[P2.030]

Understanding membrane fouling in produced water treatment: The effect of ionic strength

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Produced water is the largest waste stream generated by oil and gas production. Before disposal, this water has to be treated to remove the dispersed oil. Membranes can be used for this treatment, but fouling by the oil in the wastewater is often severe. In our research, we look into the fundamentals of membrane fouling by emulsified oil from a colloidal perspective, taking into account different parameters that play a role in colloidal and surface science (Figure 1)[1].

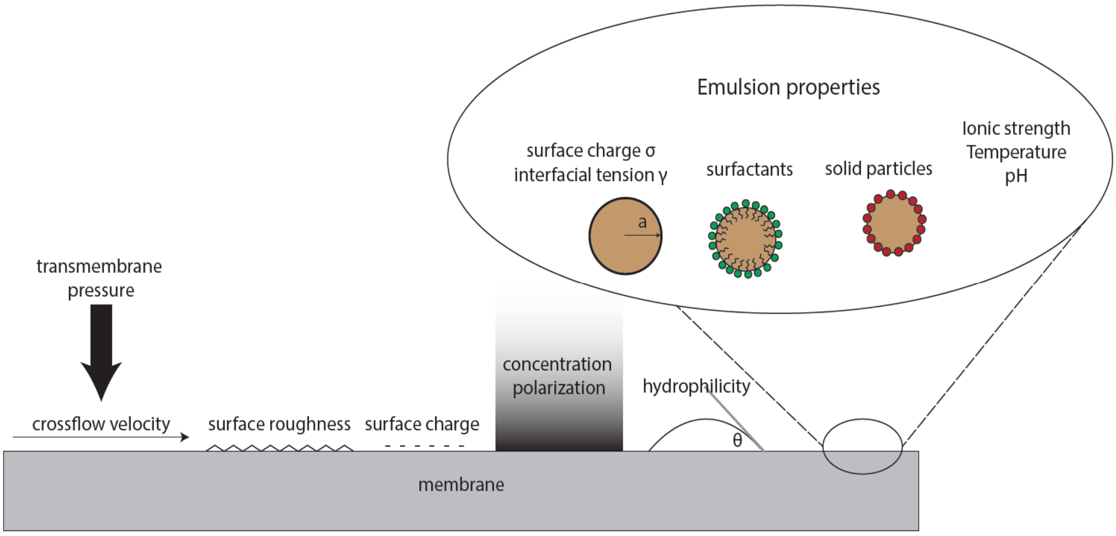

Figure 1: Parameters that play a role in membrane fouling.

To understand the interaction of oil droplets in an emulsion with a surface, flux decline experiments are compared with the adhesion of oil droplets to a glass model surface in a flow cell. This surface is modified to be hydrophilic or hydrophobic and the emulsion properties are varied to study the influence on droplet-surface interactions[2].

Figure 2 shows that increasing the salt concentration of the emulsion increases flux decline, which is a measure for membrane fouling. These curves, however, do not show what happens on the membrane surface. The results obtained with the flow cell can give additional insights.

Figure 3 shows the influence of the hydrophilicity of the surface on droplet behaviour.

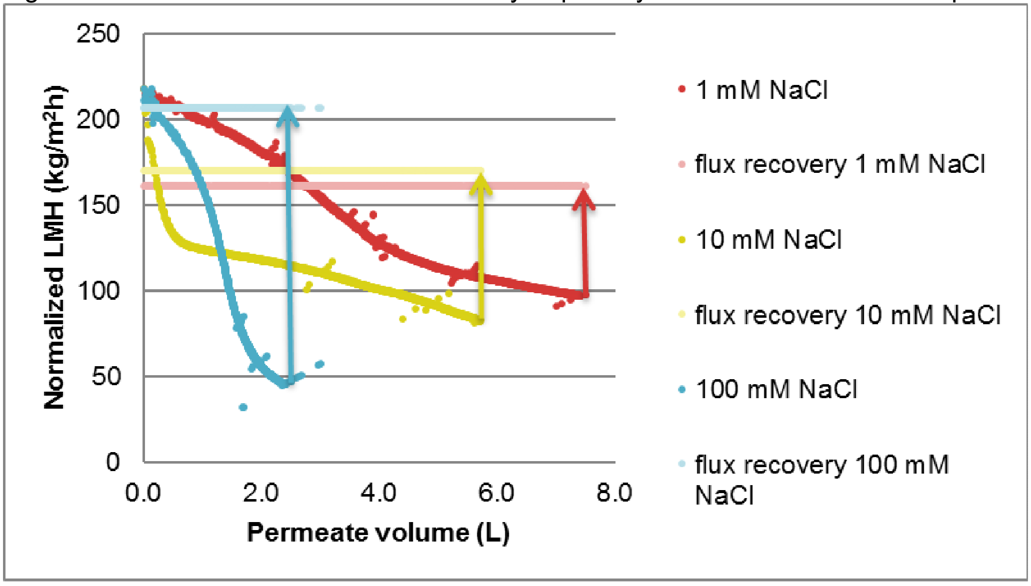

Figure 2: Flux decline curves of a UF membrane and an emulsion with varying levels of sodium chloride.

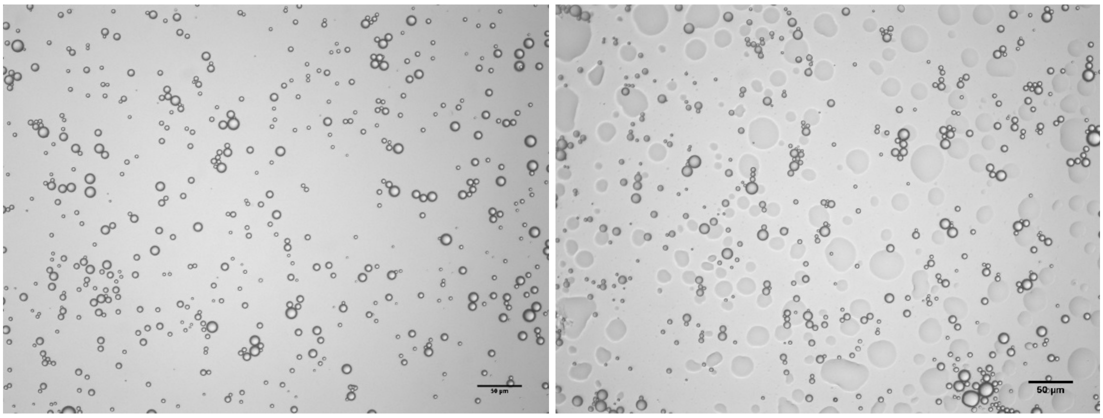

Figure 3: Oil droplets on a hydrophilic surface (left) and a hydrophobic surface (right) at 100mM NaCl.

Our results show that the fouling of membranes by oil-in-water emulsions and produced water is a complex interplay between emulsion and surface properties. We will discuss in detail how salt and the type of stabilizing surfactant affect the fouling propensity and flux recovery after physical cleaning.

[1] Dickhout et al., JCIS (2017), 487, 523

[2] Dresselhuis, et al., Soft Matter (2008), 4, 1079

Keywords: Microfiltration, polymeric membranes, colloids, produced water

[P2.031]

Impact of module geometry on the ultrafiltration behavior of polysaccharide-based vaccines

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Highly effective vaccines against diseases caused by Streptococcus pneumoniae have been developed using the capsular polysaccharide from these bacteria, often conjugated to a highly immunogenic protein. Ultrafiltration is currently used for purification and concentration of these vaccines, but there is relatively little quantitative data on the key factors controlling polysaccharide retention. In this study, we compare the ultrafiltration behavior of bacterial polysaccharides using different membrane modules to understand the effects of the module design and extent of concentration polarization on polysaccharide/conjugate retention.

Experiments were performed using several polysaccharide serotypes and the corresponding conjugates, both provided by Pfizer. Ultrafiltration data were obtained over a range of filtrate flux and polysaccharide concentrations using 500 kDa nominal molecular weight cut-off polyethersulfone membranes in stirred cells, tangential flow filtration cassettes (MilliporeSigma), and hollow fiber modules (SpectrumLabs).

Polysaccharide transmission increased with increasing filtrate flux in all 3 modules due to the effects of concentration polarization. Data for an uncharged serotype were in good agreement with predictions of the classical stagnant film model, with the lowest degree of polarization obtained in the TFF cassette due to the enhanced mass transfer provided by the screened channel. Results for the charged polysaccharides were considerably different in the dead-end and TFF systems. For example, transmission of a highly charged polysaccharide in the cassette and hollow fiber modules was below 25% over the entire range of filtrate flux, while nearly 100% transmission was obtained in the stirred cell at filtrate flux above 100 L/m^2/h due to differences in the hydrodynamics. These results provide important fundamental insights into the factors controlling the ultrafiltration behavior of bacterial polysaccharides, while guiding practitioners in extrapolating data from small dead-end filtration modules to the hollow fiber / TFF cassettes employed in manufacturing processes for these important polysaccharide-based vaccines.

Keywords: Module geometry, Ultrafiltration, Fouling, Bacterial polysaccharides

[P2.032]

Tailoring membrane surface properties and filtration performances via self-assembly of polysulfone-based amphiphilic block copolymer

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Recently, UF membranes have achieved very few improvements due to inherent material limitations and faced the great challenges including the limited control of the membrane surface and structure for high performances and antifouling properties in treating complicate solution systems. Novel membrane materials are desired to synthesize from molecular-level design approaches and to achieve the fine control of membrane structure and surface properties. Here, a particular type of amphiphilic block copolymer polyethylene glycol-block-polysulfone-block-polyethylene glycol (PEG-b-PSf-b-PEG) was synthesized through one-pot step-growth polymerization with mPEG as two ends to achieve the mobility of hydrophilic polymer chains. Without any other polymer or additive involved, the non-solvent induced phase separation (NIPS) method was used to fabricate the PEG-b-PSf-b-PEG UF membrane. The surface properties and filtration performances of UF membranes were tailored through the self-assembly behavior of PEG-b-PSf-b-PEG amphiphilic triblock copolymer combining the solvent and thermal annealing treatments in water at 90 °C. The annealed PEG-b-PSf-b-PEG membrane significantly enhanced its water flux resulting from the increased mean pore size with the improved porosity, as well as the decreased skin layer thickness, upon annealing. More importantly, the PEG-b-PSf-b-PEG membrane surface turned from hydrophobic to hydrophilic upon annealing with PEG enrichment on the surface, and exhibited the improved protein antifouling performances. Our research attempts to provide insights on the molecular-level design of membrane materials and the fine tailoring of the membrane structure and surface properties.

Keywords: Ultrafiltration, Block Copolymer, Self-assembly, Antifouling

[P2.033]

A greener membrane preparation via combined phase separation method (N-TIPS) using an environmentally-friendly solvent

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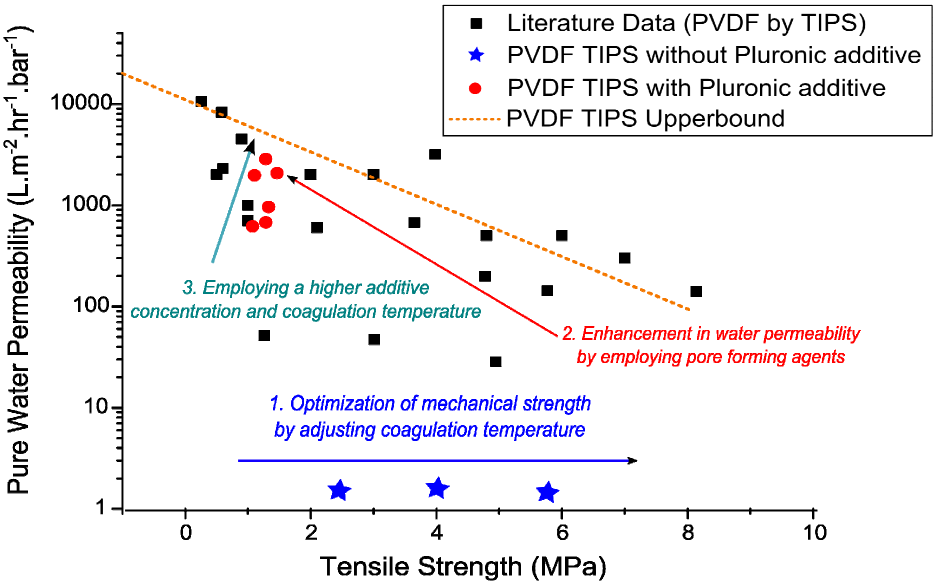
Introduction : Membrane market size is expected to reach $27 billion by 2018(1) and membrane technology is likely to be an indispensable technology in industrial processes with the advantages of environment-friendliness. However, toxicity of the solvents used in membrane preparation still remains as a pressing challenge. In fact, currently used solvents such as NMP (N-Methyl-2-pyrrolidone), DMF (Dimethylformamide), and DBP (Dibutyl phthalate) are facing regulations due to concerns over potential health and environmental issues so that finding alternatives for green membrane preparation is gaining a momentum.(2)

Methods : In this study, Pentanoic acid (Polarclean), which has shown a less impact on environment and provides a high solvent power as much as NMP(N-Methyl-2-pyrrolidone), was selected and studied for membrane preparation. The effects of polymer concentration, coagulation bath temperature and addition of additives were investigated. In order to compare performances with reported MF/UF membranes, the characterizations such as mechanical strength, pure water permeability, pore size distribution were conducted.

Results : Compared to a green solvent like DMSO, Pentanoic acid has stronger solvent power and thermal resistance, hence, more versatilities in dope composition and temperature control were allowed. In addition, Pentanoic acid is water-soluble so that it yielded synergic variation in final membrane morphology and performance.

Discussion : The greenness of Polarclean can make membrane preparation process sustainable and its high solvent power may provide future potential in membrane market. According to performance comparison using the upper bound(3), the membranes prepared in this study demonstrates the competitive performance compared to membranes reported from literature.



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(2) Jung, Jun Tae, et el. *Journal of Membrane Science*, 514, 250-263 (2016)

(3) Kim, Jeong F., et al. *AIChE Journal*, 62, 461-490 (2016)

Keywords: Greener membrane preparation, Non-solvent induced phase separation (NIPS), Thermally induced phase separation (TIPS), PVDF

[P2.034]

Development of UF hollow fiber membrane and module for pretreatment of RO process

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[Introduction]

Today, seawater desalination technologies are being studied extensively due to global water shortages. In the Middle East, seawater desalination is preferred not only for water quality but also for energy conservation. It is important to reduce the energy consumption of each unit as well as the RO process. We have studied energy saving UF membrane, module, and process.

[Methods]

Dope solution was prepared by using polysulfone polymer, NMP and additives. Hollow fiber membrane was fabricated using VIPS and NIPS processes. The hollow fiber membrane was moistened and dried to produce UF modules. Water permeability and tensile strength were measured as well as SEM images.

[Results]

The developed hollow fiber membrane was measured the water permeability of IN → OUT, OUT → IN. There was no difference in permeability when measured with a 1 inch small module. The tensile strength was 4 to 5 MPa. The permeability of sponge structure was slightly higher than finger structure, but tensile strength of finger structure was higher.

[Discussion]

The prepared hollow fiber membrane showed different water permeability and tensile strength depending on the morphology. There was no difference in water flux between IN → OUT and OUT → IN process. It would be shown different flux when the module size and area were expanded at same pressure. In the out → in process, the operating pressure must be increased because dead zones occur in larger module. For this reason, hollow fiber membrane with good tensile strength and elongation should be used at higher pressure but energy consumption is high. We are going to investigate about it as we increase the size of the module.

Keywords: UF membrane, RO pretreatment, Polysulfone, Hollow fiber membrane

[P2.035]

Study on the interfacial activation of dual surfactants in the process of forming porous membranes

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In order to regulate the microstructure of separation membranes and further investigate the mechanism of membrane preparation. Polyvinylidene fluoride (PVDF) hollow fiber membranes were fabricated by NIPS using dual surfactants (Span80 and Tween80) as the additive. Exactly, the dual surfactants have the specific value of Hydrophilic-Lipophilic Balance (HLB). Here we evaluated the Hydrophilic-Lipophilic Balance offset value (□HLB) on the membrane relative properties such as the pure water flux, SEM etc. As results indicated, in the membrane preparation process of NIPS, the surfactant could activate the interface of polymer concentrated phase when the casting dope transits from the stable region to the unstable region. Also, when the value of HLB approached to 10, the interfacial activation of the dual surfactants was obvious, eventually leading to more pores on the skin layer. Meanwhile the membrane intrinsic resistance was the lowest. They are also featured by the most probable aperture moving toward the maximum pore size. Most importantly, compared to the separation membrane without the surfactant, the pure water flux increased by 277%, reaching up to 1015 L/ (h·m^2). This research introduces a new pore-making strategy of the surfactant interfacial activation on polymer concentrated phase, which involves a novel film-forming mechanism in NIPS.

Keywords: hollow fiber membranes, non-solvent induced phase separation, Hydrophilic-Lipophilic Balance, interfacial activation

[P2.036]

Stepwise fabrication of oligoamide film on ultrafiltration membrane to control and improve its performance

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Ultrafiltration (UF) membranes are widely used in wastewater treatment, hemodialysis, food and beverage industries, and others. It is highly important to control and adjust the properties of the UF membranes according to a particular application. Here we propose a scalable method of coating the porous UF membrane by oligoamide synthesized by stepwise reaction between trimesoyl chloride (TMC) and meta-phenylene diamine (mPD) [1]. Variations in number of synthetic cycles of oligoamide induce different thickness of coating, hence different pore size.

The first stage was surface amination of polyacrylonitrile (PAN) membranes which was achieved by the partial reduction of nitrile (-CN) groups of the membrane using diethyltriamine (DETA) and sodium carbonate under heating [2] [Figure 1]. The amine content of the aminated-PAN membranes were determined by dye specific staining method using orange II.

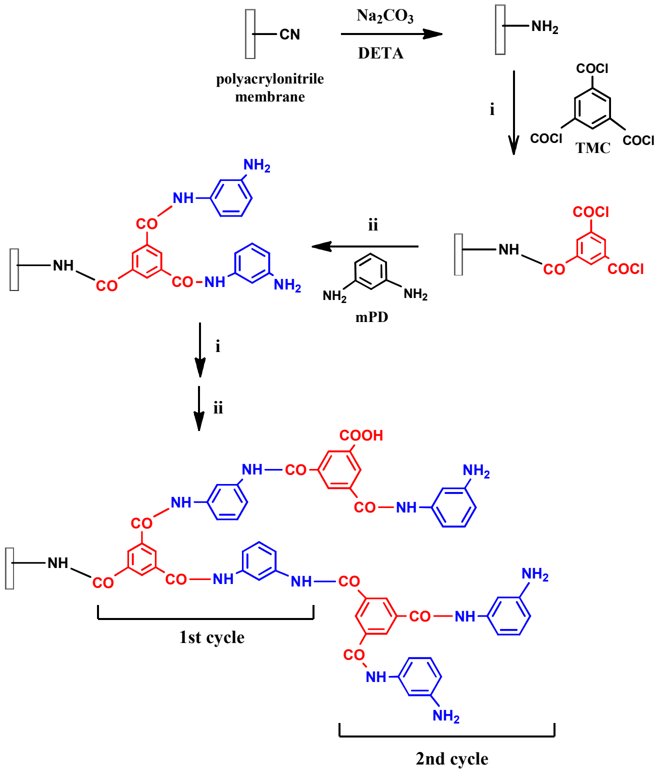

Figure1. Stepwise preparation of oligoamide on aminated-PAN membrane

Then, oligoamide coating of aminated-PAN membranes was prepared via the stepwise protocol and the surface properties of the membranes were characterized. ATR-FTIR analyses gave clear indication of polyamide peaks on the membrane surface which indicates the oligoamide formation. Filtration experiments were performed, and showed a reduction in water permeability of the modified membranes (from 535 to 69 $L/m^2h\cdot bar$ for unmodified PAN and 10 cycles oligoamide, respectively) in direct correlation with number of synthetic cycles of the oligoamide coating. The rejection of polyethylene glycol with different molecular weight range was used to evaluate the membrane transport properties, which also indicated a direct influence of number of synthetic cycles of oligoamide.

The results of this study may be used in the future to fabricate UF membranes with precise transport properties by controlling the number of synthetic cycles of oligoamide coating on membrane.

1. Steiner, Z., et al. Chem Comm **47**: 2384-2386.

2. Hong, G., et al. J Haz Mater **295**: 161–169.

Keywords: Ultrafiltration, Oligoamide, Stepwise preparation, Membrane coating

[P2.037]

Direct numerical simulation of cake formaiton in cross-flow microfiltration process

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Microfiltration of particles and microorganisms is an essential technique in various industrial processes. In the microfiltration, particles deposit on a membrane surface and form a cake layer. The cake layer leads to filtration resistance and membrane durability. In general, cross-flow microfiltration is employed because the tangential flow enables to wash away the cake layer or supress the cake formation. For optimization of cross-flow microfiltration process, it is necessary to understand the mechanism of cake formation more essentially. In this study, we investigated the factors affecting the cake formation in the cross-flow microfiltration by numerical simulations.

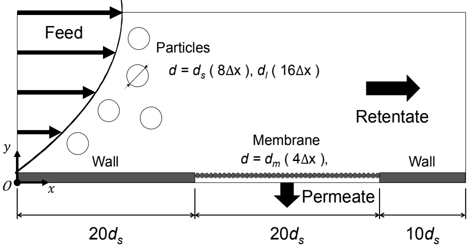

Fig. 1 Computational domain

The simulation model was based on the scheme where the discrete element method (DEM) for a particle computation and the lattice Boltzmann method (LBM) for a fluid computation are two-way coupled with the smoothed profile method[1)].

We simulated the cross-flow filtration under a constant pressure condition (Fig. 1). The solvent permeated through the membrane that was represented by small particles, and the dispersed particles accumulated on the membrane to form a cake layer. The effects of volume fraction ϕ on the cake formation were investigated. The time variation of the numbers of particles included in cake layer is shown in Fig. 2. For the all conditions the numbers increased with the increase of filtration time and reached a pseudo-steady value. The cake layer grew more drastically in the early period ϕ = 20%. This is reasonable because the feed suspension contains more particles per filtered volume for higher volume fraction. The number at psuedosteady state was higher at ϕ = 20 %, demonstrating that higher volume fraction provides a lower cake resistance. Using this model, we further investigated the effects of the other factors on cake formation.

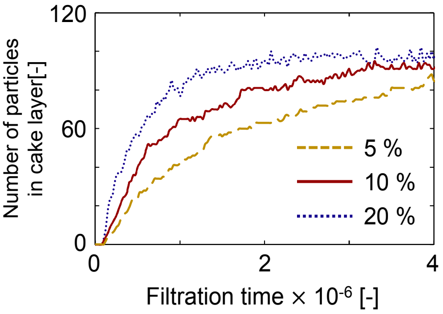

Fig. 2 Time variation of number of

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1) Y. Nakayama and R. Yamamoto, *Phys. Rev. E.* **71**, 036707 (2005).

Keywords: cross-flow filtration, microfiltration, simulation, cake layer

[P2.038]

Influence of polystyrenesulfonate on the performance and fouling properties of the polyvinylidene fluoride based ultrafiltration membranes

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Polyvinylidene fluoride (PVDF) as a thermal and chemically stable polymer, with applications in membrane fabrication, was chosen as the base polymer for the fabrication of durable ultrafiltration (UF) membranes. However, despite the physical attributes PVDF presents the issue regarding its hydrophobic nature remains a limitation. Membranes fabricated using pristine PVDF powder are prone to rapid fouling, which negatively affects their applications, performance and lifespan. This, in turn, escalates the overall operational costs due to required frequent backwashing, chemical washing, and/or membrane replacement. To address PVDF limitations and/or challenges, bulk modification of the polymer via chemical grafting with hydrophilic polystyrene sulfonate (PSS) onto PVDF was performed to improve its characteristics. The grafting of PSS was verified through $^{+}$H NMR and FTIR. UF membranes were prepared from the grafted powder via phase inversion immersion precipitation method. The morphology of the fabricated membranes was determined by SEM and AFM and the results showed a decrease in roughness with an increase in PSS loadings. Similarly, the contact angle was also found to decrease with an increase in PSS loading signifying improvement on hydrophilicity. The membranes also showed great stability over a range of temperature during DSC and TGA analysis. The resulting membranes were also tested for pure water permeability, rejection and fouling. A rapid increase in permeation was observed with an increase in PSS loading from 1 to 3 wt.%. The permeation results were complemented by excellent rejection performance of above 90 % across all formulations including the pristine membrane. An improvement in flux recovery was observed with an increase in PSS loading even though 1 wt.% PSS loading gave less flux recovery than the pristine membrane. The membranes will play a vital role in treating borehole or surface water for drinking purposes particularly around disadvantaged communities.

Keywords: Polynivylidene sulfonate, Polystyrene sulfonate, chemical grafting, fouling

[P2.039]

Study of the transfer mechanisms of a single protein solution during ultrafiltration in water/ethanol media

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Ethanol is widely used to extract valuable compounds from renewable resources. However, other separations are generally necessary to recover the target components. Ultrafiltration could be used considering that macromolecules can enter the composition of the extracts.

For safety reasons, the standard UF pilots commonly used for aqueous media cannot be used in pure ethanol. But an alternative is to achieve an appropriate dilution by water (maximum 30% ethanol v/v).

Nevertheless, the understanding of transfer mechanisms through UF membrane in water/ethanol remained a bottleneck for the UF simulation because of the change in the dielectric constant and the viscosity of the solvent mixture.

This work aimed at studying the impact of ethanol on the transfer mechanisms of a model protein (lysozyme: 14.3 $kg.mol^{-1}$, pI= 10.7, Stokes Radius =1.8 nm) during UF in water/ethanol (up to 30%). No significant protein denaturation occurred as depicted from ATR-FTIR.

The positively charged lysozyme was filtered (1 $g.L^{-1}$, 25°C, 2 bar, 4 $m.s^{-1}$, VRR=1) by a zirconia membrane (M1-Carbosep, 150 $kg.mol^{-1}$) modifying the physico-chemical environment by varying the pH (4, 7 or 9) and the ionic strength (I) with NaCl.

Regardless of the pH and the ethanol content, at I= 0 mM, the retention of lysozyme was 99%.

In 70/30 water/ethanol and I= 100 mM, the retention of lysozyme decreased significantly down to 75%, 25% and 0% at pH 4, 7 and 9 respectively, despite an increase in membrane fouling at pH 9.

The CDE model [1] (taking into account Convection, Diffusion and Electrophoretic migration) proposed in aqueous UF was used to analyse the results aiming at expanding the application range of this model.

[1] Rabiller-Baudry M., Chaufer B., Aimar P., Bariou B., Lucas D., J. Membr. Sci. 179(1), 163-174 (2000).

Keywords: ultrafiltration, protein, water/ethanol, transfer mechanism

[P2.040]

About the limits of microfiltration for the purification of different wastewater streams

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In the past, microfiltration was widely used as a pretreatment step for wastewater stream purification purposes. Experiences performed during the last years shows that microfiltration fails to maintain its performances for longer period of times. Many case studies demonstrate that the adoption of microfiltration leads to the failure of the overall process; the severe fouling of the microfiltration membranes leads to high operating costs with the consequence to make the treatment of the wastewater economically unfeasible.

The boundary flux concept is a profitable tool to analyse fouling issues in membrane processes. The boundary flux value separates an operating region characterized by reversible fouling formation from irreversible one. Bounday flux values are not content, but function of time, as calculated by the subboundary fouling rate value. The knowledge of both parameters may fully describe the membrane performances in subboundary operating regimes.

Many times, for wastewater purification purposes, ultrafiltration membranes appear to be suit better to the needs, even they exhibit lower permeate fluxes compared to microfiltration. Key to this choice is that ultrafiltration appears to resist better to fouling issues, with a limited reduction of the performances as a function of time. In other words, it appears that ultrafiltration exhibit higher boundary flux values and lower subboundary fouling rates.

In this work, after a brief introduction to the boundary flux concept, for many different wastewater streams (more than 20, produced by the most relevant industries in food, agriculture, manufacture, pharmaceutics), the boundary flux and subboundary fouling rate values of different microfiltration and ultrafiltration membranes will be discussed and compared. The possibility to successfully use microfiltration as a pretreatment step strongly depends on the feedstock characteristics and, in detail, on the particle size of the suspended matter.

In most cases, microfiltration demonstrates to be technically unsuitable for pretreatment purposes of many wastewater streams; as a consequence, the adoption of microfiltration pushes operators to exceed boundary flux conditions, therefore triggering severe fouling, that leads to economic unfeasibility of the process in long terms.

Keywords: boundary flux, fouling, failures, process feasibility

[P2.041]

Membrane biofouling control using membrane blended with quaternary ammonium compound assembled on carbon material

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Introduction

For the *in-situ* membrane surface modification, the antibiofouling efficacy is hindered by the inefficient presence of antimicrobial agents on membrane surface since they are blended with the polymers and distributed into the bulk membrane matrix. In this study, a compatible carbon carrier was adopted to assemble the quaternary ammonium compound (QAC@Carbon) for enhancing its surface segregation of polyvinylidene fluoride (PVDF) microfiltration membranes, thereby improving the cost-effectiveness in biofouling mitigation.

Methods

QAC@Carbon-blended PVDF membrane was denoted as MCQ. Membranes separately blended with carbon carrier and QAC were termed MC and MQ, respectively. XPS was performed to determine the elemental composition for surface segregation investigation. Biofouling experiments were carried out in a filtration reactor using *S. aureus* as feed solution.

Results and Discussion

Based on XPS data, MCQ had QAC/PVDF ratio of 15.1% on the membrane surface, which is 2.5-fold of the MQ (6.8%). The hypothesis of the surface segregation affected by carbon material is illustrated in Figure 1. The segregation of hydrophobic alkyl chains of QAC can cause a decline of solvent evaporation rate and decrease the exchange rate between the solvent and non-solvent during phase inversion, thus inducing a reduced QAC segregation on membrane surface. In contrast, hydrophilic carbon carrier compromised the segregation rate during the pre-evaporation process for MCQ membrane and caused less significant impacts on the exchange rate between solvent and non-solvent in the following phase inversion process.

In the biofouling experiments (Figure 2), the TMP increase rate of MCQ was lower compared to that of MC and MQ. Meanwhile, The biofilm layer on MCQ is thinner than those on MC and MQ membranes, and the relative abundance of dead cells of MCQ was clearly observed, confirming that MCQ membrane can inhibit growth of microorganisms and enable a long-term antibiofouling efficacy.

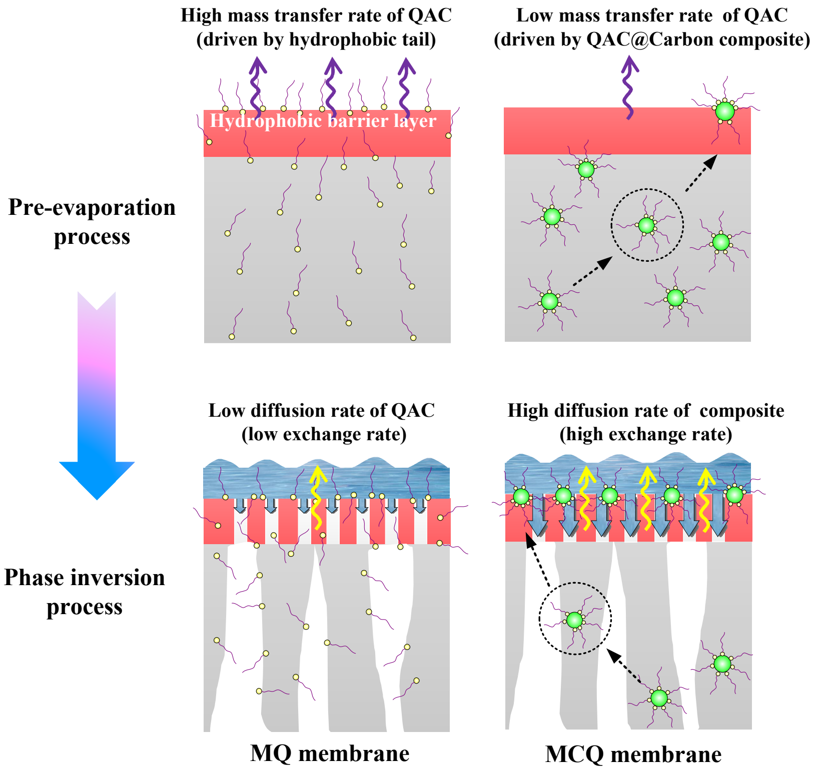

Figure 1 A schematic representation of the influence of carbon carrier on QAC segregation

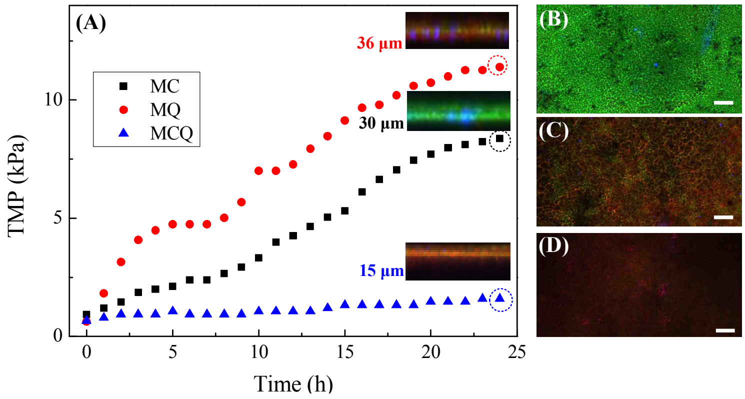

Figure 2 Biofouling behaviours of modified membrane. (A) Variations of TMP for MC, MQ and MCQ membranes as a function of time, and representative confocal microscopy side view of the biofilms formed on MC, MQ and MCQ membranes after 24-h operation; CLSM images of the biofilms of (B) MC, (C) MQ and (D) MCQ membranes after 24-h operation. Biofilms were stained with Con A (blue), SYTO 9 (green), and PI (red) for EPS (polysaccharides), live and/or dead cells, and dead cells, respectively. White bar represents a length of 20 µm.

Keywords: Antibiofouling, Membrane preparation, Surface segregation

[P2.042]

Effects of thermally induced phase separation (TIPS) parameters during fabrication of microporous polyvinylidene fluoride (PVDF) membranes using green solvent

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PVDF is widely used in membrane application during its high chemical corrosion resistance and heat resistance. Currently, TIPS method is frequently used to fabricate microporous membranes. Its high reproducibility with lower tendency for defect formation and narrower pore size distribution, rendering the method more suitable for microfiltration and ultrafiltration applications.

Membrane technology is considered a green technology compared to other conventional technologies. On the other hand, the membrane fabrication technique is not exempt from the green issues. In fact, conventional solvents used in TIPS method can potentially cause health and environmental impacts.

In this sense, many solvents have been investigated to replace the conventional solvents to green ones. Among those, a kind of citrate based solvent called ATBC provides a suitable solvent power and less environmental impacts compared to conventional solvents for membrane fabrication via TIPS method.

In this presentation, some of the key TIPS parameters that affect the membrane morphology and performance will be discussed such as the polymer concentration, polymer-solvent interaction and stretching protocol using design of experiment.

Tensile strength was increased according as an augment the concentration of polymer. By employing stretching method, it was able to improve the permeability of the membranes up to 538 LMH/bar with an 8.8 MPa tensile strength. On the contrary, the elongation at break was drastically dropped from 55% to 4%.

The polymer concentration increased up to 50wt% to improve the mechanical strength of the membranes fabricated by TIPS method. The nascent membranes were subsequently stretched to improve the porosity and permeability, while modifying the mean pore size. A DOE was conducted to optimize the stretching method among temperature, stretching ratio, and holding time as the independent factors under control. Depending on the application, suitable elongation conditions should be selected so as not to cause excessive strain while improving membrane permeability.

Keywords: Thermally induced phase separation, Microfiltration/Ultrafiltration, PVDF membrane, Green solvent

[P2.043]

Hollow fibre membranes: Effect of chemicallyenhanced backwashing on their structure and mechanical integrity

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In this study, commercially available PES membranes were used in to study the effect of chemically enhanced backwashing. This study involved subjecting lengths of inside-out filtration polyethersulphone (PES) hollow fibre membranes to varying chemical types, concentrations and durations either by soaking or spraying the fibres. Scanning electron microscopy (SEM) was used afterwards to examine the effects of the chemicals on the membrane structure.

In order to spray the chemicals, a rig was designed which operated with the aid of a peristaltic pump to introduce some pressure into the system. This is therefore more representative of a real backwashing system than soaking the fibres. Chemical types, durations and concentrations were selected to represent at least half a year of hollow fibre plant operation so that a real plant could be simulated more closely.

After soaking in 5% hydrogen peroxide for 10 minutes (in terms of chemical load expressed as

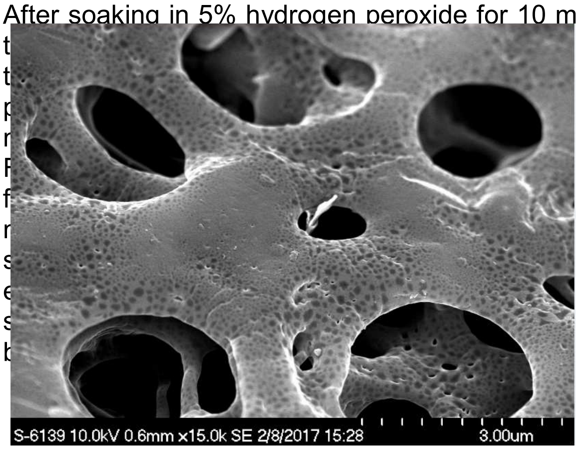

Figure 1: Soaking in 5% H2O2 for 10 mins

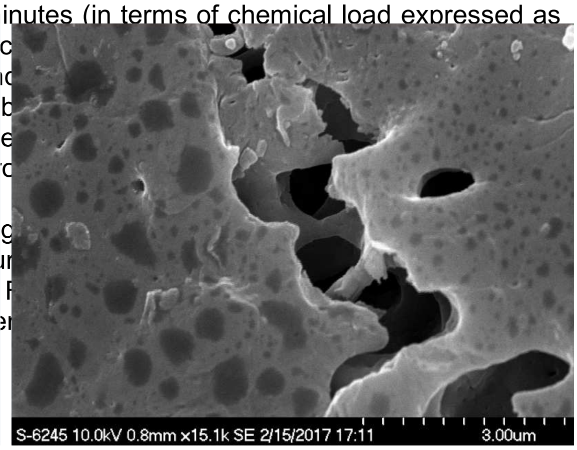

Figure 2: Deformed untreated fibre

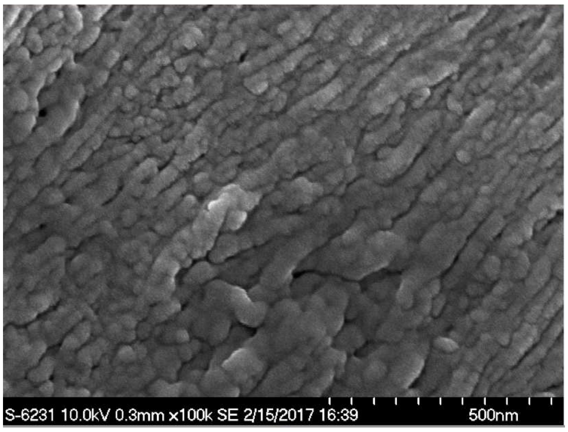

Figure 3: Spraying with 5% NaOCl for 1 hr - inner wall

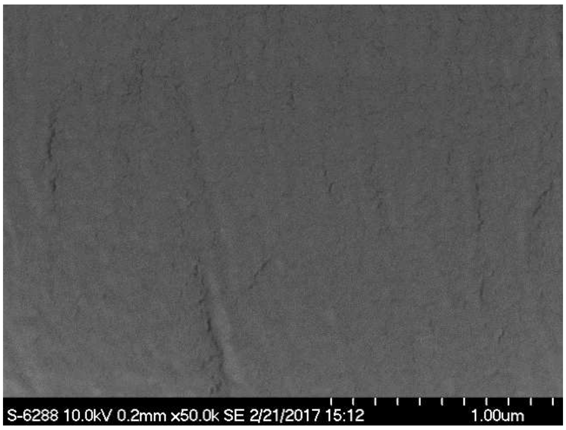

Figure 4: Untreated– inner wall

Keywords: Backwashing, Structure and Mechanical Integrity, Hollow fibre membranes, Chemically enhanced backwash

[P2.044]

PVDF/Palygorskite-g-poly(N,N-dimethylaminoethyl methacrylate) hybrid ultrafiltration membranes with enhanced flux and fouling-resistance

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PVDF is widely used in industrial applications, especially in water treatment such as microfiltration, ultrafiltration, and membrane bioreactors. Because of its poor hydrophilicity, these filters are vulnerable to the occurrence of fouling during treatment of aqueous solutions such as proteins, oils, subsequently leads to a sharp decrease in membrane permeation flux which limit applications to a certain extent. Previous works have shown that blending modification can improve the PVDF porous membrane performance in aspects of hydrophilicity, permeability, antifouling property etc. Adding inorganic nanoparticles has been extensively researched due to its simpleness. And it can improve the mechanical strength and high thermal stability of PVDF membranes.

In this study, the pH-responsive poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) modified palygorskite (PGS) was used as a hydrophilic modifier and hybrid ultrafiltration membranes were prepared. The membrane performance, especially the anti-fouling property, was then characterized. The results indicated that the modified membrane permeability was enhanced relative to the unmodified membrane, but maintained nearly unchanged retention. The maximum pure water flux was about 271 L•m-2•h-1, nearly twice that of the pristine membrane. During the filtration of BSA solution, the permeate fluxes of the modified PVDF membranes were much higher and declined more slowly than that of the pristine one. The modified fouling index analyses verified the reduced fouling tendency by incorporating PGS-g-PDMAEMA. This is a step forward in bringing organic-inorganic hybrid ultrafiltration membranes with superior properties such as environmentally sensitive performance, anti-pollution performance and easy cleaning performance for separation processes.

Keywords: PVDF, Palygorskite, PDMAEMA, Ultrafiltration

[P2.045]

Chitosan-graphene oxide lamellar membranes and application in wastewater treatment

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[3]State University of New York at Stony Brook, USA

Chitosan-graphene oxide (CSGO) nanocomposites have been investigated for various applications such as drug delivery, bone tissue engineering, and wastewater treatment due to the good stability and biocompatibility of the nanocomposites with excellent mechanical and thermal properties. GO particles help to overcome the CS drawbacks such as weak mechanical properties and the solubility of CS in acidic aqueous environments while CSGO membrane can benefit from the high performance of both the GO fillers and CS matrix. The performance and characterization of two different types of CSGO composite films were evaluated. Our results demonstrate how using different sizes of GO particles can affect the characterization and performance of these membranes. Granular GO (0.3-0.7 um in diameter) and nanoscale GO (90 nm in diameter) were used to make flat sheet membranes through solvent evaporation. Scanning electron microscopy (SEM) was used to study the morphology of the membrane. To study the molecular interactions between GO and CS, attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) was used. In addition, X-ray photoelectron spectroscopy (XPS) and high resolution x-ray diffraction (XRD) were used to determine the chemical composition and the crystallinity of the films. To study the mechanical properties of the membranes with and without GO particles, a universal mechanical testing machine (Instron) was used. Different surface and cross-section membrane morphologies were detected by using nanoscale and granular GO. In addition, the effect of the morphology on the membranes characterization and properties was investigated. Finally, the membranes were evaluated in a cross-flow system with methylene blue (MB) as a model organic contaminant to evaluate water flux and contaminant rejection. More than 90% of the methylene blue (concentrations ranging 1-100 mg/L) was rejected by CSGO membranes. Mass balances of the feed, concentrate, and permeate suggest the physical rejection is the dominant mechanism of dye removal.

Keywords: Graphene oxide, Chitosan, Membrane, Cross-flow filtration

[P2.046]

New gas separation membranes made by thermal treatment of blends of o-hydroxypolyimides and porous polymer networks

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Polymer membranes for gas separation is widely accepted as a valuable approach to separate complex mixtures of gases. However, classical approaches are not able to accomplish the needs of industry in order to obtain materials having large gas separation productivity in harsh conditions. In this context, thermal and chemical resistant polymeric materials having large gas productivities are extensively sought to be applied at industrial scale.

The use of thermally rearranged (TR) polymers for gas separation applications has marked a breakthrough, giving materials with outstanding values of productivity. TR polymers are materials where a solid state rearrangement from a rigid structure to another rigid one is carried out by a thermal treatment. Due to this conversion, materials with very high permeability and good selectivity have been obtained. In particular, some set of new gas separation membranes based on polyimides with ortho-hydroxy groups which undergo a thermal change to polybenzoxazoles (TR-PBO) have been developed. These new membranes are extremely efficient separating CO2 from other gases. In fact, these materials are so competent that their properties can be compared with carbon molecular sieves but having much better mechanical properties.

Recently, the preparation of mixed matrix membranes (MMMs), coming from a combination of a linear polymer having high gas productivity and cross-linked porous polymer networks (PPNs), has been shown as an excellent way of getting materials with excellent permeability/selectivity balances. However, the use of polymeric networks employed as load in MMMs where the polyimide matrix is going to undergo an additional thermal rearrangement (TR) process is more cumbersome due to the high thermal temperature employed in the process. Thus, the PPNs should be have degradation temperatures near 500 oC and it is well known that not many polymeric structures have this feature.

Our work recently has developed a feasible and low-cost synthetic protocol of formation of new high thermal stable PPNs, by reaction of aromatic compounds, having a required symmetry, with electron-withdrawing ketones. Some of these PPNs have shown BET surfaces larger than 800 m2/g and CO2 sorption values higher than 16% w/w at 273K (760 mmHg). Furthermore, these PPNs have shown initial degradation temperature higher than 450 oC. In this context, a new generation of gas separation membranes have been obtained by blending these PPNs with TR precursors (pristine o-hydroxy polyimides (OHPIs)), which has permitted to obtain homogeneous MMMs with excellent mechanical properties and good gas separation performances better than those of the pristine OHPI.

After a thermal treatment at 450 oC, the obtained materials showed excellent permeability to CO2, and good mechanical properties, similar or better than other TR membranes.

Keywords: Gas Separation, CO2 Capture, Thermal Rearrangement, mixed Matrix Membranes

[P2.047]

Synthesis of PVDF membranes with magnetic nanoparticles for applications in membrane distillation

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Introduction

In this work, magnetic nanoparticles (NP) were incorporated into PVDF membranes to improve their membrane distillation (MD) flux, based on a theoretically-demonstrated but never-practically-utilized effect of membrane conductivity on MD flux.

Methodology

Magnetite nanoparticles were synthesized from precursor salts ($FeCl_2$ and $FeCl_3$). The nanoparticles (1%) were then blended with PVDF (10%) in DMAc, casted on support mesh, then phase-inverted into membranes following a NIPS process (**Fig.1**). Extensive characterizations were done applying goniometric, microscopic, surface and spectroscopic methods to elucidate the structural and physiochemical properties of the membranes. A set of aggressive leaching tests were conducted using concentrated acid to study the stability of NP and the post-leaching properties of the membrane.

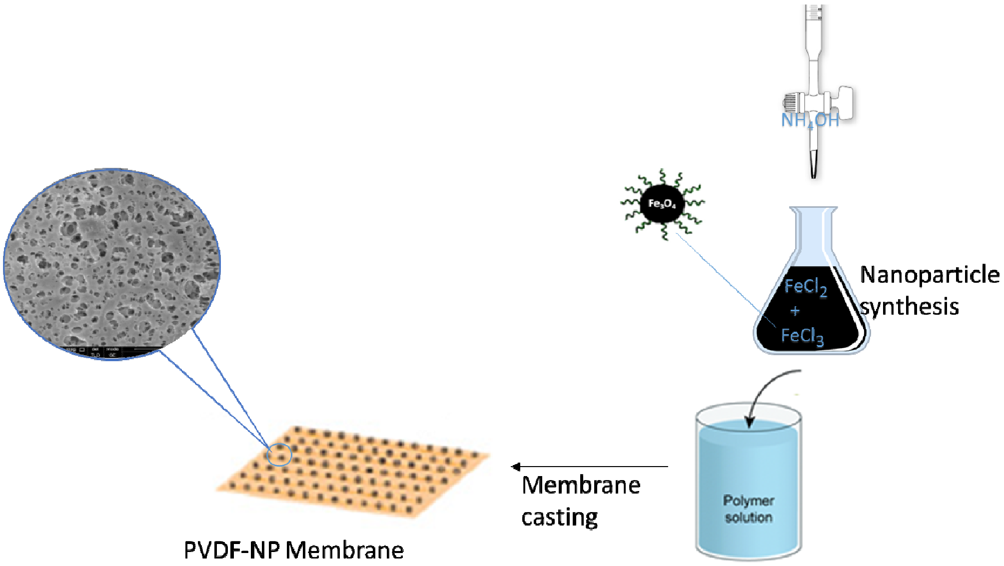

Fig. 1: **Preparation of the blend membrane**

Results

EDAX analyses showed a uniformly distributed NP within the membrane matrix. Also, as shown in **Fig.2(i),** the structure and morphology of the membrane was not affected by the addition or the subsequent leaching of the nanoparticles from the membrane. Contact angle values, which were 97.8, 99.2 and 100.1^0 for the PVDF, PVDF-NP and leached membranes, respectively, showed that the addition of nanoparticles did not compromise the hydrophobicity of the membrane. Also from the AFM data in **Fig.2(ii),** addition of nanoparticles lowered the roughness of the membrane. Significantly higher MD flux (ca. 150%) and higher salt rejection were achieved with the incorporation of magnetite nanoparticles as shown in **Fig. 2(iii)**.

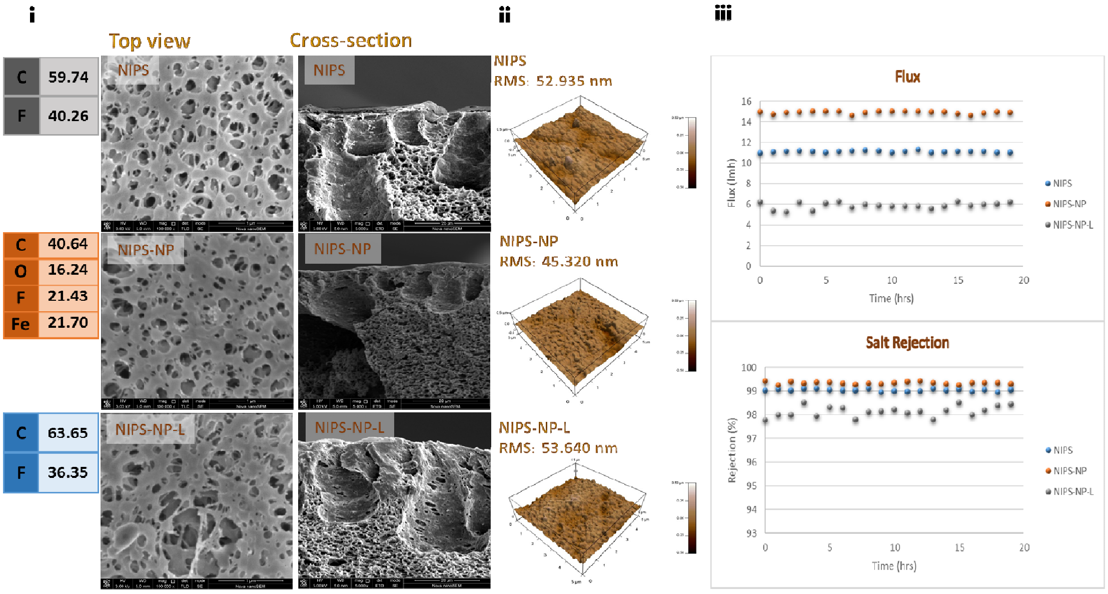

Fig. 2: (i) SEM and EDAX analyses, (ii)AFM topography, (iii) DCMD results of pure PVDF (NIPS), PVDF-NP (NIPS-NP) and leached (NIPS-NP-L) membranes

Discussion

The incorporation of magnetic nanoparticles in PVDF membranes using the method herein described improved the DCMD performance of the membrane without affecting its hydrophobicity. This is due to the coating of nanoparticles with a thin polymer layer as seen under TEM. The increase in flux is due to the presence of nanoparticles with high thermal conductivity in the membrane matrix. The NP were found stable within the membrane matrix with negligible leaching detected under normal MD operating conditions.

Keywords: Polyvinylidene fluoride, Magnetic Nanoparticles, Membrane distillation, Flux

[P2.048]

Mixed matrix membranes based on PPO with H_2-selective fillers

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We fabricated robust mixed matrix membranes (MMMs) based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and two commercial molecular sieves: Zeolite 3A and ZIF-8. The membrane preparation was optimized to allow the formation of films up to 45wt% of filler. The permeation, diffusion and sorption of He (used as a model for H_2), N_2, CH_4, CO_2 were investigated at 35, 50, 65°C.

SEM images showed good adhesion between the polymer matrix and both fillers. The dispersion of the fillers was homogeneous, with some aggregates at high loadings. DSC analysis revealed that moisture is entrapped in PPO/Zeolite systems, removable with a high temperature treatment. Conversely, PPO/ZIF-8 films were fully hydrophobic and amorphous.

Remarkable gas transport results were showed by PPO/ZIF-8 membranes, which revealed an increase of He permeability of around 800% with respect to the pure PPO and a He/CO_2 selectivity which was 15% higher at 35°C. The diffusivity is inversely proportional to the kinetic diameter of the gas, thus MMMs behave as molecular sieves. High loading PPO/ZIF-8 membranes show that relatively He solubility increase far more than that of CO_2.

The effect of temperature further enables the gas separation properties, indeed both He permeability and He/CO_2 selectivity increase sharply with increasing temperature. This aspect makes these materials even more interesting for industrial applications, which usually operate at temperature higher than the room temperature. The activation energy of the permeation and diffusion were evaluated, as well as their trend with filler content.

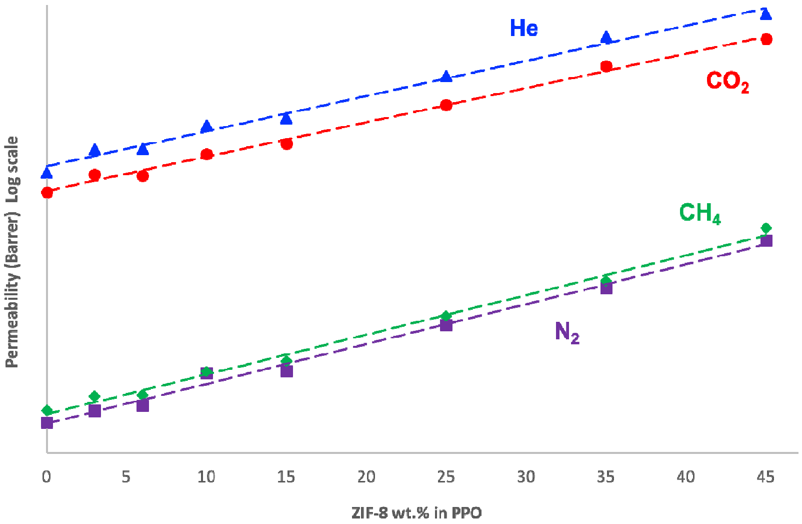

Figure 1: Enhancement of PPO membrane permeability by addition of ZIF-8 particles, at 35°C

This work has been done within the “Centre of Excellence on Clean energy” project (CUP: D82I13000250001), managed by Sotacarbo S.p.A. and funded by the Regional Government of Sardinia. The work was carried out in the framework of the project INSTM INDBO01183.

Keywords: Mixed matrix membranes, Pre-combustion separation, Hydrogen purification, Metal organic frameworks

[P2.049]

Polymer-grafted nanoparticle membranes with controllable free-volume

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Polymeric membranes used in gas separations are typically bound by permeability/selectivity limits, i.e., the Robeson Upper Bound. To be successful in a practical context, new membrane materials must exceed this current limit. We report here a membrane construct which may enable us to achieve this goal through the precise control of the polymer free volume to primarily affect molecular diffusion.

We developed a mixed matrix membrane composed of nanoparticles end-grafted with long polymer chains with varying grafted chain length and grafting density. The particular systems realized here consist of (rubbery) poly(methyl acrylate) (PMA) grafted spherical silica nanoparticles (14nm diameter) and (glassy) poly(methyl methacrylate) (PMMA) grafted silica. The materials were cast into thin films and the permeabilites of light gases measured using both steady gas permeation and transient sorption. The measured permeabilities do not follow conventional composite theory, which anticipate reduced *P* relative to the neat polymer. Instead, we find *elevated* gas permeabilities (Figure 1). This increase is controllable through variations in chain length and grafting density. For example, CO_2 permeability in PMA can be increased by up to an order of magnitude, with minor changes in CO_2/CH_4 selectivity.

The composite free volume as measured by positron annihilation lifetime spectroscopy (PALS, see Figure 2), pycnometry, and N_2 isotherms indicate that free volume is controllably altered through the grafting parameters. Further, we find that permeability increases and free volume changes are correlated. Measurements of glassy PMMA-grafted silica yield similar transport property changes, and also show a strong suppression of deleterious aging effects typical of glassy membranes. Evidently the enhanced gas transport changes in these grafted nanocomposite systems offer a novel platform for the rational design of both rubbery and glassy membranes with tunable free volume and permeability/selectivity exceeding the current best for many applications.

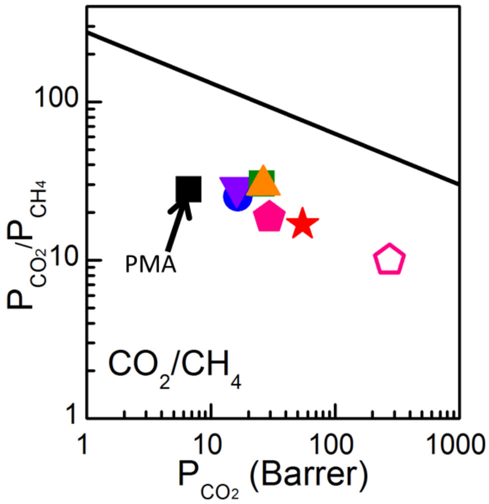

Figure1: Composite Robeson Plot

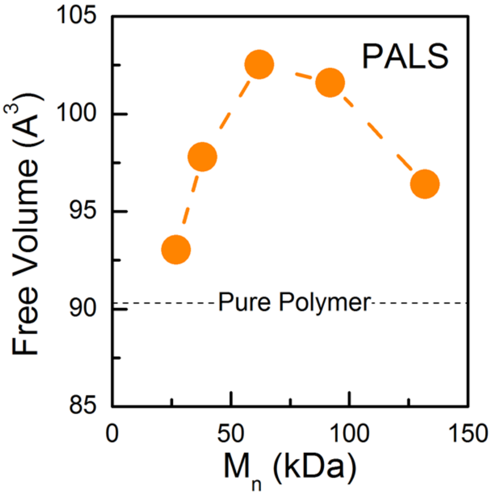

Figure2: Free volume enhancement

Keywords: PMA, grafted nanocomposite, free volume control, polymer aging

[P2.050]

Mixed-matrix membrane containing metal-organic frameworks for enhanced CO_2/CH_4 separation

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Numerous approaches had been utilised so as to enhance of CO_2/CH_4 separation capability considering that biogas upgrading could be feasible in overcoming the current increase in energy demand together with lack of diversification of available energy resources. CO_2 removal from biogas via membrane-based separation, which possesses the advantages of small plant footprint, low energy penalty and ease of fabrication into large-scale membrane modules had been focussed. However, as the performance of polymeric membranes are governed by the permeability-selectivity trade-off and the immense difficulty of fabricating inorganic membranes into large membrane areas, the incorporation of nanoporous fillers, particularly metal-organic frameworks have been proven to be feasible in improving both permeability and selectivity of a membrane.

In this study, $Zn(pyrz)_2(SiF_6)$ nanocrystals which possess pore size of 3.8 Å was incorporated into in-house polyimide membrane. This crystal had demonstrated strong CO_2/CH_4 separation capability in view of essentially zero CH_4 adsorption. Nonetheless, in our previous work[1], the submicron crystal size is still not small enough for effective gas separation. Thus, nanocrystal MOFs had been synthesised through sonochemical approach so as to create nanocrystals of close to 100 nm. The addition of 10 wt% loading into in-house polyimide was sufficient enough to overcome the Robeson Upper bound limit due to a strong improvement of CO_2 solubility and diffusivity in mixed-matrix membrane.

Furthermore, design of mixed-matrix membrane with amine-grafted HKUST-1 will be conducted. The presence of open metal sites in HKUST-1 allows the possibility to conduct post-synthetic functionalization[2] that allows enhancement in CO_2 uptake at low pressure. The inaccessibility of N_2 into the pores after grafting of amines into HKUST-1 allows an improved CO_2/CH_4 selectivity if amine-grafted HKUST-1 was incorporated into polymeric membrane. Besides, it was observed that the incorporation of amine-based adsorbents is generally more advantageous if the flue gas temperature is high.

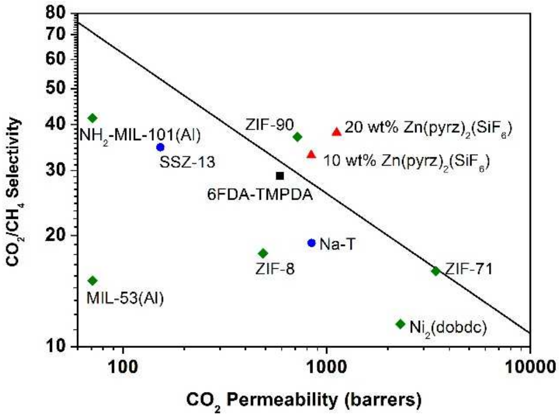

Figure 1 Performance of mixed-matrix membrane containing $Zn(pyrz)_2(SiF_6)$ nanocrystals in 6FDA-based polymers, with other fillers (zeolites and MOFs) in 6FDA-based polymers are included for comparison

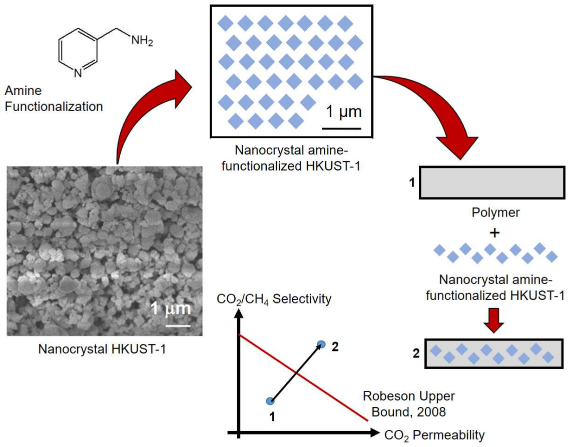

Figure 2 Executive summary of mixed-matrix membrane containing amine-functionalized HKUST-1

Reference

[1] H. Gong, T. H. Nguyen, R. Wang, T. H. Bae, Separations of Binary Mixtures of CO_2/CH_4 and CO_2/N_2 with Mixed-Matrix Membranes Containing $Zn(pyrz)_2(SiF_6)$ Metal-Organic Framework, *J. Membr. Sci.* **2015**, *495,* 169-175.

[2] C. Montoro, E. Gracía, S. Calero, M. A. Pérez-Fernández, A. L. López, E. Barea, et. al., Functionalisation of MOF open metal sites with pendant amines for CO_2 capture, Journal of Materials Chemistry, 2012, 22, 10155 – 10158.

Keywords: biogas, nanocrystal, sonochemical, post-synthetic functionalization

[P2.051]

TriNa/Pebax 2533 mixed matrix membranes for efficient CO_2 capture

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CO_2 capture and storage is gaining tremendous interests for energy, economic and environmental perspectives. Compared with conventional processes, membrane technology has presented excellent potential in CO_2 capture due to many advantages, such as no phase change, low energy consumption, ease of scale up and small footprint. Mixed matrix membranes (MMMs) comprised of a polymer as the continuous phase and a filler as the dispersed phase can offer one of the most potentially effective solutions to improve the CO_2 separation performance.

In this research, solvent-evaporation method was employed to prepare MMMs with different composition. Poly(ether-b-amide) (Pebax 2533) was chosen as polymer matrix, and the polyethylene glycol 200 (PEG200) solution of 1,2,4-triazolylsodium (TrizNa) and TrizNa were chosen as fillers. SEM, FT-IR, TGA and DSC were used to characterize the MMMs. The results show that the fillers are successfully incorporated into the polymer matrix, and the addition of all fillers have certain effects on the structure and thermal properties of the MMMs. When the filler loadings are not very high, the mechanical properties of the MMMs are still on a relatively high level. Compared with the pristine Pebax 2533 membrane, the CO_2 separation performance of MMMs are improved. When the loadings of PEG200 and TrizNa are 20wt.% and 3wt.% respectively, the CO_2 separation performance of Pebax 2533/PEG200/TriNa membrane exhibits best performance with CO_2 permeability of 219.55 Barrer, and the CO_2/N_2, CO_2/CH_4 and CO_2/H_2 selectivities of 32.33, 10.12 and 6.52, respectively. When TrizNa loading is 15wt.%, the Pebax 2533/TriNa membrane exhibits performance with CO_2 permeability of 219.01 Barrer, and the of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 selectivities of 27.40, 8.10 and 4.80, respectively. Improving operating pressure can increase CO_2 permeability and selectivities. With the increasing of operating temperature, gas permeabilities can be improved, but selectivities decrease.

Keywords: TriNa, poly(ether-b-amide), CO2, membrane

[P2.052]

Composite hollow fiber membranes using Pebax®1657/ ionic liquid/ graphene oxide mixed matrix membranes for improved CO_2 separation

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Blending ionic liquid with polyether block amide (Pebax®) to form homogeneous blends have achieved higher CO_2 flux due to enhanced CO_2 solubility, although at the expense of lower gas pair selectivity and mechanical strength. On the other hand, addition of nanofillers into the polymer matrix to form mixed matrix membranes (MMMs) increases CO_2 permeation due to increase in the tortuosity of gas diffusion pathway with simultaneous improvement in the mechanical strength. However, the incompatibility between polymer matrix and the fillers resulting in the formation of non-selective voids and lower gas selectivity is still one of the frequent challenges for MMMs.

In this work, Pebax®1657 was blended with [emim][BF_4] ionic liquid (IL) and graphene oxide (GO) to improve the CO_2 separation properties of the polymer in the form of thin film composite hollow fibers using a simple dip coating technique. The resulting Pebax®/IL/GO (1:4:0.035 w/w) hollow fibers (Fig. 1) have improved CO_2 permeability by 70% and marginally enhanced CO_2/N_2 and CO_2/CH_4 selectivities compared to Pebax®/IL (1:4). Selection of GO with high oxidation and excellent water dispersibility properties is of importance to ensure the compatibility with the polymer/IL matrix to allow thinner coating and improve gas pair selectivity.

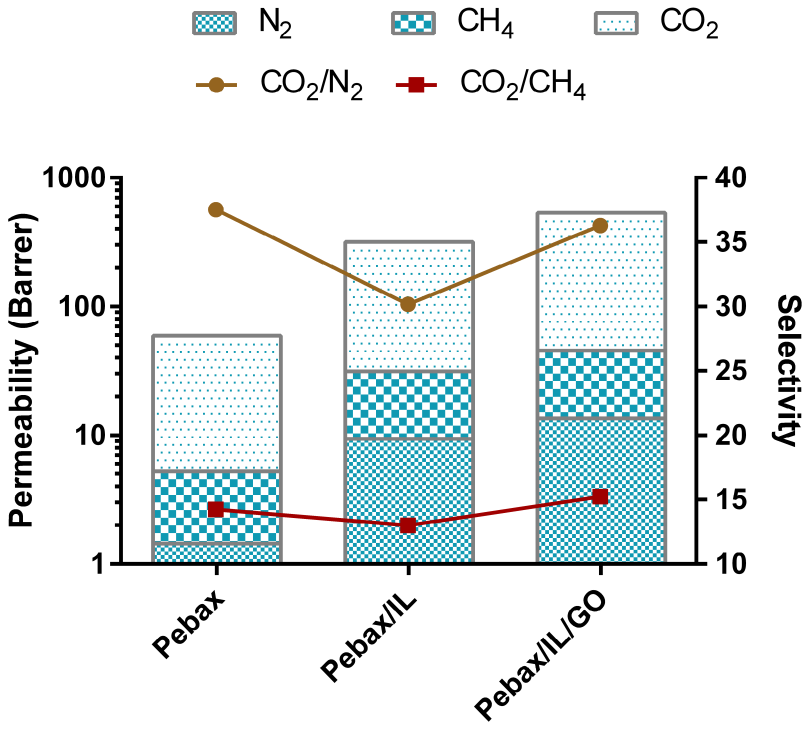

Figure 1. Effect of addition 80wt% IL and 0.07wt% GO on CO_2 separation performance at 25°C and 3 bar

Keywords: ionic liquid, graphene oxide, CO2 separation

[O7.48]

Crosslinking of polyurethane membranes for improved plasticization resistance for CO_2 capturing

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[1]Isfahan University of Technology, Iran, [2]Kyoto University, Japan

Low mechanical properties and high CO_2 plasticization limited the industrial application of polyurethane (PU) membranes. A series of a cross-linkable PU structure using a 1:3:2 molar ratio of pluronic® L-61, isophorone diisocyanate (IPDI) and 3,5-diaminobenzoic acid (DABA) was synthesized. The PU was crosslinked by a variety of crosslinking agents with different chain lengths and functionalities (hydroxyl and amine) in an esterification-based reaction to improve the mechanical properties and plasticization resistance. In order to facilitate the esterification reaction, thionyl chloride as the chlorination reagent was used to increase the conversion efficiency of carboxylic acid to acyl chloride groups. Pure gas (H_2, CO_2, N_2, CH_4) permeability experiments were carried out on the corsslinked PU (XPU) membranes. High CO_2 plasticization pressure up to 28 bar was observed for the crosslinked PU membrane with hexanediamine (XPU-HDA), which is more than two times higher than non-crosslinked PU and commercial membranes (PEBAX® 2533) (Fig.1). This chemical crosslinking of PU membranes, rigidifies the chains, reduces the dilution of the polymer and provides strong resistance to CO_2-induced plasticization. FTIR and DSC showed that the phase separation was more likely in XPUs, which is mainly related to the new crosslinked bonds within the hard segments that provide stronger interactions between the crosslinked hard segments and make them reluctant to mix with soft segment chains. An enhanced improvement of over 600% in Young's modulus and 200% in hardness for XPUs related to pristine PU was noticed. The CO_2 permeability of pristine PU decreased from 110 barrer to 77 barrer for XPU-HDA. Although gas permeability reduces slightly in XPU membranes, film formation ability and good mechanical properties and of the XPU samples facilitate their application as an ultra-thin film on the alumina support (Fig.2).

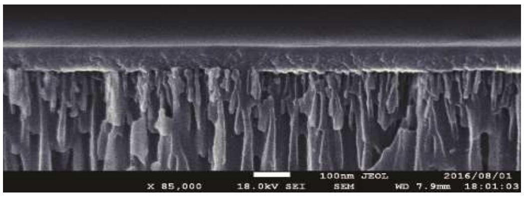

Fig 2. Cross-sectional SEM image of thin film. Scale bar is 100nm.

Keywords: Polyurethane, Carbon dioxide capture, crosslinking, plasticization

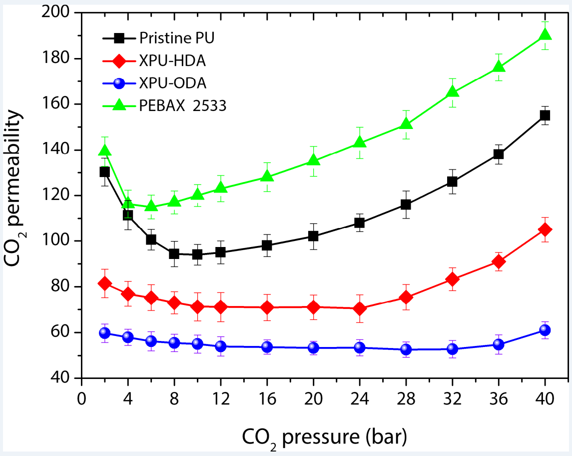

Fig. 1. CO_2 permeability of crosslinked PUs with different

[P2.054]

Improvement of the surface -wear resistance of ultrafiltration membranes with carbon nanotubes for the application of purification of fermentation products

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An ultra-filtration (UF) membrane process has been used for the purification and concentration of the metabolites, because of its high energy efficiency. However, still there are some difficulties, serious membrane fouling, in filtering highly viscose fermentation broth with conventional UF membranes. Therefore, to remove the foulants accumulated on the membrane surface effectively, physical cleaning devices such as a blade has been equipped into a membrane filtering system, and it performed good separation. But conventional UF membranes, when used for this membrane system, do not withstand long, and easily damaged during its operation because of the strong shear forces applied to the membrane surface by the mechanical cleaning devices. Such membrane system requires a new UF membrane with strong surface wear resistance. However, there is no current commercially available UF membrane with such high surface wear resistance.

So in this study, we have developed a new UF membrane with excellent surface abrasion resistance by effectively dispersing multi-walled carbon nanotubes (CNTs) throughout a UF membrane surface. Controlling the CNTs content and concentration of additives, the condition for the preparation of polyethersulfone (PES) UF membrane was optimised, and the resulting membrane exhibited excellent surface hardness and good permselective properties. The abrasion resistance of the membrane was found to be 15 times higher than the conventional UF membranes. The mean pore size of the membrane was 0.08 □m and its flux was about 549 LMH. The membrane system loaded with this membrane showed much improved performance and durability.

Keywords: ultrafilration membrane, carbon nanotubes, abrasion resistance, fermentation products

[P2.055]

A facile route for the fabrication of ultrahigh perm-selectivity thin film nanocomposite membrane with in-situ generated zwitterionic amine nanoparticles

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In the face of serious environmental pollution and water scarcity problems, membrane separation techniques, especially reverse osmosis (RO) and nanofiltration (NF), have been quickly developed. The research of mixed matrix polymeric membranes with incorporation of nanomaterials has attracted increased attention during the last two decades. In this work, we proposed a facile and simple route to the preparation of thin film nanocomposite membranes with in-situ generated zwitterionic amine nanoparticles (ZANPs) (with diameters ranging from 20 to 100 nm) (Figure 1). Chemical structures and the size of ZANP nanoparticles were determined by fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and dynamic light scattering analysis (DLS), respectively; and could be conveniently tuned by varying the concentration of the zwitterionic amine precursor and dopamine cross-linker in the aqueous solution. Subsequently, ZANP nanocomposite membranes (ZANPMs) were prepared by dip-coating the ZANP dispersion solution onto polysulfone ultrafiltration (PSF-UF) supporting layer, followed by interfacial cross-linked with 1,3,5-Benzenetricarboxylic chloride (TMC). Performances of the as-prepared nanocomposite membranes were characterized with field emission electron microscopy (FESEM), atomic force microscopy (AFM), water contact angle and nanofiltration test. The ZANPM membrane showed high water permeability (186.7 $L.m^{-2}.h^{-1}.MPa^{-1}$), which is 2 times higher than the pristine TFCM (57.5 $L.m^{-2}.h^{-1}.MPa^{-1}$) and good selectivity of MB dye, Na_2SO_4 and NaCl, respectively; (Figure 2). It was also demonstrated that the incorporation of ZANP nanoparticles increased the interfacial interaction of the selective and supporting layer, and enhanced the surface hydrophilicity, leading to an improved stability and anti-fouling properties. Therefore, this work opens up an innovative approach to construct thin film nanocomposite membranes and will be helpful to exploit advanced nanofiltration membranes for substance separation and water treatment applications.

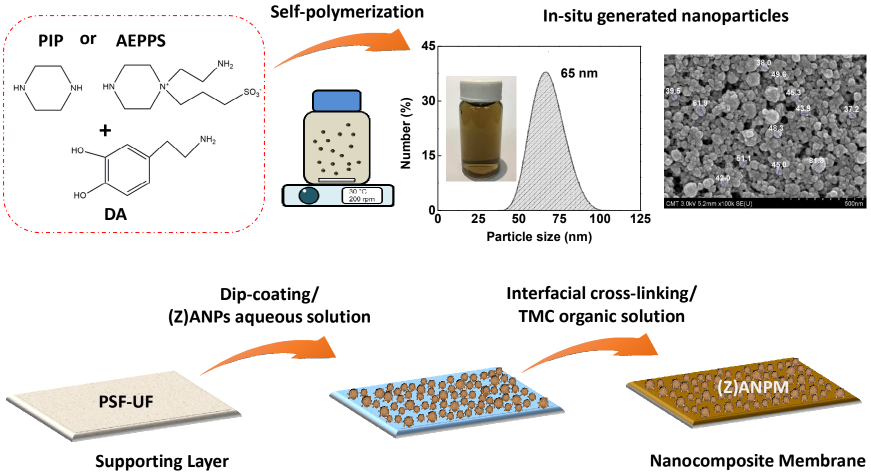

Figure 1. Schematic diagram for preparing thin-film nanocomposite membrane with in-situ generated (zwitterionic) amine nanoparticles (Z)ANPs.

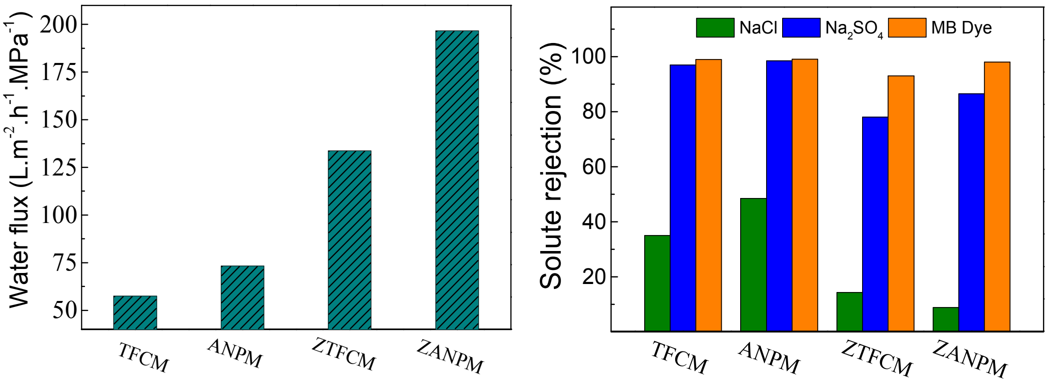

Figure 2. Nanofiltration performance of TFCM, ZTFCM, ANPM and ZANPM.

Keywords: nanofiltration, thin film nanocomposite membrane, zwitterionic nanoparticles, ultrahigh perm-selectivity

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Module optimization of endotoxin adsorbers using MRI

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Today more than 10% of the worldwide population suffers from chronic kidney disease (CKD) which is classified as a global public health concern [1,2]. Around two million of the CKD patients rely on lifesaving dialysis treatments. One of the known risks is the level of endotoxins in the dialysate stream fed to the patient during the treatment [3]. A complete removal of the endotoxins significantly improves the patient's survivability. Therefore, medical care companies, like Baxter, produce annually more than one million of the so called endotoxin adsorbers. These are dead-end filtration modules. A thorough product design is inevitable to manufacture cheap but efficient modules. Magnetic resonance imaging (MRI) is a powerful tool for membrane optimization since it non-invasively measures the fluid dynamics in opaque systems [4].

We have analyzed the potential of module optimization for Baxter's endotoxin adsorber using MRI. Particular emphasis has been put on the design of the inlet and the lid which affect the fluid dynamics. MRI measurements have been performed in-situ during filtration and the data have been analyzed using Matlab programming to create 2D flow maps. Using MRI we have visualized the interior structure of the module and the membrane could be illustrated with high contrast. Measured flow dynamics have revealed how the design of the inlet can cause maldistributions above the membrane downgrading the filtration performance.

Local flux has been resolved in the scale of hundreds of micrometers showing active and non-active filtration parts on the membrane. Time dependent cake layer evolution has been imaged showing silica particle deposition on the membrane surface. Subsequent changes in the flow have been observed depicting the higher resistance for the flow due to the cake layer.

We have shown that MRI can be extremely helpful as a tool for module design optimization.

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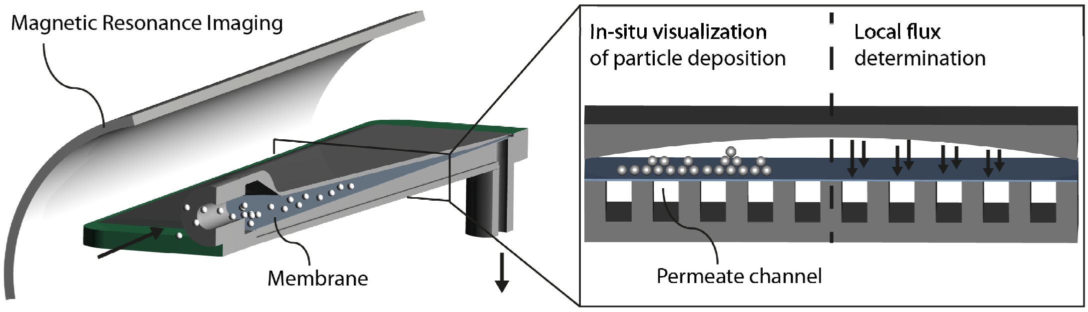

Keywords: MRI, local flux, silica filtration, fluid dynamics

[P2.057]

Fabrication of carbon nanotube/polyvinylidene fluoride composite membrane for CO_2 capture

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Increasing concerns over global warming is driving researcher to develop new technology for capturing CO_2, the major greenhouse gas emitted. Membrane gas absorption (MGA) is a new CO_2 capturing technology that combines membrane technique with chemical absorption. The key advantages of MGA are independently adjustable flow of gas and liquid, compact equipment, and relatively low energy consumption. However, development of new membrane with improved properties has been an emerging issue for its effective utilization. Among limitations of membrane, wetting is the main problem that always takes place in membrane gas absorber. In general, when membrane is used as a barrier to separate gas and liquid phase, one side of membrane would expose to gas while the other exposes to an absorbent, which could penetrate into the membrane pores, leading to lower CO_2 absorption efficiency and membrane damages in long-term operation. Membrane hydrophilicity is an important factor affecting membrane wetting. In general, membranes with higher hydrophobicity exhibit better stability because its hydrophobic surface prevents absorbent penetration into the membrane pores. This work focuses on the development of composite membranes, from carbon nanotubes (CNTs) and polyvinylidene fluoride (PVDF) for capturing CO_2 from flue gas by the MGA method. The CNT was used as the additive to improve membrane hydrophobicity. It was found that the addition of CNT has an influence on membrane surface morphology as well as membrane hydrophilicity. The feasibility study to use the as-synthesized composite membrane in CO_2 capture application by incorporating with monoethanolamine (MEA) as an absorbent will also be investigated and will be presented in the future.

Keywords: Membrane gas absorption, composite membrane, CO2 capture

[P2.058]

Properties of novel cellulose acetate propionate based materials containing reactive ionic liquid or plasticizer

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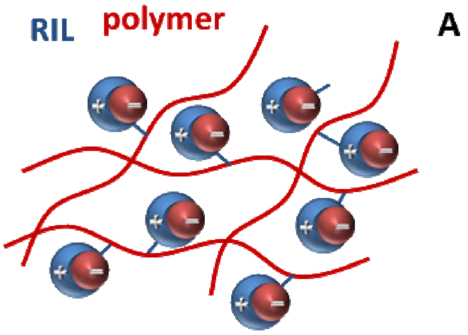
Due to their unique characteristics, ionic liquids (ILs) are used to tailor membrane properties. However, the drawback of such membranes is the gradual leaching of ILs from the membrane during exploitation.

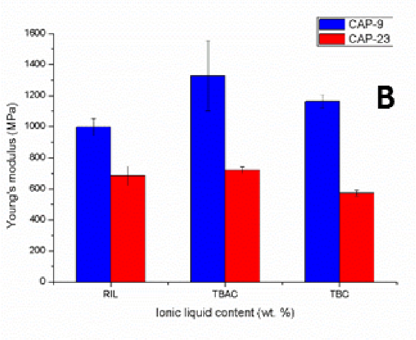
The main aim of this work was the preparation and comprehensive characterization of novel nonporous polymer membranes based on cellulose acetate propionate (CAP) with immobilized reactive ionic liquid (RIL): 3-(1,3-diethoxy-1,3-dioxopropan-2-yl)-1-methyl-1H-imidazol-3-ium bromide (Fig. A). This work was also focused on the evaluation of chemical and mechanical stability of CAP-RIL membranes in comparison to membranes plasticized using tributyl citrate (TBC) and acetyltributyl citrate (ATBC). Performed investigations broaden knowledge related with modification of membrane physicochemical properties; they are crucial in the development of membrane based technologies.

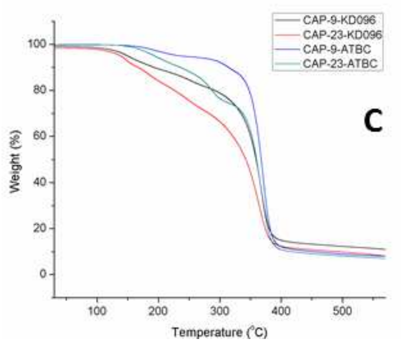
It was found that an increase of the RIL content decreases the Young's modulus and increases the elongation at break. This reflects the enhanced membranes flexibility and proves the RIL plasticization effect. The type of used component (RIL, TBC, and ATBC) possesses minor influence on membrane mechanical properties (Fig. B). Additionally, TGA analysis testifies that investigated membranes are thermally stable up to 100°C, whereas plasticized CAP based membranes show better thermal stability above 100°C (Fig. C). Contact angle measurements revealed the decreasing hydrophilic character of the membrane surface with increasing RIL content (Fig. D). The molar swelling degree is the highest in ethanol compared to water and propan-2-ol regardless of investigated membrane, whereas the RIL incorporation enhances the swelling ability of CAP based membranes (Fig. E).

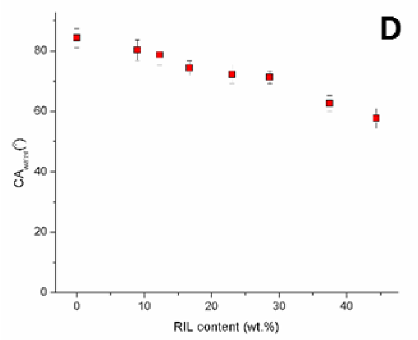
Acknowledgements

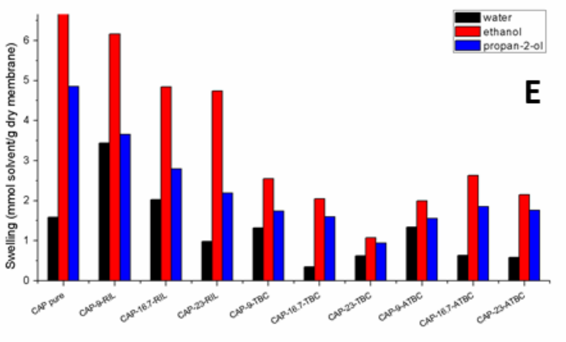
This project received founding from Polish National Science Centre (grant agreement No. DEC-2015/18/M/ST5/00635) and was supported by Hubert Curien's Partnership Program "Polonium" (35501/2016). Edyta Rynkowska is grateful for the French Government scholarship (grant No. 848642E, 878205J). This work is a part of the joint PhD of Edyta Rynkowska (Nicolaus Copernicus University in Torun, Poland and Rouen University, France).











Keywords: immobilized reactive ionic liquid (RIL), cellulose acetate propionate (CAP) MMMs, plasticizers: tributyl citrate, acetyltributyl citrate, physicochemical properties of CAP MMMs

[P2.059]

Highly porous carbon nanotube/polysulfone nanocomposite supports for high-flux polyamide reverse osmosis membranes

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Recent researches have emphasized that surface characteristics of supports play a significant role in reverse osmosis (RO) performances of thin film composite (TFC) membranes. In this study, we incorporated carbon nanotube (CNT) into polysulfone (PSf) matrix to tune the surface characteristics of PSf support for high-flux TFC membranes. The prepared CNT/PSf nanocomposite supports showed significantly improved surface porosity with maintaining both surface pore radius and hydrophobicity. Such surface characteristics were responsible for the defect-free formation of polyamide (PA) selective layer possessing large surface area which contributes to the flux enhancement. Consequently, PA-TFC membranes prepared with CNT/PSf nanocomposite supports represented improved water permeance at most 35% without losing salt rejection compared to the bare TFC membranes. The results revealed that the surface porosity of support is a dominant factor to determine the water permeance of TFC membranes rather than the pure water flux inside support itself or the thickness of PA layer. Furthermore, we propose a direction for the optimum supports through a comparison study between CNT and conventional pore formers (e.g. polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP)) as an additive into supports.

Keywords: Reverse osmosis, Support, Carbon nanotube, Nanocomposite

[P2.060]

Preparation of dual-layered nanocomposite membranes using graphene oxide and halloysite nanotubes for enhancing membrane performance in osmotically driven processes

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A novel thin-film composite (TFC) membrane with dual-layered substrate support was fabricated by double-blade casting technique using different polysulfone (PSf) concentrations for top and bottom substrate layers for both forward osmosis (FO) and pressure retarded osmosis (PRO) processes. Graphene oxide was applied for the preparation of the dual-layered FO membranes, and both GO and halloysite nanotubes were incorporated into the dual-layered substrate layer for the PRO membrane preparation. The double-blade casting approach resulted in a membrane support with a highly porous structure and a dense top skin layer on which the polyamide active layer was effectively formed.

The dual-layered TFC FO membrane with GO exhibited high water permeability and ion selectivity due to the presence of well dispersed hydrophilic GO in the PSf substrate which provided favourable condition for the polyamide layer formation. Using deionized water as feed and 1 M NaCl as draw solution (DS), it exhibited highest water flux of 33.8 $Lm^{-2}h^{-1}$, lowest specific reverse solute flux 0.19 gL^{-1} and much smaller structural parameter of 130 µm compared to single- and dual-layered GO-free TFC membranes.

The dual-layered TFC PRO membrane incorporated with GO and HNTs resulted in excellent power density of 20.6 Wm^{-2} at 24 bar using DI water as FS and 1 M NaCl as DS. The GO incorporated skin layer provided a suitable condition for polyamide layer formation while the HNTs incorporated bottom layer resulted in highly porous, hydrophilic and strong substrate that lowers the ICP and hence higher power density.

The overall results suggest that, the use of dual-blade casting is a promising technique for membrane fabrication is it provides flexible options for the optimisation of the membrane substrate layers both by altering polymer concentrations and nanomaterial incorporation in each substrate layer to produce osmotic membrane of excellent properties for FO and PRO applications.

Keywords: Dual-layered substrate, Graphene oxide, halloysite nanotubes, Mixed matrix membranes

[P2.061]

Synthesis and characterization of ZIF-71/PDMS mixed matrix membranes for the removal of ethanol and 1-butanol from water through pervaporation

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The zeolitic imidazolate framework-71 (ZIF-71)/polydimethylsiloxane (PDMS) mixed matrix membranes (MMMs) were prepared with two different PDMS systems: addition cure system and condensation cure system. The addition cure PDMS system is not compatible with ZIF-71 particles resulting in membranes with poor mechanical properties. Specifically, the imidazole ligand 4,5-dichloroimidazole impairs the cross-linking reaction between the vinyl terminated PDMS and the -SiH groups by poisoning the platinum catalyst. The membranes made with condensation cure PDMS method had good mechanical properties. Condensation cure PDMS MMMs were made with four ZIF-71 loadings: 0, 5, 25 and 40 wt%. Overall, the 40 wt% ZIF-71 loading PDMS MMMs achieved the best ethanol and 1-butanol separation performance. The maximum ethanol/water selectivity was 0.81±0.04 (separation factor of 12.5±0.3 for 2 wt% ethanol feed) and the maximum 1-butanol/water selectivity was 5.64±0.15 (separation factor of 69.9±1.8 for 2 wt% 1-butanol feed). This is the first report of the separation of 1-butanol from water with ZIF-71/PDMS MMMs to date.

Different ZIF-71 size particles were obtained by varying synthesis temperature from -20 °C to 35 °C. The particle sizes synthesized ranges from 150 nm to 1 μm. We found that ZIF-71 particle size is crucial in ZIF-71/PDMS MMMs separation performance. Submicron size ZIF-71 particles tend to agglomeration and decrease alcohol/water selectivity. Membranes made with micron-sized ZIF-71 particles had better particle dispersion in PDMS polymer matrix and achieved better alcohol/water selectivity than submicron size particles.

Keywords: pervaporation, mixed matrix membrane, biofuel, ZIF-71

[P2.062]

Preparation of PES/SPSf/graphene oxide nanofiltration hollow fiber membrane with improved antifouling and antibiofouling properties

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Pressure-driven membrane processes have been extensively applied to address the forever deteriorating water quality caused by the presence of traditional as well as newly emerging pollutants in water. However, the performance of membranes tends to be limited by membrane fouling, a process in which foulants are deposited on the membrane surface and/or within the membrane pores. It has been found that increasing the hydrophilicity of the membrane surface remarkably minimizes fouling [1]. This work describes the production of polyethersulfone (PES) based nanofiltration (NF) hollow fiber membrane blend with improved fouling resistance, controlled pore sizes as well improved antimicrobial properties by using carbon nanomaterials. The PES/sulfonated polysulfone (SPSf)/graphene oxide (GO) NF membrane blend prepared via a non-solvent induced gelation phase separation method demonstrate unique separation properties. In our work, we systematically vary the content of SPSf and GO in order to obtain optimum membrane performance. Ultrasonic through-transmission measurements were carried out to quantify the rate of membrane formation during the phase inversion process. The structural morphology and surface properties of PES/SPSf/GO membranes were studied using scanning electron microscope, atomic force microscope, electrokinetic analyser and contact angle analyser. We also report molecular weight cut-off data carried out using polyethylene glycol of various molecular weights to characterize the membrane pore sizes. So far, our results indicate that an increase in SPSf content leads to an improvement in membrane hydrophilicity as demonstrated by a decline in contact angle values. The addition of water in the dope solution significantly transformed the morphology of the membrane by changing the typical asymmetric structure with finger-like macrovoids in the sub-layer to sponge-like morphology with nanopores. It was found that the presence of GO in the membranes improved the antimicrobial properties of membranes thereby preventing biofouling by the tested bacteria. Therefore, by properly controlling the membrane pore sizes through the adjustment of SPSf and GO contents, a PES membrane capable of rejecting specific organic micropollutants from water was prepared.

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Keywords: polyethersulfone/sulfonated polysulfone, graphene oxide, hollow fiber membrane, antifouling

[P2.063]

Influence of functionalized graphene within polycarbonate membranes on the water affinity

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Graphene (G) is a mono-layer of sp^2 bonded carbon atoms with a single-atom-thick sheet arranged in a honeycomb structure. The good properties such as mechanical, electrical, thermal and high surface area have been attracting attention in different areas including in polymer composites. Graphene oxide (GO) sheets can be obtained by G oxidation process. They present the polar oxygen functional groups located on the basal plane or at the sheet edges. From GO, a lot of chemical functionalization are possible, as with APTES. The incorporation of particles within polymeric membranes can modify the sorption and permeation profiles. Bisphenol-A polycarbonate (PC) shows good properties, however, almost all the literature, usually report the effects in electrical conductivity. So this work intends to study the influence of very low particle concentrations in PC and in water affinity situations. The G was prepared by direct ultrasound exfoliation of graphite in NMP. The GO was prepared by the Hummer's method. The GO-A was synthetized by reaction with APTES. The composite membranes were prepared by solvent casting. Differential scanning calorimetry (DSC), water vapor transport (WVT) and water sorption were performed. The WVT analysis showed in generally that the vapor water flux increased in all the levels and types of particle while for the water swelling test the tendency was the decreasing in the particles presence. Thus, the sorption-difusion mechanism is related by two factors, the voids in the matrix and the surface water affinity. This information can be corroborated by DSC results. Though the T_g value for all the cases remained practically the same, the increasing of WTV is justified by local motion according to the decreasing of rigid amorphous fraction. The lower surface affinity is justified by interactions of functional groups of the particles and PC that lead the decreasing of interaction sites to water.

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Keywords: Graphene, Polycarbonate, Composite, Water vapor transport

[P2.064]

Dual-functional ultrafiltration membrane for simultaneous removal of multiple pollutants with high-performance

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Simultaneous removal of multiple pollutants from aqueous solution with less energy consumption is crucial in water purification. Here, a novel concept of dual-functional ultrafiltration (DFUF) membrane is demonstrated by entrapment of nano-structured adsorbents into the finger-like pores of ultrafiltration (UF) membrane rather than in the membrane matrix in previous reports of blend membranes, resulting in an exceptionally high active content and simultaneous removal of multiple pollutants from water due to the dual functions of rejection and adsorption. As a demonstration, hollow porous $Zr(OH)_x$ nanospheres (HPZNs) were immobilized in polyethersulfone (PES) UF membranes through polydopamine coating with a high content of 68.9 wt%.

The decontamination capacity of DFUF membranes towards multiple model pollutants (colloidal gold, polyethylene glycol (PEG), Pb(II)) was evaluated against a blend membrane. Compared to the blend membrane, the DFUF membranes showed 2.1-fold increase in the effective treatment volume for the treatment of Pb(II) contaminated water from 100 ppb to below 10 ppb (WHO drinking water standard). Simultaneously, the DFUF membranes effectively removed the colloidal gold and PEG below instrument detection limit, however the blend membrane only achieved 97.6% and 96.8% rejection for colloidal gold and PEG, respectively. Moreover, the DFUF membranes showed negligible leakage of nano-adsorbents during testing; and the membrane can be easily regenerated and reused. This study sheds new light on the design of high performance multifunction membranes for drinking water purification.

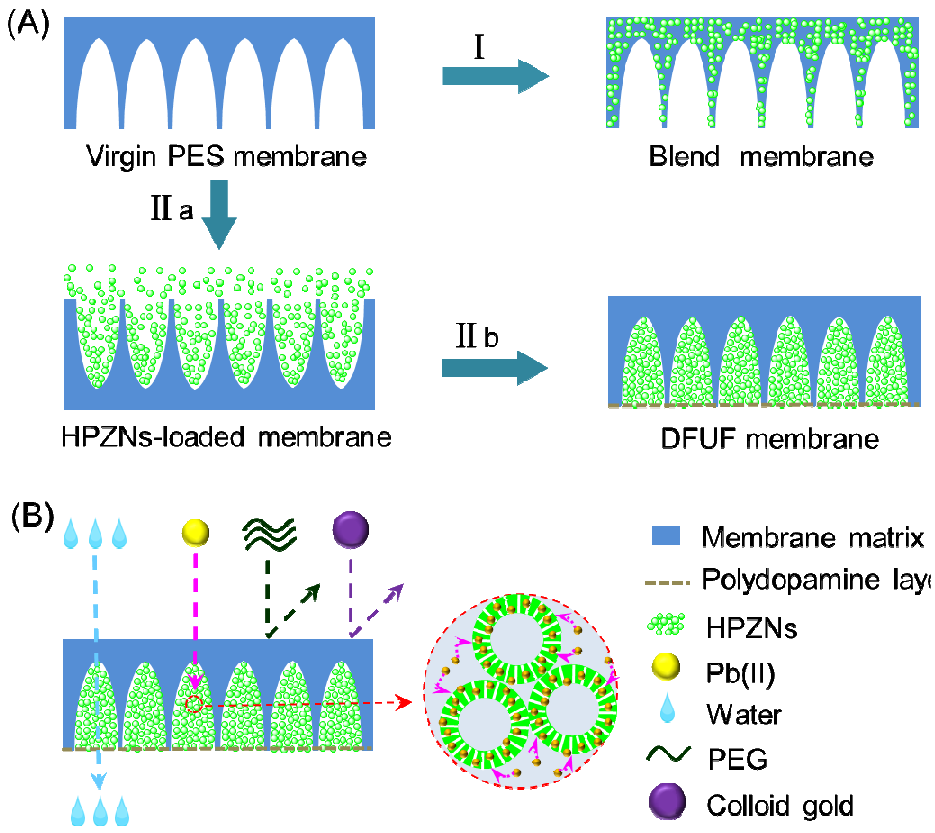

Figure 1. Schematic representation of UF membrane designs: (A) Virgin polymer UF membrane and a traditional blend membrane are both synthesized through a one-step casting method (I). A new 2-step method to form DFUF membrane (II); (B) the purification process for multiple pollutants polluted water by DFUF membrane.

Keywords: dual functional membrane, nano-adsorbents, ultrafiltration, multiple pollutants

[P2.065]

Synthesis and characterization of a novel montmorillonite-enhanced Poly(ether sulfone) heterogeneous cation exchange membrane: Mono/divalent ionic transport

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The material properties of ion exchange membranes (IEMs) play an important role in the performance of any electrodialysis process. According to the structure and preparation method of the membrane, IEMs can be categorized as homogeneous or as heterogeneous. Although homogeneous membranes have good transport properties, they are mechanically weak, while heterogeneous membranes have much better mechanical properties, easier preparation procedures, lower production costs, but unfortunately also poorer transport properties Many researchers have reported various methods to modify IEM's features. One of them is development of composite ion exchange membranes using inorganic materials in polymeric matrix. Montmorillonite (MMT) is an abundant and inexpensive layered alumino-silicate mineral that has large surface areas and a negative surface charge. A novel heterogeneous composite cation exchange membrane, composed of poly (ether sulfone), cation exchange resins, and montmorillonite as additive, was prepared by solution casting. The effects of the weight fraction of MMT on physico-chemical properties of the membranes were investigated. Our results indicated that incorporation of MMT could effectively improve the performance of the pristine heterogeneous membranes in terms of ion exchange capacity, water content and ion permeability of Na^+ and Ba^{2+}. A maximum in performance was found around 2 wt.% MMT. We hypothesize that the incorporation of clay allows for improved ion transport, especially through the modified PES matrix. Composite IEMs as proposed here could potentially bridge the gap between the homogeneous and heterogeneous membranes, leading to IEMs with good material and transport properties.

Keywords: Cation exchange membranes, Ionic transport property, Montmorillonite (MMT), Poly (ether sulfone) (PES)

[P2.066]

ZIF-L/ PDMS mixed matrix membranes for separation of ethyl alcohol and isopropyl alcohol from nitrogen

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Solvents in air can be recovered to save high-value chemicals and to minimize the effect of them on environment. Ethyl alcohol (EtOH) and isopropyl alcohols (IPA) are widely used solvents in defense, electronics, press-packaging, textile industries, are recycled from air by adsorption based solvent recovery processes. In these processes, the VOC captured by activated carbon in adsorption columns is swept by nitrogen and condensed under cryogenic conditions since the partial pressure of VOC in nitrogen is very low. The condensed VOC mixtures is then separated in to its components by distillation. In order to replace the cryogenic condensation with a condensation process taking place at higher temperatures, the partial pressure of VOC should be increased.

The objective of this study is to develop a membrane-based process to increase the VOC partial pressure in nitrogen. For this purpose, ZIF-L filled polydimethylsiloxane (PDMS) mixed matrix membranes were prepared on macro porous polyethersulfone ultrafiltration membranes. The membranes had ZIF-L loadings of 2.5 to 20 % by weight. The VOC, which is a mixture of ethyl and isopropyl alcohols, has a very low partial pressure in nitrogen (molar ratio of N_2:EtOH:IPA=1000:2.5:2.5).

The SEM images of the membranes showed that the PDMS layer has a thickness of 147 μm±10 and ZIF-L particles have been well dispersed within the polymer matrix. Pure PDMS membrane showed VOCs/N_2 separation factor of 3 with a permeability of 246 Barrer at 50 ^{0}C. The VOCs/N_2 separation factor is, on the other hand, 6 and 24 for MMMs with 2.5% and 20% ZIF-L, respectively. The respective total permeabilities of the membranes are 415 and 520 Barrer at 50 ^{0}C.

Keywords: ZIF-L, PDMS, VOCs separation, Mixed matrix membrane

[P2.068]

Polymeric membranes with well-controlled 3D structures and their applications

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This study reports the preparation of polymeric membranes with well-controlled 3D structures isoporous membranes and polymer/polymer mixed matrix membranes) via Langmuir-Blodgett technology with particulate templates and their applications in membrane distillation and gas separation. The membrane preparation consisted of four procedures in sequential.

Firstly, uniform-size particulate templates were piled up on a substrate by Langmuir-Blodgett technology (Fig.1 (1)). In this study, multiple layers of 400 nm silica particles were well arranged on silicon wafer and also 400 nm PS (polystyrene) particles on ITO glass.

At the second stage, polymer 1 solution was loaded to fill in the interstice between particles by spin coating to form polymer 1/particulate template mixed matrix membrane (Fig. 1 (2)). The membrane was then removed from substrate in a non-solvent bath. Various polymers (e.g. PES, CA, PVDF, PMMA, etc.) have been tested in our lab, and the membranes were successfully fabricated.

Next, the particulate templates inside the membrane were etched out with a suitable solvent (1% HF for silica; NMP for PS) to produce isoporous membrane (Fig. 1 (3)). Isoporous membranes could be used in numerous applications. For instance, isoporous PVDF membrane made from 15 layers of 400 nm silica templates showed a 70% larger flux in the distillation of 1 wt.% NaCl solution than a traditional phase-inversion PVDF membrane with similar thickness and pore size.

In the final procedure, polymer 2 was injected into the membrane pores to prepare polymer 1/ polymer 2 mixed matrix membrane (Fig. 1 (4)). In this way, two polymers with different properties could be combined together in a single membrane. The polymer 1/polymer 2 mixed matrix membranes were applied to CO_2/CH_4 separation in our study, and their performance was compared with pure polymer membranes.

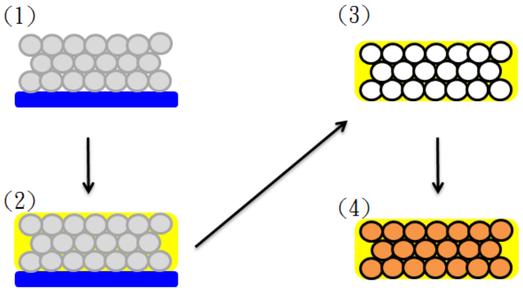

Fig. 1 The experimental procedures for fabrication of polymeric membranes with well-controlled 3D structures.

Keywords: mixed matrix membrane, isoporous membrane, gas separation, membrane distillation

[P2.069]

Graphitic carbon nitride nanosheets embedded in poly(vinyl alcohol) nanocomposite membranes for ethanol dehydration via pervaporation

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Graphitic carbon nitride (g-C_3N_4) is an innovative kind of soft two-dimensional (2D) nanomaterials. Due to its lamellar structure like graphite layers, g-C_3N_4 has attracted significant interest as a new class of filler for the fabrication of novel polymeric nanocomposite membranes. In this study, highly water-selective hybrid membranes with excellent water/ethanol separation performance and superior water channel were fabricated by incorporating g-C_3N_4 nanosheets into poly(vinyl alcohol) (PVA) matrix. g-C_3N_4 was synthesized largely via thermal oxidation “etching” methods, which applied melamine as a precursor. The ultrathin and nanoporous structures were characterized by transmission electron microscopy, Fourier transform infrared spectra, and X-ray diffraction. Due to the strong interfacial interactions among g-C_3N_4, succinic acid (Sa) and PVA matrix, the hybrid nanocomposite membranes showed both high swelling resistance as well as mechanical strength stability. In addition, the addition of g-C_3N_4 can improve the membrane hydrophilic and heat-resistant properties significantly. Importantly, membrane permeability would be improved greatly because the ordered alignment and the regular pore structure of g-C_3N_4 rendered ordered water channels for rapid transportation of water molecules. The total flux and separation factor of this new membrane can reach about 6332 g/m^2h, and 33.6, respectively. Moreover, the nanocomposite membrane exhibited an excellent long-term operating stability. After operating over 120 hours, the total flux and separation factor still maintained at about 6332 g/m^2h and 33.6 for 90 wt. % ethanol/water system at 75 □. This is a step forward in bringing organic-inorganic hybrid membranes with superior properties incorporating 2D porous fillers (g-C_3N_4, et al) for pervaporation separation processes.

Keywords: Pervaporation dehydration, Nanocomposite membrane, g-C3N4, Poly(vinyl alcohol)

[P2.070]

Preparation and characterization of fluoroalkyl modified carbons/PVDF composite membranes for membrane distillation

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Agglomeration of activated carbon (AC) particles had negative influence on performance of AC/PVDF composite membrane. To solve this problem, the AC was functionalized by fluoroalkyl groups in this study, which was synthesized via the reaction between carboxylic activated carbons and octafluoropentanol (OFP). The fluoroalkyl-AC/PVDF composite membrane was prepared by blending PVDF and functionalized AC-OFP particles via a conventional phase-inversion method. The dispersion of AC-OFP particles in membrane matrix was improved. As a result, the maximum DCMD flux increased about 35.6% from 29.8 kg/m^{2}h (PVDF/AC membrane) to 40.4 kg/m^{2}h (the PVDF/AC-OFP membrane) by just adding 0.15 wt. % AC-OFP particles.

Keywords: Polyvinylidene fluoride membrane, hydrophobic membrane, Fluoroalkyl carbon, membrane distillation

[P2.071]

Mitigation of membrane fouling: An impact of enhanced surface energy of PVDF membrane by immobilization of TiO_2 NPs on membrane surface

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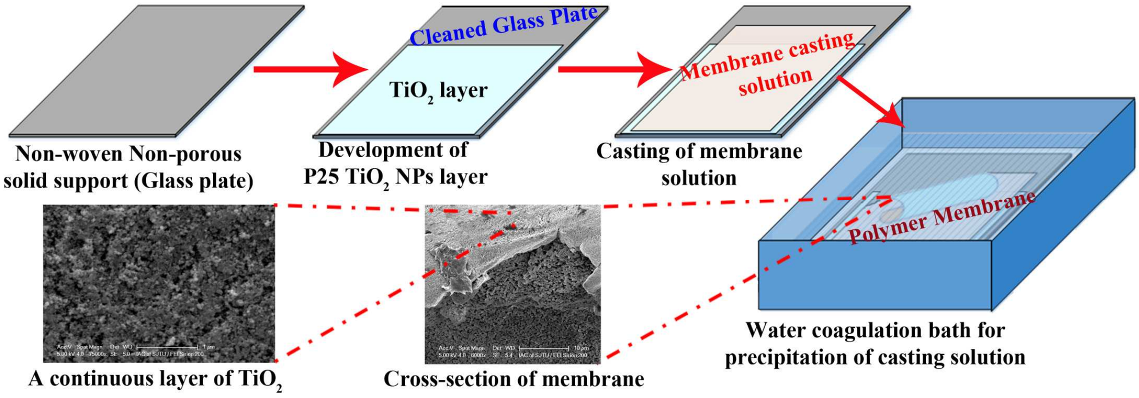
Surface hydrophilicity of membranes is considered one of the most important parameters to mitigate membrane fouling, and hydrophilicity is largely influenced by the surface energy of the membrane. We developed a facile technique [prefabrication surface adhesion of TiO_2 NPs (SaT)] to incorporate TiO_2 NPs on the surface of PVDF based ultrafiltration (UF) membrane to enhance the surface energy. For comparison, membranes without NPs [PVDF-PEG (PP)] and NPs blended in membrane matrix [PVDF-PEG-TiO_2 (PPT)] were also prepared. The reference membranes (PP and PPT) and the membranes prepared with the facile techniques (SaT-PP and SaT-PPT) were thoroughly characterized (surface energy (γ), contact angle (CA), zeta potential (ζ), surface roughness, thermal stability, physical stability, and membrane resistance) and evaluated for antifouling performances. The SaT-PP and SaT-PPT membranes showed similar and the highest γ (60.94 ± 2 mJ/m^2) followed by PPT and PP membranes (42.05 ± 5, 33.84 ± 2 mJ/m^2, respectively). The CA of SaT-PP and SaT-PPT membranes was 21 ± 2^o and of PPT and PP membranes were 49.8 ± 1.65^o and 62 ± 2^o, respectively. The ζ of SaT-PPT and SaT-PP membranes was -19.5 ± 1 and for PPT and PP membranes were -7.42 ± 2 and -1.03 ± 0.5 mV, respectively. The thermal and physical stability were maximum for SaT-PPT membrane. Whereas, surface roughness, membrane resistance, and molecular weight cut-off were least for SaT-PPT membrane. The antifouling potential of the membranes were assessed with 2 mg/L humic acid solution using a cross-flow UF system. The initial flux was adjusted to 100 L/m^2 h for 90 min UF process. Insignificant fouling was observed for SaT-PPT and SaT-PP membranes, whereas 60% and 70% fouling was observed for PPT and PP membranes. It is reasonable to believe that our developed SaT-PPT membranes will provide insightful engineering practices to benefit the broad water-treatment applications.



Keywords: Fouling mitigation, surface energy, hydrophilicity, PVDF

[P2.072]

Zeolite imidazolate framework-300 (ZIF-300) filled PEBA mixed matrix membranes for CO_2 capture

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Metal organic frameworks (MOFs) have become one of the most popular materials for developing in mixed matrix membranes (MMMs) [1, 2], owing to its high flexibility and tunable physicochemical properties. Zeolitic imidazolate framework-300 (ZIF-300), a new member of ZIFs family, is formed by coordination of metal ions Zn^{2+}, 2-dimethyimidazole and 5(6)-bromobenzimidazolate with a chabazite (CHA) topological structure. It has been proved that ZIF-300 show higher capacity and affinity for CO_2 over N_2 [3]. Therefore, incorporating ZIF-300 particles into PEBA matrix is believed to be a facial way to improve the CO_2/N_2 separation performance of PEBA membrane.

In this work, ZIF-300 particles were dispersed in poly (ether block amide) (PEBA) to prepare ZIF-300/PEBA MMMs for the separation of CO_2/N_2. The effects of different ZIF-300 loadings on membrane microstructure and gas separation performance were investigated systematically. The as-prepared materials and membranes were characterized by various techniques such as SEM, AFM, XRD, FT-IR and TGA to study their morphologies, physical and chemical properties. Meanwhlie, the gas separation performances of ZIF-300/PEBA MMMs for CO_2/N_2 were evaluated under different temperatures and pressures. The results suggested that the ZIF-300 contents had significant influence on the transport properties of the membranes. Furthermore, the dispersion of ZIF-300 particles in polymeric matrix is of great importance for the separation behaviors of the ZIF-300/PEBA MMMs. Our work demonstrated that the ZIF-300/PEBA MMMs can be expected to have potential application in CO_2 capture.

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Keywords: Mixed matrix membrane, ZIF-300, PEBA, CO2 capture

[P2.073]

A self-standing mixed matrix membrane of UiO-66/polysulfone for forward osmosis

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Mixed matrix membranes (MMMs) which usually comprise inorganic entities embedded in a polymer matrix have received a surge of interest in recent years. By incorporating some molecular sieve particles such as zeolite or metal-organic frameworks (MOFs) into the polymer, the membrane can obtained enhanced permeability while maintaining good toughness. Herein, we reported a novel self-standing UiO-66/polysulfone (PSf) mixed matrix membrane with enhanced permeability for forward osmosis. A homogeneous sulfonated polysulfone (SPSf) incorporated PSf membrane was first fabricated via solvent evaporation method. On this basis, a certain amount of UiO-66 nanoparticles with the size between 150 ~ 200 nm were introduced into the polymer matrix, and their morphologies in the PSf membrane were confirmed by SEM, TEM, and AFM. The effects of the loadings of the nanoparticles on the membrane structure and performance were systematically investigated. The results showed that the incorporated UiO-66 nanoparticles were evenly distributed in the membrane. The nanoparticles showed good compatibility with polysulfone and no obvious voids or gaps were found in the interface. The incorporation of the UiO-66 nanoparticles resulted in the formation of a large amount of microporous structure which provided sufficient channels for the transfer of water molecules. Thus the water flux of the UiO-66/PSf MMM showed an order of magnitude improvement in FO process. When using 1.25 mol/L Na_2SO_4 as the draw solution, the highest water flux reached 67.6 LMH. Moreover, the UiO-66/PSf MMMs kept good thermal stability and mechanical properties. Such MMMs indicated a new approach for designing high performance FO membranes and showed promising applications.

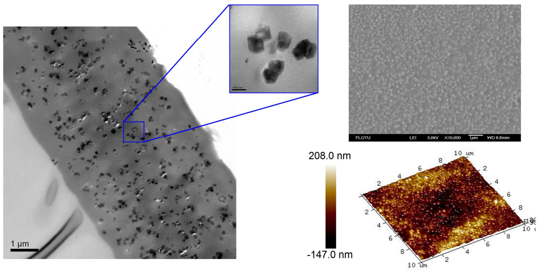

Fig. 1. Morphologies of the UiO-66/PSf mixed matrix membrane.

Keywords: mixed matrix membrane, UiO-66, polysulfone, forward osmosis

[P2.074]

Widening CO_2-facilitated transport passageways in SPEEK matrix using polymer brushes functionalized double-shelled organic submicrocapsules for efficient gas separation

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Appropriate facilitated transport carriers and water environment are two principal factors for efficient CO_2 membranes separation. In this study, the facile distillation-precipitation polymerization (DPP) and atom transfer radical polymerization (ATRP) methods are consecutively used to prepare polymer brushes functionalized double-shelled organic submicrocapsules, and the resultant organic submicrocapsules are incorporated into sulfonated poly(ether ether ketone) (SPEEK) to fabricate mixed matrix membranes (MMMs). The doubledshelled structure provides abundant facilitated carriers by the outer shell and high water retention property by the inner shell simultaneously. The organic submicrocapsules (b-IM@PMMA) are homogeneously embedded in the SPEEK matrix, and abundant amine groups on polymer brushes of outer shell increase the content of CO_2-facilitated transport sites in MMMs. The inner shell renders the organic submicrocapsules of higher water content, yielding the MMMs with enhanced water retention properties. Moreover, the incorporation of organic submicrocapsules increases the water uptake and water retention capacity of MMMs. The MMMs doped with organic submicrocapsules display better CO_2 separation performance than the MMMs doped with doubleshelled organic submicrocapsules without brushes. The polymer brushes functionalized double-shelled organic submicrocapsules act as water reservoirs to not only offer more water for the dissolution of CO_2 gas molecules, but also construct and widen interconnected continuous CO_2-facilitated transport passageways. The highest $CO_2/CH_4(N_2)$ selectivity is 73.8(76.3) for the SPEEK/b-IM@PMAA MMMs (at a CO_2 permeability of 2236 Barrer) in pure gas, surpassing the 2008 Robeson upper bound.

Keywords: Mixed matrix membranes, CO2 capure, gas separation, SPEEk matrix

[P2.075]

Highly anion-conductive imidazolium functionalized poly(ether ether ketone) microphase-separated membranes

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Anion exchange membranes (AEMs) have triggered renewed interest in fuel cells owing to their advantages over proton exchange membranes (PEMs): faster kinetics for oxygen reduction reactions, which enable the usage of non-noble metal catalysts; lower corrosion for battery materials; better fuel resistance if alcohol such as methanol is utilized. However, inadequate hydroxide conductivity hinders the commercialization of AEM fuel cells, which is primarily due to the comparatively low intrinsic mobility of hydroxide ions.

To address this, the creation of ion conduction channels with a low energy barrier is a recognized practical strategy. Microphase separation can generate well-interconnected ionic nanoaggregates and achieve greatly improved hydroxide conduction. However, the synthesis of polymers that induce microphase-separated membranes may be complex. In this study, we propose a facile approach to form microphase aggregated AEM membranes. Chloromethylated poly(ether ether ketone)s with 183% and 96% chloromethyl groups per repeat unit were obtained by controlling the reaction time, and are denoted as CMPEEK-1 and CMPEEK-2, respectively. CMPEEK-1 was first functionalized by 1-methyl-imidazole in NMP at 50 ^oC for 2 h. Measured amounts of CMPEEK-2 were added and the mixtures were maintained at 50 ^oC for another 10 h for continual imidazolization of both CMPEEK-1 and CMPEEK-2. The resulting reaction solutions, with CMPEEK-1 proportions from 0 wt% to 40 wt%, were directly cast into membranes at 60 ^oC for 12 h and heat treated at 100 ^oC for 12 h for cross-linking. The ion exchange capacities were maintained at 1.5 mmol/g by adding the same amount of 1-methyl imidazole to each reaction casting dope. The blend membrane 20 wt% CMPEEK-1 has the highest anion conductivity (Cl^- for this study) compared to the CMPEEK-2 based membrane, owing to the intrinsic compatibility of the two imidazolium functionalized PEEKs and crosslinked architecture, with dense and homogeneous blending.

Keywords: microphase-separated membrane, Anion exchange membranes, poly(ether ether ketone), imidazolium functionalization

[P2.076]

Thin film composite polyamide membranes anchored to the Poly(p-phenylene terephthamide) polymerized in the polysulfone substrate

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A new strategy of obtaining higher adhesive strength thin film composite (TFC) membrane is developed by interfacial polymerization on the Poly(p-phenylene terephthamide)/polysulfone (PPTA/PSf) in-situ blended substrate via polymerized PPTA in the polysulfone N-Methyl pyrrolidone (NMP) solution. The immobilization of PPTA in a PSf substrate is verified by FTIR and XPS. The surface performance of the PPTA/PSf substrates are characterized by FESEM, AFM and WCA measurement. And it is observed that the PPTA/PSf substrates have more open porous structures and thinner dense layer thick, more roughness surface, more wettability surface, and higher permeation flux than the PSF substrate. The compaction resistance of the substrates are evaluated by the pure water flux test vs. operation pressure, and the results indicate that the yield pressure can be improved from 1.0 Mpa (PSf substrate) to 1.6 Mpa (PPTA/PSf 8 substrate). The piperazine polyamide TFC membrane had been prepared and the cross-section and surface roughness were characterized by FESEM and AFM. It can be seen that the TFC layer linked to the starlike structure, and the surface of the TFC membrane is more roughness than the substrates while the PPTA ≤4%, but more smoothing while the PPTA ≥6%. The rejection order of the different salts is $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$. The adhesive strength between the TFC layer and the substrate is improved after in-situ blended PPTA which is demonstrated by the back flush operation. the result indicate obviously that the rejection of PA-PSf is only 53.2%, and PA-PPTA/PSf 2, PA-PPTA/PSf 4, PA-PPTA/PSf 6 and PA-PPTA/PSf 8 are remaining at 88.2%, 90.6%, 92.5, and 96.3%, respectively. In-situ blended PPTA improved not only the compaction resistance of the substrate but also the adhesive strength of the TFC layer and the substrate.

Keywords: TFC, in-situ blending, PPTA, Adhesive strength

[P2.077]

Nano-sized hollow zeolitic imidazolate framework (ZIF-8) based mixed matrix membranes for gas separation

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Membrane gas separation has attracted significant interest in recent years for industrial applications such as natural gas purification and CO_2 capture. Mix matrix membrane based on ZIF-8 has been reported recently. However, larger size of ZIF-8 in micron scale restricts the membrane performances due to the interfacial phase separation between ZIF-8 and polymer. In this study, we prepare a kind of zeolitic imidazolate framework (ZIF-8) hollow nanospheres by interfacial self-assembly of microemulsion. The ZIF-8 hollow nanospheres can disperse in a polymer excellently without any phase separation even at their high loadings. The shell and core size of ZIF-8 can be controlled easily by varing microemulsion composition and self-assembly time. The mixed matrix membranes showed significantly size dependent performances and presented enhanced gas permeability whilst the membrane selectivity to important gases remained high and constant. The proposed method highlights the potential of metal–organic framework (MOF)-based nanocomposite membranes for gas separation.

Keywords: Mixed matrix membranes, ZIF-8, Microemulsion, Gas separation

[P2.078]

Nano-aggregation suppressed thin film nanocomposite (TFN) membranes for water desalination prepared with the in-situ generation of TiO_2 additives

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We reported a promising strategy to prepare thin film nanocomposite (TFN) membranes with an in-situ generation of TiO_2 nanoparticles in active layer. Interfacial polymerization was applied to prepare thin film composite membranes and Tetra-butyl ortho-titanate (TBOT) or TiO_2 nanoparticles was used as additives. Compared with the TFN membranes fabricated by directly adding TiO_2 nanoparticles into organic phase (Ex-situ TFN), the nanoparticles in the in-situ synthesized TFN membrane (In-situ TFN) exhibited better dispersion, and higher loading of TiO_2 nanoparticles on the membrane surface was inspected. Surprisingly, at a rather low concentration of TBOT□0.6×10^{-3} mol/L□, the water flux of in-situ synthesized TFN membranes increased by more than 50% with negligible rejection loss in comparison with control thin film composite membrane. The surface properties of the membranes were investigated by scanning electron microscope (SEM), X-ray diffraction analyzer (XRD), X-ray photoelectron spectroscopy (XPS) and contact angles. These results demonstrated that in-situ generation of nano-additives could effectively suppress nano-agglomeration and improved the performance and surface features of TFN membranes.

Keywords: Interfacial polymerization, Nanocomposite membrane, nanoparticle additives, in-situ generation

[P2.079]

Amino silane (kh - 912) modified attapulgite / preparation of poly (vinylidene fluoride mixed matrix ultrafiltration membrane

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In this paper, it using amino silane (KH - 912, KH - 602 and KH - 103) to modify the surface of attapulgite (ATP), and respectively, making out to modified attapulgite like KH - 912 - ATP, KH - 602 - ATP and KH - 103 - ATP, after that, doping it into the casting solution of poly (vinylidene fluoride) (PVDF), and then preparing PVDF ultrafiltration membrane mixed matrix by the way of phase inversion method. Lastly we inspected the effect of different modifier content on the pore size of membrane, the pure water flux, microscopic structure, separation performance and pollution resistance. The experimental results showed that the addition of modified attapulgite had little influence on aperture size, the average pore size of the modified membrane and pure PVDF membrane were about 20 nm. The increasing of the content of modified attapulgite resulting in the more number of finger-like pore and more longer length of hole. When 7 wt. % of modified attapulgite content, the modified membrane possessed the largest reject rate of BSA, the best separation effect and lowest fixed pollution index. It improved the hydrophilic performance and increased the pure water flux of the membrane when different content of modified attapulgite was doped into the PVDF membrane. Besides, the more content of the modified attapulgite, the greater of the pure water flux. Comprehensive consideration, 7 wt. % of modified attapulgite content had a better performance of the modified membrane.

Keywords: amino silane, attapulgite, polyvinylidene fluoride, phase inversion

[P2.080]

Sorption enhanced mixed matrix materials for H_2/CO_2 separation at elevated temperatures

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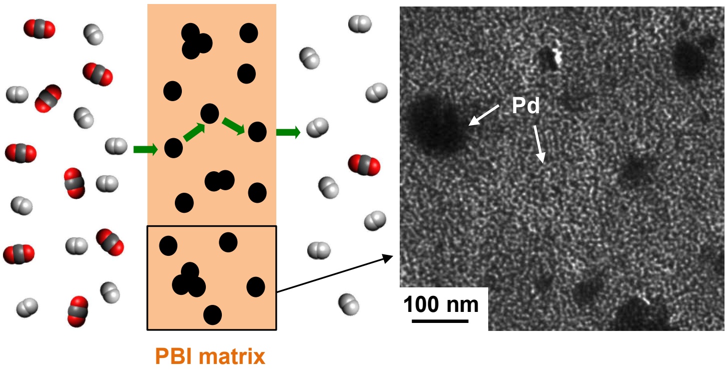

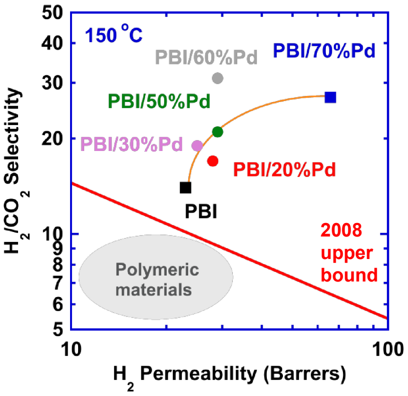

Polymeric membranes have been widely explored for energy-efficient and low-cost CO_2 capture and H_2 purification in the integrated gasification combined cycle (IGCC) processes. Conventional approaches are focused on designing rigid polymers with strong size sieving ability achieving high H_2/CO_2 diffusivity, such as poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (PBI). In contrast, we investigate mixed matrix materials (MMMs) containing PBI and palladium (Pd) nanoparticles, which have strong affinity towards H_2 and thus exhibit extremely high H_2/CO_2 solubility selectivity. Pd nanoparticles with uniform diameters of 6 - 8 nm are prepared via hot-injection approaches, which show H_2/CO_2 solubility selectivity of 840, compared with < 0.1 for typical polymers. The effect of Pd loading (0 - 70 wt%) and temperature on the pure- and mixed-gas H_2/CO_2 separation properties is thoroughly evaluated. The loading of Pd nanoparticles dramatically increases H_2 solubility and H_2/CO_2 solubility selectivity, resulting in a significant increase in H_2 permeability and H_2/CO_2 selectivity at temperatures of 100 - 200 °C. For example, adding 70 wt% Pd in PBI increases H_2 permeability from 25 to 70 Barrers, and H_2/CO_2 selectivity from 13 to 29 at 150 °C. Such performance is above the upper bound of the Robeson's plot for H_2/CO_2 separation, demonstrating their potential for industrial H_2/CO_2 separation. This poster presentation will also examine morphology of the MMMs and describe a model to elucidate the relationship of the structure and H_2 transport properties in these sorption enhanced MMMs.

Keywords: Mixed matrix membranes, Palladium nanoparticles, Polybenzimidazole, H2/CO2 separation

[P2.081]

Modelling the membrane formation dynamics using the cahn-hilliard equation, a way for controlling the membrane morphology

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We developed 2D and 3D numerical models (figure 1) coupling Cahn-Hilliard and Navier-Stokes equations [1, 2] to simulate the membrane formation dynamics by phase inversion. The phase separation process is widely used to produce porous polymeric membranes, whose morphology depend on several factors such as the polymer concentration, the solvent quality, or the mass transfer involved during the process [3]. The phase inversion is a de-mixing process involving the formation of two phases: a rich polymer phase (the final membrane after the solidification of the membrane) and a lean polymer phase (the pores of the membranes after the solvent extraction).

One of the most important challenges in the membrane formation field concerns the control of the formation mechanisms, which will have a great impact on the final membrane structure and thus on the functional properties such as the permeability and the selectivity. The elementary formation mechanisms can be optimized and monitored using computational simulation to describe the structuration dynamics once the phase inversion starts.

In this work, we used the Flory-Huggins-De Gennes theory [4] to describe the thermodynamic potential involving also hydrodynamics effects induced by the phase inversion. We first verified the linear model of the spinodal decomposition, i.e. the Cahn model involved during the first demixing period. This work investigated the effects of the polymer concentration and the temperature quench on the patterns evolution and hence on the final membrane porosity and pore connectivity. The growth laws were also determined depending on the temperature quench and the initial formulation.

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Keywords: phase separation, process, Spinodal decomposition, modeling

[P2.082]

The molecular structure and transport properties of polyPOSS-imide networks for gas separations at high pressures and temperatures

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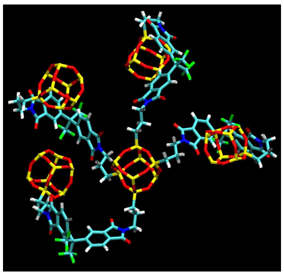
Hybrid organic/inorganic hyper-cross-linked membranes based on imides covalently bonded with polyhedral oligomeric silsesquioxanes (POSS) have recently been developed for gas-separation applications under high pressures and/or temperatures.[1] These networks exhibit different molecular sieving capabilities depending on the nature of the dianhydride precursor for the imide and the degree of cross-linking.[2,3]

In this work, we bridge the gap between experiment and the fundamental atomic-level differences for networks based on either the 6FDA or the PMDA dianhydrides by using molecular dynamics (MD) simulations.[4,5] The construction algorithms closely mimick the experimental three-step scheme, i.e. (a) the mixing of the reactants (b) the interfacial polycondensation and (c) the thermal imidization. The advanced simulation strategy ensures that the final material properties of the models match as closely as possible those of the actual materials.



Such models are able to explain the experimental differences in densities, structures, void-spaces and mechanical properties as a function of the organic precursor. Many properties which are difficult to measure experimentally can also be accessed, such as the fine details of the links (inter- to intraPOSS links, single to double links, etc…), the significant distances and angles, the energies, the water loss over the imidization reaction only, the morphology of the void space as well as the tensile stress vs. strain curves, various moduli and yield behaviour under isotropic expansion at both low and high temperatures. In addition, CO_2 and CH_4 gas molecules have now been inserted into the polyPOSS-imide models in order to characterize their sorption, swelling capabilities, trajectories and diffusivities under a large range of pressures and temperatures.

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Keywords: MD simulations, Hybrid organic-inorganic, Cross-linked, High pressures and temperatures

[P2.083]

Insight into pervaporation processes using Me-silicalite-2 membranes via a simplified molecular dynamic method

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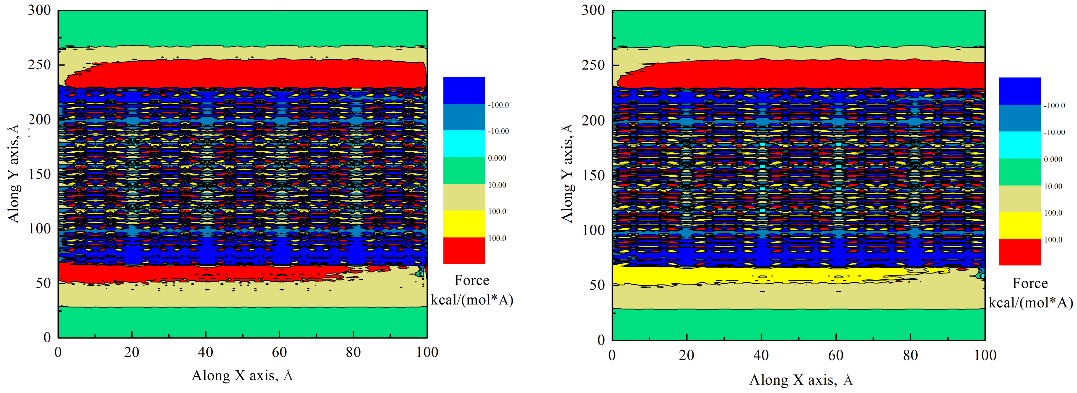
Molecular simulation methods have been considered as effective tools to reveal and predict the pervaporation properties of membrane materials, despite massive computing resources needed to perform simulations with realistic scales. This study focus on separating DMF from dilute aqueous solutions with MEL-type zeolites using simplified molecular dynamic method to avoid huge time consumption. Models of Me-silicalite-2 (Me=Sn, Ti and Zr) membranes, were prepared using PAW methods based on XRD patterns with force field parameters from Cygan's work[1]. The atoms in the membranes and in the molecules of feed solution were evenly placed on the space of the simulation box. Hence, the atomistic interaction between the feed and membrane materials could be calculated, tabulated and stored as grid energies and forces. The spacing for calculation in Figure 1 is 0.2 Å, and the results suggested insignificant difference between the traditional method and ours. Additionally, the periodical patterns within the gradient images indicated possibility to extend the scale of simulation from 10nm to nearly micrometers. The grid energies and forces were further used in the MD simulations of pervaporation process via Me-silicalite-2. Elementary results showed that, the separation factor for DMF in 5wt% solutions on Me-silicalite-2 was close to our experimental data. And introducing Ti and Sn into silicalite-2 could elevate the separation performance of membranes, which was also consistent with laboratory results. Compared with traditional MD simulation, the time consumption using the grid-based energy evaluation method could be only one hundredth in the system with Me-silicalite-2 model consist of 50 cells. Therefore, the method described here could be applied to simulate large scale membranes for the insight of pervaporation properties.



Force gradient from atomistic interaction calculations

Force gradient from tabulated grid forces calculations

Figure 1 Interaction between water hydrogen and sililicalite-2 membranes

Acknowledgements

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Keywords: Me-silicalite-2 membranes, pervaporation, grid-based energy evaluation, molecular dynamics

[P2.084]

Fabrication of ultrathin-film composite membranes via incorporating dual-layer support

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Polymeric membranes are of particular potential in effectively separating CO2 from light gases, such as N2 and CH4, which offer an attractive alternative due to their advantages including lower operating cost and facile preparation. In order to improve the CO2 separation performance, ultrathin-film composite (UTFC) membranes have been developed exhibiting much higher permeance due to the reduced diffusion pathway. In general, UTFC membranes are fabricated via incorporating gutter layer between selective layer and support layer or interfacial polymerization method. The incorporation of gutter layer on porous support decrease the possibility of forming pinhole defects so that to form ultrathin selective layer, however, the inevitable diffusion resistance and poor controllability of gutter layer bring apparent drawbacks. The interfacial polymerization method is favor of forming much thinner selective layer, while the chemical composition of membrane is limited to reactive monomers. Herein, we propose a more facile and general way to prepare ultrathin composite membranes by fabricating dual-layer support which combines the ultrathin inorganic nanoporous layer with the original porous support. In this report, I will review our works about coating polymer solutions on the composite support so as to prepare ultrathin polymer membranes, which can effectively improve CO2 separation performance and make the membrane preparation process more controllable.

Keywords: Polymeric membranes, Ultrathin-film composite (UTFC) membrane, CO2 separation, Dual-layer support

[P2.085]

Impact of swelling characteristics on the permselective properties of multi-layer composite membranes for water removal from alcohols

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The removal of water from organic solvents and biofuels, including lower alcohols (i.e methanol, ethanol, propanol, and butanol), is necessary for the production, blending, and reuse of those organic compounds. Water forms an azeotrope with many hydrophilic solvents, complicating the separation of water/solvent mixtures. The use of water-selective membranes in a pervaporation or vapor permeation process enables the removal of water from the solvents efficiently, even when an azeotrope is present. Common hydrophilic polymer membranes often swell in water, resulting in permeabilities and selectivities that are dependent on the water content of the feed mixture. Recent work has shown the benefit of overcoating a hydrophilic water-permselective membrane with a non-swelling perfluoropolymer film [1,2]. The perfluoropolymer layer reduces the activity of water in the hydrophilic polymer layer, reducing swelling in that layer. This helps to increase the water selectivity of the multi-layer membrane relative to the selectivity of the base hydrophilic polymer even at high water activity on the surface layer, usually at the expense of permeability. In this work, the effect of overcoating the hydrophilic layer with polymer films of various swelling characteristics was modeled. Top layers that swell in the solvent offer some advantages, particularly with regard to the water permeance of the multi-layer composite.

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The views expressed in this abstract are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

Keywords: pervaporation, vapor permeation, composite membrane, transport modeling

[P2.086]

Membrane contactor modelling for subsea natural gas dehydration

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A new membrane process design for subsea natural gas dehydration with the use of membrane contactor in combination with pervaporation for regeneration of the solvent (e.g., triethylene glycol) is proposed. The goal it to meet the pipeline specifications for the natural gas and simultaneously prevent transport problems such as hydrate formation. Models of the membrane processes and process simulation is required to optimize the process design and evaluate the feasibility of the system.

The developed membrane contactor model is based on a hollow fibre module configuration with absorbent inside the fibre, gas on the shell side and a porous membrane. The shell side is a one-dimensional model due to turbulent flow, assuming no changes in radial direction. Inside the fibres, the flow is laminar and a two-dimensional model is applied to describe the concentration and temperature profile. Orthogonal collocation is applied to solve the two-point boundary value problem. The model describes a system of differential equations in molar flow/concentration, temperature and pressure for both phases. Due to the high pressure in subsea operation, the vapour-liquid equilibrium model used in the flux calculation is adjusted and optimized according to reported high-pressure data[1]. The model is implemented into HYSYS with the use of MATLAB Cape-Open Unit Operation, for process simulation and optimization.

In the present work, the feasibility for subsea dehydration with membrane contactor is evaluated through modelling and process simulation. The operation conditions and membrane parameters is optimized, including sensitivity studies and dimensioning of the membrane contactor unit.

The membrane contactor model is one part needed for the system optimization and evaluation of the feasibility for the new proposed membrane process design.

The present research work is developed within the SUBPRO SFI centre supported by the Research Council of Norway, major industry partner and NTNU.

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Keywords: Natural gas dehydration, Subsea processing, Membrane contactor, Modeling

[P2.087]

Predictive study on antibacterial activity of polymerizable surfactants for membrane surface modifications

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Innovative coatings for improving the antifouling property of commercial membranes are of particular interest for enhancing the membranes lifetime and keeping their performance constant in wastewater treatments. In this direction, an innovative membrane coating based on the preparation of polymerisable bicontinuous microemulsion (PBM)[1] and using the antimicrobial acryloyloxyundecyltriethyl ammonium bromide surfactant (AUTEAB) [2] Fig. 1 was proposed.

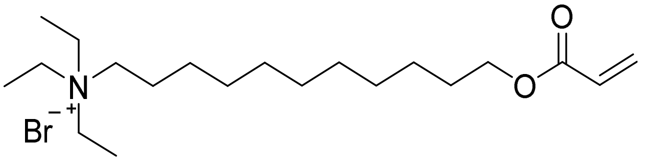

Figure 1

A molecular based modeling was carried out in this paper for predicting AUTEAB's analogues with increased antibacterial activity. Two molecular descriptors, correlated to the antibacterial property, were calculated for each surfactant conformers showing an increasing number of carbons in the aliphatic chain. Conformers distributions with respect to the selected descriptors were analyzed[2].

These distributions do not increase linearly with the growth of the aliphatic atoms. This non-linear behavior was also experimentally observed for the antibacterial activity of different QAS. Surfactants with ten or greater number of carbons in the aliphatic chain, not including the compound with twelve atoms, should show higher biocidal activity. The surfactant with fourteen atoms yields the best result. QM calculations showed that the water molecules do not affect significantly the above conclusions. The modeling predictions agree with experimental evidence related to the biocide activity of commercial surfactants as CTAB, thus, this work is of particular interest to direct the synthesis of innovative surfactants to be used in PBM techniques for obtaining biofouling resistance membranes coatings.

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Acknowledgment The work performed has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 689427 for the project VicInAqua.

Keywords: polymerizable surfactants, antibacterial activity, membranes coatings, antifouling property

[P2.088]

Polyoxometalates in polymer membranes for a more efficient fouling treatment: A nanoscale modeling

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Fouling is undoubtedly one of the major drawbacks limiting membrane-based technology in wastewater treatments. Polyoxometalates display several properties as antibacterial and capability to evolve oxygen from H_2O_2 dismutation[1]. $[PMo_{12}O_{40}]^{3-}$ and $(Ru_4(SiW_{10})_2$ polyoxometalates were suggested as fillers in membrane coatings prepared by a PBM method[2]. The exchange of $[PMo_{12}O_{40}]^{3-}$and $Ru_4(SiW_{10})_2$ with ions on surfaces functionalized with ammonium surfactants (QAS) is herein presented. Since an efficient exchange of bromide with a $[PMo12O40]^{3-}$ definitely increases the antifouling efficiency of the membranes, this exchange was simulated at nanoscale level using a Quantum and Molecular Mechanics [3] approach. The modelling predicted that this exchange takes place in a limited extent[3] due to the low QAS surface concentration and the counter ion used to neutralize the surfactant charge, crucial points to guarantee the electrostatic interaction of the $[PMo12O40]^{3-}$on the surface. *Ad hoc* measures were performed using homemade membranes and analytical measurements, performed to assess the extent of the exchange, are in good agreement with the modeling predictions.

The $Ru_4\,(SiW_{10}\,)_2$ release from PBM coatings results in the reduction of antifouling which is due to the oxygen evolution from the coatings. The second nanoscale modelling is aimed to predict the release of $Ru_4(SiW_{10})_2$, bounded *via* noncovalent bonds to QAS, in solutions containing ions. The QM/MM simulations were performed considering dilute solution of NaCl. The modeling shows that although the QAS-$Ru_4(SiW_{10}\,)_2$ adduct is very stable, the permeation of the target ions in the membrane coating can destabilize this complex.

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Acknowledgment The work performed has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement **No 689427** for the project **VicInAqua**.

Keywords: Nanoscale modeling, Polyoxometalate fillers, Membrane coatings, PBM

[P2.089]

Theoretical study of separation properties of carbon nanotubes and polyhedral carbon nano-onions

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Ab-initio approaches play an important role for predicting material-property relationships without adjustable parameters. Separation properties of carbon nanotubes (CNT) and polyhedral carbon nano-onions (PCNO) were therein analyzed using such a methodology.

The optimal nanotube diameters, able to reject low molecular weight solutes by size-exclusion, were predicted besides to the water permeability enhancement of related CNT composite membranes[1,2]. The structures of a sample solutes were first optimised hence their minimum cross-sections were calculated. Afterwards, the CNT Maximum Diameters (NTMD) as well as the inlet sizes of nanotubes with armchair and zigzag symmetries were predicted as shown in the Table.

Compounds	NTMD (Å)	SWNT (n, n)	d_{CNT}(Å)	SWNT (n, 0)	d_{CNT}(Å)
Diclofenac	14.0	(10,10)	13.6	(17,0)	13.3
Triclosan	12.5	(9,9)	12.2	(16,0)	12.5
Vanillic acid	12.4	(9,9)	12.2	(15,0))	11.7
Tyrosol	10.8	(8,8)	10.8	(13,0)	10.2
p-Coumaric-acid	10.9	(8,8)	10.8	(13,0)	10.2

Configurations of tyrosol inside a single-wall CNT (SWCNT), obtained by Molecular Dynamics, were used to validate the theoretical predictions. Significant distortions of the tyrosol ring in the (8,8) and (13,0) SWCNT were highlighted by Quantum Mechanics calculations. Thus, these nanotubes should reject the tyrosol molecules as predicted by the NTMD value.

PCNO can be considered as building blocks for new Carbon Molecular Sieve (CMS) coatings. Due to the lack of clear crystallographic structural data, models of these nanoparticles were first developed, and then used to evaluate particle-particle equilibrium distances and adhesion energies *via* QM calculations, including dispersion energy. The equilibrium distances were then used to predict separation properties of randomly assembled PCNO. The obtained morphologies, similar to CMS membranes, show not only size-discrimination, but also shape-discrimination capabilities, e.g. CO_2 vs CH_4. Studies of the adsorption capacity of these nanoparticles are also in progress as well as their functionalization.

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Keywords: polyhedral carbon nano-onions, Ab-initio approaches, CNT, CMS morphologies

[P2.090]

Modeling multiphase transport and separation in mesoporous membranes with dynamic mean field theory

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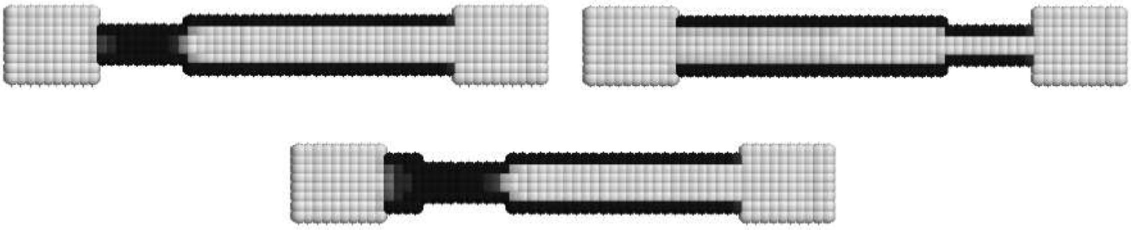
Mesoporous membranes can remove condensable components from light gases, e.g. carbon dioxide from flue gases and volatile organic compounds (VOC) from air, via mechanisms like preferential adsorption, surface flow, and capillary condensation. Design of improved membrane materials requires understanding of the effects of pore structure on the transport of gases and condensable vapors via such mechanisms, under gradients in pressure and concentration. We have recently demonstrated that dynamic mean field theory (DMFT), a coarse-grained lattice-based density functional theory, provides a computationally efficient molecular-level technique for predictive modeling of these systems. Here we present DMFT computations for several membrane applications, including permporometry and VOC recovery. For the latter, we demonstrate how the operative transport mechanisms are affected by pore variables like gas-surface interaction strength and variation in cross-sectional area. Furthermore, we show how this insight can be used to suggest new designs for mesopore structure that improve the permeation and selectivity.



density distribution of a condensable fluid (darker = more dense) permeating under a pressure gradient through three pores with different ink-bottle type geometries.

Keywords: mesoporous membranes, vapor recovery, permporometry, multiphase transport

[P2.091]

Evaluation of water permeability of novel supramolecule membrane by non-equilibrium molecular dynamics

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Water selective permeable membranes are used in various industrial processes such as seawater desalination and dehydration, however development of membranes with high water permeability is desired to improve process efficiency. In recent years, a unique water permeation mechanism with high water permeability such as aquaporin has been revealed. Therefore, a theoretical design of membranes having such a mechanism is expected to develop a high efficiency membranes. In this paper, we first evaluated the performance of such new membranes theoretically by non-equilibrium molecular dynamics method. We focused on a macrocyclic tetramers of 2-phenyl-1,3,4-oxadiazole, which are supramolecular, as a membrane structure. It has been reported that this molecule can contain water molecules in the form of chain-like in the pores inside the stacked supramolecules. We simulated the reverse osmosis process with our own code. Based on the time increment of a number of permeated water molecules, the pressure dependency of flux was predicted. Calculated flux showed that our modeled membrane achieved high water permeability of 35 kg/(m^2 s) under the pressure difference of 99 atm. Furthermore, we succeeded in improving then membrane structure to demonstrate higher water permeability by changing the atomic charge distribution in the pores and pore diameter.

Keywords: water treatment, molecular dynamics, reverse osmosis process, supramolecule membrane

[P2.092]

Modelling chemical degradation of ionomer in a polymer electrolyte fuel cell

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The work is devoted to development of a kinetic model describing the chemical degradation of the perfluorinated ionomer in the catalyst layers as well as in the membrane during the operation in a polymer electrolyte fuel cell.

The suggested model is based on the following approximations: a) hydrogen peroxide (H_2O_2) formation proceeds in both catalyst layers via the two-electron oxygen reduction (1); b) an amount of the hydrogen peroxide is reduced into water according to the reaction (2); c) the peroxide is transported via diffusion in the membrane, micro-porous and macro-porous layers; d) in the ionomer, the peroxide reacts with metal cations via the Fenton reaction and (3) builds hydroxyl radicals; e) the hydroxyl radicals split the side chains of the ionomer, which contain the functional groups; f) the boundary conditions are identically to the conditions defined in [1].

(1) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $E_{2eORR} = 0.695$ V 2e oxygen reduction

(2) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E_{H2O2d} = 1.760$ V H_2O_2 reduction

(3) $Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^{\cdot} + H_2O$ Fenton reaction

The model has been applied to analyze the effects of operating parameters such as pressure, temperature and relative humidity on the degradation of the perfluorinated ionomer in the operating fuel cell. The model enables to monitor time-dependent changes in the ionic conductivity of the membrane, the thickness of the membrane and the catalyst layer, acid group concentration of the ionomer as well as the amount of HF and CO_2 released.

Acknowledgment. The work has been financially supported by the Austrian Research Promotion Agency (FFG), the Austrian Ministry for Transport, Innovation and Technology (BMVIT) and the company AVL List GmbH: Program “Mobilität der Zukunft”, Project “FC-DIAMOND” (No. 850328, 2015-2018) - PEM Fuel Cell DegradatIon Analysis and MinimizatiON MethoDology Based on Joint Experimental and Simulation Techniques.

[1] Wong K, Kjeang E. Macroscopic in-situ modeling of chemical membrane degradation in polymer electrolyte fuel cells // Journal of the Electrochemical Society 2014, 161 (9): F823-F832.

Keywords: polymer electrolyte fuel cell, hydrogen peroxide formation, ionomer degradation, HF release

[P2.093]

Numerical simulation on direct contact membrane distillation: Optimization of hollow fiber membrane module

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Introduction

Direct contact membrane distillation (DCMD) technology is promising membrane desalination process which is based thermally driven desalination process. DCMD process able to use not only fresh water desalination but also resource concentration. In order to scale-up for commercialization of DCMD process, membrane module design and optimization are required. In this study, numerical simulation model is developed to optimize membrane performance of hollow fiber module regarding membrane thickness and porosity. To validate of the model, lab-scale experimental study is conducted simultaneously.

Method

For hollow fiber DCMD membrane model, continuity, incompressible steady-state Navier-Stokes, convection, and convection-diffusion equations are considered. The membrane is made by PTFE and properties are as follow, 358 μm thickness, 83 % porosity, 200 mm length. To validate hollow fiber DCMD membrane model, membrane performance is evaluated under various operating conditions regarding to feed water concentration and temperature of feed and permeate.

Results

Based on the experimental results and developed hollow fiber model, performance of hollow fiber DCMD are evaluated by varying membrane thickness and porosity. According to membrane properties, membrane performance – vapor flux and temperature are changed. Comparison between performances of change of membrane thickness and porosity, we are able to see the factor that have more impact on performance.

Discussion

Based on the results, optimal hollow fiber DCMD membrane properties – thickness and porosity is able to the basis of membrane module design for large-scale application.

Keywords: direct contact membrane distillation, hollow fiber, modeling, optimization

[P2.094]

Evaluating the slug flow in flat sheet membrane module using experimental and numerical methods

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Aeration induced two-phase flow, which is widely used in membrane bioreactors for fouling control, behaves as slug flow in flat sheet membrane configurations due to the effect of the restricted space between membrane sheets on the flow of bubbles. This study investigates the surface shear and strain induced by slug flow between two membrane sheets in a non-Newtonian fluid using both numerical and experimental methods.

Three strain gauges were attached on a FS membrane module (0.02 m^2) submerged in a bench-scale membrane tank (0.0007 m^3) (Fig. 1) to measure the local strain. Coarse bubbles (aeration intensity 75 $m^3/m^2/hr$) were sparged into 1.0 g/L xanthan gum solution, which has comparable rheological properties and surface tension properties to activated sludge (MLSS 16.7 g/L) collected from North Head WTP (Manly, Australia). A 3D CFD model, incorporating an experimentally calibrated rheology model and surface tension model, was developed for the membrane tank using ANSYS FLUENT® 17.2. The one-way system coupling was used to transfer simulated membrane surface force to ANSYS transient structural model to simulate the membrane strain. All simulations were performed on a 48 core processor.

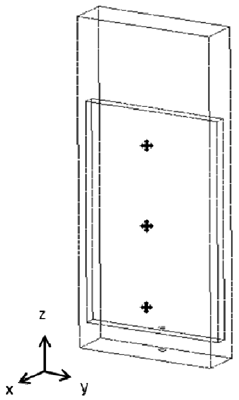

Fig. 1: Schematic representation of the bench-scale membrane tank

The simulation results showed that rising slug flow established a periodic shear stress and pressure difference on the two sides of membrane and therefore lead to periodic strain on membrane sheet. The time-averaged strain on membrane increased along height with the largest strain of 5.0×10^{-4} obtained near the top. The CFD-Transient Structural Model was validated by comparing simulated strain with experimentally measure strain within an error of 6%. The approach demonstrates how numerical techniques can be used to model performance of fouling control methods (aeration) in terms of shear on the membrane surface and changes in membrane structure that may impact integrity and membrane life.

Keywords: numerical simulation, flat sheet membrane, slug flow, strain gauge

[P2.095]

Mixed gas transport and solubility in glassy polymers: A predictive modelling approach

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The analysis of transport and sorption of gas mixture in polymers is fundamental for gas separation membranes development, and for the evaluation of their performance under real process conditions. However, very few modelling approaches are suitable for that description, especially for glassy phases.

A general transport model proved its ability to describe pure gas permeability and solubility in glassy polymers, considering diffusivity as the product of the molecular mobility and a thermodynamic factor, related to concentration dependence of penetrant chemical potential, and relying on the nonequilibrium thermodynamics for glassy polymers (NET-GP). In parallel, a simple exponential dependence on penetrant concentration is used to describe mobility behaviour, which contains the only two adjustable parameters of the model: infinite dilution penetrant mobility and plasticization factor.

The transport model is extended to mixed gas transport in glassy polymers, in the usual limit of small penetrant concentrations in the matrix, typical in gas separation membranes. Experimental permeability data of CO_2/CH_4 mixtures in conventional or innovative glassy membranes have been examined, and described by the present model, with no need of any additional parameters with respect to the pure gas case. The NET-GP approach represents accurately the multicomponent solubility in glassy polymers, as already proved previously, and the transport model accounts for the presence of a second component through its concentration dependence of the diffusion coefficient. The model describes well the experimental permeability data for all the systems investigated in wide ranges of feed pressure.

Interestingly, the model is able to highlight competitive sorption phenomena among the two penetrants, and the effects produced on both solubility and diffusivity coefficients. Furthermore, polymer dilation induced by CO2 is also considered, together with resulting plasticization effects.

Keywords: Mixed gas permeability, Multicomponent diffusion, Glassy polymers, NELF Model

[P2.096]

Molecular simulations of mixed-gas permeation in polymer membranes: Challenges and improved methodologies

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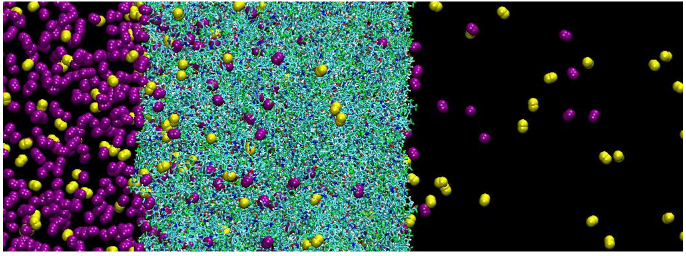
Molecular Dynamics (MD) simulations complement experiments by providing detailed informations at the molecular level. However, polymer models require special techniques to generate pre-relaxed starting configurations and fully-atomistic models of a membrane of realistic thickness are very demanding in terms of computational resources. The common procedure is to build bulk models periodic in three dimensions, which are representative of the membrane core. Skin-effects are then studied using specific surface models with explicit gas reservoirs.

As for most permeation experiments, gas transport simulations are usually carried out using pure gases. Such simulations describe the transport and estimate the diffusion and solubility coefficients of the specific gas in the membrane (*J. Membr. Sci.* **2016,** 520, 385). The ratio of the pure permeabilities for two different gases then leads to the ideal selectivity of the membrane. However, when real membranes are run under mixed-gas conditions, their actual separation factor is often different from the ideal value. It is thus pertinent to investigate whether MD simulations can shed light on these mixed-gas effects.

Within this context, the methodology depends on the nature of the model. In the surface models, the mixed-gas nature of the feed can be monitored in the reservoirs. Sorption and diffusion occur naturally, as will be shown for O_2/N_2 separation in a 6FDA-6FpDA polyimide. On the other hand, there are no explicit reservoirs in the bulk models. We will present a novel iterative method that fixes the pressure and changes the number of penetrant molecules in the polymer phase to obtain an uptake in equilibrium with a mixed feed gas of fixed composition. Limiting gas diffusivities will be estimated using the Trajectory Extending Kinetic Monte Carlo method. This will be illustrated by N_2/CH_4 separation in the aforementioned polyimide. The extension to multi-phase gas feeds will also be discussed.



Keywords: MD simulations, Transport, Mixed-gas, Polymer membranes

[P2.097]

Impact of ethanol on transfer of charged solutes in water/ethanol media in ultrafiltration, nanofiltration and reverse osmosis

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Ethanol is widely used to extract target components from renewable bio-resources. But generally complementary separations are required that could be achieved by UF, NF and RO.

Except the lack of resistant membranes and the safety of these harsh filtration conditions, one of the drawback is the lack of fundamental knowledge on transfer mechanisms of solutes (inorganic salts, small organics, polysaccharides, proteins…) in pure ethanol.

To that, in a first step we considered the impact of ethanol in media where the main solvent remained water (dilution of ethanol extracts). For safety reasons, the upper chosen limit in ethanol was 30 % v/v.

In this study, charged solutes were filtered in water/ethanol 100/0 and 70/30 v/v in cross-flow filtration:

○ UF: the rejection of a positively charged protein (lysozyme 14,3 $kg.mol^{-1}$) varied between 0 and 99% depending on the pH and the ionic strength I with a zirconia membrane (M1-Carbosep, 150 $kg.mol^{-1}$).

○ NF: in the range 6-28 bar, the rejection order between NaCl and $CaCl_2$ ($I= 8.6 \times 10^{-3}$ $mol.L^{-1}$) was reversed compared to that in water with a polypiperazine amide membrane (NF270, 180 $g.mol^{-1}$)

○ RO: the rejection of a negatively charged azo-dye (Tropaeolin O, 293 $g.mol^{-1}$) decreased from 97% at I=0 to 94% at $I= 100 \times 10^{-3}$ $mol.L^{-1}$ (NaCl) at 20 bar with a polyamide membrane (TFC HR)

Addition of 30% ethanol induces an increase in viscosity and a decrease in the dielectric constant. The diffusion coefficients, and the electrophoretic mobility of charged solutes are divided by two; the decrease in the dielectric constant would modify electrostatic interactions. Nevertheless, results highlight that electrostatic interactions remained efficient in presence of 30% ethanol in UF, NF and RO.

The role of osmotic pressure (NF, RO) would also be discussed as well as the impact of the confinement of solvents in the membrane pores.

Keywords: ultrafiltration, nanofiltration, reverse osmosis, transfer in water/ethanol

[P2.098]

Conceptual methodology for membrane cascade design to separate solutes of intermediate retentions in highly different concentrations thanks to a method inspired from that of McCabe-Thiele

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Université de Rennes 1, France

The commercial available membranes often have not sufficient selectivity for fractionating mixtures into single solutes or enriched fractions. Membrane cascades with recycling between stages are promising solutions to overcome this issue (**Figure 1a**). However, there is still a lack of conceptual methodology for their design.

Therefore, the method of McCabe-Thiele, originally developed for distillation, was adapted.

For membrane separation of 2 components in 1/1000 proportions the graphical method required the use of a log-log plot. 3 types of curves based on experimental data are needed that links the mole fraction of a compound in the retentate and in the permeate stream (**Figure 2**):

○ One partitioning curve for a given stage and a given VRR; one specific curve per VRR.

○ For the permeate retreatment section, an operating curve gives the relationship between the retentate of a given stage and the permeate of the previous stage; one specific straight line per stage.

○ For the retentate retreatment section, an operating curve gives the relationship between the permeate of a given stage and the retentate of the previous stage; one specific straight line per stage

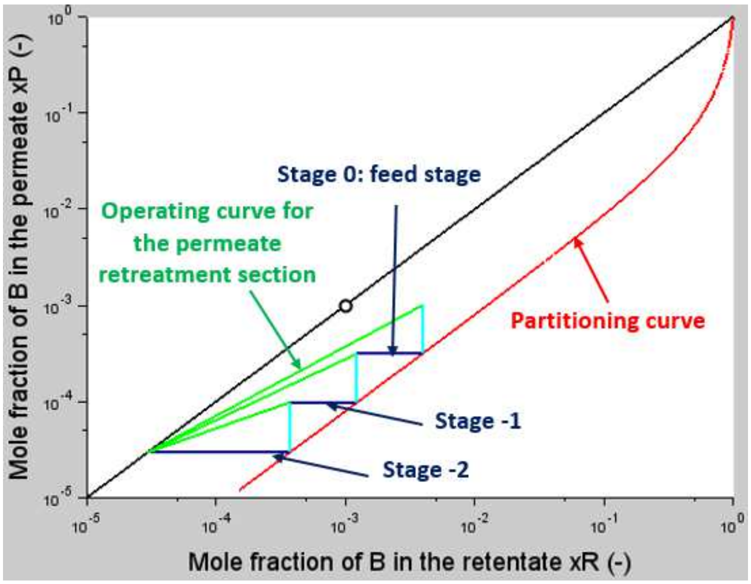

Figure 2: Graphical construction of the method inspired from that of McCabe -Thiele

This method was applied for the separation of solutes A (Retention=30%) and B (Retention=88%) in mixture ([A]=1 M and [B]=1 mM). The goal of the separation was set at more than 70% of A extraction in permeate and at least 97% of B recovery in retentate that cannot be fulfilled with a one-stage process

Several configurations can be initially proposed (**Figure 1a**). Applying the McCabe-Thiele method (**Figure 2**) permeate retreatment with 3 stages was expected to reach the goal (**Figure 1b**).

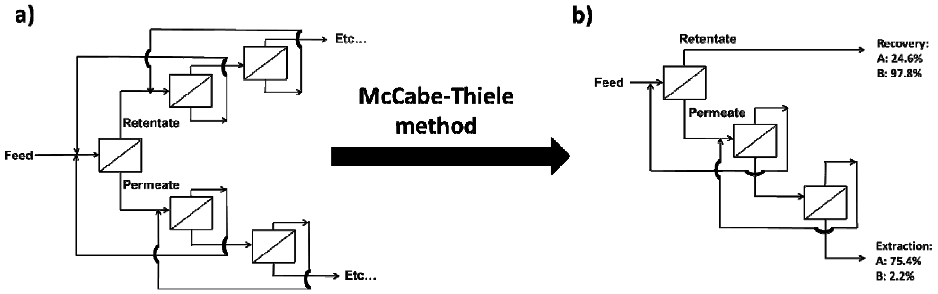

Figure 1: a) initial possible design of membrane cascades – b) 3 stages cascade drawn from McCabe-Thiele method

Keywords: cascade membrane design, McCabe-Thiele method

[P2.099]

A combined experimental and computational study of interactions between organic solutes and polyamide reverse osmosis membranes

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People's access to drinking water is a major challenge for the coming decades, not only for the developing countries but also for the industrialized states. This global issue is further aggravated by factors such as pollution and the inequality of its distribution.

Despite the technological importance of the reverse osmosis (RO) process, the molecular mechanisms of water and solute transport through RO membranes are not well understood, particularly at the molecular level. Several studies showed that rejection of uncharged solutes by RO membranes cannot be described by a simple sieving effect ruled by the relative size between these solutes and the free volumes within the membrane skin layer. However, getting quantitative information regarding solute / membrane affinity is extremely challenging because RO membranes are essentially thin-film composite materials, the skin layer of which does not represent more than ~ 0.1 % of the total membrane thickness.

In this work we investigated the separation performance of a commercial thin-film composite polyamide RO membrane with respect to three organic molecules with identical molecular mass (100 g/mol): 4-aminopiperidine, pinacolone, and methylisobuthyl ketone. The interaction energy between the different solutes and the membrane phase was computed from molecular dynamics simulations. The resulting sequence was found to correlate well with experimental rejections. Molecular simulations showed that the total solute-hydrated membrane interaction is governed by both solute-confined water and solute-polymer interactions. Sorption of the different organics within the membrane active layer was further determined from attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). A nice agreement was obtained between interaction energies computed from molecular simulations and the partitioning coefficients inferred from ATR-FTIR spectroscopy. Moreover, both ATR-FTIR and molecular simulations indicated a dramatic decrease in the organic solute diffusivity inside the RO membrane.

Keywords: Reverse osmosis, molecular simulations, membrane affinity

[P2.100]

Novel permeation mechanism in water permeable membranes investigated by non-equilibrium molecular simulation

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In this presentation, novel concept for achieving high water permeation through membranes was suggested and theoretically confirmed by using non-equilibrium molecular dynamics (MD). Recently, much attention has been paid to water transport in aquaporins because aquaporins are membrane water channels that play critical roles in controlling the water contents of cells and show high water flux. Hydrogen bonds between water molecule and well distributed charged amino acids on the water channel are believed to give high water flux and perfect water selectivity against any ions. Therefore, by resembling aquaporin, we prepared several water channel models in which atomic charges were distributed uniformly in the one dimensional pore wall to control molecular orientation of permeating water molecules. MD simulations using these models clarify that orientation of water molecules during the diffusion are well controlled with keeping hydrogen bonding to charged atoms in the pore. Moreover, effect of flux on structural factors such as pore diameter and distribution of charged atoms are investigated to clarify the optimal structural parameters to achieve molecular orientation control concept. To consider the application to reverse osmosis, non-equilibrium MD (NEMD) are employed for same models. NEMD simulations showed a pronounced water flux when molecular orientations of water in the pore were well controlled. We found that the interaction with pore wall decreases the surface barrier when water molecule enter the pore from aqueous phase and becomes to increase the driving force of continuous permeation from feed side to permeate side. More details of results including dependency of flux and dynamics on pressure difference will be presented at the conference.

Keywords: nanofiltration, non-equilibrium molecular dynamics, pressure-driven permeation, molecular orientation control

[P1.138]

Effects of dianhydrides precursors on molecular weight and thermal stability of hydroxy-polyimide membrane

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Polybenzoxazole (PBO), made by the thermal rearrangement of a hydroxyl-polyimide (HPI) formed from diamine and dianhydride precursors, is currently a very popular polymer in membrane research fields. Everything from its permeation properties to the path of its formation have been studied. However, a glaring paucity within these studies exists: there are no studies that directly compare the dianhydride precursors of the polyimides and their effects on the molecular weight and thermal stability of the resulting polyimides. This ongoing research reports on preliminary results of a study involving four dianhydrides, where we show that all four of them can be made into polyimides in conjunction with the diamine 2,2’-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (bisAPAF). We also report on the effects of the dianhydride on the number average and weight average molecular weights of the hydroxyl-polyimides. High molecular weight HPSs with the pattern PMDA<HPI-BTDA<HPI-ODPA were formed coupled with good thermo-oxidative stability. The ranking of thermal stability is HPI-BTDA<HPI-PMDA<HPI-BPDA<HPI-ODPA. FTIR analysis was used to identify the chemical changes in the polymer, while TG-DSC analysis confirmed synthesized polymers’ thermal stability and potential conversion to PBO structure via thermal treatment.

Keywords: Polybenzoxazole, Thermal rearrangement, Membranes, Gas separation

[P2.102]

Application of open-source CFD package (OpenFOAM) to membrane distillation modeling

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We investigate fluid dynamic and thermodynamic behaviors of membrane distillation (MD) processes of flat sheet and hollow fiber membrane modules using open-source computational fluid dynamics (CFD) package, OpenFOAM. OpenFOAM is a multi-physics simulation tool, which recently became very popular in academic as well as industrial CFD communities. Having several types based on condensation schemes, MD is truly a multi-physical phenomena, containing momentum, energy, and mass transfer across two interfaces: one between feed stream and membrane, and the other between membrane and distillate stream. Length scales associated to MD processes include microscopic motion of vapor molecules, meso-scopic transport through pores, and macroscopic fluid flow with thermodynamic phase transition. Although accurate and rigorous MD simulations require information exchange between different length scales, it is formidable task to investigate MD processes from molecular dynamics level to continuum fluid dynamics phenomena. In this paper, key transport mechanisms in each sub-domains of MD modules are fundamentally discussed to have at least one (out of three) transfer mechanisms as a perturbation, leaving the other two in a strongly correlated phase in each membrane region. Module-scale simulations visualizes the transient, correlated momentum/energy/mass transfer phenomena of direct contact membrane distillation and vacuum membrane distillation. The present method of OpenFOAM for MD processes can significantly enhance design and optimization techniques for MD modules/stacks in industrial applications.

Keywords: Computational Fluid Dynamics, OpenFOAM, Membrane Distillation, Multi-scale simulation

[P2.103]

OpenFoam simulation for direct contact membrane distillation (DCMD)

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OpenFOAM (OF) is a multi-physics simulation package containing a number of solvers for engineering and physics applications, specifically including computational fluid dynamics. OF has currently more than 80 solvers for fluid dynamics, reactive flow, combustion, direct numerical simulation, heat transfer, particle-tracking, molecular dynamics, electrodynamics, (mechanical) stress analysis of solid, and finance. Membrane distillation is a complex and coupled phenomena of momentum, energy (heat), and mass transfer in three separated regions. Each region has two dominant transfer mechanism, under which mass transfer can be treated as a perturbation. The water evaporation on the membrane surface is a molecular phenomena and the feed and distillate stream is macroscopic continuum phenomena. The order of magnitude in the length scale varies from 0.1 micron to 0.1 meter. In this light, it is a difficult task to seamlessly couple the evaporation of water molecules, vapor migration through membrane pores, and fluid flow in membrane modules. In this paper, we propose a simulation method to eliminate the length-scale restriction, and converge governing equations at the three levels into one phenomenological model containing material properties of porous MD membranes and their influence on MD performance.

Keywords: Computational Fluid Dynamics, Direct contact membrane distillation, OpenFOAM, Multi-physics simulation

[P2.104]

The role of water activity (a_w) in water transport through membranes

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The vapor pressure of water contained in two commercially available membranes was measured. The water concentration isotherm produced a “material osmotic density” a quantifiable expression of a membrane’s hydrophilicity. The water activity measurements of ternary mixtures composed of water-NaCl-membrane and contact angle measurements of water-NaCl mixtures indicate the membrane’s propensity to de-wet solutions of even modest salinity below the macroscopic scale. The de-wetting of pores was evaluated as a quantum event at the molecular to meso-scale that allows the membranes to violate the principle of microscopic reversibility and thus explains the unidirectional function of asymmetric membranes. The propensity of a membrane to de- wet suggests that water transport through membranes is limited by the available number/volume of pathways which may correlate to the membrane’s material osmotic density, a quantifiable measure of hydrophilicity. The material osmotic density can be incorporated into a quantitative model of water transport through a membrane based on available and continually wetted pathways. This proposed facilitated transport model of water flux is fundamentally different than established thermodynamic-gradient solution-diffusion models of water flux.

Keywords: membrane hydrophilicity, water transport, water activity, wetting

[P2.105]

Preparation of Amphotericin B-Ergosterol structures and molecular simulation of water adsorption and diffusion

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In this study, molecular simulation was used to explore the structural characteristics and transport performances of amphotericin B-ergosterol (AmBEr) channels. A molecular dynamics (MD) technique was used to construct two types of molecular models of AmBEr channels: single-layer channel (SLC) and double-layer channel (DLC) as shown in Fig.1 (a) and (b). MD simulation revealed the difference of structure, channel diameter, interior affinity, and transportation behavior between SLC and DLC AmBEr models (Fig. 2). The Monte Carlo (MC) method was adopted to investigate the sorption behaviors in these channels. The intramolecular properties and intermolecular interactions indicated that the feasibility of simple model construction method adopted in this study. The internal diameter and channel shape showed that the funnel type AmBEr channels, which led to high permeability and selectivity performance. The special tunnel shape was reflected in the diffusion calculation that showed as high displacement of water molecules in two types of channel models as bulk water, and water permeabilities for these AmBEr models were estimated as shown in Table 1 based on the solution-diffusion model. The water molecule-channel hydrogen bond distribution and snapshot analyses of adsorption site revealed that the affinity between amphotericin B monomer and water molecule. The novel chemical structure of amphotericin B monomer has both the hydrophilic and hydrophobic segments at the same time, which was reflected in the unique shape of an water adsorption isotherm. That is, the unique three stepwise increases were observed in adsorption behavior for water molecules.

The results of the structure and water transport properties of AmBEr channel, as shown by the MD technic and MC methods, provided valuable information that would have been hard to obtain from actual experiment. The simulation techniques can be useful for structural characterization of the channel and estimation of transport behavior of the molecules in AmBEr channels.

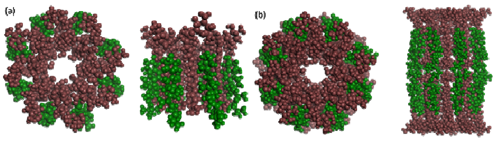

Fig. 1 (a) Single layer AmBEr channel top view (left) side view (right), and (b) Double layer channel AmBEr channel top view (left) side view (right) (red: Amphotericin B, green: ergosterol)

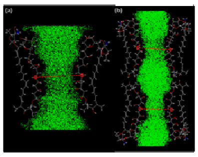

Fig. 2 Section vies of SLC (left) and DLC (right) simulation channel

Table 1 Water molecule transport properties of AmBEr simulation

	SLC	DLC
Solubility Coefficient [mole/Pa m^3]	4.75	2.66
Diffusivity Coefficient [m^2/s]	1.3×10^{-9}	2.1×10^{-9}
Permeability [mole m /(m^2 s Pa)]	6.2×10^{-9}	5.6×10^{-9}

Reference

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Keywords: Amphotericin B, Ergosterol, Molecular Dynamic Dimulation, Water Transport

[P2.106]

Preparation of thin-film composite membranes with tailored structure using novel amine monomers for nanofiltration

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Fundamental understanding on the effects of different monomers on thin-film composite (TFC) membrane properties is necessary in order to tailor desired membrane pore structure and separation performance. In this work, TFC membranes were successfully prepared via interfacial polymerization (IP) of TMC and novel aliphatic amines containing ether bond. The chemical features and morphology of the thin-film layer were confirmed by XPS, ATR-FTIR and SEM, while the surface properties of the membrane were characterized by water contact angel and zeta potential measurement. The separation performance of the membranes were evaluated by a cross-flow device as well as a zero-pressure diffusion experiment.

The results revealed that the novel monomers were successfully incorporated into the membranes. The resultant membranes showed a relatively rough surface with sphere-like pattern. Besides, the membranes fabricated with novel monomers exhibited less hydrophilicity and surface charge compared to PIP-TFC membrane, which indicated a weaker affinity to water molecules.

With the increase of the proportion of aliphatic amines in the aqueous phase, the resultant membranes could all maintain a high Na_2SO_4 rejection(>99%). While two out of the three novel membranes exhibited a rather low rejection for NaCl (<17%), which indicated that the membrane possessed high selectivity for SO4$_2$- /Cl-. Finally yet importantly, the pore structures of the membranes were characterized by the diffusion of small molecules through the thin-film.

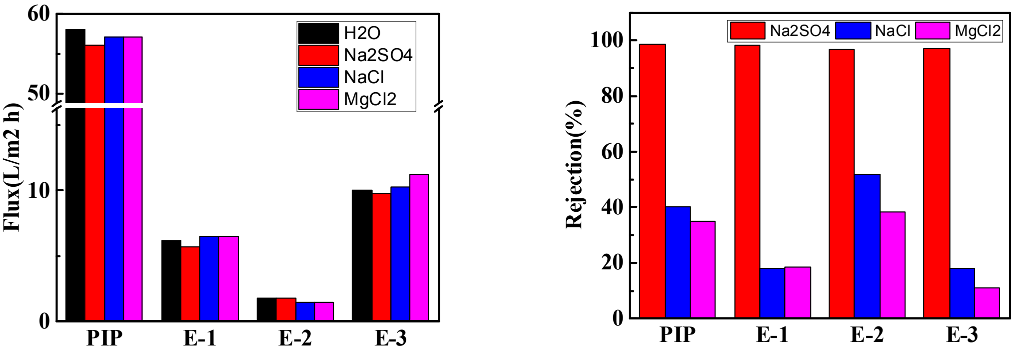

Fig.1. The permeate flux and salt rejection of PIP-TFC membranes and membranes prepared in this work

Keywords: thin-film composite membrane, interfacial polymerization, monomer, nanofiltration

[P2.107]

Transport performance of nanofiltration membranes in metallurgical and mining efflents: Modelling the separation of oxyacids (H_2SO_4 and H_3AsO_4) from metallic species (Cu, Zn)

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[1]Universitat Politècnica de Catalunya (UPC), Spain, [2]Water Technology Center (CETaqua), Spain, [3]Catalan Institute for Research and Advanced Studies (ICREA), Spain

Membrane technology has gained importance over the past decades for treat wastewaters. Among the features that could affect the separation performance, the effect of chemical equilibrium was little studied and was proved to be noticeable. The existence of chemical equilibrium in waters could imply the presence of non-charged solutes (e.g. magnesium sulphate partially dissociates) or the formation of complexes among elements in solution (e.g. hydrometallurgical waters or acid mine drainage, in which ions complexes with sulphate or remain freely). Acidic waters generated in the metallurgical and mining industry circuits are characterized by the presence of high content of oxyacids (e.g. H_2SO_4, H_3AsO_4) with metallic species (Cu, Zn, Ni, Co, Cd).

Nanofiltration (NF) membranes have proved to be an effective technique for brine desalination and also for acidic metal stream treatment to purify the acid (e.g. H_2SO_4) from arsenic acid (H_3AsO_4) and concentrate metals in solution. In order to study the impact of chemical equilibrium in the separation performance, several experiments were carried out with synthetic solutions by varying feed concentration. Experiments were performed with a flat sheet NF270 membrane (based on polyamide active layer) in a cross-flow. Trans-membrane pressure was varied (from osmotic pressure to 18 bar), while feed temperature and cross-flow velocity were kept constant (0.7 m/s).

Results were fitted according to solution-diffusion model, in which reactive transport was coupled. The contribution of all the ions to solute permeation was determined by the calculation of the membrane permeance to ion. This parameter was determined for each ion in solution, including the free ions or the complexes. Model fitted properly rejection curves for the ions in solution, being the standard deviation from experimental data less than 10 %.

Mathematical model allowed predicting the behaviour of elements in solution, which confirm the applicability of solution-diffusion model coupled with reactive transport.

ACKNOWLEDGMENTS

This research was supported by the Waste2Product project (CTM2014-57302-R) financed by the Spanish Ministry of Economy and Competitiveness (MINECO) and the Catalan Government (Project Ref. SGR2014-50-SETRI), Spain. As well, Xanel Vecino thanks MINECO for her Juan de la Cierva contract (ref. FJCI-2014-19732) and Julio López for his pre-doctoral grant (ref. BES-2015-075051).

[P2.108]

High-flux nanofiltration membranes filled with zwitterion-poly(dopamine) modified multiwall carbon nanotubes

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Recently, lots of researches have been focus on the incorporation of nanomaterials in nanofiltration membranes (NFMs), which can produce low-resistance channels for high water permeability. Multiwall carbon nanotubes (MWCNTs), as a kind of nanomaterials, have been generally used to prepare mix matrix membrane. However, agglomeration and weak compatibility make it difficult to incorporate and well disperse in NFMs. Consequently, modified MWCNTs (MMWCNTs) have been widely concerned. Zwitterions with high hydrophilicity are becoming promising materials for nanofiltration membranes, which can be used to obtain MMWCNTs with well dispersity. N-aminoethyl piperazine propane sulfonate (AEPPS) with the amine groups can crosslink with 1, 3, 5-benzenetricarboxylic chloride (TMC) and immobilize MMWCNTs in polyamide matrix. However, traditional ways of anchoring zwitterions on MWCNTs is complicated. As we know, dopamine, a mussel-inspired catechol-amine, can normally self-polymerizes to form poly-(dopamine) ,which can strongly adhere on virtually any type of solid surface and undergo versatile reactions with molecules presenting amine groups. Therefore, poly-(dopamine) can act as an interlayer between MWCNTs and AEPPS, which provides a facile way to anchor AEPPS on MWCNTs.

In this work, MMWCNTs were prepared by co-deposition of poly-(dopamine) and AEPPS on the surface of MWCNTs. Then the MMWCNTs were dispersed in PIP aqueous solution and NFMs were prepared via interfacial polymerization. The MMWCNTs and NFMs were characterized by FTIR, XPS, TGA, TEM and AFM. At optimized conditions, the water flux of the PIP/MMWCNTs/TMC membrane was 12.7 L m^{-2} h^{-1} bar^{-1}, 1.8 times as high as the pristine PIP/TMC membrane without sacrificing the rejection of Na_2SO_4. Furthermore, all the NFMs showed good nanofiltration stability during the long-term operation. This work gives a facile and general method to obtain high flux NFMs filled with MMWCNTs.

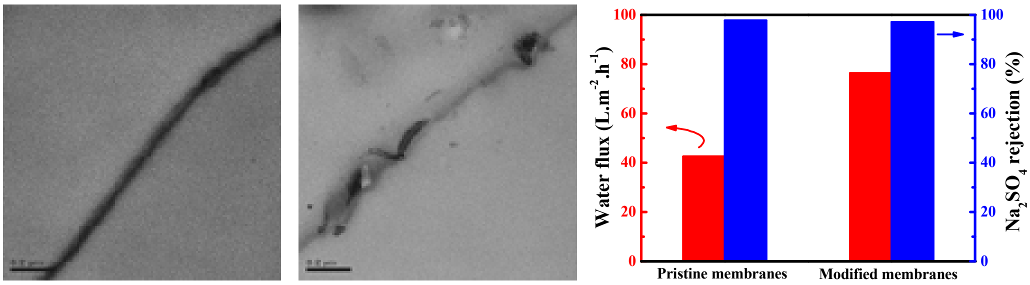

Figure 1. TEM images of PIP/TMC (left), PIP/MMWCNTs/TMC (middle), the performance of NFMs (right)

Keywords: Nanofiltration, High-flux, Zwitterion, Carbon nanotubes

[P2.109]

Carbon molecular sieve membranes supported by stainless steel porous substrate

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Carbon molecular sieve (CMS) membranes have the potential to separate organic solvents due to their micropore structure and good solvent stability. A variety of polymer precursors can be used to create CMS membranes. While hollow fiber membranes incorporate large area of membranes into small volumes, the spinning process itself is not an efficient way to quickly screen materials. A platform is needed to screen potential polymer precursors and pyrolysis conditions.

We will present our research on CMS membranes supported by stainless steel hollow fiber porous substrate. Torlon®/stainless steel particle hollow fibers were spun and subsequently sintered into a porous substrate. Polymer precursor membranes were fabricated by dip coating the stainless steel fibers into the polymer solutions. The quality of dip–coated membranes is affected by the following factors: polymer solution solvent type, polymer concentration, dip coating atmosphere, substrate roughness, and drawing speed. By optimizing those parameters, we successfully dip coat polymer membranes including, Matrimid ®, PVDF, PIM-1 and 6FDA-DAM. Those polymer membranes can be pyrolyzed into defect-free CMS membranes. Our results show that stainless steel porous hollow fibers are an efficient platform to probe the organic solvent permeation properties of a variety of CMS microstructures.

Keywords: stainless steel porous substrate, hollow fiber, dip coating, polymer precursor

[P2.110]

Preparation and characterization of nano-filtration membrane to improve acid-resistance property

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1. Introduction

Nanofiltration (NF) membrane is used for the industrial wastewater that NF demand has greatly expanded for many new interesting applications such as for removal of rare-metal in abundant acids, separation/purification in organic solvents and etc. Abundant acids like HCl, H_2SO_4, HNO_3 and other rare metals can be potentially separated using NF membrane via recycling waste resources system. The acidic effluents industrial has being demanding a durable NF membrane to separate rare-metals from the waste acid solution. This study carried on to prepare a novel acid resistance of NF membrane with increasing rare-metal separation capacity in prolonged exposure process.

2. Methods

The acid-resistance NF membrane was prepared by the interfacial polymerization with reaction of aliphatic amine and trimesoyl chloride (TMC) on a porous PSf support membrane, followed by thermal treatment. We used in melamine and sulfanilamide as additive in order to improve the water flux and acid resistance. The acid resistance tests were carried out with 2000ppm $MgSO_4$ and NaCl feed water stream under an operation pressure of 75 psi for 30 min with effective membrane area of 27.01 cm^2.

3. Results and Discussion

The optical NF membrane exhibited a rejection of 98 %, and a water flux of 33 GFD with $MgSO_4$ feed water, and the NaCl rejection was 20%. The initial value of water flux and rejection of optical NF membrane has been maintained in four weeks in H_2SO_4 solution of 15 wt%. The structure and characteristics of the membrane were determined by ATR-FTIR, XPS and FE-SEM.

Keywords: Nanofiltration membrane, Acid-resistance, Interfacial polymerization

[P2.111]

Investigation of the impact of ethanol during nanofiltration of salts in water/ethanol mixtures

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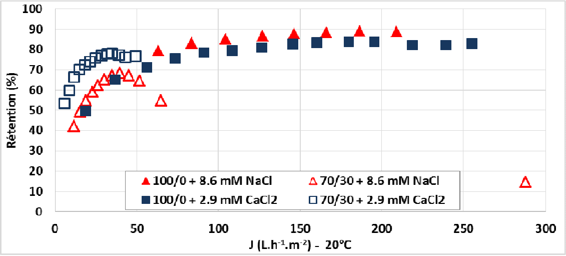
Ethanol is often used as a solvent for extraction of compounds from raw renewable materials. Nevertheless, complementary separation, for instance by nanofiltration, is generally necessary to enrich the medium in the target components. However, the conventional membranes are not always compatibles with pure ethanol. An alternative is to carry out NF in water/ethanol mixture after appropriate dilution (maximum 30% ethanol).

This study aimed at showing the impact of ethanol on retentions of inorganic salts (NaCl 0-1 mol.L^{-1} or $CaCl_2$ 0-0.033 mol.L^{-1}) in water/ethanol mixtures (100/0 to 70/30 v/v), with NF270 membrane (polypiperazine amide, FilmTec, MWCO 180 g.mol^{-1}).

During NF of water/ethanol mixtures, the permeate flux J decreased as the ethanol percentage increased. It was confirmed that neither the difference in osmotic pressure nor the concentration polarization has an impact on J. This suggested that the flux reduction was due to ethanol transport in the membrane (non- swollen) pores.

In water, at ionic strength I= 8.6x10^{-3} mol.L^{-1}, NaCl retention (Ret_{NaCl}) and $CaCl_2$ retention (Ret_{CaCl2}) reached a plateau as the flux increased. On the contrary, in water/ethanol 70/30, retention dropped when fluxes were high enough indicating a change in the transfer mechanisms (**Figure 1**).

The membrane selectivity I=8.6x10^{-3} mol.L^{-1} changed in presence of ethanol. Indeed, Ret_{NaCl} was higher than Ret_{CaCl2} in water whereas the order of retentions was reversed in 70/30 mixture.



Ret_{NaCl} is lower in 70/30 mixture than in water. Results suggested that electrostatic repulsive interactions existed in both medium but have less impact in 70/30 mixture. In contrast, Ret_{CaCl2} was higher in 70/30 mixture than in water, which was more surprising and suggested a reversal of the membrane's charge. This assumption needs to be validated by measurements of the membrane streaming potential.

Figure 1: Ret_{NaCl} and Ret_{CaCl2} (I=8.6x10^{-3} mol.L^{-1}) in water and in 70/30 water/ethanol mixture.

Keywords: transfer mechanism, water/ethanol, inorganic salts, nanofiltration

[P2.112]

Study of the influence of water matrix on the rejection of organic acids in low pressure reverse osmosis membranes using factorial experimental design methodology

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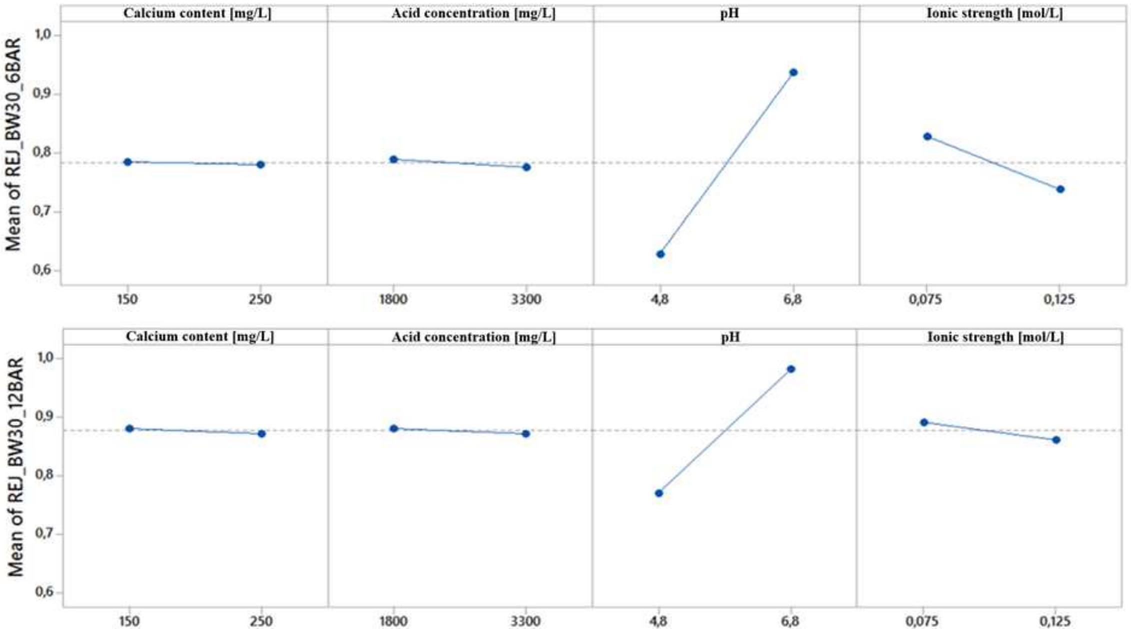
The present work investigates the influence of the water matrix on organic acid rejection in nanofiltration and low pressure RO. The experiments were designed by the factorial planning methodology to allow the understanding of the phenomenon in a multivariate scenario.

Ionic strength, pH-value, acetic acid concentration and calcium content were the selected design factors through prior statistical analysis of samples from a hydrolysis reactor. Experiments were carried out on a cross-flow membrane unit equipped with NF90 and BW30 (Dow Chemicals) membranes at 6 and 12 bar, 25°C and 0.22 m/s cross flow velocity.



the other hand, the ionized acid fraction also increases with pH-value due to the displacement of the acid-base equilibrium.

Ionic strength presented also well significant influence on acid rejection, but with a decreasing trend, as a result of the compensation of the negatively charged groups on the membrane surface and the positive ions present in the solution (K^+ and Ca^{2+}) (Fig. 1). The positive significance and magnitude of the synergic effects of the other factors (acetic acid concentration and calcium content) demonstrate the non-linear behaviour of the rejection, indicating that the water matrix has complex influences on the membrane process and, therefore, the one-factor-at-time experiments cannot be the best approach in rejection studies. Additionally, it was verified that influence of water matrix depends on the operational pressure: similar changes on water matrix resulted in a lower performance difference at high pressure.

Keywords: organic acid rejection, NF/LPRO, factorial experimental design

[P2.113]

Acid resistant nanofiltration membrane fabrication and performance

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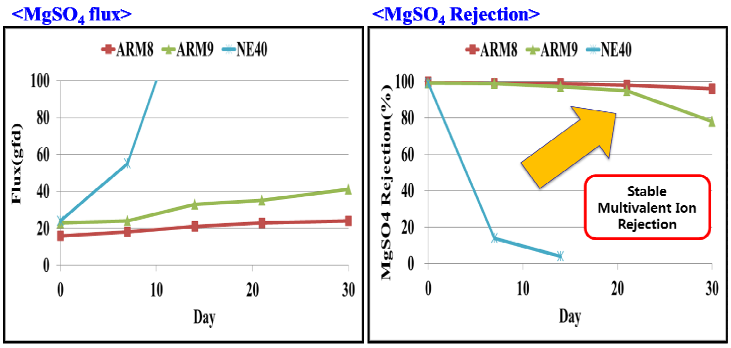
Nanofiltration Membranes (NF) are membranes which incorporate nanometer sized pores to selectively separate larger ionic and organic species from water. These membranes are most often made of polymer thin films and are used in water softening applications to remove scale forming divalent ions such as calcium or magnesium. Recent developments in nanofiltration technology have expanded the use of these membranes in a variety of new areas such as pharmaceuticals, industrial chemical production, and pretreatment for seawater desalination. As such, nanofiltration membranes which can survive in harsh conditions such highly acidic environments has drawn great interest in the industry. Acid resistant nanofiltration membrane (ARM) was fabricated using interfacial polymerization of a specially formulated polyamide onto a polysulfone support layer. ARM showed extreme durability in highly acidic environments. As compared to a regular NE40 (commercial NF), ARM showed little change in flux and divalent ion rejection after being exposed to acid for 30 days. The ARM membranes are still in its initial stages but in extreme acidic situations (15% sulfuric acid soaking), ARM showed stable performance in comparison to regular grade NF membranes which saw losses in both flux and rejection.



<$MgSO_4$ flux>

<$MgSO_4$ Rejection>

Test Condition: 2,000 ppm $MgSO_4$, 75 psi, 25℃, 15% H_2SO_4 solution soaking

Keywords: Nanofiltration, acid resistant, membrane, polyamide

[P2.114]

Preparation of integrally polyimide-based composite solvent resistant nanofiltration membranes by interfacial polymerization for enhanced solvent resistant performance

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Most solvent - resistance nanofiltration (SRNF) membranes were prepared by phase inversion method. However, they could not meet the demand of high permeability for organic solvent separations. Till now relative few research works were focused on interfacial polymerization technique owing to the adherence difference between the different materials used for the ultrafiltration (UF) substrate and the dense skin layer.

Here we fabricated polyimide (PI) ultra-thin skin layer onto porous PI UF substrate by interfacial polymerization and subsequent imidization and cross-linking. M-phenylenediamine (MPD) and 1,2,4,5-benzene tetramethyl acyl chloride (BTAC) were used as aqueous and organics monomers, respectively. Dopamine was taken as a kind of monomer in the aqueous solution to build a powerful binding between PI substrate and PI skin layer. Since both the substrate and the skin layer were PI polymer after imidization, we cross-linked both layers simultaneously by ethanediamine to enhanced the interconnectivity between them.

The results demonstrated that integrally PI SRNF membrane were fabricated. FTIR-ATR, Raman and XPS indicated that PI skin layer had been formed successfully after the imidization, and dopamine had participated in the reaction. The integrally PI SRNF membrane showed relative high permeability, it could achieve ethanol permeate flux of 12.04 L m^{-2} h^{-1} at 1.0MPa with RB rejection of 97.31% under optimized conditions and after post activated by DMF. The integrally PI SRNF membranes with dopamine addition showed enhanced solvent resistance. After immersion in organic solvents such as DMF, DMAC, DMSO and NMP, the membranes still remained RB rejection of 97.23% for 6 weeks in DMF and of 75.42% for 4 weeks in NMP and were more stable than those fabricated without adding dopamine monomer.

In this way we successfully fabricated a kind of integrally PI-based dopamine-containing composite SRNF membranes with excellent solvent resistance and good separation performance.

Keywords: solvent resistance nanofiltration, interfacial polymerization, imidization, dopamine

[P2.115]

UV and EB cross-linked polysulfone based membranes for versatile applications

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In separation technology, polymeric membranes have found wide application. Cross-linking procedures are needed to enhance the stability of commonly used polymers such as polyimides and poly(aryl sulfones), which are not sufficiently resistant to heat and harsh solvents (i.e. aprotic solvents). Chemical cross-linking of membranes has so far mainly been performed to apply them in solvent resistance nanofiltration (SRNF) [1]. However, this method is not suitable for polymers without reactive groups, e.g. poly(aryl sulfones) or poly(ether ether ketones). Hence, there is a need to design an efficient method for post-synthesis cross-linking of such polymers.

In this work, two environmentally friendly irradiation methods were applied in this work, namely ultraviolet (UV) and electron beam (EB) cross-linking. Non-solvent phase inversion method has been used to synthesize the membranes, followed by UV or EB curing[2,3]. Semi-interpenetrating polymer network (SIPN) of a linear polysulfone and a cross-linked polyacrylate formed the matrix of the membranes. The effect of the type and concentration of the photo-initiator and cross-linker functionality on the curing efficiency and membrane SRNF performance were investigated in depth, together with the membrane chemical stability. Besides, different irradiation doses were applied to tune the different curing parameters.

Good performing SRNF membranes with superior chemical stability and various morphologies from macrovoid to sponge-like structure, have been produced by appropriately tuning the synthesis conditions. The influence of phase inversion parameters (i.e polymer concentration, co-solvent type and concentration, evaporation time) on SRNF membrane performance was also studied in order to achieve the most optimal system. The mechanical characteristics, the effect of casting thickness and the surface properties of the membranes cross-linked by both irradiation methods were further investigated. Additionally, the swelling behavior of UV-cured thin PSU films as function of different curing parameters (i.e. radiation dose and cross-linker functionality) was analyzed with ellipsometry.

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Keywords: Phase inversion, Cross-linking, UV and EB-curing, Polysulfone membranes

[P2.116]

Use of green solvents in membrane preparation

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Aim of this work is to replace traditional solvents in membrane preparation by green/bio-solvents. A while set of carbonates, glycerol derviatives and bio-based solvents were screened on their possibility to dissolve common membrane polymers and create porous structures via the process of phase inversion.

Cellulose acetate (CA) was then selected to prepare nanofiltration membranes by using methyl lactate as green solvent.

Different concentrations of CA solutions were prepared in methyl lactate. All membranes were obtained by water induced phase inversion. Filtrations were performed at 25 °C under pressures ranging from 3 to 15 bar using rose bengal solutions. Membranes morphology and internal structure were characterized using scanning electron microscope (SEM).

With increasing cellulose acetate concentrations (8 to 20%) during membranes preparation, rejections increased from 40 to 99.5%, while permeances decreased from 35 to 2.35 L/m^2 h bar (figure 1).

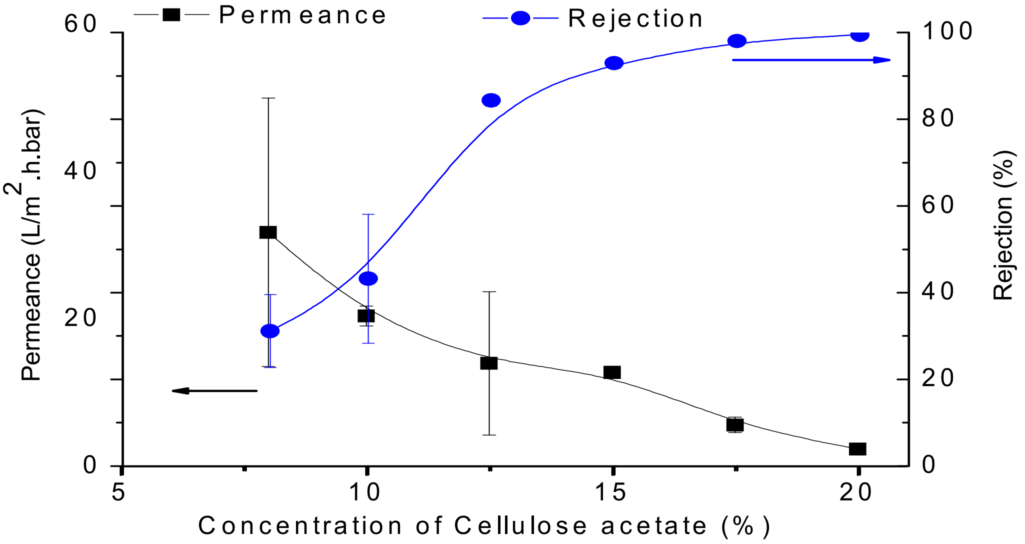

Figure 1 Effect of concentration of cellulose acetate in the membrane preparation solution on rejection and permeance using aqueous rose bengal solutions.

Keywords: Green solvents, ,, Cellulose acetate, Phase inversion, nanofiltration

[P2.117]

Screening of membranes to treat ACN-based feeds in SRNF

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Introduction

A range of commercially available and lab-made membranes was screened for use in feeds containing acetonitrile (ACN). ACN was selected as it is one of the most widely used solvents in pharmaceutical industry and surprisingly absent in earlier SRNF work. The selected membranes ranged from the tight nanofiltration range to the lower end ultrafiltration range, prepared from different membrane chemistries and with different membrane preparation methods.

Methods

Multiple dyes were tested as probe molecules to study the retention behavior of the membranes in ACN. Gel content measurements were conducted on the membranes and interaction parameters with ACN, the dyes and the membranes were calculated to link physico-chemical properties to separation performances.

Results

ACN was found to be a very appropriate solvent for SRNF-applications, as most membranes reached high fluxes and retentions, comparable to those obtained in most other solvents. As most membrane polymers did not dissolve in ACN, membrane crosslinking is not even strictly necessary to ensure stability of the membranes when applied in these feeds.

Discussion

The screened membranes all showed permeances that are higher than in other known solvents, thanks to the low viscosity of ACN. For example, membranes based on TBPEEK and PSf showed an average permeance in ACN that is over 20 times higher than in IPA, whilst keeping their mechanical integrity. For the commercial Duramem® membranes, a nice MWCO-curve could be constructed from the retention data. This was not possible for most other membranes, which showed an unexpected low retention for the dyes Safranine O and Crystal Violet. The commercial SolSep membranes gave good retentions for most dyes but often at the expense of a lower permeance.

In particular, PI-based membranes seem very suitable for SRNF-filtrations with ACN as a solvent. Other polymers tend to swell more, causing lower retentions and very high fluxes.

Keywords: Solvent resistant nanofiltration membranes, ACN, Industrial applications, High-throughput testing

[P2.118]

Application of composite cellulose membranes for nanofiltration of aprotic solvents

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Aprotic solvents are widely used in petrochemical, pharmaceutical, and paint-and-coatings industry. Thus, there is a problem of aprotic solvents regeneration for their further use. Organic solvent nanofiltration process may be one of the cleaning methods. For successful and efficient implementation of this process, membrane should be mechanically and chemically stable in organic media. In this regard, such polymer as cellulose generates much interest. However, due to the presence of strong hydrogen bonds in the structure, cellulose dissolution is a problem that complicates membrane forming. N-methylmorpholine-N-oxide (MMO) is one of the most practically interesting solvents that offer massive opportunities of the membrane structure regulation. Thus, the purpose of this work was the separation of model mixtures based on aprotic solvents by using cellulosic composite membranes prepared from the solutions in MMO.

Composite membranes were formed from 12% cellulose solutions in MMO and characterized in permeability terms to aprotic solvents and rejection of anionic dyes OrangeII (O) (MW=350) and Remazol Brilliant Blue R (R) (MW=626). The membranes have been tested for nanofiltration of aprotic solvents. The solvent permeability has changed from 0.11±0.02 to 2.5±0.4 kg/(m2*h*bar) in the following order: DMSO>NMP>DMFA>THF>acetone. The rejection of the anionic dyes (O) and (R) has been found to range within 15-85% and 42-94%, respectively, on the solvent nature. Furthermore, experiments in sorption of aprotic solvents were performed, showing a marked difference in the interaction of certain solvents with the membrane material. A low degree of cellulose swelling in THF (37%) was detected, and higher degree of cellulose swelling was in DMSO (230%). In addition, it has been found that the rejection of solutes by the composite membranes correlates with the degree of cellulose swelling. A rejection of ≥90% has been achieved for (R), which has the larger molecule, at a cellulose swelling ratio of 100% or higher.

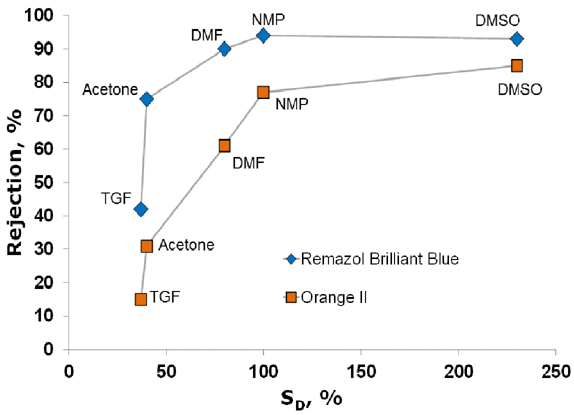

Figure 1. Rejection coefficients of Orange II and Remazol Brilliant Blue R as a function of the degree of swelling of cellulose membranes in organic solvents.

This work was done at TIPS RAS with financial support from Russian Scientific Foundation (project no. 14-19-01775).

Keywords: Cellulose, N-methylmorpholine-N-oxide, Composite membranes, Aprotic solvents

[P2.119]

Enhancing antibiofouling property of thin-film composite polyamide nanofiltration membrane by constructing double-layered PEO structure

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Membrane fouling caused by adsorption of organic macromolecular especially protein, impacts membrane performance and life, remains technical difficulties and challenges. In this study, we report a hydrophilic nanofiltration membrane with double-layered PEO structure to improve antifouling property. The first PEO layer (selective layer) was fabricated by interfacial polymerization between trimesoyl chloride and mixed amines mainly containing O,O’-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine) on porous polysulfone support membrane. The antifouling property against bovine serum albumin (BSA in solution at PH=7.4) for the nascent polyamide membrane with single PEO layer is not satisfactory with a highest water flux recovery of 63.6%. Therefor a second interfacial polymerization was carried out between Jeffamine and unreacted carbonyl group in the selective layer to establish another PEO layer on nascent polyamide layer. Then composite polyamide nanofiltration membranes with double-layered PEO structure were obtained. The experimental results show that the permeation-separation performance of membranes with double-layered PEO structure has little variation compared to that of single-layered membranes with a highest pure water flux of 51.7 $L\cdot m^{-2}\cdot h^{-1}$, and Na_2SO_4 rejection of 95.3%. This maybe due to the fact that the second PEO layer is comb-like structure without cross-linking between Jeffamine and trimesoyl chloride. While the antifouling property against BSA is significantly improved by the additional PEO layer with a highest water flux recovery of 99.6%. The experiment results also demonstrate that membranes with the double-layered PEO structure are more hydrophilic than the membrane with single-layered PEO□which lead to the improvement of antifouling property.

Keywords: Antifouling, PEO, Double-layered hydrophilic structure, Nanofiltration

[P2.120]

Role of reverse cation diffusion in forward osmosis biofouling by microalgae

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The process of forward osmosis, characterized in low-energy consumption and low membrane fouling, has been increasingly penetrated into the field of microalgae separation from water. In this work, the role of reverse cation diffusion in forward osmosis (FO) biofouling was investigated by microalgae including *Chlorella vulgaris and Scenedesmus obliquus*.

The FO biofouling was first compared by the SE culture medium after the separation of algal cell using CTA membrane and draw solution of NaCl, $MgCl_2$ and $CaCl_2$. The FO biofouling behavior including the water flux decline and the biofilm composition was related to the reverse cation diffusion.

The results showed that the reverse calcium diffusion led to significantly more severe water flux decline in comparison with reverse magnesium and sodium permeation for both of microalgae, and the soluble algal product (SAP) on the membrane was expectedly higher. When the same DOC of 20 mg L^{-1} in the SAP was used as the feed and the same osmotic pressure of 1 mM NaCl was controlled, the flux decline of three fourth and the SAP content of two times was observed for the $CaCl_2$ draw solution, indicating that FO biofouling was enhanced by the complexation of calcium ions to SAP.

The role of calcium cation on the SAP, the algal cell itself, and the broth was further investigated. The continue decrease of feed DOC followed by an abrupt increase verified the speculation that algal cells leaked more carbohydrates after interacting with the calcium. This work was endeavored to propel the integration of forward osmosis with traditional field of microalgae separation from water.

Keywords: Forward osmosis, Microalgae, wastewater, Soluable algal product (SAP)

[P2.121]

Characterization of a thermoresponsive chitosan derivative as a potential draw solute for forward osmosis

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[1]Chung Yuan University, Taiwan, [2]University of Arkansas, USA, [3]Zhejiang University, China

A thermoresponsive chitosan derivative was synthesized by reacting chitosan (CS) with butyl glycidyl ether (BGE) to break the inter- and intramolecular hydrogen bonds of the polymer. An aqueous solution of the thermoresponsive CS derivative exhibits a lower critical solution temperature (LCST) than CS, and it undergoes a phase transition separation when the temperature changes. Successful incorporation of BGE into the CS was confirmed by FTIR and XPS analyses. Varying the BGE content and the concentration of the aqueous solution produced different LCST ranges, as shown by transmittance vs temperature curves. The particle size was observed by scanning electron microscopy, which revealed that the particles were smaller and well dispersed at 15 °C, whereas the particles became larger and tended to aggregate at 60 °C. A similar trend was observed with the mean particle size measured using dynamic light scattering. Positron annihilation lifetime spectroscopy data also revealed the reversibility of the particle properties as a function of temperature. Microstructure analysis showed that the particles had larger free-volume sizes at 15 °C than at 60 °C. The particles were also found to be nontoxic with 92% cell survival. A simple forward osmosis (FO) test for dye dehydration revealed the potential use of the thermoresponsive chitosan derivative as a draw solute with a flux of 8.6 L/m2 h and rejection of 99.8%.

Keywords: Forward osmosis, draw solute, flux, foulimg

[P2.122]

Investigating organic fouling and cleaning of aquaporin based forward osmosis membranes

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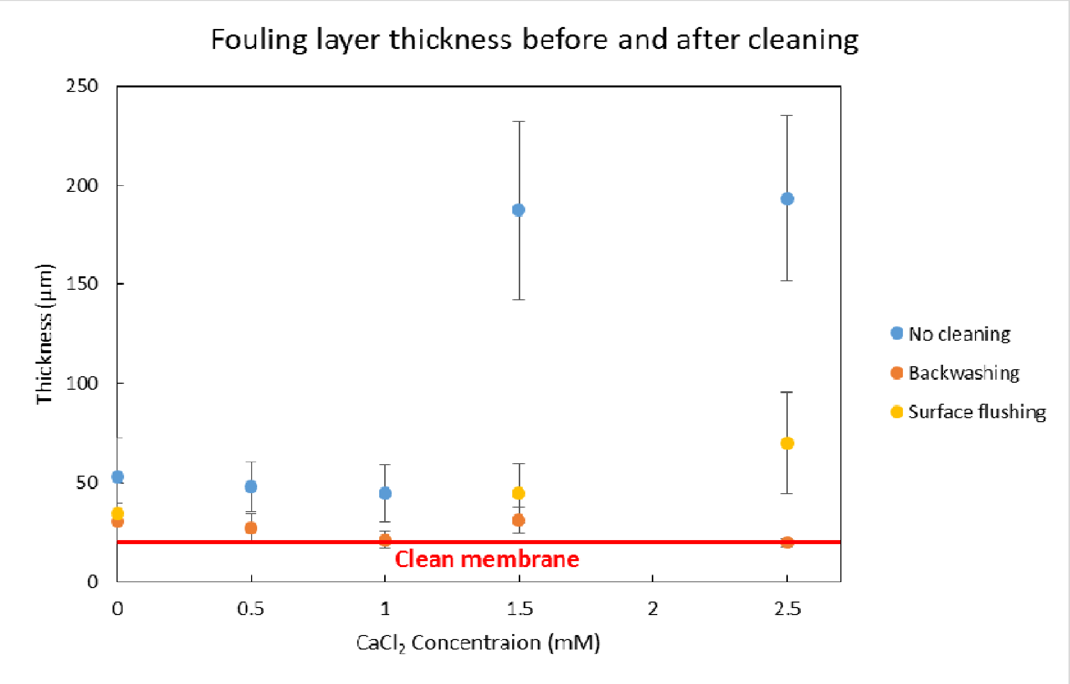
Effective cleaning strategies are an integral part of membrane processes as they can maintain production and prolong membrane life, therefore reducing replacement costs and time losses. The aim of this study is to assess the performance of surface flushing and osmotic backwashing of fouled aquaporin forward osmosis membranes in terms of flux recovery and fouling layer removal.

The membranes were fouled with alginic acid (AA) and $CaCl_2$ and then cleaned for 1 minute. Since Ca^{2+} is known to enhance AA fouling, the Ca^{2+} feed concentration was varied to assess how different fouling severities impact cleaning efficiency. During surface flushing, both sides of the membrane were rinsed with deionised water. During backwashing the draw solution was 0.7 M NaCl and the feed was deionised water. The fouling layer before and after cleaning was imaged using confocal microscopy in order to determine the thickness.



Fouling thickness against Ca^{2+} concentration (feed: AA 200 mg/L, $CaCl_2$, DS: 0.7 M NaCl; Aquaporin Inside^{TM}; AL-FS mode).

The fouling thickness increases by 360% when the $CaCl_2$ concentration increases from 0 to 2.5 mM Ca^{2+} as the Ca^{2+} binds with carboxylic groups in the AA forming a dense gel layer.

Backwashing is superior to surface flushing, especially at higher Ca^{2+} concentrations: for 2.5 mM, backwashing removes 99% of the fouling layer and restores 100% of the flux while surface flushing removes only 58% and restores 76% of the flux. This shows that for more severe fouling, only backwashing is effective for the removal of fouling in FO membranes. Other parameters affecting fouling characteristics and their impact on BW efficiency will be studied next.

Keywords: Forward osmosis, Fouling, Cleaning, Aquaporin

[P2.123]

The effect of structures of supporting membranes on the antifouling property of forward osmosis membrane in AL-DS mode

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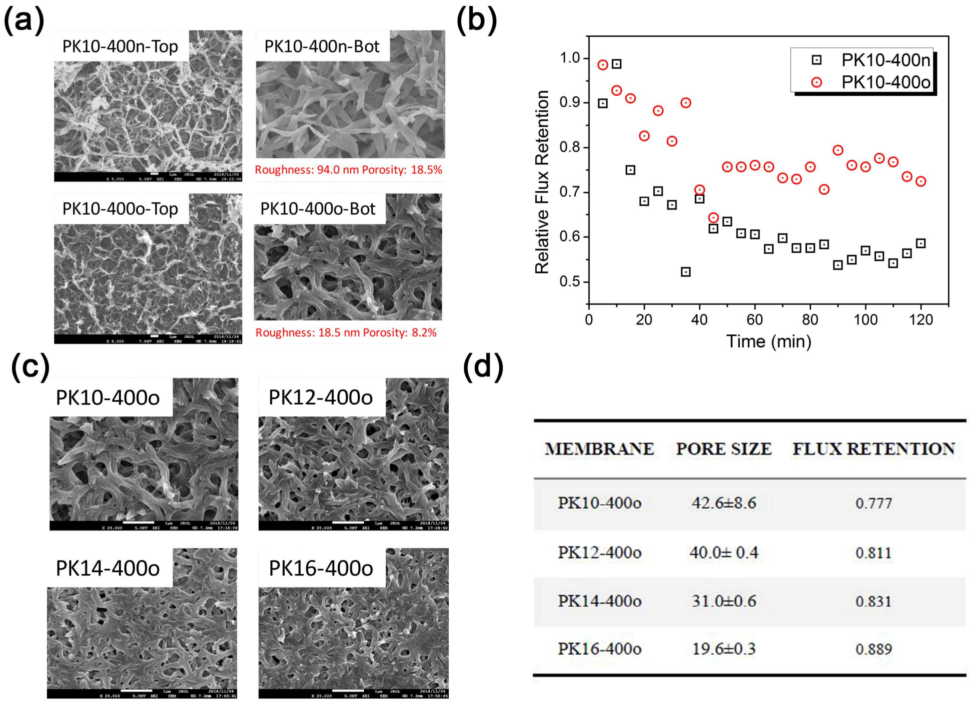
In recent decades, osmotic-driven membranes (i.e., forward osmosis (FO) and pressure retard osmosis (PRO) membranes) have nourished progress in water treatment and energy production to simultaneously address water resource shortage and energy crisis. FO membrane fouling problem, especially in active-layer-facing-draw-solution (AL-DS) or PRO mode, has attracted wide attentions. Scientists have proposed several methods to improve the antifouling property of FO membranes by designing the double-skinned FO membrane [1] and improving the hydrophilicity of the supporting membranes [2]. However, there is still lack of fundamental research on the relationship between the structures of supporting membranes and antifouling property of FO membrane in AL-DS mode. Here, we design and prepare a series of polyketone (PK)-based FO membranes with various supporting membranes to study the antifouling property. Sodium alginate is used as the model foulant.

The effect of the orientation. Two PK-based FO membranes are prepared by introducing the active layer on each side of the supporting membrane. It is found that the antifouling property of the membrane with smooth surface and lower surface porosity is much better (Figs. 1a and 1b). That is because that the foulant easily enters the more porous structures, resulting in the more sever fouling. *The effect of the surface pore size.* FO membranes with different supporting membranes were prepared. The antifouling property of FO membranes increases with the decreasing surface pore sizes of supporting membranes (Figs. 1c and 1d). However, other factors, including the surface porosity, roughness and structural parameter, may affect the antifouling property, which will be investigated in our following research.



MEMBRANE	PORE SIZE	FLUX RETENTION
PK10-400o	42.6±8.6	0.777
PK12-400o	40.0± 0.4	0.811
PK14-400o	31.0±0.6	0.831
PK16-400o	19.6±0.3	0.889

Fig. 1. (a, c) SEM images and (b, d) antifouling property of PK-based FO membranes.

References:

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[2] Li, et al., *Environ. Sci. Technol.* **2014,** *48* (16), 9898-9907.

Keywords: forward osmosis membrane, antifouling, AL-DS

[P2.124]

Separation of inorganic components from industrial wastewater via a hybrid forward osmosis -reverse osmosis system

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Driven by increasing need for sustainable water and energy, new technologies are being developed to provide these critical resources without waste. Renewable bio-feedstocks can be pyrolyzed to produce energy along with a single waste stream: wastewater containing residual hydrocarbons and inorganics from the energy production step. Here we assess the potential for a hybrid forward osmosis (FO) - reverse osmosis (RO) system to reclaim all inorganic components of this complex wastewater. FO performs the first separation while RO regenerates the FO draw solution. This dual membrane configuration provides two key advantages. First, the FO membrane protects the more fouling-prone RO membrane. Second, two selective membrane barriers ensure the quality of the RO permeate. Transport through each of these membranes can be customized by independently adjusting the pH of both the feed (wastewater) and the draw solution. By exploiting the pH-dependency of speciation for different contaminants (e.g., ammonia and cyanide), wastewater components can be sequestered in different parts of the hybrid system to achieve optimal fractionation. We quantified the transport and recovery of ammonia, cyanide, nickel, and zinc species across the FO membrane as a function of pH, recovery, and draw solution concentration. A stable water flux of 2 L m-2 h-1 was achievable when a 1 M NaCl draw solution was paired with raw wastewater. For wastewater at pH 5.0, NH4+ (183 mg-N/L in the feed) was undetectable in the draw solution while neutral HCN was only minimally rejected. These data support the potential feasibility of fractionating inorganic species at different membrane stages through adjustment of pH. Our preliminary results suggest that the FO-RO hybrid system could be an effective process for reclamation of industrial wastewater.

Keywords: FO-RO hybrid, Forward osmosis, Industrial wastewater, Sustainability

[P2.125]

Fabrication of thin-film composite membranes with improved mechanical robustness for energy generation using thin woven fabrics

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The objective of this work is to develop thin-film composite (TFC) membranes with enhanced mechanical robustness and improved performance for use in osmotic energy harvesting. Pressure-retarded osmosis (PRO) requires a high-pressure gradient across the membrane; therefore, mechanical robustness is a required characteristic for PRO membranes. Creating robust membranes by increasing thickness is not a good option, as membrane permeability is inversely proportional to thickness. Furthermore, thick membranes suffer from high levels of internal concentration polarization.

To attain the project objective, we prepared novel TFC membranes using thin woven fabrics with tensile strength higher than 50 MPa. These fabrics are thinner than the polyester backing found commonly in commercial TFC membranes. Membranes were fabricated by casting a support layer on the fabric via phase inversion followed by interfacial polymerization. Testing included measurements of mechanical strength using an INSTRON machine to evaluate the mechanical robustness of the composite membranes, scanning-electron microscopy (SEM) to visualize membrane morphologies, water permeation and salt rejection tests to compare the performance among the novel TFC membranes, and PRO runs to estimate the structural parameter and maximum power density achievable.

Results show that the novel TFC membranes have higher mechanical strength than the commercial TFC membranes. SEM images showed a good coupling between the fabrics and the support layer, as well as a fully sponge-like cross-section. Additionally, water permeation and salt rejection results showed no significant difference with the type of fabric used for backing. Ultimately, PRO testing showed that the novel TFC membranes had higher power density compared to commercial TFC membranes, and in general they had structural parameters below 200 micron.

These findings support the idea that the use of thin woven fabrics as membrane supports has potential for maintaining membrane robustness in TFC membranes, which is needed for high water flux, and enhanced power generation.

Keywords: thin-film composite membrane, woven fabrics, mechanical strength, pressure-retarded osmosis

[P2.126]

Fundamental study on ionic liquid-based draw solution for forward osmosis membrane process

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Forward osmosis (FO) membrane process is an emerging membrane technology for desalination. In FO membrane process, the osmotic pressure across a membrane provides driving force for drawing water. One of the key challenges of the FO membrane process is the lack of effective draw solution (DS), which can be easily separated and recovered from water. In this study, we focused on the applicability of aqueous solution of ionic liquids (ILs) as a DS of a FO membrane process. Because ILs are organic salt, its aqueous solutions could give high osmotic pressure. Furthermore, some ILs show lower critical solution temperature (LCST)-type phase separation, which could allow to regenerate the ILs-based DS and to recover water easily.

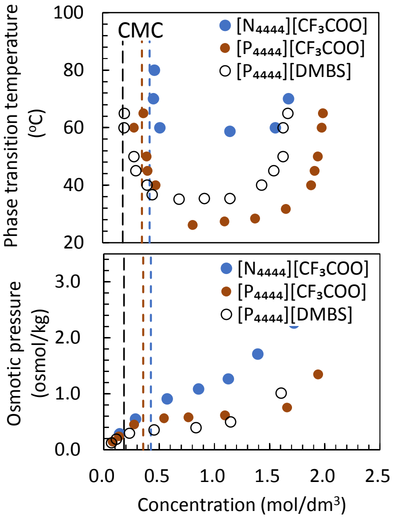

Fig. 1 Effect of IL concentration on the phase transition temperature and the osmotic pressure of the LCST-type IL-

We investigated the relationship among the structure of ILs, and osmotic pressure and LCST type phase diagram of the aqueous solutions of ILs. From the osmotic pressure measurement, it was found that the osmotic pressure of the aqueous solutions dissolving hydrophilic ILs increased linearly with the increase of the IL concentration, whereas the aqueous solutions of LCST-type ILs showed almost constant osmotic pressure within a certain range of IL concentration. From the critical micelle concentration (CMC) measurement, it was found that the aqueous solutions of LCST-type ILs showed CMC. From the results, it was suggested that aggregation of LCST-type ILs strongly affect not only the osmotic pressure but also the phase diagram (Fig. 1).

To examine the performance of the developed LCST-type IL-based DS, water permeability and ILs leakage during FO membrane process were evaluated. Some IL-based DS showed lower IL leakage than NaCl solution with keeping high water permeability of more than 0.06 LMH/bar. From the results, it was suggested that IL-based DS could useful in the FO membrane process because of its high osmotic pressure, low leakage and LCST-type phase separation property.

Keywords: Forward osmosis membrane process, Draw solution, Ionic liquid, Lower critical solution temperature

[P2.127]

Design considerations for plate-and-frame forward osmosis membrane system

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The optimal module for forward osmosis (FO) membrane has been developed and commercialized for water treatment process like desalination and water reuse. Currently, there are three kinds of modules, related to the type of FO membrane used. For example, plate-and-frame (PF) and spiral-wound (SW) modules, for flat sheet membrane; hollow fiber (HF) modules for this type of membranes. Among these three types of modules, the plate-and-frame (PF) configuration has the lowest pressure drop because it has low membrane packing density and the two solutions (draw and feed solutions) flow through simple flow path like flat, rectangular channels. This low pressure drop is a good merit for FO process. A few previous FO module studies was focused on SW modules but there is currently no study about PF FO module. Since flow patterns and flow resistance in the feed and draw channels can be different and affected by specific module design, the experimental investigation about PF FO module is needed. Especially, the performance test of the elements connected in series is required to design FO water treatment systems. For this study, 9 PF FO elements are used and 3, 6, and 9 elements connected in series can be individually operated. In this experimental setup, SCADA (Supervisory Control and Data Acquisition) system was installed for data acquisition, logging and control of the plant variables. Through PLCc (programmable logic controllers) and VFDs (variable-frequency drives), two pumps were controlled to obtain the desired flow rates. This study analyzes the structural features of the PF FO membrane module via an experimental approach and presents the design considerations of PF FO systems. In addition, the performances, such as water flux, water recovery, and volume concentration factor, were compared for flow rates, osmotic pressure differences, and number of elements (that is, membrane area used).

Keywords: forward osmosis, membrane module, plate-and-frame, structural features

[P2.128]

Maximum power transfer for osmotic energy conversion

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Pressure retarded osmosis (PRO) is an energy conversion process in which the chemical potential across a salt gradient is converted to mechanical energy via engineered osmosis. The osmotic process occurs across a semipermeable membrane that is loaded with a hydro turbine. The expanding volume of pressurized solution drives the turbine providing useful work.

This paper investigates the influence that operating conditions have on power transfer in a PRO energy conversion system. A simplified analog circuit representation of the process is used to demonstrate by analysis and simulation that maximum power transfer requires for the PRO process to occur with case specific source flow rates and outlet resistances. Transfer functions are derived and a closed loop control strategy is developed to demonstrate that target conditions can successfully be maintained under variations in both the source and the load, thereby achieving maximum power transfer.

Keywords: Pressure retarded osmosis, Salinity gradient energy conversion, Maximum power point tracking, Modeling

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Analysis of limiting factors in pressure retarded osmosis system (PRO) using the fluid-dynamic model to improve the performance

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Introduction

The Pressure retarded osmosis (PRO) system uses a salinity gradient to enhance the water flux through a semi-permeable membrane and sustainably generates electricity by a turbine. However, there are some limiting factors to decrease the efficiency of the PRO system like internal concentration polarization (ICP), external concentration polarization (ECP), and reverse salt permeation (RSP). To optimize PRO's performance, the effect of limiting factors on the PRO performance should be analyzed to suggest desirable membrane geometry and operating condition for the PRO system.

Method

In this study, two types of polymers, thermally rearranged poly(benzoxazole) (TR-PBO) and sulfonated poly(arylene ether sulfone) (BPSH), were utilized to fabricate support layer *via* electrospinning. And then, polyamide selective layer was coated on the surface of each membrane by interfacial polymerization. The PRO performance of the developed membranes was measured with a lab-scale PRO apparatus. And, the fluid-dynamic model was used to clarify the impacts of three limiting factors on the PRO performance.

Result

TFC-BPSH40 (A: 2.0 LMH*bar^{-1} and R: 95.8%) shows higher water permeability and rejection than TFC-PBO (A: 1.5 LMH*bar^{-1} and R: 95.0%). As a result, TFC-BPSH40 has better power density (11.5 W*m^{-2}@15bar) compared with TFC-PBO (10.5 W*m^{-2}@15bar).

Discussion

The limiting factors indicated that TFC-PBO had a higher resistance than TFC-BPSH40, which was induced by the hydrophilicity difference of the developed membranes. On the contrary, the ECP of TFC-BPSH40 is higher than that of TFC-PBO due to high water flux of TFC-BPSH40. The analysis suggests that thin, hydrophilic and highly porous structure would be helpful to decrease ICP. Moreover, an increase of flow rate at draw side would be also helpful to suppresses ECP.

References

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Keywords: Pressure retarded osmosis, Robust membrane, Fluid-dynamic model, limiting factors