-RE). Definitively, the brine of photothermal SGMD mixed with seawater generated ca. 1.3 W/m^2_{MP} of Blue Energy. Using saline solutions as feed helped to reduce stack resistance while membrane selectivity affected unfavorably.

Overall, photothermal materials were found to be beneficial to overcome the bottleneck of MD whereas the hybridization of MD with SGP-RE paves the way for the advent of a circular Blue Economy. Integration of two membrane-based processes led better exploitation of raw materials and lower energy consumption under the process intensification concept.

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Microplastic pollution and membrane processes

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Abstract

Plastic pollution is a major concern considering the disastrous impact that it has on the environment and humans. The world plastic production is constantly increasing with a production rising from 335 million tons in 2016 to 348 million tons in 2017 [1]. The significant increase and widespread in worldwide production of plastics produces huge amount of plastics waste on land that enters in the aquatic environment causing growing alarms [2]. Furthermore, as microplastic (MP) is able to adsorb other common environmental contaminants, such as metals, pharmaceuticals, and others, it can cause diseases such as cancer, malformations in animals and humans, reduced reproductive activity, reduced immune response [2].

Nowadays, the 98% of MP is retained from wastewater treatment plants (WWTPs) but MP with a size smaller than 20 μm and NP is not retained, therefore WWTPs plants are supposed to be one of the major responsible for the plastic pollution in wastewater effluents [2]. A removal efficiency of 98% is achieved by the tertiary treatment, producing an effluent of almost drinking-water quality. However, the limited application of tertiary treatments in the WWTPs coupled with the huge amount of treated wastewaters to obtain water with different quality are a source of plastic in the effluents. Among the tertiary treatment processes, membrane operations can offer an effective solution to the microplastic and nanoplastic pollution in the effluents. To date, the application of membrane technology in the removal of microplastic is still limited, the last year registers a certain increase of study in which conventional membrane separation process and MBR are combined with the other existing treatment processes to reach a more effective removal of microplastic contaminants from wastewaters. Preliminary studies suggest that membrane technology may represent a useful solution in well-designed treatment processes to limit plastic pollution.

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Investigation of Novel Low-Fouling Membranes Performance in a Lab-Scale Side-Stream Membrane Bioreactor

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Abstract

The ultimate goal of membrane filtration is to separate molecular contaminants from a solution by a membrane to deliver water quality complying with the demands of required standards for reuse. Its combination with biological processes led to development of membrane bioreactor (MBR), which produces clarified and hygienically safe effluent [1-3]. Due to its modular design, reduced tank size with compact and small treatment facilities, MBR is a promising water treatment technology with reduced environmental impact [1,4]. One of the challenging issues of MBR operation is notably membrane fouling, which collectively refers to the phenomena of molecule adsorption, pore clogging, gel layer or cake build-up induced by the rejected contaminants that tend to accumulate on the membrane surface [5]. It is a fundamental constraint on all membrane processes and is still actively investigated in the field of wastewater treatment since it leads to high drops of permeability in MBR modules. As a consequence, frequent membrane cleaning or replacement to regain membrane permeability are required [4-5]. Recovery of permeability for fouled membranes include air scouring, backwashing as well as chemical cleaning. However, they result in reduced MBR performance, increased energy consumption and additional operative costs [6]. Thus, recently novel low-fouling membranes based on polymerisable bicontinuous microemulsion (PBM) coating were developed as a promising approach to mitigate fouling [7-10].

Two types of ultrafiltration (UF) membranes - commercially available polyethersulfone (PES) as the standard porous membrane and novel ultraviolet light emitting diode (UV-LED) based PBM coated membrane were modularised in lab-scale side-stream MBR. Membrane fouling was observed by subjecting the membranes to 0.1 g/L humic acid solution as model foulant representing a typical organic component of wastewater. In order to assess fouling propensity, a flux-step method to study critical flux was developed with a laboratory side stream membrane unit [11]. Membrane fouling was investigated between 20 – 60 L/m^{2}h (LMH) with dramatic change of transmembrane pressure (TMP) upon reaching critical flux above 45 LMH. Characterised by a sudden rise in TMP, critical flux was

obtained by the flux-step method where each step was an increment of 12 LMH for a fixed time duration. For comparative study, three membrane module parameters were monitored, viz., volume flow maintained at 28 L/H, permeate flux varied in steps and TMP. Analysis of total organic carbon (TOC) rejection and change in pigmentation confirmed by visual appearance of collected permeate indicated contrast in permeate quality. Novel PBM coated membrane exhibited potential for longer duration of operation holding constant permeability at higher TMP with lesser fouling than commercial PES membrane. Thus, stress test conditions to attain the critical flux in lab-scale MBR while monitoring its membrane fouling and stabilising its flux gives an opportunity to evaluate applicative strategies of the novel low-fouling PBM coated membranes in improving MBR efficiency.

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UNIVERSITÁ DELLA CALABRIA

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Theoretical Models for Membrane Capacitive Deionization for the design of Modular Desalination Processes

Author: Ulrich Hellriegel

A promising approach for energy efficient water desalination is the technology of membrane capacitive deionization (MCDI). To make it deployable for sustainable drinking water production, not only pilot scaled concepts but also modelling strategies have to be developed, so future plants can be designed.

In this PhD project, modelling tools, which are easy to handle are developed that the design of desalination plants with MCDI modules can be simplified. Theoretical models for single parts inside a MCDI module for mass transfer, adsorption and fluid dynamics are reviewed, modified and adapted. FEM models have been compared with 0D-models. The solution diffusion model for RO / NF has been implemented and combined with the suitable MCDI models. Lab scale experiments and pilot scale tests with a commercial MCDI module and model water were conducted for the evaluation of the theoretical models and their discussion.

For the laboratory tests, a commercial module from Voltea B.V (C-3 Development Kit) is used, to reproduce realistic values. As model feed, different deionized water-NaCl-solution are used, partly loaded with magnesium and calcium.

The semi-analytical 0D-models, like modified Donnan (mD) and amphoteric Donnan (aD) models, are solved with Microsoft Excel and MathWorks Matlab. FEM- and a combined model, using Nernst-Planck-Poisson (NPP) equations to rebuild the Gouy-Chapman model of the electric double layer (EDL), which are mainly responsible for the adsorption of ions as well as the Navier-Stokes equations for the fluid dynamics, are solved partly coupled in a 2D room with the program COMSOL Multiphysics (5.2-5.3).

The different models are compared with experimental data and the most promising are showing that they are valid for different ranges of applied voltages to the MCDI cell (see Figure 1), due to different meso- and microporic adsorption effects. The mD-model shows promising results for the salt adsorption capacity (SAC) with higher applied voltages, which is the usual applied range of cell voltages in MCDI technology. Furthermore it is solvable with less computational time than the NPP-model. Hence the 0D model is more suitable for a designing tool for water treatment plants with MCDI modules.

To achieve higher degrees of accuracy, these two models and the solution diffusion model for RO are being combined and a calculation tool is set up with the COMSOL Multiphysics application builder.

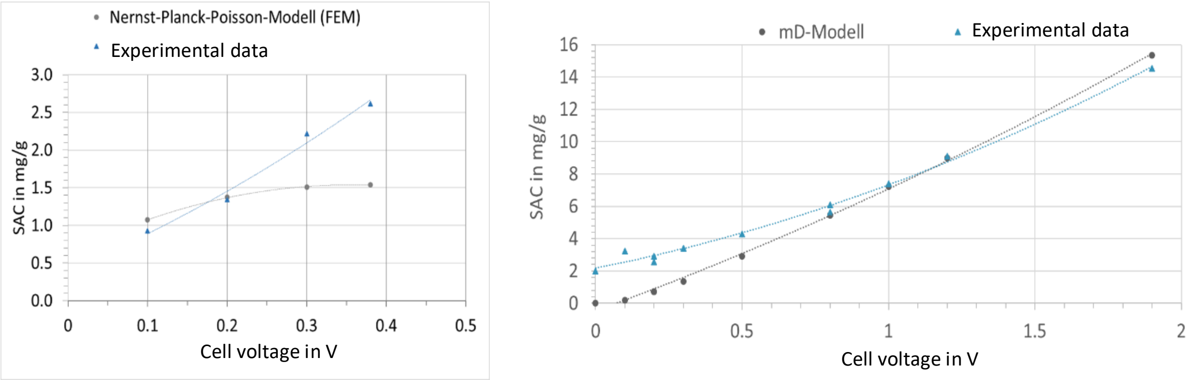

Figure 1. *Comparison of models with experimental data. Left: 2D-FEM model, right: 0D semi-analytical*

MFI Zeolite Membranes and Vacuum Membrane Distillation: a Combination for Desalination

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Abstract

Water is an essential resource for assuring socio-economic development and maintaining healthy ecosystems. However, the urbanization and industrialization caused a growing scarcity of fresh water. In this scenario, seawater is the most abundant source to obtain drinking water and/or water for industrial and agricultural use [1]. Membrane technology seems to be extremely important for solving water shortage problems [2]. In fact, polymeric membranes are widely used at industrial scale for seawater desalination. On the other hand, they present different drawbacks as low chemical stability, fouling and short lifetime. Inorganic membranes (main types are ceramic, silica, zeolite and carbon) characterized by high thermal, mechanical and chemical stability can be used when polymeric ones fail [3]. The zeolite membranes unlike all other inorganic membranes present also pore size at molecular scale and so can separate liquid and gas mixtures of species with similar size and shape. In particular, MFI membranes with pore size (of about 5.5 Å) lower than different hydrated ions can achieve good salt rejections [4, 5].

We developed zeolite membranes with a length of 30 cm by means of the secondary growth method coupled with the cross flow seeding procedure and using a fast heating profile for the template removal (calcination step) [6, 7]. The prepared membranes were characterized in desalination process by vacuum membrane distillation. Salt rejections of 99.9% were obtained for feeds ranging from 0.2 M to 0.9 M. The highest flux (20.6 kg m^2 h) was measured for the 0.2 M feed, by working at 70 °C and 120 L/h [7]. While, a further permeate treatment (e.g., by RO) was required for 1.2 M feeds [7]. A comparison with literature data evidenced as these membranes showed higher fluxes and salt rejections than other inorganic membranes tested for water desalination.

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Investigating membrane distillation: thermal performance and low-temperature applications

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Abstract

Membrane Distillation (MD), being able to theoretically reject 100% non volatile compounds present in aqueous streams, is an interesting tool for water and wastewater treatment. The hydrophobic character of the microporous membranes used avoids the passage of liquid, allowing only water vapor and volatiles to be transferred from the feed to the permeate side. This means that in the same membrane module all toxic/undesired non volatile species can be retained in the retentate, while producing a high-quality permeate. New strategies were investigated to reduce the specific thermal energy consumption associated to MD, such as the coupling of Direct Contact Membrane Distillation (DCMD) with Air Gap Membrane Distillation (AGMD) [1], and to increase the water production by novel designs of DCMD flat membrane modules [2]. Moreover, the application of Vacuum Membrane Distillation (VMD) in the food industry, to concentrate at low temperatures the coffee extracts [3] and the date juices [4] was studied. Still related to the coffee industry, a new unit, the Vacuum Membrane Dryer (VMDr), was used to dehydrate and recover the caffeine from the washwater produced during the caffeine extraction by supercritical CO_2 [3]. The efficiency of DCMD in treating at low temperatures (up to 50°C) aqueous solutions of urea was also analyzed, pointing out the need of developing membranes and modules "ad hoc" to improve the trans-membrane flux and, then, the productivity of the system.

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Recovery and purification of plant-derived compounds as biopesticides coming from tomato leaves

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Abstract

Pesticides are widely used in agriculture for the protection of crops from pests and consequently to increase crop productivity. However, the intensive use of pesticides can have a negative impact on the environment and humans. In recent years, plant-derived compounds used as biopesticides have received growing interest as a safe alternative to synthetic pesticides for sustainable agriculture. In this context, the tomato leaves represent a renewable source of biodegradable biopesticides such as oligogalacturonides for natural plant protection.

This work aims to recover/purify polysaccharide components from tomato leaves by aqueous extraction coupled with membrane operations. In this work, an integrated membrane-assisted biorefinery strategy was used to decrease the complexity of the solution, to extract the biomolecules of interest and to fractionate them. In particular, the extraction of biomolecules by varying the pH of the extracting solution was investigated. The aqueous extract coming from acidic treatment was then processed by ultrafiltration (UF, 30-50 kDa). Subsequently, the permeate coming from first UF step was treated with a second UF step (using membranes with lower MWCO, 5 kDa) for carbohydrates purification. For each step, membranes with different physical-chemical properties were investigated in terms of permeate flux, fouling index and bioactive compounds (carbohydrates, proteins, biophenols) rejection.

Results showed that i) the acidic treatment of extract permitted to increase the amount of carbohydrates released in the solution; ii) the regenerated cellulose membrane of 30 kDa allowed the removal of proteins from the extract in the retentate side with low carbohydrates and biophenols rejection and fouling index compared to other membranes tested; iii) the second UF stage, carried out

using polyethersulfone membrane, permitted the production of an enriched fraction of carbohydrates in the permeate side. In the future work, insecticidal effects of purified fraction of carbohydrates will be evaluated.

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Production of a phytotherapic with anticancer properties by intensified and integrated membrane systems

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Abstract

The high toxicity of chemotherapy and the resistance of cells to it in breast cancer treatment pushed the research in finding new candidates drugs. The use of plant material as source for new drugs is an already established method in pharmaceutical industry, but the need to find innovative sustainable production systems capable of converting vegetal materials into bioactive molecules using greener production processes and renewable material as a source of new drugs is a challenge.

In this work, a non-commercially available pure compound present in olive oil is produced by an integrated membrane process, using olive leaves as starting material and it has been tested *in vitro* for its potential antiproliferative activity on breast cancer cells. The integrated membrane process is composed by a membrane bioreactor (MBR) and a membrane emulsification (ME) process. In the MBR, the conversion of oleuropein extracted from olive leaves in oleuropein aglycone was carried out. The poor water soluble oleuropein aglycone (OLA) was then extracted in a green organic solvent to stabilize it.

A conversion of oleuropein in OLA of about 93%, for five consecutive reaction cycles in the MBR was obtained. The OLA produced was then extracted by ME in a green solvent reaching 90% of extraction efficiency and tested on two different line of breast cancer cells . Results of *in vitro* antiproliferative activity on breast cancer cells demonstrated that OLA compound inhibited anchorage-dependent and -independent cell growth and induced G0/G1 cell cycle arrest in both breast cancer cells tested. In particular, it enhanced the cyclin-dependent kinase inhibitor p21Cip/WAF1, p27 and p53 expression and decreased cyclin D/E expression at both mRNA and protein levels. In addition, it induced apoptosis (increased cleavage of PARP and caspace 3/8, enhanced Bax-Bad/Bcl-2-Bcl-XL ratio, marked DNA fragmentation) in both breast cancer cells. In conclusion, the synthetized compound showed antiproliferative and pro-apoptotic activities against breast cancer cells, suggesting it as a potential agent for breast cancer treatment, also in the occurrence of resistance to hormonal therapies [1].

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Membrane-based devices for controlled drug delivery

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Abstract

In the last decades, controlled drug delivery became one of the most important field in modern medication for maintaining the plasma concentration of a drug in the therapeutic range as well as for reducing the administration frequency and the occurrence of side effects. In particular, the scientists focalised their attention on the development of innovative release systems due to their advantages over traditional formulations [1, 2]. In this context, the production of membranes-based transdermal release devices offers the possibility to by-pass the gastrointestinal thus avoiding both, its irritation and the first-pass inactivation at liver level. Other advantages are the increase of drug bioavailability and therefore the improvement of the patient compliance [3]. Up to date different natural and synthetic materials for developing transdermal patches were exploited. Among them, mixed matrix membranes zeolite loaded (developed at CNR-ITM) were promising as potential devices for the controlled release of gemfibrozil [4], ibuprofen [5] and tramadol [6]. All the investigated systems exhibited a linear release kinetic; as it is required in the case of transdermal controlled delivery systems. Recently, we prepared poly(vinyl alcohol)-based membranes for the administration of the cardio selective beta-blocker metoprolol, which is used as antihypertensive and for the angina pectoris and myocardial infarct treatment [7]. Results of *ex-vivo* release experiments and data from different mathematical models (applied for understand the release mechanism of these membranes) showed a zero-order release profile of metoprolol.

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Zeolite membranes to control new solid formulations of Extra Virgin olive oil

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Abstract

This study deals with the design and manufacture of pure and hybrid synthetic (Mixed Matrix Membranes, MMMs) zeolite scaffolds (containing various amount of zeolite crystals dispersed in a polymeric matrix) to obtain new biomaterials. These scaffolds can potentially be used in the field of translational medicine to obtain innovative results to address tumorigenesis mechanisms with the promotion of an effort to deal with technical methods and information. Since olive oil has beneficial effects in healthy human cells and slows down and/or inhibits cell growth, the aim of this work was to monitor the protective and beneficial antitumor effects of olive oil in a new solid formulation (Spread Bio-Oil) on cancer cell cultured on zeolite scaffolds. In order to investigate the cytotoxicity of the new bio-oil spread and to test antiproliferative activity on the cancer cells we used two phenotypically different human breast cancer cell lines (MCF-7 and MDA-MB-231) seeded on various morphologies of zeolite membranes. We report the fabrication and characterization of pure and hybrid (MMMs) zeolite membranes and evaluated the intensively cell adhesion, spreading and cell growth by adhesion test, MTT, optical microscopy analyses and Scanning Electronic Microscopy (SEM) microphotography analyses. Our results demonstrate that both cell lines adhered and grow on all zeolite surfaces and that both show better viability after Spread Bio-Oil treatments. All cell adhesions are a specific membrane-type and, in particular, MCF-7 cells interact and adhere preferentially on pure zeolite membranes. Cancer cells seem to recognize and prefer the characteristics of the supports according to the following trend: Co-ZSM-5>Co-S-1>13X. Moreover, Co-ZSM-5 zeolite membranes were the best scaffolds and MDA-MB-231 cells after administration of Spread Bio-Oil showed less viability with respect to MCF-7 responding better to all concentrations of the innovative food. Our data indicate that Spread Bio-Oil decreases at very low concentration values (5, 10, 25, 50, 100, 200 and 300 μg/mL) cell proliferation in a dose- and time-dependent manner. The work confirms both the superiority of pure zeolite scaffolds for cultures of human normal and cancer cells and Spread Bio-Oil as an innovative food preserving all the beneficial and healthy properties of the extra virgin olive oil from which it derives[1].

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