Membrane Science and Technology (MST2019)

Nanyang Executive Centre @ NTU, Singapore

13-14 June 2019

ABSTRACT BOOK

NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

Singapore Membrane Technology Centre
Nanyang Environment and Water Research Institute

MEMBRANE SOCIETY IN SINGAPORE
MEMSIS

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MST2019 Day 1 on 13 June 2019, Thursday

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TIME	**DAY 1 PROGRAMME**			
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POSTER

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2	Biofouling prevention of drinking water Reverse Osmosis membrane by Vanillin: Comparative Metagenomics	Smita Pal, Asifa Qureshi, Hemant J. Purohit Academy of Scientific & Innovative Research (AcSIR), India
3	Preparation and performance of nonwoven fabric reinforced PVDF/GR hollow fiber composite microfiltration membrane	Xiujuan Lan, Huiying Chen, Yubin Hong Suntar Environmental Technology Co., Ltd, China
4	Improved rejection ability of interfacially synthesized polyester thin-film composite membrane by surface cross-linking	Zhenhua Lü, Meihong Liu and Sanchuan Yu Zhejiang Sci-Tech University, China
5	Triblock copolymer polymersomes incorporating Aquaporin Z proteins for biomimetic membranes	R. Gorecki, D. M. Reurink, M. M. Khan, K. Trzaskus and C. Helix-Nielsen Technical University of Denmark
6	Design and fabrication of hierarchical porous membrane for flow-through removal of aqueous micropollutants	Dongxue Yao, Na Ma, Ying Pan, Jian Yin, Jianqiang Meng Tianjin Polytechnic University, China

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7	Synthesis of thin film composite polyamide membranes: Effect of chemical additives in aqueous and organic phases on membrane morphology and performance	Meng You, BinFei Wang, Hua Wang, Jianqiang Meng Tianjin Polytechnic University, China
8	Effect of UV Treatment and PEG Grafting on Polysulfone Membrane Surface to Improve Hydrophilicity for Wastewater Treatment	S. Ruangdit, T. Chittrakarn, C. Kaew-on and S. Sirijarukul Prince of Songkla University, Thailand
9	Dye Sensitizer of Chlorophyll as Mixed with TiO2 nanoparticle in photocatalytic for enhancing the hydrogen production	W. Bootluck, N. Junchoo, N. Meesiang, W. Khongnakorn and T. Chittrakarn Prince of Songkla University, Thailand
10	Tailoring the characteristics of graphene oxide membranes for gas separation and water purification	T. Foller, X. Jin, F.Wang, Y. You, R.K. Joshi University of New South Wales, Australia
11	Versatile Through-Hole Membranes with Ordered and Tuneable Pore Geometry	Him Cheng Wong, Mei Chee Tan, and Hong Yee Low Singapore University of Technology and Design

PLENARY SESSIONS

Robust Micro-Tubular and Micro-Monolithic Ceramic Membranes

Kang Li

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ABSTRACT

Growing applications of membrane processes in water and energy pose new and interesting demands on both membranes and its process design. At Imperial, our research spans from new membrane development to its applications in separation and reaction. We have developed new fabrication techniques for polymeric, ceramic and metallic membranes, especially in hollow fibre/micro-tubular geometry with diameter between 0.5 and 2 mm. These membranes have unique purposely-designed wall structures to suit different applications, including filtration, gas separation, emission control and fuel cells. Such fabrication techniques have also been extended to micro-monolith (i.e. multi-channels), for example, 2-mm diameter ceramic tubes with 6-7 parallel channels with either symmetric or asymmetric geometries.

The designed membranes with the unique wall structures can be further functionalised with advanced nanomaterials or catalysts, and multiple functions can be integrated into an one-single device. The functional nanomaterials currently being investigated include graphene, graphene oxide, metal-organic frameworks (MOFs), and they can be in the form of thin films deposited on the surface of the membrane support or granules packed in the unique wall structures of the membrane. For example, we have developed micro-tubular graphene oxide thin films to extract water from organic solvents, and a novel adsorption/filtration column containing MOF nanoparticles to get rid of bacteria and heavy metal ions from contaminated water. The micro-monolithic membranes can also be incorporated with catalysts to construct micro-reactors or fuel cells. Our research on these micro-reactors has been regarded as one of the most important progresses in the field. This presentation will focus on the new membrane fabrication techniques and applications of these purposely-designed membranes in separation and reaction.

3D Printed Thin Film Composite Membranes

Jeffrey R. McCutcheon

Al Geib Professor of Environmental Engineering Research & Education
Department of Chemical & Biomolecular Engineering
University of Connecticut

ABSTRACT

Interfacial polymerization, while effective at making thin film composite desalination membranes of high permeability and selectivity, is a relatively uncontrolled process that prevents tuning of polyamide film thickness or roughness. A new approach is presented which uses electrospraying to deposit monomer solutions in nanoscale droplets directly onto a substrate where they subsequently react to form the crosslinked polyamide film essentially on any surface. This printing approach enables film thickness control to 4 nm resolution (~20 nm total thickness) and achieves films with a root mean square roughness as low as 2 nm. The higher performing membranes in this study exceeded both the permeance (as much as a 10-fold improvement) and selectivity (notably higher salt rejections) of commercially available reverse osmosis membranes in addition to their substantially lower roughness. The method is also scalable and potentially reduces chemical consumption in membrane fabrication by over ten-fold.

Biofouling of Membrane Systems for Drinking Water Production: Diagnosis, Prediction and Prevention

J.S. Vrouwenvelder

Water Desalination and Reuse Center,
Division of Biological and Environmental Science and Engineering, King Abdullah University of Science and Technology

ABSTRACT

High quality drinking water can be produced with membrane filtration processes like reverse osmosis (RO) and nanofiltration (NF). As the global demand for fresh clean water is increasing, these membrane technologies are increasingly important.

One of the most serious problems in RO/NF applications is biofouling - excessive growth of biomass - affecting the performance of RO/NF systems. This can be due to the increase in pressure drop across membrane elements, the decrease in membrane permeability or increase in salt passage. These phenomena result in the need to increase the feed pressure to maintain constant production and to clean the membranes chemically.

The presentation contains (i) an short overview of the Water Desalination and Reuse center and the three flagship research projects, (ii) and for biofouling an overview of new tools to monitor and characterize biofouling: fouling simulator development, sensitive pressure drop measurements, MRI and imaging and three-dimensional numerical modelling to simulate biofouling, and (iii) new insights derived with these tools, pilot and full-scale RO/NF installation studies, and (iv) new potential biofouling control strategies.

Bioinspired Zwitterionic Membranes Design, Development, and Applications

Yung Chang

R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Taoyuan 320, Taiwan

ABSTRACT

Stable blood compatibility of membranes used in contact with human whole blood is highly desirable for blood-inert devices. The design and development of nonfouling membranes are therefore critically important in biomedical applications, which are highly desirable in the design for human blood-contacting membrane systems. However only a very limited number of synthetic materials are regarded as good hemocompatible candidates. It is suggested via bio-inspiration that a nanoscale homogenous mixture of balanced charge groups from polyzwitterionic materials is the key to controlling ideal nonfouling properties. An important characteristic of a zwitterionic structure is that it should have both a positively and a negatively charged moiety within the same side chain segment while maintaining overall charge neutrality. A set of functional properties is generally used to guide the design of new non-fouling polymer brushes in contact with human blood: they should be hydrophilic and electrically neutral, and hydrogen bond acceptors rather than hydrogen bond donors. For the polyzwitterionic materials, they can be further classified into polybetaines such as 2-methacryloyloxylethyl phosphorylcholine (MPC), sulfobetaine methacrylate (SBMA), and carboxybetaine methacrylate (CBMA). The advantages of nonfouling zwitterionic materials include the simplicity of synthesis, ease of applicability, abundance of raw materials, and availability of functional groups. Our team in R&D Center for Membrane Technology (Taiwan) mainly focuses on the study of bioinspired structure for their fundamental zwitterionic molecular designs as well as the development for potential biomedical applications. This talk will summarize our center’s fundamental developments related to the designs of membranes using zwitterionic materials.

KEYWORDS

Bio-inspired, zwitterionic, membranes, nonfouling, blood compatibility

Strategies for Thin Film Composite Membranes Targeting CO_2 Separations

Michael D. Guiver[1,2], Zhihua Qiao[2,3], Song Zhao[2], Zhi Wang[2], Chongli Zhong[3], Shaofei Wang[2], Zhongyi Jiang[2]

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ABSTRACT

At Tianjin University, we have explored several strategies for making thin film composite membranes for CO_2 separations. Using few-layered selective skin layers of graphene oxide (GO) supported on ultrafiltration membrane substrates, CO_2-selective channels can be created by interspersing the layers with CO_2-philic borate or short polyethylene glycol units [1,2] These interlayer filler materials serve multiple functions: (1) as crosslinkers and as spacers to stabilize and to control the *d*-spacing between the layers (2) to create a chemical environment, which is CO_2-philic, and (3) to create a 'water' environment to facilitate CO_2 transport.

Recently, we reported a new class of porous frameworks used to membrane materials: metal-induced ordered microporous polymers (MMPs) [3]. They are readily synthesized from functional polymers, small organic linkers and divalent metal ions. The linkers coordinate with metal ions, resulting unit cells from self-assembly along the polymer chains. Three-dimensional frameworks form as 50-100 nm nanoparticles. Compared with conventional MOFs, hybrid MOF MMPs have improved crystal size controllability and hydrolytic stability. Large-area MMP/mPSf membranes were made very simply by coating dilute MMP dispersions onto modified polysulfone (mPSf) substrate, resulting in defect-free ultrathin gas-selective coated layers. One composite membrane MMP-3/mPSf had a CO_2 permeance of >3000 GPU and mixed gas CO_2/N_2 (15/85) selectivity of 78, and was stable under both humidified and dry gas feeds. Another MMP-1/PSf membrane had a CO_2 permeance of >5500 GPU and mixed gas CO_2/N_2 selectivity of 35. The CO_2 permeance and mixed gas selectivity are promising because they in the desired region for CO_2 capture applications at DOE cost targets, and practical membranes can be fabricated, potentially at a large scale. Newer research is currently targeting *in situ* fabrication of large-area ultra-thin MOF CO_2-selective surfaces on polymeric membrane supports.

REFERENCES

[1] *Energy & Environ. Sci.* **9** (2016) 3107-3112.
[2] *Angew. Chem. Int. Ed.* **56** (2017) 14246-14251
[3] *Nature Materials* **18** (2019) 163-168

Novel Approaches towards IFP for the Preparation of GS, (SR)NF and RO Membranes

Ivo Vankelekom

KU Leuven, Belgium

ABSTRACT

Interfacial polymerization (IFP) has been the standard for years to prepare RO and NF membranes for aqueous applications. When considered for use in extreme conditions of pH or temperature, in solvents (solvent-resistant NF) or in water/solvent mixtures (solvent tolerant NF), many of these membranes fail due to limited chemical stability or excessive swelling.

In this presentation, novel IFP-approaches (new monomers, new reaction types, other solvent phases, new preparation methods) will be presented that lead to membranes that can successfully be operated under these conditions. First, novel support materials will be presented that allow the deposition of such stable layers on it and their subsequent operation under these harsh conditions. Finally, a link will be laid to membranes for gas separation where chemical stability is a prerequisite to create plasticization resistance and operation in highly contaminated gas streams.

Day 1
13 June 2019

Session 1: Advanced Membrane Materials I

Two-dimensional Materials for Membrane-Based Molecular Separation

Sui ZHANG

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ABSTRACT

Two-dimensional (2D) materials such as graphene, graphene oxide and molybdenum disulphide (MoS_2) are emerging candidates to potentially perform fast and selective molecular separation for membrane applications. In this talk, I will summarize our recent efforts in the preparation and application of various types of 2D membranes, including single-layer graphene membranes, layered 2D membranes based on stacked 2D nanosheets and mixed matrix membranes. Apart from commonly seen inorganic 2D materials, 2D polymer-based membranes will also be briefly discussed.

Single-layer graphene provides the thinnest possible separation layer (atomic thickness) and the possibility of pore creation across graphene to allow size-based molecular sieving of different molecules. One of the key challenges is the transfer of graphene onto the membrane support in a defect-free and scalable way. Effective pore creation is another concern. By combining pore creation during graphene formation and direct casting, graphene membranes that allow solute diffusion at a rate of at least 2-times faster than commercial membranes have been prepared for dialysis.

2D materials may also be packed to form multi-layered structure which allows molecular passage and separation via the interlayer spacing. Compared to graphene oxide, MXene and other 2D inorganic materials, MoS_2 show exceptional stability in organic solvents. We prepared two types of MoS_2 nanosheets using different methods, one rich in multi-layer structure and the other rich in mono-layer nanosheets. The structure, stability and performances of the resultant stacked MoS_2 membranes were compared. To achieve high rejection and good stability, a ‘bridging’ agent is employed to regulate the interlayer spacing and nanosheet alignment of multi-layer MoS_2 membranes, leading to improved rejection and stable performances over one week.

In addition, to enable cost-effective and scalable membrane preparation, a 3-step layer-by-layer (LbL) method has been proposed to prepare mixed matrix membranes containing MoS_2 nanosheets. With a thin layer of < 50 nm, the mixed matrix membrane can achieve ethanol permeance –selectivity that surpasses the hypothetical upper bound, e.g., 92.9 % rejection for Victoria blue B (VBB, MW 506.08) with an ethanol flux of 11.4 L m^{-2} h^{-1} bar^{-1}.

In the last, membranes based on 2D conjugated polymers and their application for gas separation will be briefly introduced.

Smart Gating Membranes with Responsive Nanogels as Functional Gates

R. XIE[a,b], F. LUO[a], X.X. FAN[a] and L.Y. CHU*[a,b]

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ABSTRACT

Smart gating membranes, as emerging artificial biomimetic membranes, have the ability to self-adjust their permeable and separative characteristics in response to stimuli from the environment.[1] Until now, the simple creation of smart or intelligent gating membranes possessing synchronous large flux, and strong mechanical strength as well as significant responsive characteristics was thought to be very challenging. Here, a new strategy for the easy and controllable production of satisfactorily-performing smart gating membranes, through the construction of response nanogels *in situ* in the surfaces of membrane pores by virtue of a vapor-induced phase separation (VIPS) process, is designed and developed. Taking poly(*N*-isopropylacrylamide) (PNIPAM) nanogels as functional gates, the available thermo-responsive smart membranes exhibit large flux, an excellent mechanical property and significant thermo-responsive characteristics simultaneously. Meanwhile, the resultant novel thermo-responsive catalytic membranes with silver-nanoparticle-loaded PNIPAM nanogels as thermo-responsive gates and catalysts show both satisfactory thermo-responsive characteristics and catalytic properties. Such catalytic membranes are able to adjust the throughput in light of the feed reactant concentration and maintain high catalytic conversion in the meantime through alteration of the reaction temperature. The outcomes offer valuable instructions for the design and production or even high-volume manufacture of smart membranes with an expected performance. The new strategy suggested is applicable to producing diverse functional materials with pores modified by responsive or non-responsive nanoparticles in diverse utilizations.

Moreover, the previously reported smart membranes were mainly featured with single gating model, *i.e*. positively or negatively responsive membranes, however, it is still a great challenge to design and prepare smart membranes with dual responsive performance till now to meet the practical needs. A novel dual pH-responsive smart gating membrane is proposed by skillfully blending poly (*N,N′*-dimethylamino-2-ethyl methacrylate) (PDMAEMA) microgels into poly(ether sulfone) membrane as functional gates via liquid-induced phase separation (LIPS) method. The as-prepared membrane is featured with both positively pH-responsive characteristics in acidic environment and negatively pH-responsive characteristics in basic environment. The mechanism of the dual pH-responsive performance is attributed to the pH-responsive volume change of PDMAEMA microgels embedded in the membrane, and the pH-responsive hydrophobicity and stiffness of the microgels, respectively. As a result, the permeability of this novel membrane is increased at first and then decreased with increasing the environmental pH value. The dual pH-responsive property of the prepared membrane is reversible and repeatable. The dual pH-responsive membrane proposed in this study provides a novel gating mode for design and development of

pH-responsive smart membranes, which is highly potential for myriad applications, such as sewage treatments, sensors, controlled release of drugs and so on.

KEYWORDS

Smart gating membranes; Catalytic membranes; Thermo-responsive; dual pH-responsive; Silver nanoparticles

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Nafion-based Low Hydrated Polyelectrolyte Multilayer Membranes for Enhanced Water Purification

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ABSTRACT

Micropollutants present in drinking water is more and more becoming a concern for human health and environment. [1] Waste water from hospitals, industry, and domestic households results in an accumulation of micropollutants in river and surface waters resources. To prevent micropollutants from ending up in our drinking water, membrane filtration of ground and surface water promises to be a simple method to provide clean and safe drinking water. However, new and advanced membranes need to be developed in order to remove all micropollutants in an efficient manner.

Layer-by-layer (LbL) assembly of oppositely charged polyelectrolytes is a highly effective and proven method to tune and modify membrane performance. [2] This versatile technique makes use of alternately dip-coating two oppositely charged polyelectrolytes on a surface, thereby creating a polyelectrolyte multilayer (PEM). [3] Such a PEM is easily applied on all geometries and for this reason, a porous hollow fiber support can be used. When a tight ultrafiltration (UF) membrane is used as a support, LbL allows a thin film to be coated on the UF-support, thereby creating a nanofiltration (NF) membrane. [2] A NF-membrane can be used as a separation device to remove divalent ions or heavy metals, to recover dyes, or to remove natural organic matter and micropollutants.

To make a PEM, various polyelectrolyte pairs can be used which all give different separation properties. A promising system that has high retention towards monovalent salts, is the combination of polyallylamine (PAH) and polystyrene sulfonate (PSS). Although this system provides high salt retention, a major limitation is that the separation is mainly based on Donnan exclusion. With Donnan exclusion, separation is based on the charge between the solutes and the membrane. For this reason, small and uncharged micropollutants (such as bisphenol A and atrazine) will still permeate through the membrane. [4] In order to create a PEM-membrane that has reverse osmosis properties, the PEMs have to be made denser. Subsequently, separation can be based on size exclusion. To make a PEM denser, several techniques can be used; crosslinking of the PEM and more hydrophobic polyelectrolytes can be used to reduce the swelling of PEMs. In this study, we incorporate Nafion, a hydrophobic polymer, into PAH/PSS multilayers to reduce swelling.

Nafion is a highly fluorinated polymer with a repeating sulfate moiety. Due to the sulfate group, the polymer can act as a polyanion and can interact with polycations in a LbL manner. [5] In this study, we show by ellipsometry that terminating a PAH/PSS multilayer with just a single layer of Nafion decreases the swelling by half. Through water contact angle measurements, we show that the PEM becomes more hydrophobic after a terminating-layer of Nafion. The change in multilayer properties when terminating with Nafion is shown in Table 1. In addition, we show that we can successfully prepare a PAH/Nafion multilayer on top of a PAH/PSS multilayer, increasing the influence of Nafion on the properties of the entire PEM.

Table 1: Water contact angle and swelling of a $[PSS/PAH]_8$, $[PSS/PAH]_8PSS$, and $[PSS/PAH]_8Nafion$ multilayer.

	Contact angle (°)	Swelling (%)
$[PSS/PAH]_8$	54 ± 2	24 ± 2
$[PSS/PAH]_8PSS$	36 ± 1	20 ± 1
$[PSS/PAH]_8Nafion$	92 ± 2	11 ± 1

We also show that Nafion enhances the separation performance of the membrane. When terminating with Nafion, the permeability of the membrane decreases by half. Moreover, the molecular weight cut-off decreases from 300 to 260 $g{\cdot}mol^{-1}$, showing that a Nafion-terminated PEM-membrane is denser. Subsequently, when the membrane is used for the separation of micropollutants, as shown in Figure 1, overall retention increases. Retention is especially high for uncharged and negatively charged micropollutants. In addition, both salt and micropollutant retention increases further when multiple PAH/Nafion layers are deposited on the membrane surface. We conclude, that terminating with just a single layer or multiple layers of Nafion drastically alters the PEM properties and enhances the performance of a PEM-membrane.

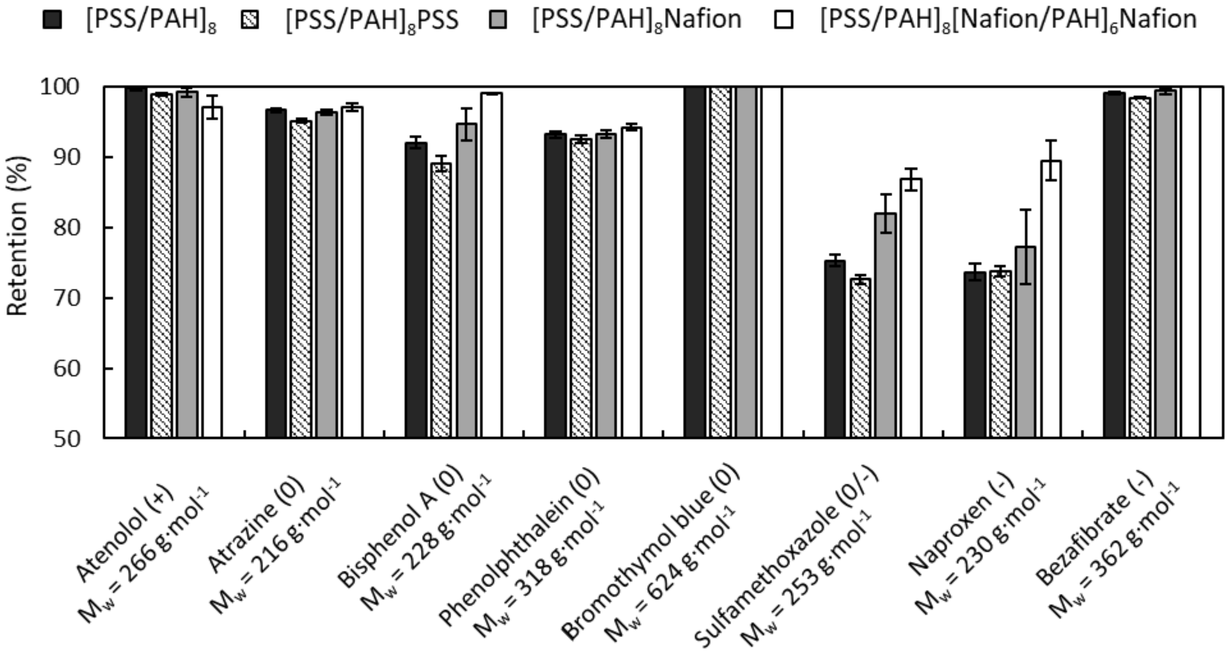

Figure 1: Micropollutant retention of a $[PSS/PAH]_8$ (black column), $[PSS/PAH]_8PSS$ (patterned column), $[PSS/PAH]_8Nafion$, (grey column), and $[PSS/PAH]_8[Nafion/PAH]_6Nafion$ (White column) PEM-membrane.

KEYWORDS

Polyelectrolyte multilayers; Nafion; swelling; micropollutants

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Development of Poly(Phthalazinone Ether)s Membrane Materials for Energy and Water Treatment Applications

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ABSTRACT

Poly(phthalazinone ether)s with good thermal stability and chemical stability are promising membrane materials [1]. Thermally stable ultrafiltration and nanofiltration membranes, proton exchange membranes and anion exchange membranes prepared from poly(phthalazinone ether)s have been reported. In this paper, we described the recent development in novel poly(phthalazinone ether)s membrane materials for energy and water treatment applications.

Sulfonated poly(aryl ether sulfone) composite nanofiltration membranes were fabricated via coating method with poly(phthalazinone ether)s membranes as substrates. Three kinds of sulfonated poly(aryl ether sulfone)s with different amounts of phthalazinone moieties were used as coating materials. The membrane prepared from sulfonated poly(phthalazinone ether sulfone) (SPPES) with more phthalazinone moiety groups showed high water flux and salt rejection. The rejection of the three composite membranes decreased slightly with the solution temperature rising from 20 to 90 °C, while the SPPES composite membrane showed a higher increase in flux than others. SPPES composite membranes show better thermal stability than others.

Novel poly(phthalazinone ether ketone ketone)s bearing sulfonic acid groups on pendant phenyl rings (SPPEKK-DB) were prepared from poly(phthalazinone ether ketone ketone)s containing pendant phenyl groups through postsulfonation method.

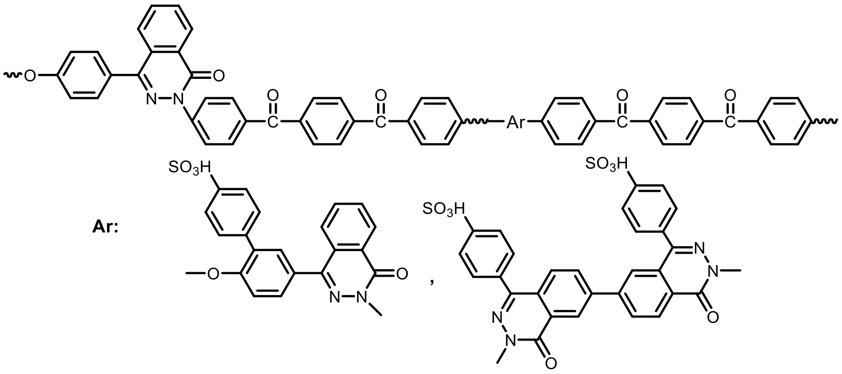

Fig.1. Chemical structure of poly(phthalazinone ether)s with pendant sulfonic acid phenyl groups

The structure of SPPEKK-DB was confirmed by FTIR and NMR, and was showed in Fig.1. Proton exchange membranes prepared from SPPEKK-DB show good oxidative stability and high proton conductivity. The proton exchange membranes were stable more than 4 hours in Fenton' reagent (2ppm $FeSO_4$ in 3%H_2O_2) at 80°C.

Vanadium redox flow battery (VRB) systems can be used as large-scale energy storage devices, which are suitable for un-interruptible power supply and emergency backup [2]. Ion exchange membrane is one of the key components in VRB system. To improve the properties of membranes, poly(phthalazinone ether)s amphoteric ion exchange membranes (AIEM-Q/S) were prepared from brominated poly(phthalazinone ether ketone) and sulfonated poly(phthalazinone ether ketone) through convenient and low-cost process (blending and quaternary amination). AIEM-Q/S membranes contained both quaternary ammonium and sulfonic acid groups. This makes it easy to regulate the permeability of different vanadium ions and water transport. VO^{2+} and V^{3+} permeability of AIEM-Q/S membranes were 96.0-99.7% and 98.4-99.8% less than that of Nafion115, respectively. AIEM-Q/S membranes showed much lower static water transport volume than Nafion115. Energy efficiency of VRB with AIEM-Q/S membranes reached 90%, higher than that of Nafion115 (86.5%). AIEM-Q/S membranes exhibited low vanadium permeability and water transport volume and good comprehensive performance, which have the promising to use in VRB.

KEYWORDS

Poly(phthalazinone ether)s, Membrane Materials, Ion Exchange Membranes, Nanofiltration membranes

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Thin Film Nanocomposite Membranes Containing Water-Stable Metal-Organic Cages for Desalination

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ABSTRACT

The introduction of porous nanofillers into the polyamide selective layer of thin film composite (TFC) membranes is a promising strategy towards improved flux and selectivity for reverse osmosis membranes. However, the solid-state incorporation of porous additives is constrained by poor compatibility between the fillers and polyamide layer. In this study, rationally chosen metal-organic cages (MOCs) with ideal stability, solubility and porosity characteristics are successfully utilized as filler materials for TFN membranes. Mono amino compound was further used to tune the structure of the polyamide selective layer and then the performance of the TFN membrane following the “defective ligand” strategy. The optimized TFN membranes exhibit up to 3.2-fold increment in water flux without compromising the salt retention characteristics.

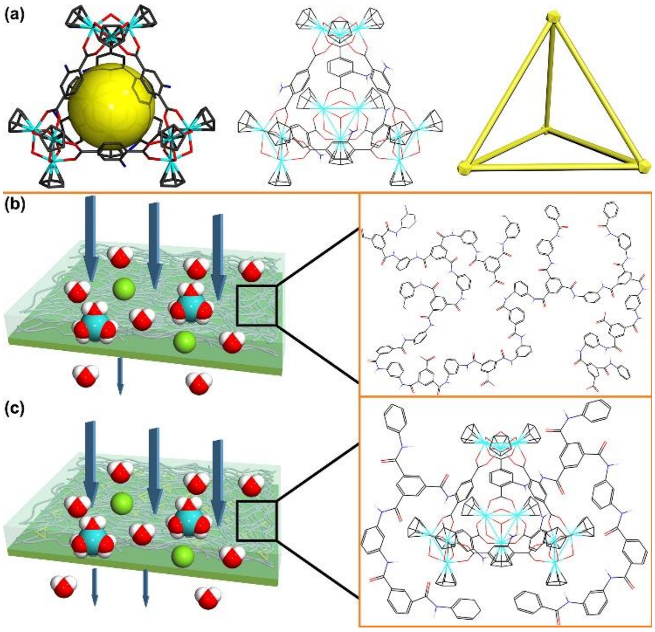

Figure 1. The crystal structure of MOC and the aperture size (a). Schematic of TFC membrane and the proposed chemical structure of the polyamide layer (b). Schematic of TFN membrane and the proposed chemical structure of polyamide layer (c). Color code: O red, N blue, C black. Counter ions Cl-, DMF molecular, and H atoms are omitted in Figure 1a for clarity.

KEYWORDS

Thin-film nanocomposite membranes • metal-organic cages • desalination application • water stability • cross-linked cages

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Session 2: Membrane for Wastewater Treatment and Industrial Application I

Membrane Bioreactor for Wastewater Treatment: Technological Advancement and Experiences Beyond the Laboratory

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ABSTRACT

Membrane bioreactors (MBRs) is a matured technology that has gained increasing popularity in treating both municipal and industrial wastewaters and it is anticipated to lead to the next generation of biological-based wastewater treatment technologies. MBR process combines a biological treatment process and a membrane filtration process for final solid liquid separation. Currently, research have been actively pursued to enhance the efficiency and sustainability of MBR process, especially to tackle issues related to membrane fouling. Strategies have been established such as development of new membrane materials, modification of membranes and new module designs to reduce membrane fouling. The first part of this presentation focuses on the technological advancement in membrane designs. Tremendous efforts are underway based on the advancement in science and technology such as application of nanomaterials to enhance the antifouling properties and robustness of the membranes. The explorations of various novel functional materials and modification techniques will be covered. The system design and operation of a commercial-scale MBR, jointly operated by Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia (UTM), will also be highlighted. The future perspective of MBR in terms of design of hybrid system and augmentation of biogas production will also be briefly discussed. In the second part of the presentation, the route to achieving success in both laboratory and commercial scale will be highlighted. With the surging needs to translate the fundamental knowledge to practical application in order to serve the community, translational research is one of the main direction of membrane science and technology development. The factors and roadmap of this translational efforts will be presented.

Superwetting Nanofibrous Membrane for Oil/Water Separation: Mechanism and Applications

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ABSTRACT

Nanofibrous membranes obtained through electrospun method have been widely used in the fields of environmental engineering and separations due to their unique properties of high porosity, large surface area and controllable structure [1]. Especially, nanofibrous membranes have been considered as exceptional candidates for oil/water treatment because of their intrinsic microstructure obtained by the random assembling of nanofibers and super-low mass transfer resistance [2]. However, separation mechanism of nanofibrous membrane for oil/water separation is rarely discussed as well as the antifouling properties. In this presentation, except for the construction of superwetting nanofibrous membrane, we will endeavor to illustrate the separation mechanism of nanofibrous membrane for emulsions. In addition, antifouling properties of the nanofibrous membrane will be discussed based on the analysis of different forms of water (non-freezable, freezable and free water) on membrane surface and the interactions between membrane surface and foulants. Separation performance and the proposed mechanism were presented in Figure 1.

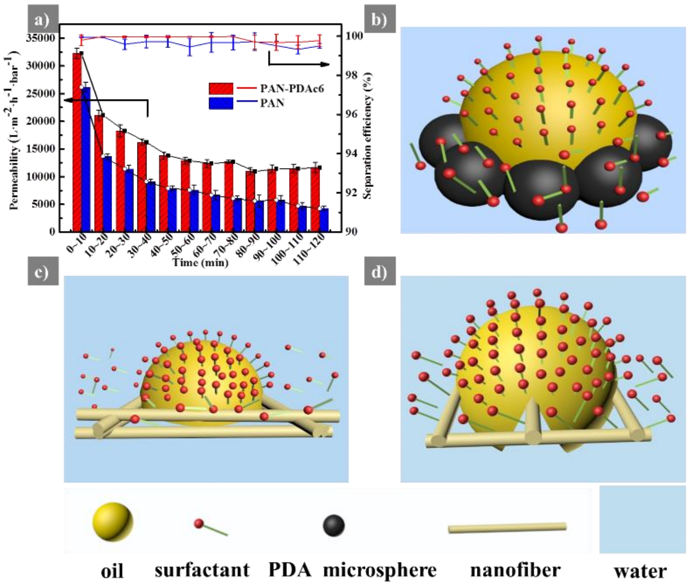

Figure 1. Separation performance and the proposed separation mechanism.

KEYWORDS

Nanofibrous membrane; Superwetting; Antifouling; Oil/water separation.

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Development and Evaluation of Nanofibrous Composite Membranes for Extractive Membrane Bioreactors

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ABSTRACT

Extractive membrane bioreactors (EMBRs) are promising technologies for highly saline organic wastewater treatment, which combines an aqueous-aqueous extractive membrane process and biodegradation [1-3]. As shown in **Fig. 1**, the target contaminants diffuse through an extractive membrane and are metabolized by the active biofilm attached on the downstream membrane surface and microorganisms in the bioreactor [4]. The benefit of EMBRs is that the biomass is not exposed to the potentially hostile feed conditions (high salinity, pH extremes *etc.*). The critical part in the EMBR process is the extractive membrane possessing high organic transfer coefficients and high rejections to acid, caustic, inorganic salts and water [3].

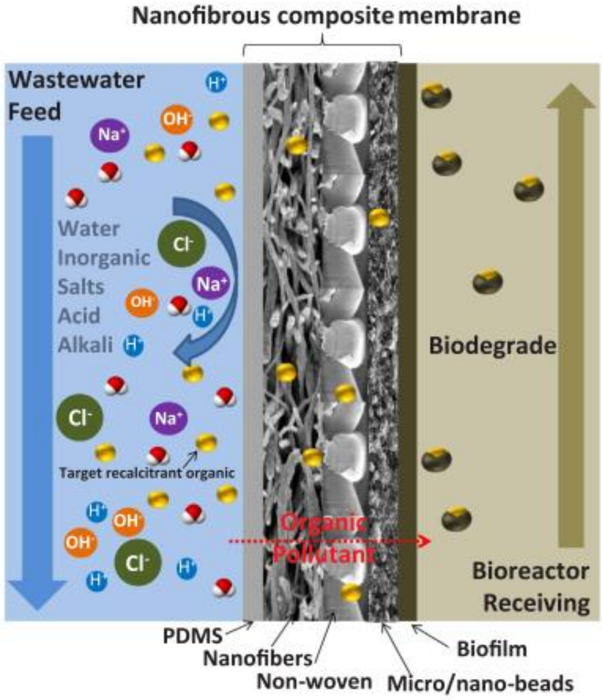

Fig.1. Schematic illustration of an extractive membrane bioreactor (EMBR) and an as-designed nanofibrous composite membrane.

In these works, novel nanofibrous composite membranes have been designed, developed and evaluated in EMBRs [5, 6]. In the first part of works, we studied the effects of membrane surface properties on the membrane-attached biofilm on the receiving side [5]. Two nanofibrous composite membranes with a superhydrophobic surface (code as NC) or a superhydrophilic surface (code as M-NC) have been developed. Compared to commercial polydimethysiloxane (PDMS) tubular membranes, both NC and M-NC possessed 10 times higher phenol extraction efficiency in an aqueous-aqueous extractive membrane process. The fouling-releasing fluoro-polymeric surface of the hydrophobic NC was able to attenuate the tendency of microbial attachment and encourage biofilm scouring from the membrane surface in the S-EMBR. In contrast, more polysaccharides were present in the biofilm on the poly (ethylene glycol) (PEG)-modified M-NC surface, which acted as adhesives to tightly immobilize the biofilm on the membrane surface. Lastly, the NC which exhibited a higher stable k_0 of 5.7×10^{-7} m/s in 12 days of submerged EMBR (S-EMBR) operation, has been tested in a pilot S-EMBR to treat actual industrial wastewater. It showed a stable and competitive k_0 of 6.5×10^{-7} m/s in 31 days operation, demonstrating its feasibility for hostile industrial wastewater treatment.

We further investigated the coupled effects of membrane roughness and hydrodynamic conditions on membrane performance in both crossflow EMBR (CF-EMBR) and S-EMBR processes[6]. Less biofilm was observed on the smooth PDMS surface. In contrast, the ridges and valleys on the membrane surface were able to provide a more favourable micro-environment for microorganisms and protect them from external stresses. The mature micro-colonies could clog the membrane support and enhance concentrated ICP, resulting in a significant reduction of k_0's by more than 58%.

In our recent works, in order to precisely control the thickness of PDMS selective layer, electrospray has been employed to deposit the PDMS layer on PVDF nanofibrous substrate surface. The thickness of PDMS could be reduced to 1.7 μm, which result in significant enhancement of k_0 to 48.8×10^{-7} m/s. It is hoped that our works can motivate the EMBR process for highly saline organic wastewater treatment in industrial large-scale applications.

KEYWORDS

Extractive membrane bioreactor; nanofibrous composite membrane; Electrospinning; highly saline organic wastewater

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Biocarriers Facilitated Gravity-Driven Membrane (GDM) Reactor for Decentralized Wastewater Reclamation

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ABSTRACT

Globally, providing reliable wastewater treatment in rural areas with low population densities and dispersed households is a challenge (Massoud et al. 2009). Especially, in many scenarios (such as shortage of fresh water supply), the treated water from the decentralized wastewater treatment systems needs to be adopted for non-potable reuse purposes such as toilet flushing, gardening, irrigation, etc. (Gikas and Tchobanoglous 2009). Conventionally, constructed wetland, media filters, lagoons, and bioreactors have been widely used as decentralized wastewater treatment or reclamation processes (Fernandes et al. 2013, Vega et al. 2003, Wu et al. 2011). However, in some situations, these traditional methods cannot guarantee the treated water to meet the increasingly strict wastewater discharge or non-potable reuse standards.

Recently, gravity-driven membrane (GDM) filtration have received great attention as a decentralized process in treating surface water, rainwater, greywater, and sewage water (Ding et al. 2017a, Ding et al. 2017b, Pronk et al. 2019, Tang et al. 2016, Wu et al. 2019). The advantages of the GDM process include that (1) it can produce superior treated water due to high membrane separation efficiency; (2) it is an economic process due to its lower capital cost (no permeate suction pump) and operation cost (without requiring physical and chemical cleaning) compared to other membrane processes such as membrane bioreactors (MBRs).

To further improve GDM membrane performance and permeate quality, activated carbon media were attempted to be integrated with the GDM system by coating them on membrane surface, or as pretreatment filter, or by packing them inside of GDM reactor (Ding et al. 2018a, Ding et al. 2018b, Tang et al. 2018a, Tang et al. 2018b). However, nutrient removal in the reported biocarriers facilitated GDM systems was not explored, which was considered as an important parameter in wastewater treatment for satisfactory discharge or reclamation. In conventional MBRs, several studies have illustrated high nutrient removal efficiencies under intermittent aeration conditions in a single reactor (Capodici et al. 2015). The same approach may also be suitable for the biocarriers facilitated GDM system to achieve simultaneous carbon and nutrient removal from wastewater.

Therefore, this study aims to compare organic and nitrogen removal, membrane performance, microbial community, and energy consumption in granular activated

carbon (GAC) facilitated GDM systems in treating real wastewater under different intermittent aeration cycles (intensity and frequency). To illustrate the feasibility of GAC+GDM system as a decentralized wastewater treatment process, energy consumption analysis of GAC+GDM systems under different operation conditions was also performed.

The results showed the GAC+GDM reactors with intermittent aeration produced the permeate with DOC concentrations at 2.7-7.8 mg/L, ~56-64% lower than that in the control reactor (3.7-16.9 mg/L). In detail, the removal efficiencies of small organic fractions in the reactors with intermittent aeration, i.e., building blocks (~86-93%), NMW neutrals (~88-91%) and NMW acids (~98-100%), were greater than those in the reactor without aeration (~80%, ~77%, and ~92%, respectively). The removal efficiency of TN (~26.5-37.1%) in the GAC+GDM reactors with intermittent aeration was approximately 2-3 times greater than that of reactor without aeration (~13.5%).

In addition, the stabilized permeate flux was achieved at ~0.9, 2.0, 2.6, and 3.5 L/m^{2}h in the GDM reactor without aeration, with aeration at 30 min on/60 min off (0.5 L/min), with aeration at 60 min on/60 min off (0.5 L/min), and with aeration at 60 min on/60 min off (2 L/min), respectively (Figure 1a). The intermittent aeration significantly reduced the cake layer resistance and therefore improved ~130-300% the permeate flux compared to control without aeration (Figure 1b). The analysis of biofilm cake layer on the membrane surface indicated that the amounts of biopolymers on the membranes in the intermittent aerated reactors (2.2-6.2 µg/cm^2) were remarkably lower than that in the reactor without aeration (43.4 µg/cm^2).

At the end of filtration operation, the biofilm samples were collected from the GAC particles and the fouled membranes. The microbial community compositions of these samples were analyzed in terms of prokaryotic and eukaryotic community. In detail, Chlorobi, phototrophic bacteria that grow under strictly anoxic conditions, was predominant in the biofilm cake layer in the absence of aeration. While, high abundance of Nitrospirae (Nitrospira genus) were found in the biofilm cake layers in all three reactors with intermittent aeration, accounting for 33.6-59.5%. Ciliophora (38.4%), Chlorophyta (18.6%), and Cryptomycota (18.5%) were predominant eukaryotes on the membrane biofilm layer in the reactor without aeration, but they showed relatively low abundances in those reactors with intermittent aeration. While, Rotifera, a type of aerobic and oligotrophic eukaryote, was the major phylum on the membrane biofilm layer in the reactors with intermittent aeration (30.8-69.6%), whereas it accounted for only 1.1% on the membrane biofilm layer in the reactor without aeration. Interestingly, in the GAC biofilm layer, although a highly similarity of prokaryotic communities was present in the reactors with different aeration conditions, the eukaryotic communities appeared to be significantly different.

The total energy consumption was estimated at 0.003, 0.052, 0.155, and 0.170 kWh/m^3 in the GDM reactor without aeration, with aeration at 30 min on/60 min off (0.5 L/min), with aeration at 60 min on/60 min off (0.5 L/min), and with aeration at 60 min on/60 min off (2 L/min), respectively. Nevertheless, the GAC+GDM reactor with intermittent aeration (0.052-0.170 kWh/m^3) appears to have a competitiveness compared to the conventional activated sludge (~0.3-0.4 kWh/m^3) (Van Dijk and Roncken 1997) and MBR processes (~0.6-6.1 kWh/m^3) (Fenu et al. 2010, Gil et al. 2010). This study suggested that a GAC+GDM reactor with low aeration intensity could be promising as a decentralized wastewater treatment process in terms of water quality and operating energy consumption.

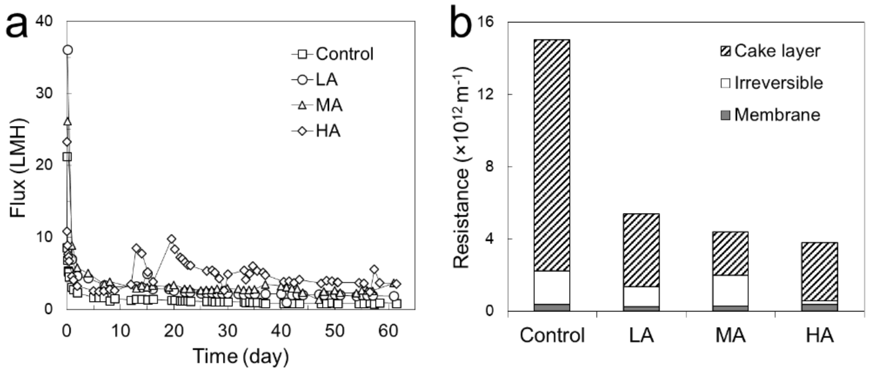

Figure 1. (a) Permeate flux developments and (b) filtration resistance profiles in the GAC+GDM reactors. Control: without aeration; LA: 30 min on/60 min off (0.5 L/min); MA: 60 min on/60 min off (0.5 L/min); HA: 60 min on/60 min off (2 L/min).

Table 1. Dissolved organic fractions in the feed and permeate of GAC+GDM systems (Control: without aeration; LA: 30 min on/60 min off (0.5 L/min); MA: 60 min on/60 min off (0.5 L/min); HA: 60 min on/60 min off (2 L/min).

Organic fractions (µg/L)	Stage 1			Stage 2		
	Feed	Control	HA	Feed	MA	LA
		permeate	permeate		permeate	permeate
Biopolymers	832.4 (±183.1)	36.3 (±30.7)	57.0 (±29.6)	2672.8 (±1036.9)	33.8 (±26.2)	142.6 (±172.7)
Humic substances	3255.6 (±580.5)	479.8 (±88.8)	227.2 (±88.8)	2496.2 (±610.3)	272.6 (±85.0)	370.4 (±118.2)
Building blocks	1799.8 (±424.2)	404.7 (±117.0)	234.6 (±90.2)	2232.2 (±423.6)	175.4 (±51.6)	274.6 (±98.6)
NMW neutrals	3429.2 (±462.0)	746.0 (±197.7)	630.4 (±162.6)	2143.6 (±680.7)	340.4 (±296.9)	276.0 (±185.8)
NMW acids	647.2 (±290.1)	31.8 (±10.5)	14.6 (±9.4)	286.8 (±573.6)	35.2 (±35.3)	16.4 (±16.4)

KEYWORDS

Biofilm; Gravity-driven membrane reactor; Granular activated carbon; Hydraulic retention time; Intermittent aeration; Microbial community

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Superwetting Membranes for High-Performance Separation of Oil-in-Water Emulsions

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ABSTRACT

Accidents of oil spill and other oil-related industries generate tremendous oily wastewater every year. Separating or collecting oil from the oily water has become a worldwide tough subject, especially for the separation of emulsified oily water (oil-in-water emulsions) with a wide oil droplet size distribution from micrometers to nanometers. The critical change in separating oil-in-water emulsions using membranes is to reduce oil fouling, as oil especially viscous oil is easy to adhere on and thus foul membrane surface. Direct result of oil fouling is the quick decline of membrane flux and separation efficiency. Recently, the developments of superhydrophilic and underwater superoleophobic membranes provide an encouraging strategy for separating oil-in-water emulsions with significantly improved anti-oil-fouling property.

Generally, the anti-oil-fouling property of superwetting membranes is determined by the surface hydrated layer which can protect the membrane surface from oil contacting and adhering on. The stronger the hydration ability, the better the anti-oil-fouling performance. Based on this guiding ideology, we fabricate a polyionized hydrogel polymer sodium, polyacrylate-grafted polyvinylidene fluoride, (PAAS-g-PVDF) *via* an alkaline-induced phase inversion process.[1] The PAAS-g-PVDF exhibits outstanding anti-adhesion and self-cleaning property to high-viscous crude oil in aqueous environment. The underwater crude oil contact angles (CAs) of PAAS-g-PVDF and PAAS-g-PVDF-coated substrates are all above 165° with ultralow crude oil adhesive force of nearly zero. Moreover, the membrane made of PAAS-g-PVDF-coated copper mesh can effectively separate crude oil/water mixtures with extremely high water flux up to 50,000 $Lm^{-2}h^{-1}$ driven only by gravity, and with very high separation efficiency above 99.99% (oil content in the filtrate water after one-time separation is as low as 0.5 ppm). Most importantly, the membrane is fouling-free from crude oil and easily recycled for long-term use.

Hydrogels with strong hydration ability and low adhesive superoleophobicity are ideal materials for modifying membranes to achieve efficient and antifouling separation of oil-in-water emulsions. However, a key challenge in fabricating hydrogel-modified microfiltration and ultrafiltration membranes is to design an ultrathin hydrogel layer with both sufficient anti-oil-fouling ability and controllable thickness, thus not blocking the micro- and nanosized membrane pores. Inspired by the novel harsh-environment-tolerant superoleophobicity of alginate-rich seaweed, we achieve the construction of an ultrathin Cu^{2+}/alginate hydrogel multilayer with controllable thickness at the nanometer scale on a polymer ultrafiltration membrane *via* a layer-by-layer self-assembly method.[2] Both the nanosized pores and the high flux of original membrane are well-maintained. The Cu^{2+}/alginate multilayer modified ultrafiltration membrane behaves a biomimetic superhydrophilicity, underwater superoleophobicity and

antifouling ability for crude oil. It is capable of efficiently separating crude oil-in-water emulsion with a high water flux of 1230 $Lm^{-2}h^{-1}bar^{-1}$, an ultrahigh efficiency of 99.8%, and an outstanding antifouling and cyclic ability. What's more, the membrane exhibits good salt-tolerance, antibacterial ability and long-term stability.

A strategy for developing advanced superwetting membranes with both ultrahigh flux and ultrahigh efficiency is to constructing superwetting membranes with both nanosized ultrathin thickness and nanosized pore size. We design a single-walled carbon nanotube (SWCNT) membrane with controllable thickness of 30-150 nm and pore size of 80-10 nm *via* assembling SWCNTs into a porous network membrane.[3] To endow the SWCNT membrane with superhydrophilic and underwater superoleophobic property, anatase TiO_2 nanoparticles and polyethylenimine (PEI) are modified on SWCNT surface *via* surface coating or surface grafting, respectively.[4,5] Benefiting from the unique membrane structure and superwetting property, the fabricated SWCNT nanocomposite membranes exhibit ultrahigh flux up to 30,0000 $Lm^{-2}h^{-1}bar^{-1}$ for separating various oil-in-water emulsions, which is 2 orders of magnitude higher than commercial filtration membranes, simultaneously with very high separation efficiency above 99.96% and outstanding antifouling ability.

KEYWORDS

Superwetting membrane, ultrathin membrane, oil-in-water emulsion separation, anti-oil-fouling, ultrahigh flux.

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Session 3: Nanofiltration/Organic Solvent Nanofiltration

Nanomaterials-assisted Construction of Nanofiltration Membranes with Improved Permeability

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ABSTRACT

Nanofiltration (NF) membranes with ultrahigh permeance and high rejection are highly beneficial for efficient desalination and wastewater treatment. Improving water permeance while maintaining the high rejection of state-of-the-art thin film composite (TFC) NF membranes remains a great challenge. Herein, we report the fabrication of a TFC NF membrane with a crumpled polyamide (PA) layer via interfacial polymerization on a single-walled carbon nanotubes/polyether sulfone composite support loaded with nanoparticles as a sacrificial templating material, using metal-organic framework nanoparticles (ZIF-8) as an example. The nanoparticles, which can be removed by water dissolution after interfacial polymerization, facilitate the formation of a rough PA active layer with crumpled nanostructure. The NF membrane obtained thereby exhibits high permeance up to 53.5 $Lm^{-2}h^{-1}bar^{-1}$ with a rejection above 95% for Na_2SO_4, yielding an overall desalination performance superior to state-of-the-art NF membranes reported so far. Our work provides a simple avenue to fabricate advanced PA NF membranes with outstanding performance.

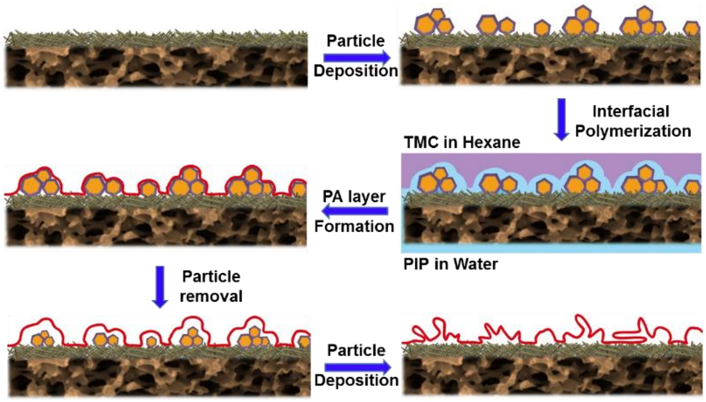

Figure. Nanoparticle as sacrifical template to creat NF membrane with increased area.

KEYWORDS

Nanofiltration membrane; SWCNT interlayer; nanoparticles template; high permeance

High Solvent-Resistant and Nanoparticles-Incorporated Thin Film Nanocomposite Membranes for Organic Solvent Nanofiltration

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ABSTRACT

Organic solvent nanofiltration (OSN), also termed as solvent resistant nanofiltration (SRNF), is an emerging technology for molecular separation and purification of organic substances [1-3]. The core component of OSN technology is OSN membranes, which should provide not only high solvent permeance and high solute rejection, but good solvent resistance as well.

Most OSN membranes belong to the family of integrally skinned asymmetric (ISA) membranes prepared by phase inversion [2]. Generally speaking, most ISA membranes suffered from inherent limitations of tight skin layer, which resulted in a relative low solvent permeance [4]. Recently, thin film composite (TFC) membranes which are characterized by an ultra-thin ‘‘separation barrier layer’’ prepared via interfacial polymerization (IP) on the top surface of a chemically different porous substrate have gained much attention for OSN applications [5].

So far, most of the studies on TFC OSN membranes focused on the PA skin layer preparation via IP reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on a crosslinked polyimide (PI) substrate. However, there were no strong interactions such as covalent bonding between the skin layer and the underline substrate, which may significantly affect the solvent resistance and long-term separation performance.

Thus, for an ideal OSN membrane prepared by the IP process, the enhanced solvent resistance should come from not only the skin layer but also the substrate, as well as the interfacial material compatibility between these two membrane components. Inspired by the fact that crosslinked PI has excellent solvent resistance, we suggested that a PI skin layer might be more compatible with the PI substrate and the further post crosslinking might form an integrally crosslinked PI-based OSN membrane which might be more resistant to organic solvents.

Taking advantages of the exceptional adhesion performance of dopamine (DA) on a variety of substrate materials and the promising chemical stability of PI polymers in OSN applications, here we reported a new class of DA-containing integral PI-based OSN membranes (consisting of both the PI skin layer and the PI substrate materials) via IP reactions and a further imidization process. During the IP process, MPD, DA, and 1,2,4,5-benzene tetracarboxylic acyl chloride (BTAC) were used as an aqueous monomer, an aqueous additive, and an organic monomer, respectively. We proved that amide bonding formed between MPD and the PI substrate during the immersion of the substrate in the aqueous MPD solution, thus providing a strong binding between the substrate and the subsequently formed skin layer of polyamide acid (PAA) which was formed during the IP reaction of MPD and BTAC. DA could also help to build a

strong binding between the substrate and the skin layer during the same IP process, since it contains amine group. The subsequent imidization step converted the PAA molecules of the skin layer into PI polymers, which was quite similar to that of the substrate.

As both the skin layer and the substrate had essentially similar PI molecular structures, the final crosslinking step crosslinked not only the inner molecules of the skin layer and the inner molecules of the substrate, but also the interface molecules between the skin layer and the substrate so as to form a wholly crosslinked (or termed as “integrally”) PI-based composite OSN membrane with improved solvent resistance.

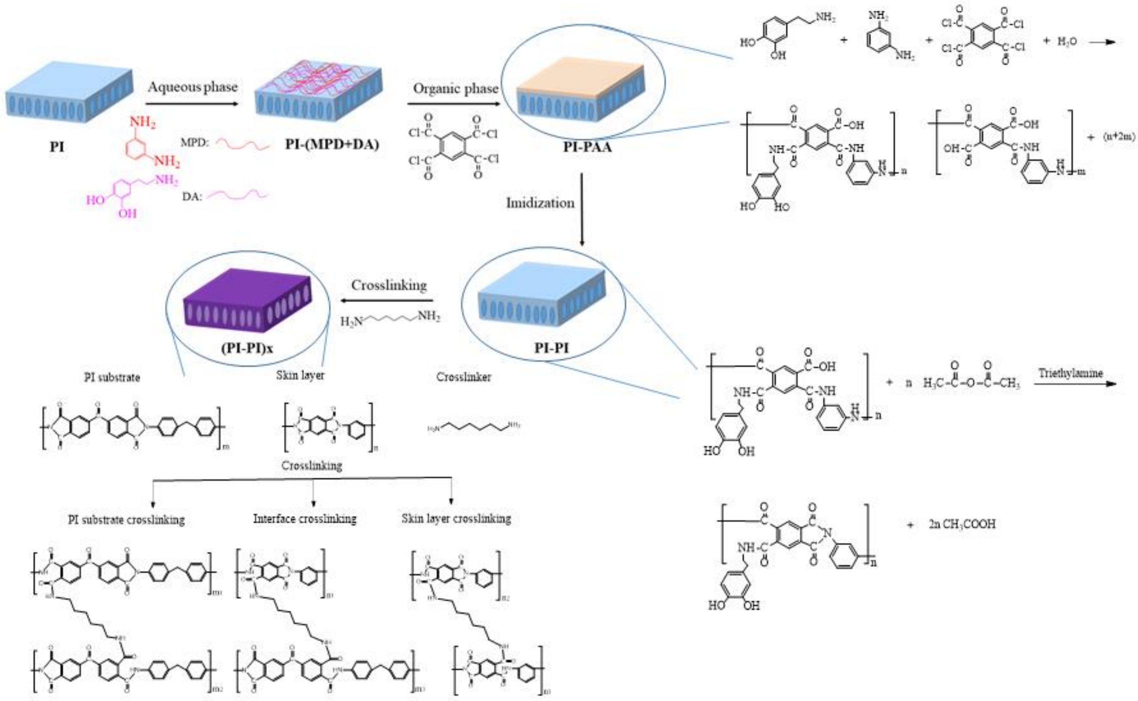

Figure 1. Schematic illustration for the fabrication of the integrally crosslinked PI-based composite OSN membranes.

The fabricated OSN membranes under optimal preparation conditions exhibited an ethanol permeance of 20. 3 L m^{-2} h^{-1} MPa^{-1} with a rejection of 98% for Rhodamine B (RDB, 479 Da) and exhibited an outstanding organic solvent resistance without compromising separation performance after the persistent immersion in *N,N*-dimethylformamide (DMF) at 80 °C for two weeks, as well as an ethanol permeance of 11.5 L m^{-2} h^{-1} MPa^{-1} with a rejection of 99.9% for Rose Bengal (RB, 1017 Da) during the filtration test for RB/DMF solution at room temperature for 7 days, indicating a promising prospective in OSN applications.

Furthermore, we investigated the incorporated of nanoparticles to fabricate thin film nanocomposite (TFN) OSN membranes with improved separation performance. We choose covalent organic frameworks (COFs) due to their specific characteristics such as porous structures, relatively low density, desirable solvent stability, as well as the characteristics that they can formed covalent bonds with the membrane matrix. The new class of COFs-incorporated TFN OSN membranes were prepared via IP reaction of MPD and TMC with the presence of COFs nanoparticles in the MPD aqueous solution, followed by chemical crosslinking and solvent activation. The prepared TFN membranes exhibited an improved surface hydrophilicity and a decreased skin layer thickness, which led to a 46.7% increment in the ethanol permeance (up to 79.8 L m^{-2} h^{-1} MPa^{-1}) compared to those of the COFs-free membranes, as well as an increased RDB rejection (up to 99.4%).

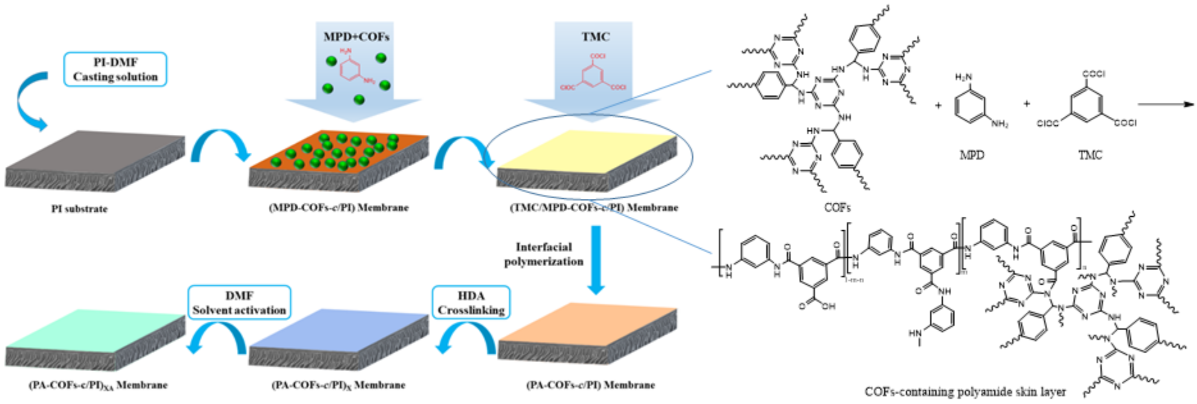

Figure 2. Schematic illustration for the fabrication of the TFN OSN membrane with COFs incorporated inside the PA skin layer.

Moreover, the prepared TFN OSN membranes exhibited an excellent solvent resistance after being statically immersed in DMF at ambient temperature over 100 days, and after being consecutively cross-flow filtrated using RB/DMF solution at ambient temperature over 7 days, both with no significant changes in the separation performance. Furthermore, they showed only minor decrease in flux and rejection after being statically immersed in DMF at 80 °C over 14 days, which proved a strong potential in OSN applications.

KEYWORDS

Organic solvent nanofiltration (OSN); Interfacial polymerization (IP); Thin film nanocomposite (TFN); Nanoparticles

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Amine Functionalised Boron Nitride $BN(NH_2)$ Nanosheet-Studded Nanofiltration Membranes with Enhanced Flux and Fouling Resistance

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ABSTRACT

Currently, nanofiltration (NF) is the most widely employed advanced treatment option in surface water purification due to high separation performance, facile design and operation, and cost-effectiveness [1,2]. Nevertheless, gradual decline of permeate flux with time due to organic fouling which results from the deposition of natural organic matter (NOM) onto the membrane surface and formation of a gel layer is still a significant challenge in the sustained operation of the NF process [3,4].

A potential strategy to minimise the fouling propensity is surface modification of NF membranes through incorporating hydrophilic nanofillers within the selective layer. In most cases, the modified surface will exhibit higher hydrophilicity and negative charge density, favouring the inhibition of organic fouling phenomenon [5-7]. However, partial/complete captivity of nanofillers within the selective film can hamper the exploitation of the full potential of the material in boosting the membrane fouling resistance properties. Moreover, some of the nanofillers are reported to be incompatible with the polymer matrix, and will aggregate upon incorporation or leach out during the filtration, thus creating more defects in the polymeric network [8-10].

To address these shortcomings, the current study reports on the fabrication of unique thin film nanocomposite (TFN) membranes studded with amine functionalised boron nitride $BN(NH_2)$ nanosheets. The advantages of using $BN(NH_2)$ nanosheets is that they can be produced via a facile, low cost, and environmentally-friendly approach, unlike the complex synthesis methods reported for various nanomaterials which depend on the consumption of numerous chemicals, and generate hazardous waste and toxic gas [11]. Also presence of amine functional groups and electron-deficient B atoms at the edges of nanosheets make them highly hydrophilic and negatively charged, in turn [11-13]. Therefore, $BN(NH_2)$ nanosheets are ideal nanofillers for enhancing the fouling resistance of NF membranes.

Fabrication wise, the thin film was synthesised through interfacial polymerisation (IP) reaction between piperazine (PIP) at 0.35 wt % in water and trimesoyl chloride (TMC) at 0.3 wt % in n-hexane to form a polypiperazine amide (PPA) layer over a polyether sulfone (PES) ultrafiltration (UF) membrane support. After the PPA film formation and prior to heat curing at 50 ˚ C, the membrane was brought into contact with an aqueous solution of $BN(NH_2)$ nanosheets at 0.003 wt % in water to stud the PPA layer. The control and the modified membranes are referred to as PPA and PPA-BN, respectively.

Fabricated membranes were characterised through scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle (CA), and streaming potential measurements results of which are presented in figure 1. Compared with the nodular structure of the PPA membrane in Figure 1(a), the PPA-BN membrane clearly exhibits the presence of $BN(NH_2)$ nanosheets on its surface as shown in Figure 1(b). Also AFM studies in Figure 1(a) and (b) revealed that the PPA-BN membrane with an average roughness (R_q) of 6.09 nm possesses a smoother surface than the PPA at 12 nm, which can be attributed to the coverage of the background nodular texture with horizontally-oriented nanosheets during the post-functionalisation stage. According to XPS results in Figure 1(e), $BN(NH_2)$ nanosheets are bound to the PIP-TMC network through covalent B–C bonding arising from the reaction of B atoms at the edges of nanosheets with available C atoms of the unreacted COCl groups on the PIP-TMC network [11,14]. Referring to Figure 1(f), CA and streaming potential measurements confirmed the greater hydrophilicity and negative charge density of the PPA-BN membrane compared to the control PPA. Higher hydrophilicity of the PPA-BN membrane originates from the availability of polar amine functional groups in the structure of $BN(NH_2)$ nanosheets, and their tendency to form hydrogen bonds with water molecules [11,15]. Also, the enhanced negative charge density is linked to the Lewis acidity and electron deficient nature of B atoms available at the edges of nanosheets, and the affinity of their vacant P orbitals to acquire hydroxyl ligands in water [11-13]. Conclusively, characterisation results reveal that the PPA-BN membrane with a smooth, hydrophilic, and negatively charged surface possesses a greater potential over the PPA counterpart to retard the organic fouling.

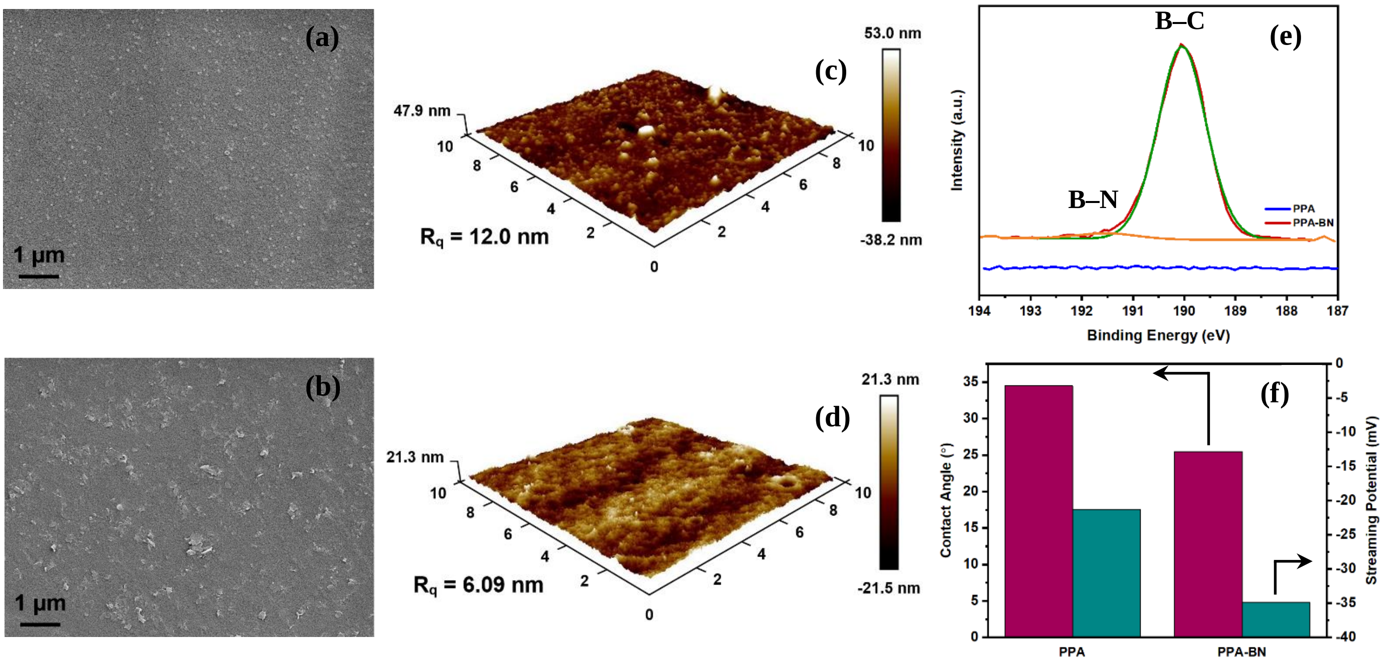

Figure 1. Characterisation results of nanosheets: SEM micrographs of (a) PPA and (b) PPA-BN surfaces, 3D AFM images of (c) PPA and (d) PPA-BN surfaces, (e) high resolution XPS B1s spectra of membranes, and (f) contact angle and streaming potential (measured at pH 7) values of membranes.

Cross flow filtration experiments at 0.6 MPa were conducted to evaluate the permeation and fouling resistance properties of membranes, results of which are tabulated in Table 1. Accordingly, the PPA-BN membrane exhibited 36.9 % enhancement in pure water flux to 45.9 LMH, from 28.9 LMH for the PPA. This improvement is ascribed to the greater hydrophilicity of the PPA-BN which contribute to the formation of a hydration layer above the membrane surface. Additionally, the smooth surface provides a frictionless pathway for the passage of water molecules and an overall faster flow [16].

Reversible/irreversible fouling resistance and recoverability trends of membranes were investigated through filtration of 200 ppm sodium alginate (SA) and bovine serum albumin (BSA) solutions during three fouling-pure water cleaning cycles. At the termination of the third cycle, it was revealed that the total fouling (R_t) of the PPA-BN membrane was approximately 50 % less than that of the PPA, and the flux recovery ratio (R_{re}) was better for the former. The improved fouling resistance and recovery of the PPA-BN membrane was attributed to its negatively charged hydrophilic surface, repelling the organic matter away from the membrane and alleviating the fouling phenomenon [17,18].

Table 1. Filtration performance of the fabricated membranes in terms of flux and fouling resistance.

Membrane	Pure Water Flux (LMH)	R_t – SA (%)	R_{re} – SA (%)	R_t – BSA (%)	R_{re} – BSA (%)
PPA	28.9	24.2	96.8	19.4	90.0
PPA-BN	45.9	11.9	97.9	11.0	93.0

In conclusion, fabrication of TFN membranes studded with BN(NH_2) nanosheets is an effective approach in enhancing the flux and minimising the extent of organic fouling.

KEYWORDS

Nanofiltration membrane, thin film nanocomposite, functionalised boron nitride, flux, fouling control.

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2D Nanowires Film Supported Nanofiltration Membrane for High-Efficient Desalination with Fast Water Permeance

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ABSTRACT

Nanofiltration (NF) membranes with ultrahigh permeance and high rejection are highly beneficial for efficient desalination and wastewater treatment. Improving water permeance while maintaining the high rejection of state-of-the-art thin film composite (TFC) NF membranes remains a great challenge. Herein, we report the fabrication of a TFC NF membrane via interfacial polymerization on 2D nanowires film/microfiltration composite support, such as single-walled carbon nanotubes/polyether sulfone composite support and cellulose nanofibers/ polyether sulfone composite support. Using this novel 2D nanowires film/microfiltration composite membrane as support instead of the use of traditional polymer-based underlying layers, a defect-free polyamide selective layer for NF membrane with thickness of as thin as 12 nm is achieved due to the high porosity and interconnected pore structure of 2D nanowires network (Figure 1). The obtained NF membrane exhibits an extremely high performance with a permeating flux of 32 l $m^{-2}h^{-1}bar^{-1}$ and a rejection rate of 95.9% to Na_2SO_4. Furthermore, we design a crumpled polyamide (PA) layer via interfacial polymerization on 2D nanowires/polyether sulfone composite support loaded with nanoparticles as a sacrificial templating material, using metal-organic framework nanoparticles (ZIF-8) as an example. The nanoparticles, which can be removed by water dissolution after interfacial polymerization, facilitate the formation of a rough PA active layer with crumpled nanostructure, which can effectively increase the effective filtration area of NF membrane. The NF membrane obtained thereby exhibits high permeance up to 53.5 l $m^{-2}h^{-1}bar^{-1}$ with a rejection above 95% for Na_2SO_4, yielding an overall desalination performance superior to state-of-the-art NF membranes reported so far. Our work provides a simple avenue to fabricate advanced PA NF membranes with outstanding performance.

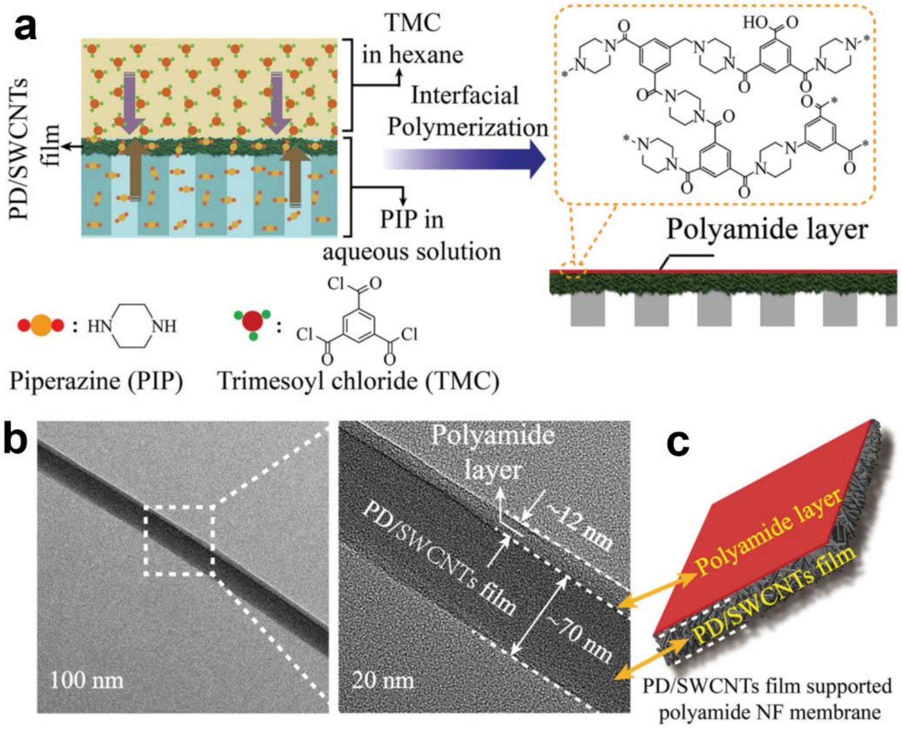

Figure 1 a schematic of interfacial polymerization process for preparing PD/SWCNTs film supported ultrathin polyamide NF membrane. **b** Cross-sectional TEM image of polyamide layer covered PD/SWCNTs film. **c** The schematic structure of PD/SWCNTs film supported polyamide NF membrane.

KEYWORDS

Nanofiltration, 2D nanomaterials, ultrafast water permeance, desalination

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Polyamide Composite Membranes Incorporated with Fluorinated Organic Nanoparticles for Organic Solvent Nanofiltration

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ABSTRACT

Nanofiltration as an environmental friendly and high efficient separation technique, has been wildly used in liquid-phase separation, such as the seawater/ brackish water desalination, wastewater treatment as well as chemical products' separation and purification. Recently, researchers have paid more and more attentions in developing high performance membranes using for organic solvent nanofiltration (OSN). However, there is still a big challenge to prepare polymeric membranes with both high perm-selectivity and good stability in OSN process. In this work, we have proposed a facile and versatile approach for the fabrication of polyamide composite membrane incorporated with fluorinated organic nanoparticles (FONs) on porous supporting membrane. The hydrophobic FON nanoparticles were formed via the oxidative polymerization of M-phenylene diamine (MPD), dopamine (DA) and 1H,1H,2H,2H-Perfluorodecanethiol (PFDT). The Hydrophobic FON nanoparticles could reduce the membranes surface energy and produce interface channels, facilitating organic solvent transporting through the membrane. Thus, there is a promising prospect to exploit advanced polyamide composite membranes for substance separation and purification in OSN process.

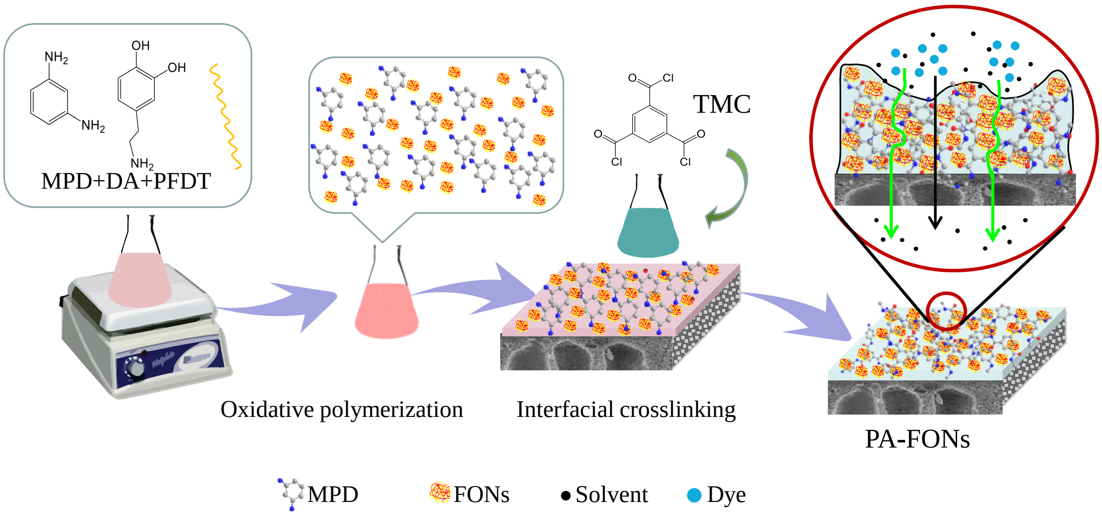

Fig.1. Schematic diagram for fabricating polyamide composite membrane incorporated with fluorinated organic nanoparticles (FONs).

KEYWORDS

Organic solvent nanofiltration; Membrane; Fluorinated; organic nanoparticle

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Session 4: Emerging Membrane Processes (FO, PRO, MD)

Low Energy Desalination Technologies: Forward Osmosis-Reverse Osmosis Hybrid System

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ABSTRACT

More than half of the current desalination plants use reverse osmosis (RO) technology. However, RO is energy intensive and thus expensive. Forward osmosis (FO) and freezing desalination (FD) offer attractive alternatives in terms of the development of more sustainable desalination technology.

FO process uses the natural chemical potential difference between a highly saline draw solution (DS) and a feed solution (FS) to induce natural osmosis through a semipermeable membrane. An FO process may be viewed as a pretreatment for downstream unit processes, especially for water with high scaling or fouling propensity. During this process the FS is concentrated while the DS becomes dilute. Energy limitation of RO process can be mitigated by combining it with FO process because RO feed water can be diluted by FO process (It is called as FO-RO hybrid system). For wastewater reuse, FO process can use wastewater or effluents as the FS and seawater as the DS. Further water resources can be recovered from the wastewater and diluted seawater can be used as the FS to RO. Synergistically coupling FO with RO produces an exceptionally robust, multi-barrier system for wastewater reuse and desalination.

With the aid of cold energy from regasification of liquefied natural gas, FD is an emerging technology for seawater desalination because of its low energy characteristics and insensitivities to fouling problems. The FD can overcome limitations of both membrane- and thermal-energy-based desalination processes. Extant studies concerning FD have primarily focused on ice-quality and productivity enhancement. Numerous crystallizer designs operating under various conditions have been investigated to achieve highest possible fresh-water purity. Few post-treatment techniques have also been developed to boost quality and productivity of fresh water.

KEYWORDS

Desalination, Forward Osmosis, Freezing Desalination, Water Reuse

ACKNOWLEDGEMENTS

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Janus Membrane with Unparalleled Forward Osmosis Performance

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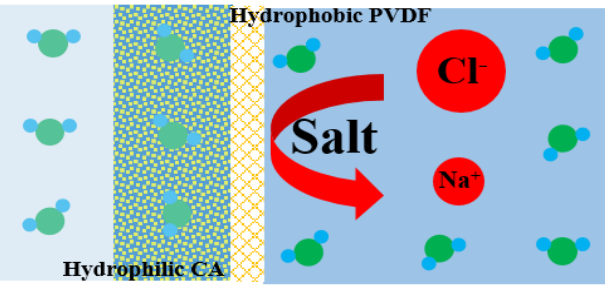
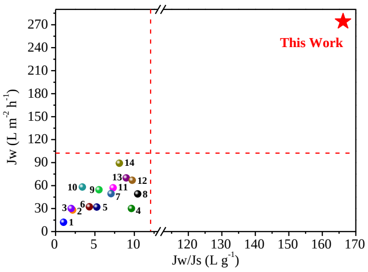
ABSTRACT

We report the use of porous Janus membranes for forward osmosis (FO). A porous Janus FO membrane, comprised of a hydrophilic cellulose acetate layer and a hydrophobic polyvinylidene fluoride (PVDF) nanofiber layer, was fabricated by electrospinning. The resultant membrane exhibited outstanding FO performance, with a high water flux of 274.2 L m^{-2} h^{-1} and a low reverse salt flux of 1.65 g m^{-2} h^{-1} using 1 M NaCl draw solution. Different from the state-of-the-art thin film composite (TFC) membranes, the prepared Janus membrane demonstrates unparalleled FO performance via a nanofluidic diode model, whose high selectivity is determined by the air gap within the hydrophobic nanofiber layer that can effectively prevent the reverse salt diffusion. Wetting of the hydrophobic layer is the crucial issue in Janus FO membranes, which deserves further attention to extend the osmosis longevity.





KEYWORDS

Porous Janus membranes, Forward osmosis, Air gap, Nanofluidic diode

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Development of an Optimization Algorithm for Full Scale Forward Osmosis Plant Design

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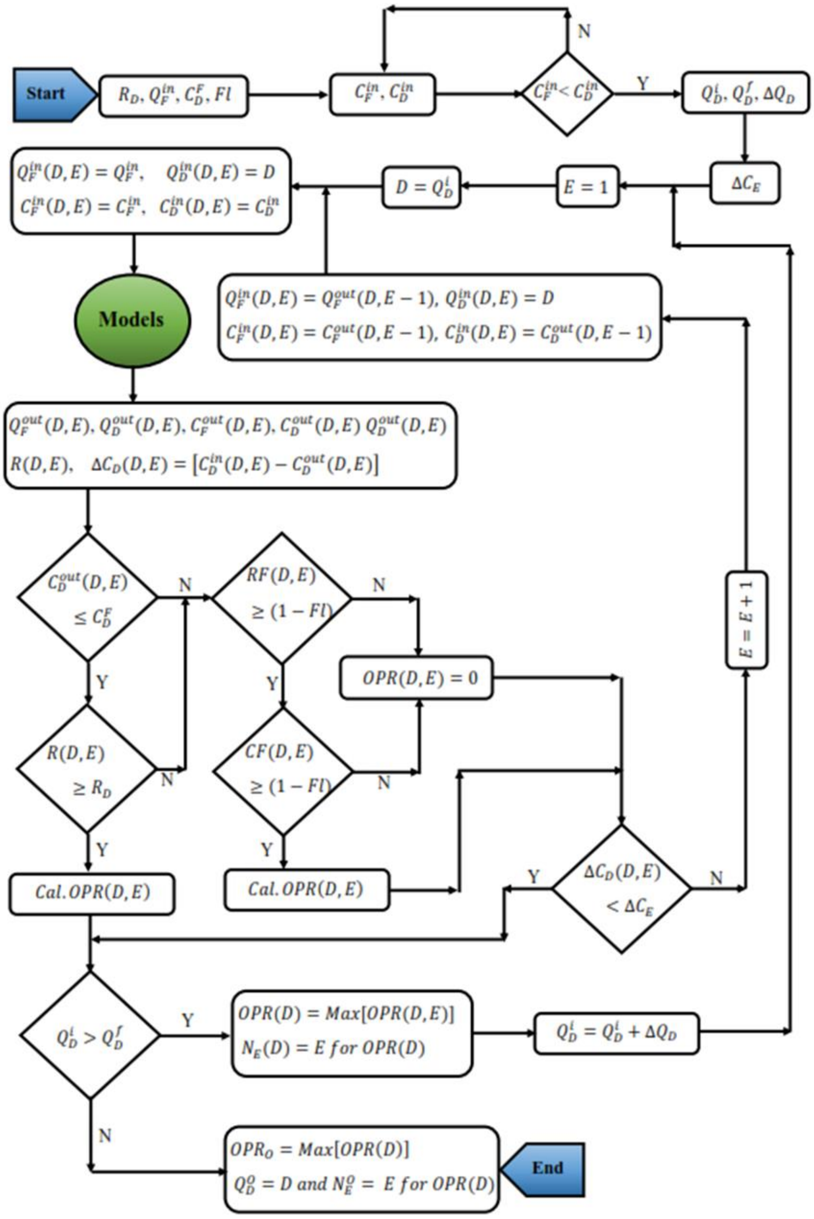
ABSTRACT

Low energy consumption and less fouling propensity of forward osmosis (FO) processes demonstrated it as a promising membrane filtration technology. Irrespective of the applications, performance of a full scale FO plant is defined by its production capacity, final draw solution (DS) concentration and feed solution (FS) recovery rate, which are significantly influenced by various design variables and operating parameters. Moreover, these parameters have both favorable and adverse effects on the process performance [1-3]. Hence, it is required to optimize the operating conditions to design an efficient plant. However, most of the FO process optimization studies so far are lab-scale analysis. But it is difficult to translate the findings of these studies for a full-scale system. Although some recent experimental studies optimized the full-scale system, but these studies are applicable for a specific application and for a narrow range of operating conditions [4, 5]. Therefore a full-scale theoretical analysis is necessary for various applications and broader range of operating conditions.

Only a few theoretical studies have been conducted to optimize the full-scale FO system. Most of these studies did not consider the actual dimensions and solution flow configurations of the membrane module. Hence, the findings of these studies are mostly inapplicable for the real applications. Moreover, these studies optimized the operating conditions by maximizing the recovery rate only. But, it was found that the recovery rate and DS dilution factor are inversely related [6, 7]. Therefore, the optimum design variables and operating conditions should be selected considering both recovery rate and concentration requirement. Thus, the main aim of this study is to optimize the design and operating conditions of a full scale FO plant. It developed a set of mathematical models to theoretically estimate the system performances. These performances were then compared with the experimental results to validate the models used for this study. Finally an overall performance index and a novel optimization algorithm was developed for the optimization of the system.



Nomenclature

Symbol

C: Concentration
J: Flux
N: Number
Q: Volumetric flowrate
R: Recovery rate
RF: Recovery fraction
CF: Concentration fraction
Fl: Flexibility
OPR: Overall performance rating

Superscript

in: inlet
out: outlet
i: initial
f: Final

Subscript

D: Draw Solution
E: Element

Fig.1. Developed optimization algorithm for the parametric optimization of FO plant

A complete theoretical framework was developed to determine the optimum operating conditions and design parameters of an FO system. The framework begins with the calculation of thermodynamic properties of FS and DS. Considering the membrane characteristics and concentration of the solutions, the local water flux and reverse salt flux were calculated. As the total water permeation through a large membrane area cannot be calculated directly, the membrane area was discretized to sufficiently smaller areas and the models were then applied iteratively to the discrete areas according to the directions of the flow. Changes in the flowrates and concentrations were estimated by solving the mass balance equations employing the finite difference method. Finally for the optimization, a new performance parameter, overall performance rating (OPR) was proposed, which combined the recovery rate and final DS concentration with the number of membrane elements. OPR is defined as the percentage of overall design target achieved per element. It was formulated by the multiplication of recovery fraction (RF) and concentration fraction (CF). However, the RF is defined as the ratio of actual recovery rate achieved to the desired recovery rate. Whereas, the CF is a ratio of targeted final concentration to the actual final concentration. In order to prevent the overdesign, the maximum values of RF and CF were considered one. The proposed optimization method was implemented by calculating OPR for several sets of operating conditions and selecting the operating conditions which provide the maximum value of OPR. Instead of searching the optimum conditions within the whole range, it only searches when both the actual recovery rate and the final concentration are in an acceptable proximity (5%) to the targeted recovery rate and concentration. The proposed optimization algorithm is described in Fig. 1.

Table 1 Calculation of optimum performance rating (OPR)

No. of Element	**1**	**2**	**3**	**4**	**5**	**6**
Recovery Rate (%)	17.68	30.53	40.57	48.56	54.94	60.02
RF	0	0	0	0.97	1	1
Final Concentration (M)	0.25	0.17	0.13	0.12	0.10	0.097
CF	0	0	0	1	1	1
OPR	0	0	0	**24.28**	20	16.67

First of all, the simulation results were compared with the findings of our previous experimental study [4] to validate the models. A commercial 8040 spiral wound thin film composite FO membrane element was used for the experiments. NaCl solutions of 0.6 M (equivalent to seawater) and 0.02 M (equivalent to wastewater) concentration was used as DS and FS. The FS and DS outlet of the first element was used as the inlet of the second element and so on. These experiments were conducted up to 4 elements. Comparison showed that the simulation results (average water flux, FS and DS outlet flowrates and concentrations of the elements) are in a very good agreement with the experimental results. However, the average deviation from the experimental results was only ≈ 7%. Followed by the validation, the optimization algorithm was employed to optimize the operating conditions. Table 1 explains the optimization algorithm depicted in Fig. 1. Considering the RF, CF and number of elements, the maximum OPR (24.28% objective/element) value was achieved when 4 elements were used in a pressure vessel. In comparison, the experimental study also showed that the optimum number of elements in a pressure vessel was 4 [4].

The above discussion shows that the proposed algorithm satisfied the experimental findings. Thus, the algorithm can be employed as a very useful tool to design and operate an efficient FO system.

KEYWORDS

Forward osmosis; Simulation, Design parameters; Operating conditions; Optimization;

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Thin Film Nanocomposite Membranes Incorporated with Zeolite for Power Generation Through Pressure Retarded Osmosis

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ABSTRACT

Energy and water issues are the two main global challenges faced by the human in the past decade. The rapid growths in global energy consumption and greenhouse gas emissions have encouraged the exploration of renewable energy sources as substitute fuels. Osmotic pressure gradient energy released from the mixing of water streams with different salinities is an unexploited resource of renewable energy. By employing a semipermeable membrane to control the mixing process, the osmotic pressure gradient energy can be generated in terms of electrical power via pressure retarded osmosis (PRO) without causing adverse environmental impacts. This work presents the fabrication of thin film nanocomposite (TFN) membranes which are customized to offer high flux in forward osmosis (FO) and high osmotic power in PRO. In this study, the TFN membrane was fabricated by forming a polyamide thin film on the polysulfone substrate through the interfacial polymerization process. Zeolite loading in the polyamide layer was in the range of 0.05-0.3 wt%. Field emission scanning electron microscope (FESEM) and atomic force spectroscopy (AFM) studies indicated that zeolite was successfully embedded in the polyamide layer of the membrane. The lowest contact angle was obtained at 61.08° when 0.1wt% of zeolite was used. Similarly, the 0.1wt% zeolite modified membrane resulted in higher water flux in both RO (9.66 L/m^{2}h) and FO (5.8 L/m^{2}h) experiments. TFN membrane incorporated with zeolite exhibits power density of 1.73 W/m^2.

KEYWORDS

Thin Film Nanocomposite (TFN), Zeolite, Reverse Osmosis (RO), Forward Osmosis (FO) and Pressure Retarded Osmosis (PRO)

Pressure-Retarded Membrane Distillation for Low-Grade Heat Recovery: The Critical Roles of Pressure-Induced Membrane Deformation

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ABSTRACT

Pressure-retarded membrane distillation (PRMD) is an emerging membrane process to recover energy from low-grade heat sources. The applied hydraulic pressure on the cold-water side in PRMD may strongly affect both energy conversion efficiency and membrane performance. Here, we report the first systematic study on this critical issue. A commercial nanoporous polytetrafluoroethylene membrane was evaluated as a general membrane sample over a range of applied pressures from 0 to 10 bar at a temperature difference of 40 ˚C. Our results show that the theoretically projected constant water vapor flux decreases significantly with the increase of the applied pressures, which can be attributed to the severe membrane deformation induced by pressures. The membrane in the active-layer-facing-hot-solution orientation is mechanically unstable with the complete loss of water vapor flux under 2 bar. In contrast, the membrane in the active-layer-facing-cold-solution orientation can still work under 10 bar. Combining theoretical analysis and detailed characterization of membrane physical structures, we show that the properties of membrane active layers (i.e., pore size, porosity, and thickness) deteriorate under elevated pressures. Deformed membranes have lower permeability and higher temperature polarization in PRMD, resulting in the observed lower water vapor fluxes. Our results suggest that improving the mechanical stability of membranes would be the first critical step in realizing practical applications of PRMD for low-grade heat recovery. Potential research directions for developing novel PRMD membranes are also proposed.

KEYWORDS

pressure-retarded membrane distillation; low-grade heat recovery; membrane deformation; temperature polarization

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Session 5: Advanced Membrane Materials II

Bioinspired Membranes and Membrane Processes

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ABSTRACT

Learning from the exceptional composition, structure, formation process and functions of natural materials, a number of bioinspired membranes have been designed and fabricated using cell membrane, lotus, mussel, nacre, aquaporin as representative prototypes and biomineralization, bioadhesion, self-assembly as major tools. These membranes have exhibited fascinating properties and outstanding performances such as high permeability, multiple selectivity, superior stability. Meanwhile, these membranes have played critical roles in solving energy, environment and water stress. Bioinspiration, as the powerful platforms for sustainable innovation and exploitation of membranes and membrane processes, have broad implications in exploiting innovative membrane materials and intensifying diverse membrane processes. This presentation will give a brief survey on the fabrications, applications as well as perspectives of bioinspired membranes and relevant membrane processes.

Preparation, Characterization and Performance of Zeolite Templated Carbon as Filler in Polysulfone Membrane

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ABSTRACT

The zeolite templated carbon (ZTC) was used as a novel filler for the preparation of mixed matrix hollow fiber membranes (MMMs). Two different ZTCs with distinct pore characteristics were used and their effect on the gas permeation performance of the MMMs was studied. We synthesized the ZTC by different methods of carbon filling into the zeolite-Y channels. The ZTC referred to as ZTC-imp was prepared via impregnation method with sucrose as carbon source [1]. Meanwhile, the carbon filling by furfuryl alcohol impregnation followed by propylene-chemical vapor deposition (CVD) was referred to as ZTCimp-CVD. X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and BET analysis were used to observe the structural morphology of the ZTCs. Results showed that ZTC-imp possess not only microporous carbon domain, but also disordered carbon deposition on the external surface of zeolite. These external carbon layer have randomly distributed mesopores and the partial ordered micropores was observed in the inner region of the ZTC. On the contrary, the two step process of impregnation-CVD is more favorable for suppressing the deposition of external carbon layer with high portion of microporous carbon, reflecting faithful replication of zeolite by the ZTC [2]. The ZTCImp-CVD exhibited higher pore structural ordering, larger surface area and higher porosity than those of ZTC-imp. No surface modification was conducted for ZTCs prior adding with the dope solution. The MMMs were fabricated by blending 0.25 wt% ZTC via dry-jet wet spinning process with polysulfone (PSf) as the membrane matrix [3]. Membrane morphological and thermal properties were examined by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC). Addition of ZTCs lead to the minimal change in the shift of diffraction angle, indicating slight changes on the polymer chain packing with the possibility of good dispersed ZTC particles. Moreover, FESEM analysis supported that defect-free membranes were observed for all MMMs, the thermal stability was also found to be enhanced with an improvement of glass transition temperature (T_g). Single gas test results exhibited that the measured permeances for all gases tested and selectivities for all separation were increased with the addition of ZTCs. PSF/ZTCimp-CVD MMM recorded the higher permeances improvement for CO_2 (98%), O_2 (108%) and H_2 (127%) with CO_2/CH_4, O_2/N_2, H_2/CH_4 and CO_2/N_2 selectivity of 59.79, 6.26, 120.74 and 33.43, respectively. These higher permeance enhancement can be ascribed due to its larger surface area and porosity providing higher adsorption capacity for gases. Meanwhile, higher selectivity can be attributed

to the highly defined pore structure of ZTCImp-CVD allowing good size–selective

capability. The ordered pore structure and higher surface area of filler play an important role in the overall performance of MMMs. The results lead to the conclusion that such filler could be a promising candidate for a novel mixed matrix membrane for CO_2, O_2 and H_2 separation.

Table 1 Characteristics of the ZTCs

Sample	**S_{BET}[a] (m$_2$/g)**	**V_t[b] (cm$_3$/g)**	**d_p[c] (Å)**
Zeolite-Y	656	0.344	8.04
ZTC-imp	1254	0.950	15.4
ZTCImp-CVD	2939	1.929	12.2

[a] BET surface area
[b] Total pore volume
[c] Mean pore width size

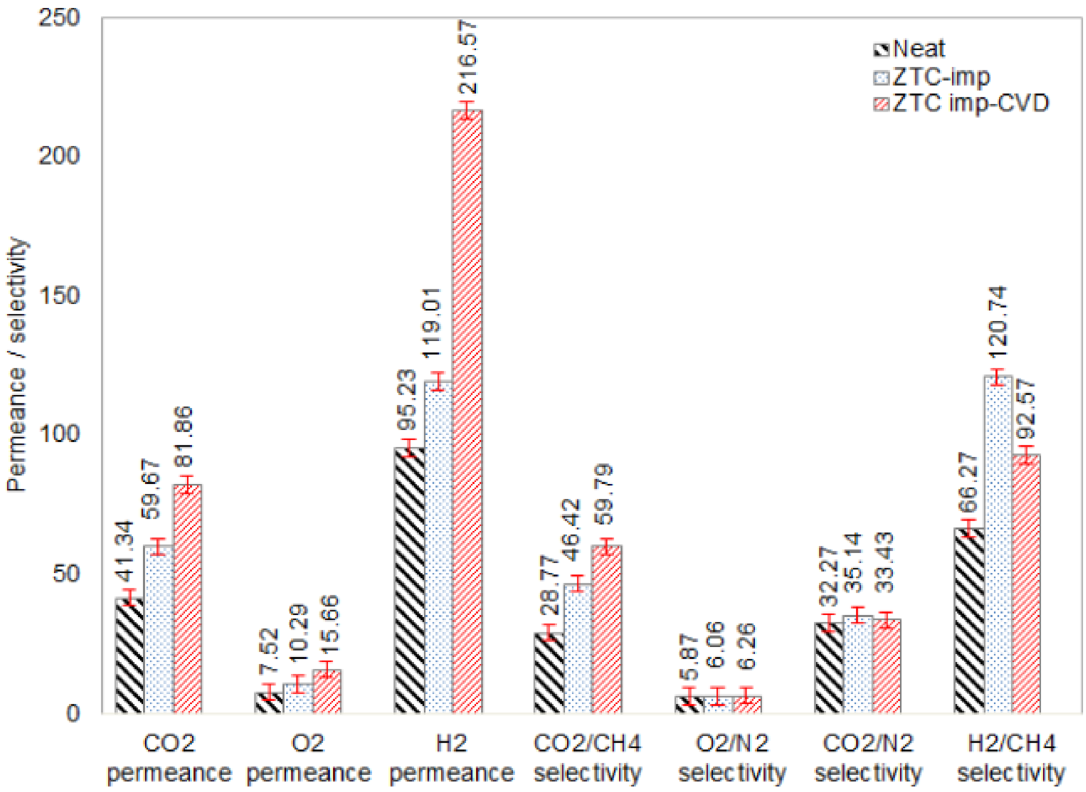

Figure 1 Gas permeation properties of PSF and PSF/ZTC MMMs

KEYWORDS

Zeolite templated carbon, synthesis routes, hollow fiber, mixed matrix membrane, gas separation

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Compatibility of Cross-Linking Polymers in Polymer Inclusion Membranes (PIMs) and Their Effect on Membrane Performance, Stability and Morphology

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ABSTRACT

Emerging as an alternative to traditional solvent extraction, PIM-based separation has been attracting considerable attention in recent years [1]. The main reasons behind the interest in PIMs are based on their better stability over other liquid membranes (e.g. supported liquid membranes (SLMs)) and their capability of performing simultaneous extraction and back-extraction [2,3]. PIMs have superior mechanical properties and chemical resistance than SLMs due to the extractant being immobilized between the entangled chains of their base-polymer, which minimizes its leaching to the adjacent aqueous phase(s). Yet PIMs' stability and rate of extraction should be improved further in order to have the potential to replace solvent extraction in industrial applications. Hence with the aim of improving the PIMs' performance, the present research applies the cross-linking polymerization approach [4] in the manufacturing of PIMs with one of the following extractants: di-(2-ethylhexyl)phosphoric acid (D2EHPA), Aliquat-336 (a mixture of quaternary alkylammonium chlorides) or trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos®-104). The ability of these membranes to extract Zn(II) (D2EHPA-based PIMs), SCN^- (Aliquat-336-based PIM) and Au(III) (Cyphos® IL104 based PIM) as model target analytes, was assessed and compared with their non-cross-linked counterparts.

Three different base-polymers such as poly(vinyl chloride) (PVC), poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) and cellulose triacetate (CTA) were examined in the preparation of PIMs along with two different cross-linking polymers namely poly(ethyleneglycol dimethacrylate) (PEG-DMA) and polyethyleneglycol divinylether (PEGDVE). Effectiveness of three different initiators (i.e., 2,2-dimethoxy-2-phenyl acetophenone (DMPA), triarylsulfonium hexafluorophosphate (TASHFP) and triphenylphosphine oxide (TPO)) in initiating the cross-linking process were examined, and the most effective initiator for each crosslinking polymer was selected. The cross-linking conditions (i.e., amount of initiator and UV-irradiation time) were optimized for each possible base-polymer and cross-linking polymer combinations. The compatibility of different extractants with all base-polymer and crosslinking polymer combinations was also examined and the outcomes are listed in Table 1. Successful PIMs (i.e., homogeneous and mechanically stable) were then exposed to UV-light (365 nm, 1.2 mW cm^{-2}) to induce the cross-linking.

Table 1. Physical appearance of PVC/PVDF-HFP/CTA based PIMs with different cross-linking polymers and extractants (× Not successful, √ Successful).

Extractant	Cross-linking polymers			Base polymer
	PEG-DMA		PEGDVE	
	DMPA	TASHFP		
D2EHPA	×	×	×	PVC
Aliquat 336	✓	×	×	
Cyphos® IL 104	×	×	×	
D2EHPA	✓	✓	✓	PVDF-HFP
Aliquat 336	✓	×	×	
Cyphos® IL 104	✓	✓	✓	
D2EHPA	✓	✓	×	CTA
Aliquat 336	✓	✓	✓	
Cyphos® IL 104	×	×	✓	

The extraction performance of all successful PIMs was then assessed. Membranes with D2EHPA, Aliquat 336 or Cyphos® IL 104 as the extractant were immersed in a feed solution composed of Zn(II), SCN^- or Au(III), respectively. For all successful crosslinked PIMs, the corresponding non-cross-linked membranes were also prepared and used for extraction experiments in order to compare their performance. For all three base-polymers, with Aliquat 336 as extractant, cross-linked membranes extracted larger amounts of thiocyanate than the corresponding non-cross-linked membranes. Similarly, PEGDMA cross-linked CTA-D2EHPA membrane extracted considerably larger amounts of Zn(II) than the corresponding non-cross-linked membrane. While PEGDVE cross-linked PVDFHFP-D2EHPA membrane was more efficient in extracting Zn(II) than its non-cross-linked counterpart. Cyphos® IL 104 based membranes were deployed for the Au(III) extraction from highly acidic feed solutions. Both CTACyphos® IL 104-based cross-linked and non-cross-linked membranes extracted an equivalent amount of Au(III) and these membranes appeared not to be suitable for prolonged use under acidic conditions. On the other hand, the PVDF-HFP- Cyphos® IL 104 based cross-linked membrane was more stable under acidic conditions and extracted much larger amounts of Au(III) than its non-cross-linked counterpart. Therefore, PVDF-HFP-Cyphos® IL 104 based cross-linked membranes were further used to extract Au(III) from electronic waste dissolved in aqua regia.

Thermal stability of the membranes was analyzed by thermogravimetric analysis (TGA) to verify whether the incorporation of the cross-linking polymer affected the membrane's thermal stability compared to the corresponding non-cross-linked membrane. Results clearly indicated that the inclusion of the cross-linking polymer in the membrane did not compromise its thermal stability.

The morphology of the membranes was also investigated by atomic force microscopy (AFM) and differences in topography were observed between cross-linked and noncross-linked PIMs. Figure 1 shows topographic images of a PVDF-HFP membrane, a cross-linked PVDF-HFP membrane, a cross-linked and a non-crosslinked PVDF-HFPbased PIM. These images illustrate that cross-linking creates surface roughness leading to an increase in the membrane specific surface area which could subsequently result in faster extraction.

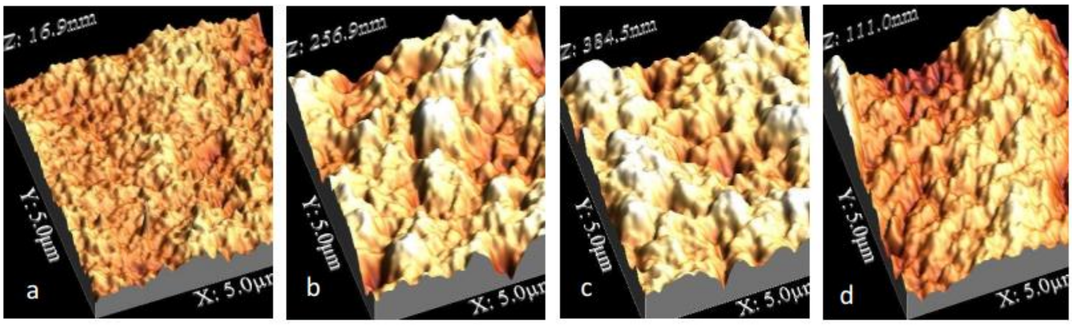

Figure 1. AFM topography of membranes containing a) PVDFHFP b) PVDFHFPPEGDVE-TASHFP c) PVDFHFP-PEGDVE-TASHFP-D2EHPA d) PVDFHFP-D2EHPA.

KEYWORDS

polymer inclusion membrane (PIM), cross-linking polymers, extraction, zinc(II), gold(III)

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Morphology of $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.7}Sr_{0.3}M_NO_{3-\delta}$ Membranes Prepared by Various Ratio of PEG-H_2O Additive

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ABSTRACT

$La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF 7328) and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM 73) are two perovskite oxides who have the ability to supply oxygen from their lattice oxygen into an oxidation reaction. With this special property, the perovskites may be used as an oxygen transport membranes for oxygen separation [1] as well as catalyst for methane partial oxidation [2]. Due to their special oxygen transfer mechanism, the membranes must be very thin to give the highest oxygen flux but strong enough not to crack or broken during the operation. Therfore, an asymmetric form of the membrane, where a thin layer of perovskite oxides supported by porous, thick layer, both of which made of the same perovskite materials is prefered. Such form is called asymmetric membrane.

The flat sheet which has finger-like structure of pores and a thin dense layer is excellent membrane for oxygen separation and methane conversion. The thin, dense layer will increase oxygen permeation.

Phase inversion method, followed by sintering method is a common method for preparing asymmetric perovskite membranes [3]. By using the method, membrane pores can be designed in such a way by controlling the difffusion rate of solvent-non solvent exchange, which can be manipulated by introducing an additive in dope solution [4]. The pores can also be modified by varying the nonsolvent, which has the ability to dissolve the additive as well as the solvent, but not able to dissolve the membrane material.

In this resereach, water was used as nonsolvent and PEG 8000 Da was used as the additives while PESf (polyether sulfone) and NMP (n-methyl pyrollidone) were used as the polymer matrix and solvent, respectively. The composition to make dope mixture is given in Table 1. In order to get more understanding on the effect of PEG and water addition into dope mixture, the ratio of PEG/water was varied and the resulted morphology, pore structure, and performance for oxygen conducting of perovskite membrane were studied.

Table 1. Composition in membrane preparation.

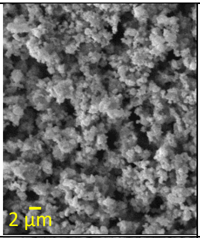
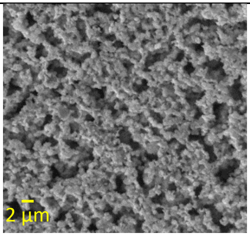
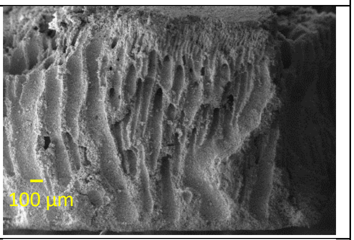
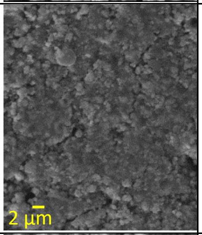
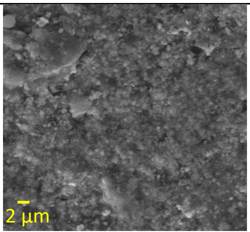
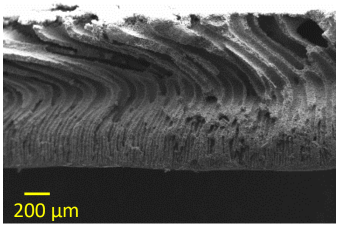
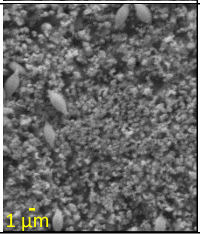
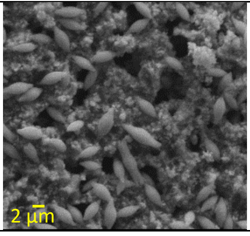
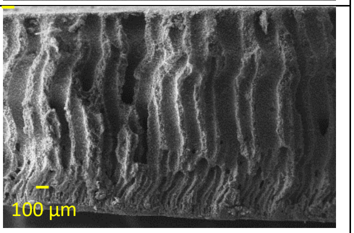
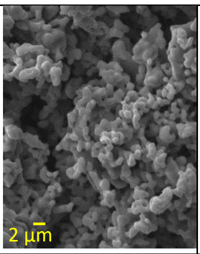
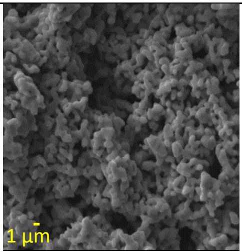
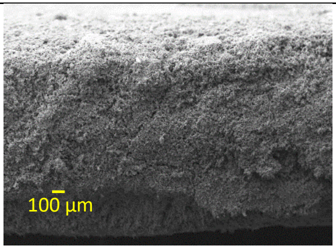
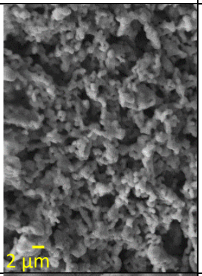
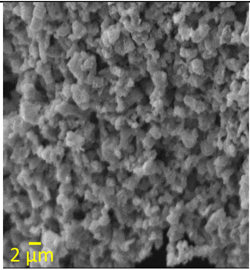
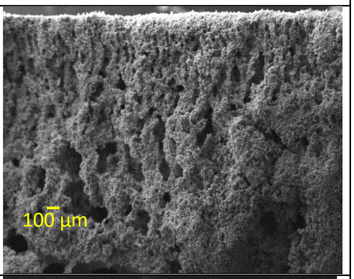
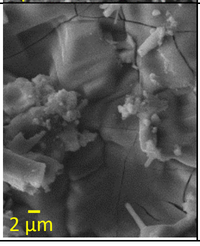
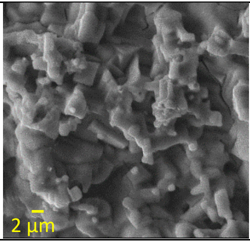
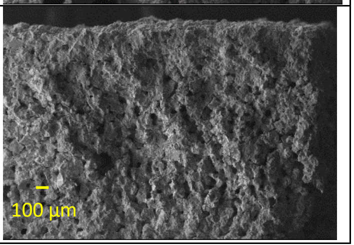
LSCF 7328 (wt%)	LSM 73 (wt%)	PESf (wt%)	NMP (wt%)	Additive (wt%)		Code
				PEG	H_2O	
52.1	-	6.7	41.2	-	-	A1S
47.1	-	6.7	41.2	3.5	1.5	B1S
47.1	-	6.7	41.2	4	1	C1S
47.1	-	6.7	41.2	4.5	0.5	D1S
47.1	-	6.7	41.2	5	0	E1S
-	52.1	6.7	41.2	-	-	A2S
-	47.1	6.7	41.2	3.5	1.5	B2S
-	47.1	6.7	41.2	4	1	C2S
-	47.1	6.7	41.2	4.5	0.5	D2S
-	47.1	6.7	41.2	5	0	E2S

In this research, the ratio of PEG 8000:H_2O were varied from 5.0:0.0, 4.5:0.5, 4.0:1.0, 3.5:1.5 and 0.0:0.0 (wt% : wt%). Crystal structure of perovskite was characterized by XRD. Meanwhile, morphology and pore structure of membrane were determined by Scanning Electron Microscopy (SEM). TGA (Thermogravimetric Analyes) were carried out to study the calcination and sintering method while the performance of perovskite membranes was determined by measuring oxygen flux from the membrane.

SEM analysis results are presented in Figure 1. Each asymmetric membrane has finger like structure of their pores and a thin but dense perovskit layer on top of the membrane.

Saljoughi et al. [13] explains that some factors that can affect the pores formation process are molecular weight of polymer additive, concentration of additive, and the choice of solvent-nonslvent. Based on Figure 1, LSCF membrane has better pore uniformity compared to LSM membrane. It indicates that each powder have their characteristic during membrane formation using phase inversion process. The uniformity of pore's might influenced mechanical and oxygen conducting properties of both membranes, generally membrane which has good uniformity of structure would have better mechanical properties. On the other hand, the thickness of dense layer LSCF membrane was thinner than LSM membrane. It was predicted that oxygen flux of LSCF membrane would greater than LSM membrane.

Figure 1. Morphology of: (a) LSCF 7328 and (b) LSM 73) membrane at different PEG:H_2O ratio

Additive (wt%)		Bottom Surface	Top Surface	Cross Section
PEG	H_2O			
(a) LSCF 7328				
0	0			
4	1			
5	0			
(b) LSM 73				
0	0			
4	1			
5	0			

The oxygen flux measurement showed that indeed LSCF 7328 membrane using different PEG:H_2O additive have higher oxygen flux than LSM 73 membrane. addition of PEG 8000 that reaches 5 wt% on the membrane LSCF 7328 or LSM 73 increases the membrane pore size and other parameters such as porosity and pore volume.

KEYWORDS

LSCF 7328, LSM 73, Perovskite oxide, PEG

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Session 6: Membrane for Wastewater Treatment and Industrial Application II

Resource Recovery from Wastewater and Urine using Membrane Technology

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ABSTRACT

Human urine contributes 85-90% of nitrogen, 50-80% of phosphorus and 80-90% of potassium in only 1% of the total wastewater volume, which requires significant treatment costs. Using raw human urine as a direct agricultural fertilizer source is limited, due to its distinct odour, high pH ranges, pathogen risk associated with faecal cross-contamination, and the presence of high concentrations of pharmaceuticals. Urine nitrification with novel-membrane bioreactor and membrane distillation processes is proposed to overcome these drawbacks. It can recover all nutrients in form of very concentrated solution or dry fertiliser, which is beneficial for self-sufficiency and food security, especially for crops with nitrogen deficiency. Only a few research groups have processed and converted source separated human urine into a valuable product. The aim of the research is to achieve the maximum urine biological stability and membrane distillation at minimum operation cost for the production of urine-based fertilizer. Furthermore, to assure the safety and quality of urine-produced fertilizer, the Nutrient Film Technique is used for the cultivation of hydroponic lettuce.

Recovery of Acetone from an Industrial Acetone-Water Mixture using Pervaporation

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ABSTRACT

Acetone is a common solvent widely used in a number of industries. Acetone-water mixtures are either used as a cleaning agent or generated when water is used to remove residual acetone in certain industrial processes. Distillation (Figure 1a) is a common method for recovering acetone from acetone-water mixture, however, it is energy intensive and requires a relatively large footprint compared to the membrane processes. Pervaporation is a membrane process which can selectively extract acetone from acetone/water mixture at a lower temperature of around 50 °C. By incorporating this membrane processes as an intermediary step prior to distillation (Figure 1b), energy requirement for acetone recovery could be reduced. The recovery of acetone from industrial acetone/water mixtures via pervaporation was investigated in this study.

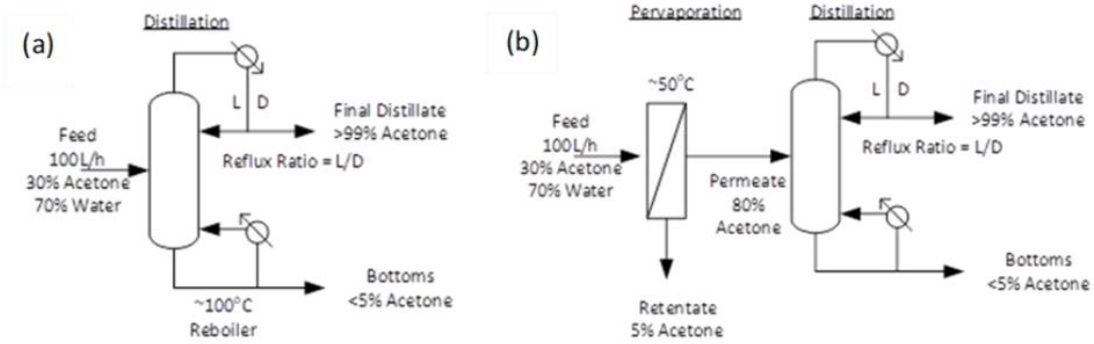

Figure 1 (a) Conventional Distillation (b) Pervaporation/Distillation Hybrid

Acetone recovery was studied using a lab-scale pervaporation system operated under varying cold trap temperature, vacuum pressure and feed concentration. Commercial pervaporation membrane (0.005 m2) was used for the recovery of acetone from industrial samples. Acetone concentration was determined using Total Organic Carbon (TOC) analyser. In this study, permeate with acetone concentration as high as 80% w/w could be recovered from industrial samples containing < 30% w/w acetone under optimized operating conditions. The effect of varying operating conditions on permeate flux and quality, as well as the impact on energy requirement, will be discussed.

KEYWORDS

Acetone recovery, Pervaporation

Treatment of Synthetic Industrial Wastewater Using Electrospun Polystyrene in Direct-Contact Membrane Distillation

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ABSTRACT

By the year 2050, around 52% of the world's population are expected to live in water-stressed regions. Hence, it is necessary to fulfill the present demand of clear water access. The demand of wastewater treatment and desalination is expected to expand, as per the World Health Organization, to protect up to 4 billion of the world's population from running out of clean water access [1,2]. Membrane distillation (MD) is a well-known non-isothermal separation process that utilizes the difference in vapor pressure to generate pure water with improved quality. In the Middle East, there is a growing demand for water desalination technologies and statistics have shown water production capacities of 38.8 million cubic meter per day [3,4]. Many recent reviews summarized the water purification technologies and porous membrane materials with referral to membrane properties in MD [5–10]. The majority have stated that the best technique used to produce thin distillation membranes is electrospinning. This effective method generates very thin membranes with fiber sizes ranging from a nanometer up to a submicron. In MD, it is typically preferred to have a non-wetted membrane with pore sizes ranging between 10 nm and 1μm [11].

In this work, a bench-scale direct-contact membrane distillation (DCMD) unit was performed under optimum process parameters of feed and distillation inlet temperatures of $T_{Feed} = 60^oC$ and $T_{Dist} = 20^oC$, respectively. A flow rate of 0.03 L/min was used to avoid wetting of the fabricated membrane. A hydrophobic polystyrene flat sheet was prepared by our group using a custom-made electrospinning apparatus. The effect of varying concentrations on the hydrophobic polystyrene membrane was studied using a high concentration feed (C1 ≈ 75,500 ppm) and another feed of lower concentration (C2 ≈ 25,200 ppm). A high salt rejection rate of 99% was achieved. The morphological structure was analyzed using SEM. Conductivity measurements have confirmed an improved permeate quality of 99%. Thus, as per the DCMD performance of the polystyrene membrane, the generated permeate from the feed is compatible with the industrial water reuse. As per literature, almost 50% of global desalination plants exist in the GCC. Yet, the utilization of produced water (i.e. rejected brine) from Qatari desalination plants in DCMD was rarely reported. Hence, the output of this study greatly contributes to existing DCMD technologies in the petrochemical industries worldwide, specifically in the gulf desalination plants, towards the production of fresher water.

KEYWORDS

Polystyrene electrospun membranes, Synthetic brine, Produced water, Permeate flux, Salt rejection

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Hierarchically-Structured Janus Membrane Surfaces for Enhanced Membrane Distillation Performance

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ABSTRACT

Commercial hydrophobic polyvinylidene fluoride (PVDF) membranes are vulnerable to membrane fouling and pore wetting, hampering the use of membrane distillation (MD) for the treatment of surfactant- and oil-containing feed streams. To address these challenges, we designed novel Janus membranes with multi-level roughness to mitigate foulant adhesion and prevent pore wetting. Specifically, fouling- and wetting-resistant Janus MD membranes with hierarchically-structured surfaces were tailored via a facile technique that involved oxidant-induced dopamine polymerization followed by *in-situ* immobilization of silver nanoparticles (AgNPs) on commercial PVDF hollow fiber substrates. These membranes demonstrated outstanding anti-fouling properties and salt rejection performances in comparison to membranes with single-level structures. We ascribed the membranes' excellent performances to the coupled effects of improved surface hydrophilicity and self-healing mechanism brought about by AgNPs. Furthermore, the newly engineered membranes exhibited antibacterial properties in *Bacillus acidicola* solutions as evidenced by clear inhibition zones observed on a confocal laser-scanning microscope. The development of hierarchically-structured Janus MD membranes with multi-level roughness paves a way to mitigate membrane fouling and pore wetting caused by low surface tension feed streams in the MD process.

KEYWORDS

Membrane Distillation; Janus Membrane; Multi-level Hierarchical Structure; Silver Nanoparticle; Polydopamine

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Session 7: Gas separation I

Ceramic Membranes Engineering for Liquid and Gas Separation Processes

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ABSTRACT

Ceramic membranes have unique properties such as high thermal stability, chemical resistance, mechanical strength and high potential in pore size engineering. Then, this type of membranes, have been developed for different strategic applications; water and wastewater treatments, production of food materials (i.e. protein, lactose, …) concentrates, gas separation and purification (i.e. hydrogen, helium, …) processes, in the last decades. In our research groups, ceramic membranes are pore size engineered for application in microfiltration (MF), ultrafiltration (UF), nanofiltation (NF) and gas separation processes. For water and wastewater treatments, the prepared ceramic membranes with pore size engineered in nanomertic scale, result in high quality water according to the national and international standards. Disinfection of water and wastewater by the prepared membranes is superior compared to the conventional methods, because the carcass of microorganisms is removed from the final treated water. In dairy industries, whey proteins are separated from wastewater of cheese production units by the prepared nanostructured ceramic membranes and purified with different purities (WPC34, WPC80, …) using ultrafiltration/diafiltration processes. In gas separation and purification processes, applying selective membrane layers on the prepared nanostructured ceramic supports, results in membranes for different applications such as: H_2 purification as a clean fuel, CO_2 capturing from flair gases, etc. Then it can be concluded that the nanostructured ceramic membranes will play a crucial role in strategic industries, in the near future.

KEYWORDS

Ceramic membranes, Pore size engineering, Liquid and Gas Separation Processes

Asymmetric Flat-Sheet Matrimid5218 Membranes Incorporated with Nitrogen-Doped Graphene Nanosheets for Highly Selective Gas Separation

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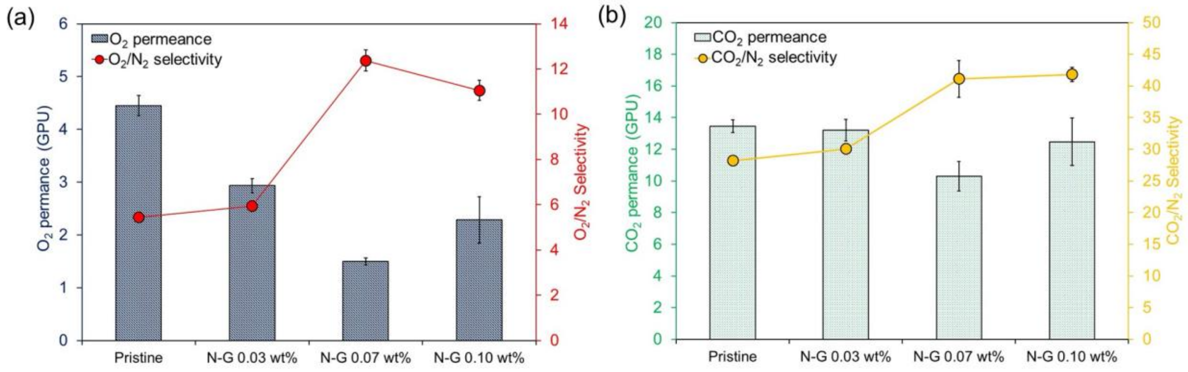
ABSTRACT

Cryogenic distillation and adsorption are the major gas separation technologies in the industry. These technologies produce high-purity gases, but they are energy-intensive. On the contrary, membrane-based technology is a simple and energy-efficient process since it uses only gas diffusion rate differences to separate the gases, and no phase changes and intermittent cycles are involved. However, one of the drawbacks of membrane-based technology is that the produced gas purity and production scale remain insufficient to match that of cryogenic distillation and adsorption. Particularly, polymeric membranes suffer from a permeability-selectivity trade-off which limit their separation performances. To address this challenge, various nanomaterial fillers have been incorporated into polymer matrices to realize mixed matrix membranes (MMMs). The fillers should possess high capacity to adjust the gas transport and physicochemical properties of the MMMs [1]. Recently, two-dimensional (2D) graphene nanomaterials, particularly graphene oxide (GO), have received widespread attention owing to their several attributes such as good compatibility with polymer matrices, relatively well-dispersion in solvents, high-aspect-ratio, easy functionalization and effective gas barrier [2]. When incorporated into a polymer matrix, the impermeable GO nanosheets can facilitate highly tortuous pathways for transport of gas molecules, which could lead to a restriction of the larger molecules’ diffusion, but a less hindered diffusion for the smaller gas molecules. As a result, membrane selectivity could be improved.

Taking this into account, we developed asymmetric MMMs containing low-content nitrogen-doped graphene (N-G) via a phase inversion method. For our membrane fabrication, we selected a commercial polyimide, Matrimid5218 as our polymer matrix because of several advantages, such as cost-effectiveness, high chemical resistance, high thermal stability, high solubility in specific solvents, and good processability [3]. The N-G nanosheets were found to have a good interfacial compatibility with the polyimide due to their nitrogen and oxygen functional groups. Moreover, the hydrophobicity of N-G nanosheets minimize their release into water during the phase inversion stage. To investigate the effect of adding low-concentration N-G on the membrane performances, we fabricated MMMs with different loadings of N-G (0.03, 0.07, and 0.10 wt%). Then, we characterized the membranes using different techniques (i.e., X-ray diffraction, scanning electron microscopy, Fourier-transform–infrared spectroscopy, thermogravimetric analyzer, and gas sorption analyzer). Finally, we evaluated the gas separation performance of the membranes with air (O_2/N_2 =21/79) and CO_2/N_2 mixture gas (CO_2/N_2 = 20/80). Figure 1 shows the gas separation performance of the fabricated membranes. While the O_2 and CO_2 permeances decrease with the incorporation of N-G nanosheets into the membrane, the O_2/N_2 and CO_2/N_2 selectivities demonstrate a remarkable increment by 126.9% and 45.8%, respectively. We attributed this to the tortuous pathways created by the N-G

nanosheets in the membranes, which severely hindered the diffusion of the larger N_2 gas molecules but exerted less transport resistance on the smaller CO_2 and O_2 molecules. Our results show the successful fabrication of asymmetric MMMs and that low-content N-G nanosheets are effective in elevating the gas selectivity of the membranes.



KEYWORDS

Gas separation, Matrimid, nitrogen-doped graphene, mixed matrix membrane

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ZIF-8@PIM-1 Composite Membrane Prepared By $Zn(OH)_2$ Nanosheet as Template to Achieve Gas Separation

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ABSTRACT

Membrane-based separation process can efficiently reduce the energy consumption and pollution the environment compared to traditional approaches.[1, 2] Nevertheless, membrane separation process is limit by the lack of stable membrane material with high permeability and high selectivity. ZIF-8 as a subspecies of MOF (Metal nodes or metal clusters, coordinated to multifunctional organic linker.)[3, 4, 5] has attract plenty of attentions to research in recent years. Due to ZIF-8 with high specific surface area and suitable pore size, was widely used in gas separation and catalysis. However, the pristine ZIF-8 is difficult to apply for the membrane separation process. And the application of pure polymer membrane is limit by Trade-off effect.[6] Mixed matrix membranes (MMMs) combine the merits of inorganic material and organic material normally has superior selectivity and permeability compared to the pure polymer matrix membrane.[7]

Here, the application of ZIF-8 is successfully via $Zn(OH)_2$ nanosheet as template to convert. The $Zn(OH)_2$ nanosheet were prepared via Zinc nitrate and ethanolamine in a certain ratio. it is advantageous for the dispersion of $Zn(OH)_2$ nanosheet with a large amount of amino groups and hydroxyl groups. Polymers of intrinsic microporosity (PIMs) as a porous organic polymer exhibits excellent performance for CO_2 capture. PIM-1 is selected as a polymer matrix to achieve high permeability and high selectivity of CO_2. The ZIF-8 is directly used as an inorganic filler material can form defects in the polymer, making the selectivity of the MMMs reducing. Therefore, a homogeneous $Zn(OH)_2$@PIM-1 mixed matrix membrane was prepared through $Zn(OH)_2$ nanosheets as inorganic fillers. The ZIF-8@PIM-1 MMMs were prepared via converting the $Zn(OH)_2$@PIM-1. The ZIF-8@PIM-1 membranes exhibits an excellent performance for CO_2/N_2. The 5% ZIF-8@PIM-1 membrane exhibit the permeability of CO_2 is up to 8043 Barrer and the ideal selectivity is 22.7, surpassing the 2008 Robinson's up bond by a wide margin.

Table 1. Gas permeability (P) of X ZIF@PIM-1 membrane (1 Barrer = 10^{-10} [cm^3 (STP) cm]/ (cm^2 s cm Hg)).

Membranes	**Pure gas Permeability (Barrer)**						**Ideal Selectivity**
			D [10^{-7} cm^2/s]		**S [10^{-2} $cm^3/(cm^3cmHg)$]**		
	CO_2	**N_2**	**CO_2**	**N_2**	**CO_2**	**N_2**	**$\alpha(CO_2/N_2)$**
3% ZIF-8@PIM-1	6406	295	12.3	5.0	52.1	5.9	21.7
5% ZIF-8@PIM-1	8043	354	15.9	7.7	50.5	4.6	22.7
10% ZIF-8@PIM-1	13515	677	26.3	10.9	51.3	6.2	20.0

KEYWORDS

$Zn(OH)_2$ nanosheet , ZIF-8, PIM-1, membrane separation

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Engineering Membranes for Enhancing O_2/N_2 Separation

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ABSTRACT

Membrane-based O_2/N_2 separation technology offers a multitude of competitive advantages including cost-effectiveness, energy-efficiency, robust process design and small plant footprint over conventional separation technologies [1, 2]. At the center piece of this technology, membranes are instrumental in enabling a high-performance O_2/N_2 separation for realizing the aforementioned advantages. Herein, we summarize our group's recent efforts in engineering different array of membranes for O_2/N_2 separation. Our research spans across different membrane designs including asymmetric hollow fiber membranes, mixed-matrix membranes (MMMs) to carbon molecular sieves (CMS) membranes. Specifically, Matrimid® hollow fiber membranes with a thin dense layer were fabricated using a non-solvent induced phase inversion (NIPS) method. Upon coating with a polydimethylsiloxane (PDMS) layer, defect-free hollow fiber membranes with O_2 permeability of 42.0 GPU and O_2/N_2 selectivity of 4.8 were successfully demonstrated. Furthermore, graphene-based materials, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs) and zeolites fillers, such as graphene oxide (GO), HKUST-1, SNW-1 and (hierarchical) zeolite-5A, have been integrated into various polymer matrices for fabricating MMMs [3]. Promising enhancements in membrane performances were observed. Notably, by carbonizing the MMMs incorporating 20 wt% zeolite 5A, we were able to achieve a high O_2 permeability of 185 barrers accompanied by a O_2/N_2 selectivity of 5.5, surpassing the 2008 Robeson upper bound limit.

KEYWORDS

O_2/N_2 separation, hollow fiber membrane, mixed-matrix membrane, carbon molecular sieves membrane, Robeson upper bound

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Session 8: Novel Membrane and Membrane Processes

Membrane Fouling Control in Anaerobic Membrane Bioreactor Based on Quorum Quenching

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ABSTRACT

Quorum quenching (QQ) is an effective method to control membrane biofouling in aerobic membrane bioreactors (Kim et al. 2013; Jiang et al. 2013). However, it is not clear if QQ is feasible in an anaerobic membrane bioreactor (AnMBR) (Meng et al. 2017). In this study, *Microbacterium*. sp that has QQ capability was embedded in alginate beads, known as QQ beads (QQB), and applied in a lab-scale AnMBR to investigate their potential in fouling control.

The hollow fiber membrane with pore size of 0.1 μm and surface area of 0.007 m2 was used in the AnMBRs (volume=1 L). The membrane flux was fixed at 8 $L/m^2 \cdot h$ (LMH) and hydraulic retention time (HRT) of the reactors was 18.5 h. The total suspended solids were maintained at 5000±100 mg/L, transmembrane pressure (TMP) was logged under constant flux. The TMP changes in the three phases operation of control, vacant beads (VB) and QQB are described in Figure 1d and -30 kPa was considered as the experimental endpoint in this study. Control, VB and QQB phases lasted for 6 days, 8 days and 45 days, respectively. The results suggest the positive effect of QQB strategy to prolong membrane fouling while the AnMBR was in steady state. It is clear that the TMP represent a quick rise to -30 kPa in a very short period of time when TMP began to rise. With the addition of QQB, the operating period of AnMBR-QQB reactor was prolonged by about 8 - 10 times at constant flux operation before reaching the pre-set maximum TMP.

Table 1 shows the COD removal performance with average efficiency of 97.98, 98.84 and 98.75% for control, VB and QQB phase, respectively. The methane production during the entire experiment was also reported. A significant improvement in methane production occurred during the transition from VB phase to QQB phase. That was mainly attributed to the addition of QQ bacteria that changed the microbial community structure in the original sludge system, and the new system may be more conducive to the growth of Methanogens.

The profiles of polysaccharides (PS) and proteins (PN) in EPS and SMP were investigated in different phases (Figure 1c). A 35.42% lower concentration of polysaccharide in loosely bond EPS (LB-PS) was observed during the QQB phase compared to the control phase. When the TMP jump occurred, the concentration of LB-PS increased slightly, but still significantly lower than that in the control and VB phase (36.76 vs. 43.74 and 46.27 mg/g·VSS). Similar trend of polysaccharide in SMP (SMP-PS) was observed. Protein in loosely bound EPS (LB-PN) and polysaccharides in tightly bound EPS (TB-PS), were at low concentration and there was no significant change during the three phases (0.41 - 0.70 mg/g·VSS). It is noteworthy that the

content of protein in SMP (SMP-PN) and tightly bound EPS (TB-PN) did not show a clear trend. The maximum concentration of SMP-PN was observed at the beginning of the QQB phase. When the TMP jump occurred, the SMP-PN concentration decreased again. The PS and PN content in loosely bound EPS and tightly bound EPS extracted from the membrane foulant was also described in Figure. 1c. The amount of PS was relatively consistent and low in both LB - and TB-EPS for all phases. Compared to the control phase, TB-PN and LB-PN were remarkably lower in the foulant from the QQB phase.

The observation of EPS and SMP changes is in good agreement with the concentration of AHL in membrane foulant (Figure 1b). In the bulk liquid and membrane foulant, the total EPS content was reduced by 15.19% and 75.32% in QQB phase compared to control phase, respectively. Thus, the decline of EPS content in fouling layer should be the main reason for mitigating membrane biofouling. Among the EPS components in foulant, the amount of protein decreased significantly, 80.98% and 82.83% reduction, for QQB phase compared to control and VB phase, respectively. This is consistent with the report in Weerasekara et al. (2014), which showed the protein content was the main factor affecting membrane biofouling. In short, *Microbacterium* sp. could reduce AHL levels in foulant (Figure 1b), which in turn suppressed the EPS production and biofilm formation, thus prolonged the MBR operation.

The AHL concentration in the effluent from control and QQB operating phases as well as in the biocake of three phases is shown in Figure 1b. Firstly, the C7-HSL dominated in the control and QQB effluent, with an average concentration of 18.60 ng/L and 21.01 ng/L, respectively. Its concentration accounted for more than 90% of all AHLs, which indicated that the long-chain signal molecules secreted by quorum-sensing bacteria in the sludge system are more easily degraded by the quencher enzymes secreted by the QQ bacteria. Secondly, C4-, C8-, and 3OC6-HSL appeared in the course of operation but at extremely low concentrations, with an average of 0.49 - 2.59 ng/L. When membrane fouling occurred in the control phase, the concentrations of C8-, C12-, C14-, 3OC8-, and 3OC12-HSL in the effluent increased slightly. In QQB phase, the concentration of C4, C8, and C14 increased significantly when membrane biofouled.

The concentration of AHLs in the biocake is also an important factor to reflect the relationship between the AHLs and the EPS content of the system. The AHLs types and corresponding concentration in the biocake in the control, VB and QQB phases are shown in Figure 1b. C4-, C8-, and C14-HSL were the main AHL compounds detected, and a very small portion of 3OC14 was also present in the biocake of the three phases. It should be noted that the concentration of each AHL in the QQB phase was much lower than that in control and VB, especially C4- and C14-, which decreased from 27.08 ng/g·VSS and 237.37 ng/g·VSS in the control phase to 2.27 ng/g·VSS and 0.93 ng/g VSS, respectively. Meanwhile, C8-HSL also showed a significant decrease, although the magnitude of the decline was not as large as C4-HSL and C14-HSL.

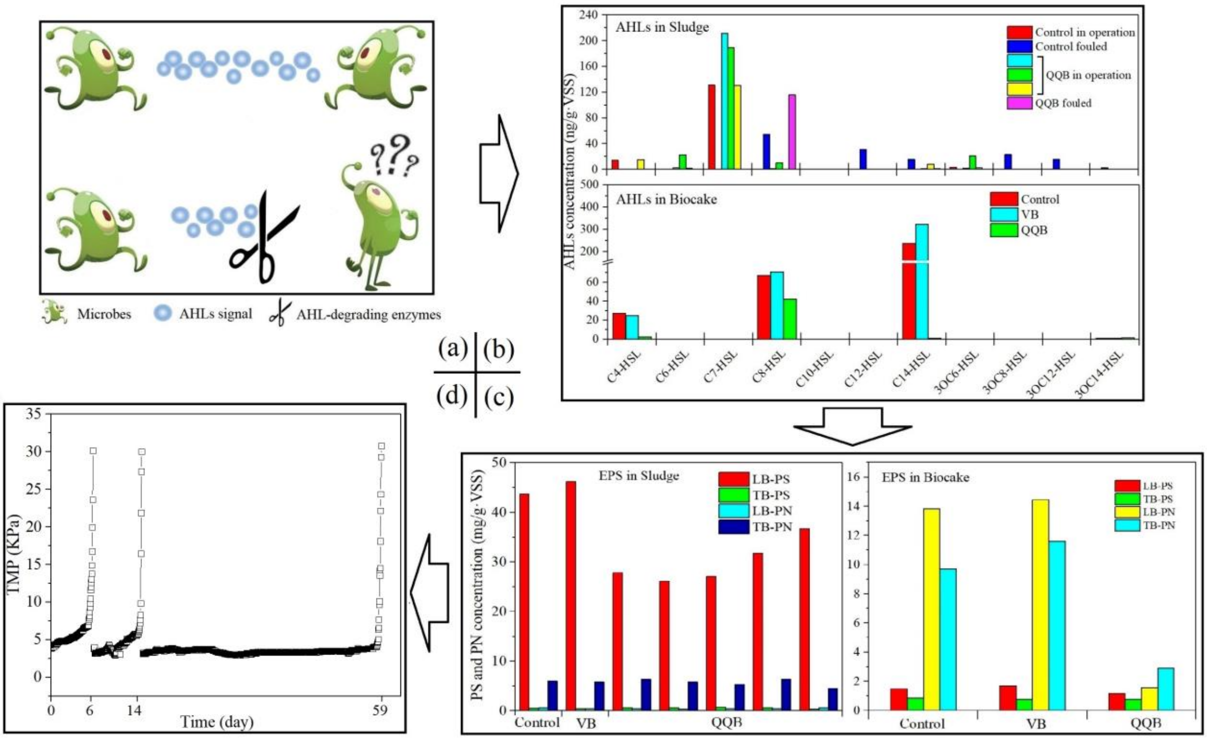

Figure 1 (a) Theory of quorum qunenching. (b) AHL levels in the bulk liquid and foulant. (c) EPS content in the mixed liquor and biocake. (d) TMP profiles in different operating phases.

Table 1 Performance of AnMBR for COD removal and methane yield.

Index	Control	VB	QQB
COD removal (%)	97.98	98.84	98.75
Average methane yield (mL/g COD)	269.29	266.11	341.95

KEYWORDS

Quorum quenching; AnMBR; Membrane fouling control; AHLs.

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A Handy-making Process for Fabricating PVA-based Interpenetrating Polymer Networks (IPNs) with High Performance of Desalination by Pervaporation: From Theory to Practice

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ABSTRACT

In order to prepare high-performance pervaporation (PV) membranes with more stable structure and shorten the crosslinking period, two candidate crosslinkers including 4-sulfophthalic acid (SPTA) and acrylic acidco-2-acrylamido-2- methylpropylsulfonic acid (P(AA-AMPS)) were preliminary evaluated using molecular simulations, which considered both their thermodynamic compatibility and crosslinking efficacy with the host polymer (polyvinyl alcohol, PVA). Effects of the crosslinkers' aggregation state on thermodynamic compatibility were systematically discussed. In addition to the mobility of crosslinking functional groups (-COOH), their probability to contact with -OH from PVA is another key factor affecting the crosslinking efficacy. Moreover, by adding catalyst, the crosslinking time of PVA and P(AA-AMPS) could be reduced from 2 h to 10 min at temperatures between 110-120 ℃. Compared with our previous work (S-PVA film) [1], PVA/P(AA-AMPS) IPN not only had a higher crosslinking efficacy but also exhibited better hydrostability. The desalination performance of the PVA/P(AA-AMPS) IPN composite PV membranes reached to a high water flux of 57.9 ± 1.7 kg/m^{2}h at 70 ℃ with a NaCl rejection greater than 99.5 % for 35000 ppm NaCl water solution. The fast crosslinking rate, high hydrostability of the PVA/P(AA-AMPS) IPN polymer, and excellent desalination properties of the resulting composite PV membranes make this method very promising for industrial scale-up.

KEYWORDS

Pervaporation desalination, PVA/P(AA-AMPS) IPN, Molecular simulation, Composite membrane

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Application of GO/rGO Membranes for Purification and Separation

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ABSTRACT

We have developed a method to make graphene oxide (GO) membranes with proper control in structure and morphology to be ideally used water purification, selective separation and adsorption. Recently, we have successfully employed our GO membrane to remove Natural Organic Matters (NOMs) from water. Our study shows that GO membranes can reject ~100% of NOM while maintaining high water flux. Furthermore, we have developed a technique that allows controlled reduction of graphene oxide to tune the interlayer spacing and make it suitable for desalination. The reduced graphene oxide (rGO) can have huge potential for desalination applications owing to its appropriate interlayer spacing (0.34–0.37 nm) that enables it to block salt ions as small as Na+ with high precision. However, the fabrication of uniform rGO membranes is a great challenge because of the loss of its polar functional groups during preparation from graphene oxide (GO). We have also utilised GO/rGO membranes for desiccation application. We conducted experimental study on the adsorption and desorption behaviour of water in GO/rGO membranes as a function of relative pressure. We have observed that our membranes can adsorb maximum of 0.58 gram of water per gram of GO (g g^{-1}), which is much higher than silica gel a commercial bench mark desiccant material. To further extend GO membrane's adsorption application we conducted ionic and molecular adsorption behaviour of GO membranes. Our results suggest that GO membranes can have potential to be used as ionic/molecular sponge. Our GO/rGo membranes also demonstrate excellent molecular sieve behavior when used for separation.

Water/Salt Transport Properties of Cellulose Triacetate Nanocomposite Films

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ABSTRACT

The synergized optimization of water flux and salt rejection by blending with inorganic fillers has been achieved for the polyamide (PA) thin film nanocomposite (TFN) membrane. However, it is difficult to characterize its mass transport properties due to the very thin and heterogeneous PA film. In this work, we select cellulose triacetate (CTA) as the base to prepare hybrid films and their transport properties were studied according to solution-diffusion theory. A series of inorganic fillers, such as reduced graphene oxide (rGO), zeolites, ZIF-8, SiO_2 and graphene oxide (GO) were incorporated. The blending of inorganic fillers leads to enhanced glass transition temperature (T_g) and density, shows little effect on the water transport property but dramatically decreases salt permeability values, which are nearly ten-fold of that of the CTA film. The blending of GO can densify and hydrophilize CTA simultaneously, which is most promising for a desalination application. The increased water uptake should contribute to its increased water permeability, while the decreased free volume size and FFV value and various interactions between the ions (Na^+, Cl^-) and GO sheets account for salt permeability decrease. For the different rGO/CTA films, compared with the GO/CTA films, the water permeability increased at certain C/O ratio, which are due to slip flow enhancement increases with hydrophobicity owing to the less interaction with water. At the same time, the salt permeability decreased by five times. In all, we expect that mixed matrix RO membranes prepared with a certain amount of inorganic particle (such as ZIF-8, GO or rGO) have the potential to increase water flux and salt rejection simultaneously.

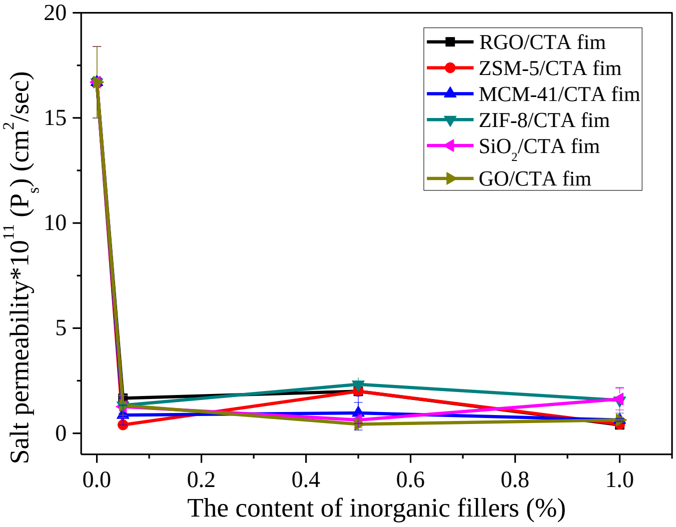

Fig.1 Salt permeability as a function of the inorganic fillers content

KEYWORDS

Water/salt transport properties; Organic/inorganic hybrid film; Solution- diffusion; Reverse osmosis; Desalination

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Design and Development of Layer-by-Layer Based Low-Pressure Antifouling Nanofiltration Membrane Used for Water Reclamation

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ABSTRACT

Recent studies have confirmed the advantages of low-pressure nanofiltration (NF) membranes in integrated nanofiltration membrane bioreactor system followed by the reverse osmosis (RO) process for high recovery water reclamation [1]. However, fouling of low-pressure NF membranes restricts their application in providing high quality feed to subsequent RO process. In this study, an antifouling low-pressure NF membrane was designed and fabricated via rapid co-deposition of polydopamine (PDA)/polyethylenimine (PEI) on electrostatic layer-by-layer (LBL) assembled polyethersulfone (PES) flat sheet membrane followed by crosslinking with glutaraldehyde (Fig. 1a). The optimized resultant membrane (LBL-cPP) presented approximately 11 LMH/bar pure water permeability with more than 90% rejection divalent cations under 2 bar pressure. The newly developed selective layer exhibited excellent antifouling performance and chemical stability ascribing to the inherent hydrophilicity of PDA/PEI and dual covalent reaction of PDA with the LBL layer. By feeding real municipal wastewater, the LBL-cPP membrane also achieved superior permeate quality (Fig. 1b), leading to lower RO fouling rate in subsequent RO unit as compared to commercial NF 270 membrane. Further organic foulant analysis indicated that 96.8% of dissolved organic carbons were effectively removed by the LBL-cPP membrane. Specifically, the novel NF membrane demonstrated high removal rate (> 93%) for foulants with low molecular weights which was largely responsible for RO fouling, while maintaining the desired flux recovery rate and reduced cleaning frequency. This study demonstrates the potential of PDA/PEI modified low-pressure NF membranes in designing efficient and sustainable water reclamation technology.

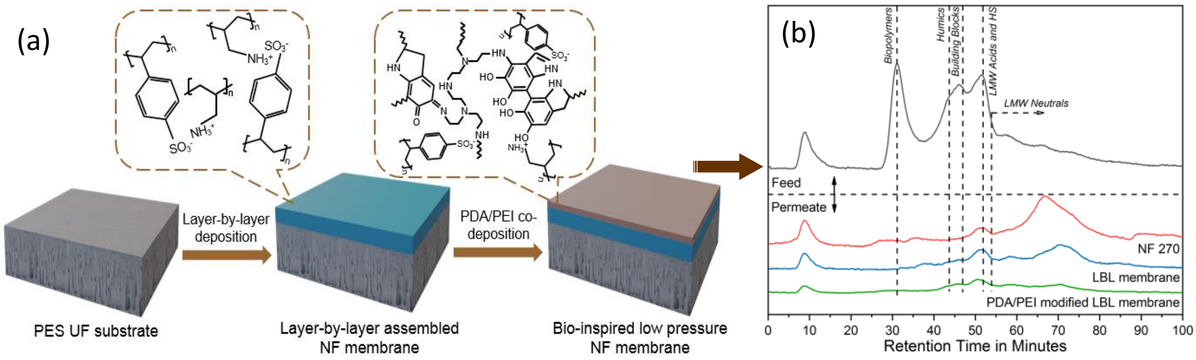

Fig.1(a) illustration of membrane preparation, (b) permeate quality of NF membranes.

KEYWORDS

Polydopamine; Layer-by-layer; Nanofiltration; Membrane fouling; Water reclamation.

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ACKNOWLEDGEMENTS

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Session 9: Nanofiltration/Reverse Osmosis

Facile Preparation of Ceramic Nanofiltration (NF) Membranes with Controllable Molecular Weight Cut-Off (MWCO)

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ABSTRACT

In this research, we proposed a facile preparation of ceramic nanofiltration (NF) membranes by the filtration of Al-Zr nanoparticles (35 nm ~ 360 nm), which blocked and narrowed pores of ceramic ultrafiltration (UF) membranes. The successful deposition and calcination of nanoparticles enabled the formation of selective nanoparticle layer inside of UF membrane pores. Moreover, the molecular weight cut-off (MWCO) of ceramic NF membranes had strong correlation with the size of Al-Zr nanoparticles, and it was formulated using Hagen-Poiseuille equation and Stokes-Einstein equation to predict the MWCO at various sizes of Al-Zr nanoparticles. We successfully prepared ceramic NF membranes with MWCO of 1000 Da, 2000 Da, 5,000 Da, and 10,000 Da based on the correlation model. The prepared ceramic NF membrane could be applied in the separation of fine chemicals and biochemical products, which required narrowly distributed pores with robust operations.

High-Performance Thin Film Composite (TFC) Membranes: Design Consideration Underneath the Polyamide Thin Film

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ABSTRACT

Despite the commercial success of thin-film composite (TFC) technique for reverse osmosis (RO) and nanofiltration (NF) membrane production, overcoming the longstanding “trade-off” relationship between permeability and selectivity of TFC membranes remains a global challenge. Since the separation properties of TFC membranes are determined by the polyamide thin film active layer, extensive research efforts have been put on altering the layer formation chemistry or intrinsic nanostructure to simultaneously improve its permeability and selectivity. But the critical role of the underlying porous substrate on the membrane separation performance was often overlooked. Not only formation of the polyamide layer is greatly affected by the substrate surface properties and pore structures, water transport through the TFC membrane is also largely governed by the structural feature of the substrate underneath the polyamide layer.

In this study, we firstly investigated how the configurations of the porous substrate influenced the desalination performance of the TFC membrane. Comparing to flat sheet membrane substrates, hollow fiber substrates were found to possess positive impact in terms of both water permeability and salt rejection, provided that the fiber mechanical strength is sufficient to withstand high pressure operation. Subsequently, we demonstrated the relationship between the substrate surface pore profile and the TFC membrane separation behavior. Manipulating the substrate surface pore profile for water flow path improvement was proved efficient in enhancing the TFC membrane water permeability. Afterwards, we extended the idea of flow path improvement from optimizing conventional polymeric substrates to the structural design of nanomaterial-based membranes.

The involvement of nanomaterials has been proved to significantly improve the TFC membrane permeability and selectivity. For example, our earlier studies introduced a single-walled carbon nanotube (CNT) interlayer to substitute the conventional polymeric membrane substrate underneath the polyamide thin film, and resulted in greatly improved .[1,2] However, the role of the nanomaterial in such improvement is still unclear. Rising from the idea of flow path improvement underneath the polyamide layer, this study systematically investigated the effect of the nanomaterial-based interlayer. It is experimentally extrapolated that the water permeability enhancement should mainly be attributed to the improved flow path underneath the polyamide layer. By optimizing the structure of the underlying CNT interlayer, TFC membranes with outstanding water permeability of ~40 L m^{-2} h^{-1} bar^{-1} and monovalent/divalent ion selectivity above 20 was obtained. This study clarifies ambiguities concerning the effects of the underlying porous substrate as well as the nanomaterial involvement on the TFC membrane performance, and provides insight into designing highly permeable and selective TFC membranes.

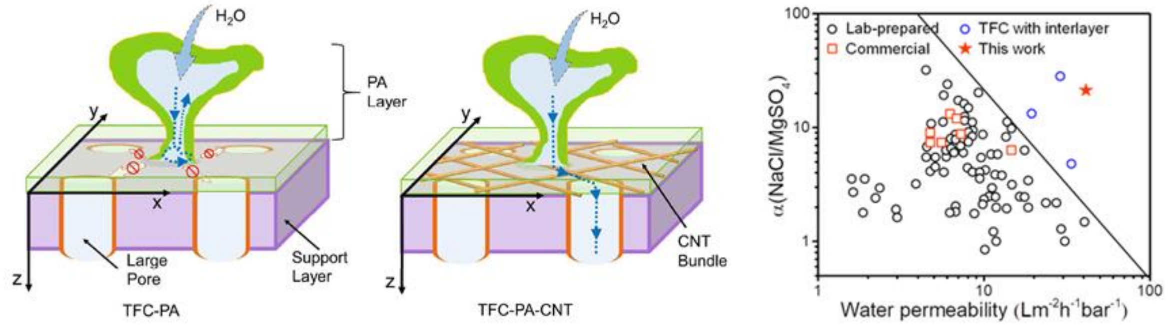

Fig. 1. Effect of the CNT interlayer on the TFC membrane performance[3,4]

KEYWORDS

Thin film composite membrane, high flux, porous substrate, nanomaterial, flow path

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Z. Yang, C. Tang *et al.* Tannic Acid/Fe^{3+} Nanoscaffold for Interfacial Polymerization: Toward Enhanced Nanofiltration Performance. *Environ. Sci. Technol.* **2018**, *52*, 9341-9349.

From Micro to Nano: Polyamide Thin Film on Ceramic Tubular Membranes for Nanofiltration

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ABSTRACT

Interfacial polymerization is an effective technique to synthesize high performance thin film membranes such as polyamide membranes. However, it is still very challenging to apply the technique on ceramic hollow fibres or tubular membranes which offer a strong mechanical strength and an excellent chemical resistance. Previous studies have shown the importance of substrate surface pore size, and an intermediate layer with small pores <10 nm was usually required for synthesizing polyamide thin film on ceramic substrates [1-2]. In this study, we demonstrated that thin polyamide layer can be synthesized directly on microfiltration ceramic tubular membranes with a surface pore size 0.1-0.2 microns via interfacial polymerization without an intermediate layer. The thin polyamide layer with a thickness 30-40 nm was successfully coated on the inner surface of the ceramic substrate by circulating the monomers: branched polyethyleneimine (PEI), piperazine, (PIP) and trimesoyl chloride (TMC) through the membrane lumen. The thin film layer showed good integration with the ceramic substrate, and could withstand high pressure (at least 10 bar). The mechanical property of the synthesized polyamide thin film was also examined using the pin-point method on the AFM, and the modulus of the thin film was measured. The thin film composite membranes demonstrated excellent nanofiltration performance with a pure water flux of 16-18 LMH bar^{-1} and a molecular cut-off of ~250 Da. The membranes also showed good salt rejections, with rejection rates >90% for $CaCl_2$, $MgCl_2$ and $MgSO_4$. With excellent chemical resistance, the composite membranes can be applied in applications involving organic solvents and a large pH range. Our study also demonstrated the potential use of commonly available microfiltration ceramic substrates for value-added applications.

KEYWORDS

Interfacial polymerization, Polyamide thin film, Ceramic membranes, Nanofiltration

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Toward Enhancing the Chlorine Resistance of Reverse Osmosis Membranes: An Effective Strategy via an End-capping Technology

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ABSTRACT

Polyamide reverse osmosis (RO) membranes suffer performance decay when exposed to free chlorine because of their unique chemical structure. The decay limits their lifespan and increases operating cost. Herein, the secondary interfacial polymerization method was performed, for the first time, using isophthaloyl chloride (IPC) as the chain-terminating reagent, to eliminate the negative effect when the unreacted amino groups interact with chlorine. The surface zeta potential of the as-prepared membrane remained almost constant over a wide pH range, which greatly demonstrated the high conversion ratio of the end-capping procedure. However, neither the surface morphology nor the separation properties were conspicuously influenced. Because of the absence of the terminated amino groups in the polyamide layer, the IPC-modified membrane exhibited significantly improved chlorine resistance, particularly at high pH. Its desalination performance remained unchanged as the total chlorine exposure approached 10,000 ppm·h, whereas only 80.3% of the NaCl was rejected by the unmodified membrane under the same condition. Such SIP technology can be applied directly to the commercial SW30 seawater desalination membrane, making it more tolerant to free chlorine. Overall, our results strongly proved the IPC-assisted end-capping process as a promising, practicable, and scalable technology for enhancing the chlorine resistance of an RO membrane.

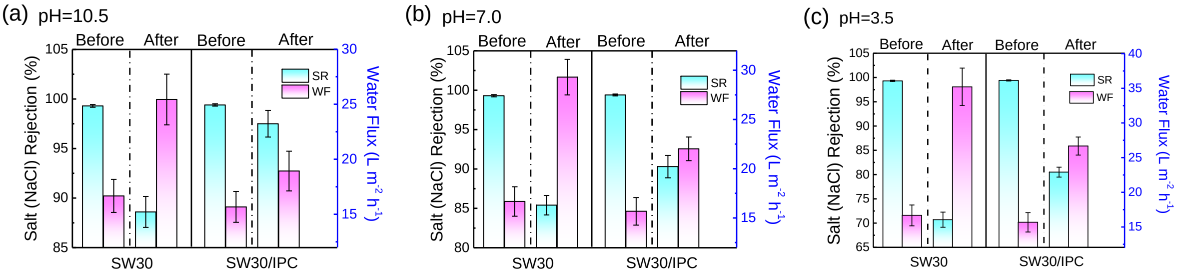

Figure 1. Water flux and salt rejection of SW30 and SW30/IPC membranes before and after Cl exposure at 10,000 ppm·h (1000 ppm NaClO solution for 10 h) and (a) pH 10.5, (b) pH 7.0, and (c) pH 3.5. Solution pH was adjusted using 1 M HCl (aq.). After static immersion in NaClO solution, each membrane sample was removed, washed thoroughly with DI water, and fixed to the RO cell to measure desalination performance. The RO test was performed using an effective membrane area of 12.56 cm^2 and 2000 mg L^{-1} NaCl as feed solution at a crossflow rate of 9.95 cm s^{-1}. The separation test was performed at a constant pressure of 15.5 bar. SW30/IPC membranes were treated with 2.0% IPC.

KEYWORDS

Reverse osmosis membrane, Chlorine resistance, End-capping, Seawater desalination

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Positively Charged Nanofiltration Membrane Based on Polyvinyl Chloride Copolymer

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ABSTRACT

A polyvinyl chloride (PVC)-based positively-charged nanofiltration membrane was fabricated from polyvinyl chloride-graft-poly(N,N-dimethylaminoethyl methacrylate) by heating and crosslinking treatment (Fig. 1). We characterized the surface chemical compositions, membranes structures, surface hydrophilicity and surface charges of the prepared membrane. The estimated membrane pore diameter is 1.98 nm and the pore diameters are in the range of 0.5–2.0 nm. The membrane exhibits excellent water permeability (9.3 L m^{-2} h^{-1} bar^{-1}) and salt rejection (93.1% with $MgCl_2$ solution). Both the heating treatment and crosslinking reaction can diminish the pore size of the precursor membrane. The membrane hydrophilicity is improved after quaternization, leading to higher water permeability compared with the membrane treated by heating only. Moreover, surface quaternization and crosslinking offer the membrane excellent pressure resistance and long-term stability. The prepared nanofiltration membrane has great promise in many applications including water softening and multivalent ion removal [1, 2].

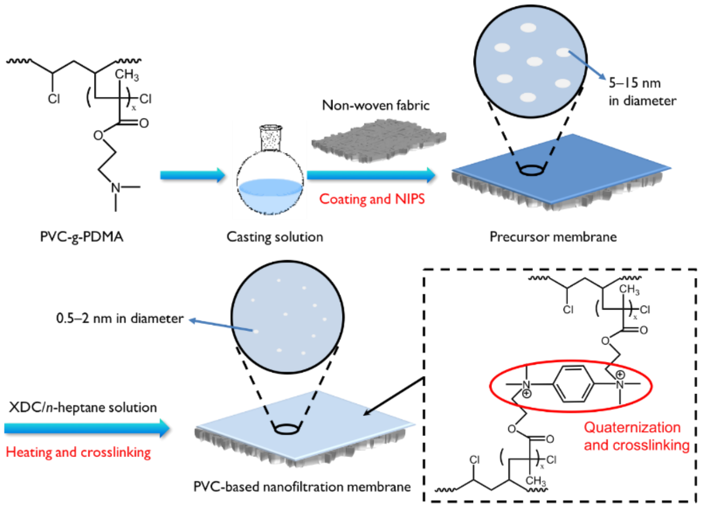

Fig. 1. Procedure for the preparation of the PVC-based nanofiltration membrane.

KEYWORDS

Polyvinyl chloride; Nanofiltration membrane; Positively charged membrane; Quaternization.

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Session 10: Gas Separation II

Nickel Hollow Fibre Membranes for High Temperature Hydrogen Separation and Production from Reforming Reactions

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ABSTRACT

High temperature hydrogen-selective membranes can be applied as membrane reactors for many hydrogenative reactions for simultaneous hydrogen separation and production. Conventional Pd membrane cannot be applied for this purpose due to its high material cost, low chemical stability and the quick poisoning by other impurity gases. However, nickel membrane can overcome these shortcomings and thus shows the potentials for these advanced applications. In this presentation, we show our recent progress in developing metallic nickel hollow fibre membranes for high temperature hydrogen separation and production from water gas shift or methane reforming reactions. The nickel membrane exhibits excellent thermal and chemical stability in the reformate gas atmosphere.

Constructing CO_2-Philic Membrane by Adjusting EO Chain Ratio for Sustainable CO_2 Separations

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ABSTRACT

The numerous of carbon dioxide (CO_2) emissions in the atmosphere accelerates global environmental issues, it is necessary to effectively carbon capture and separate for CO_2. Membrane-based separation process has a great advantage to achieve efficient CO_2 capture.[1,2] Nevertheless, the lack of appropriate membrane materials limit the membrane-based application. The ether oxygen bond of PEO chain can interact with CO_2 in an electric quadrupole moment, the PEO material is considered as one of the best materials for preparing gas separation membranes for CO_2 capture. Porous organic polymer nanosheet (PON) with nitrogen-rich functional groups and phenol groups, exhibit greatly "N_2-phobic, CO_2-philic" properties and extremely CO_2-philic, making the PON with high CO_2 adsorption capacity.[3,4] Currently, commercial membranes are polymeric membrane (PES, PAN and so on). However, the application of polymer membrane is limited by the Trade-off effect. Due to the EO segments have a strong affinity for CO_2, and PEG 400 with a large number of EO segments and hydroxyl groups, it can effectively prepare homogeneous mixed matrix membranes. PON and PEG 400 can be efficiently achieve CO_2 capture with ultra CO_2-philic. It is necessary to fabricate a mixed matrix membrane (MMM) combine the merits of PON and PEG 400 to achieve efficiently CO_2 capture.[5]

Here, Pebax 1657 was chosen as polymer matrix via incorporating PON with PEG 400 CO_2-philic material to achieve CO_2 capture. By introducing CO_2-philic PEG 400 and N_2-phobic PON, the CO_2 solubility and CO_2 diffusivity in hybrid membrane was enhanced. The permeability of the pristine pebax 1657 membrane for CO_2 and N_2 were 94 Barrer and the ideal selectivity of CO_2/N_2 is 32 at 30°C. Through change the content of PEG 400 and PON, the performance of CO_2-philic membrane exhibit the CO_2 permeability is 392 Barrer, which is 4.17 times than the original Pebax 1657 membrane; the ideal selectivity of CO_2/N_2 is approximately 2.50 times higher than the pristine Pebax 1657 membrane and up to 112. Respectively, and part of the membranes has surpassed the Robeson's upper bound (2008). This CO_2-philic membrane provide a general method for improve the CO_2 transport of advanced membranes.

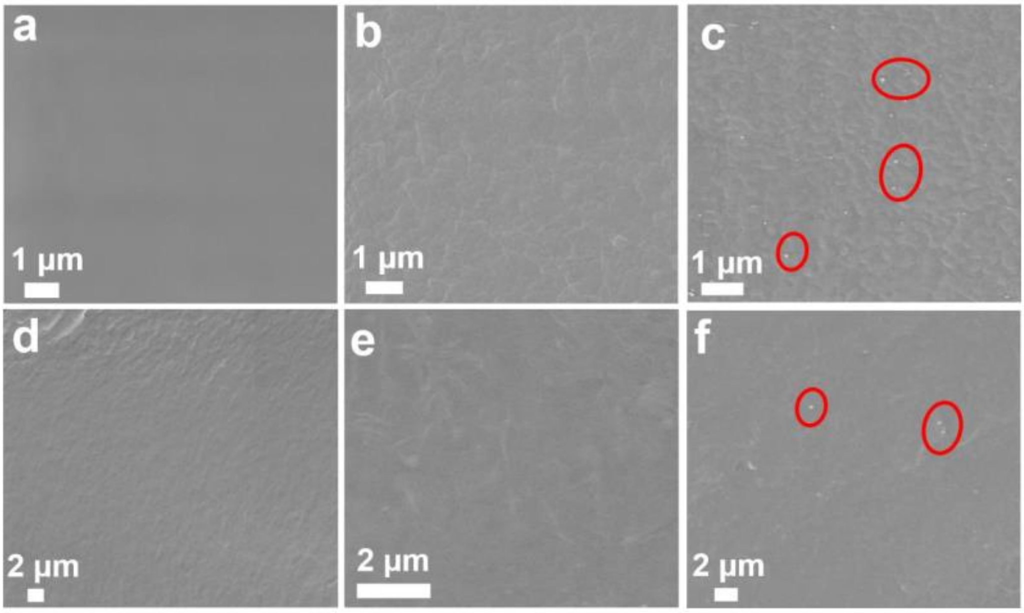

Fig. 1. Surface and cross-sectional SEM images of a serious of Pebax 1657: (a), (d) pure Pebax 1657 membrane; (b), (e) pure Pebax 1657 with PEG 400 (1.5 wt%) membrane; (c), (f) put the PON into mixed solution of Pebax 1657 and PEG 400 (1.5 wt%), (the red circled area shows PON particle).

KEYWORDS

Porous Organic Polymer Nanosheet, CO_2-Philic membrane, N_2-phobic, CO_2-philic.

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Plasticization Resistance-Enhanced CO_2 Separation at Elevated Pressures by Mixed Matrix Membranes Containing Flexible Metal-Organic Framework Fillers

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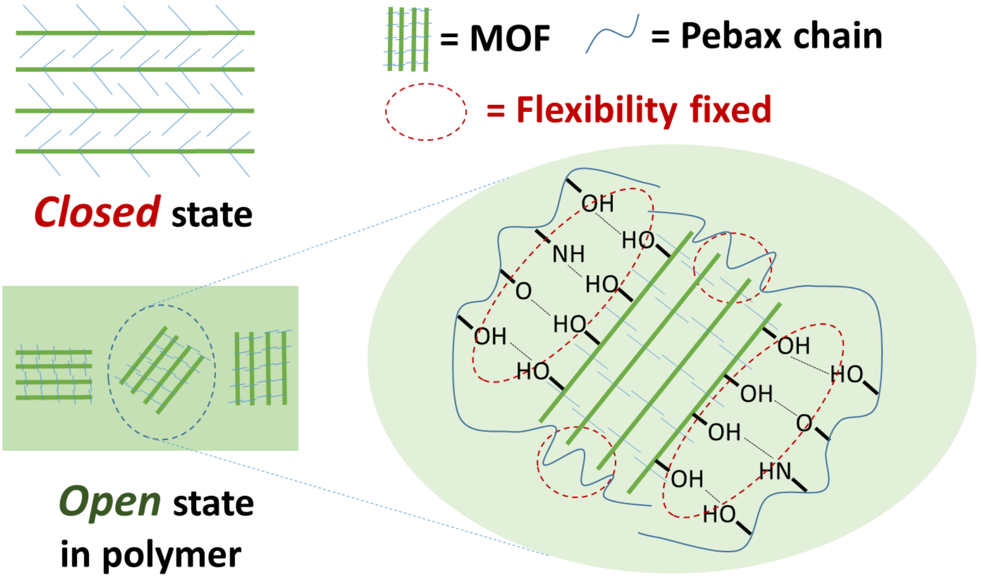
ABSTRACT

Although precise design has advanced the separation capability of polymer membranes, the inability to maintain their performance under real process conditions involving elevated pressures and moisture has prevented their smooth transition into practical applications. Specifically, plasticization of polymers is a unique challenge to membrane-based CO_2 separation. Herein, we show that the dispersion of a flexible metal-organic framework (MOF) within a polymer matrix allows the retention of high gas separation selectivity even at a transmembrane pressure of 12 bar, which is highly desirable for practical applications involving compressed feed streams. The strong interactions between MOF fillers and polymer matrices reduce the chain mobility of polymer, contributing to the enhanced plasticization resistance. X-ray diffraction (XRD) analysis indicates that channel closure of the flexible MOF in polymer is avoided, also suggesting strong MOF-polymer interactions (Scheme 1). Importantly, observation of XRD-detectable phase changes in flexible MOFs is a useful strategy to reveal the interactions between flexible MOFs and the matrices.



Scheme 1. Schematic representation of dispersing flexible MOFs into polymer membranes to enhance their resistance toward plasticization.

KEYWORDS

Mixed matrix membranes; Metal-organic frameworks; Anti-plasticization; CO_2 capture; High pressure gas separation

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NH_2-Co/ZIF-8 embedded PEO Based Mixed Matrix Membranes for Efficient CO_2 Separation

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ABSTRACT

The ever-increasing carbon dioxide concentration in the earth's atmosphere is one of the fundamental challenges of mankind in the 21st century [1]. CO_2 contributes to global warming and sooner or later the human body will also start to directly suffer from it. Thus, there is an urgent need to reduce the CO_2 level by capture at the point sources of emissions. Membrane technology for CO_2 capture has attracting more and more attention nowadays because the membrane-based CO_2 separation process has well-known advantages of low-energy consumption, operational simplicity, and low pollution over other techniques [2]. Currently, most of the commercial membranes are polymeric membrane and the development of such polymeric membrane is limited by trade-off effects between permeability and selectivity. In addition, the stability and life span of the polymeric membrane is also an issue.

Mixed matrix membranes (MMMs) composed of metal organic framework (MOF) fillers embedded in a polymeric matrix represent a promising alternative for CO_2 capture. This method can provide a highly desirable membrane that could combine the high separation performance of the fillers and pure polymer membrane. The match of transport properties and the interphase compatibility between a given filler and a polymer are very important for preparing the MMMs with attractive properties [3]. Zeolite imidazole frameworks (ZIFs) is a subclass of MOFs in which tetrahedral divalent metal ions (Zn^{2+}, Co^{2+}) are linked to imidazole derivatives through coordination bonds, and it has been widely used for CO_2 capture membrane. However, it is worth noting that inorganic zeolites generally exhibit poor compatibility with organic polymers and often require additional surface modification to avoid non-selective interfacial voids. The ethylene oxide (EO) units have a great attractiveness for CO_2, and PEO is one of the best CO_2-philic polymer material and follows the dissolution-diffusion model [4].

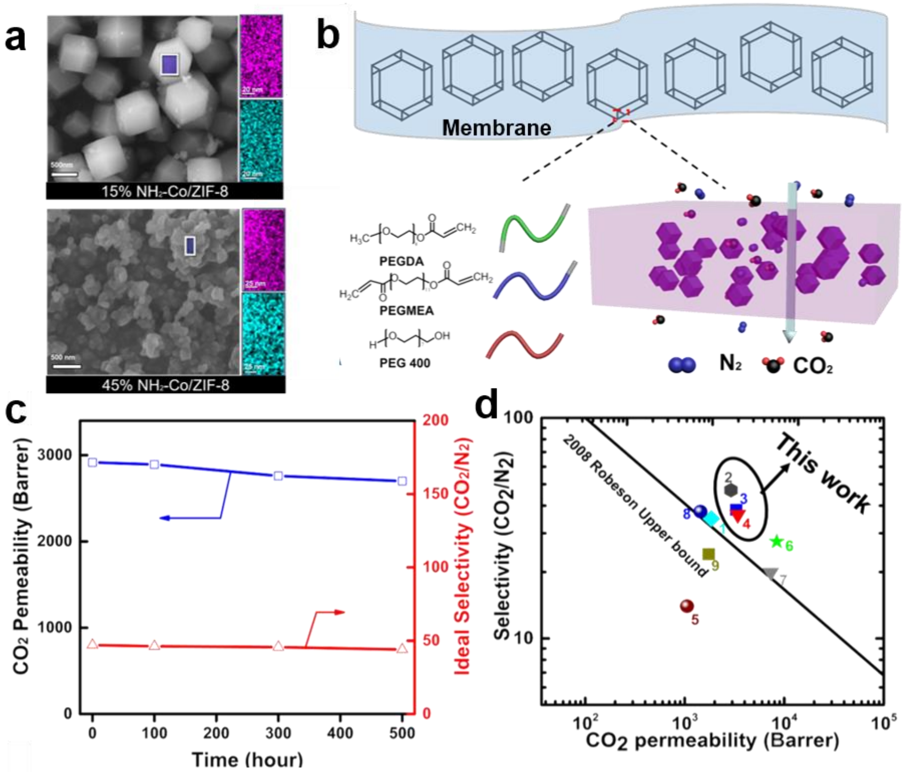

Fig. 1 (a) SEM and EDS images of NH_2-Co/ZIF-8; (b) The NH_2-Co/ZIF-8 PEO membrane structure model and its CO_2 and N_2 molecular penetration diagram; (c) Long-term stability of 30% NH_2-Co/ZIF-8 (5%) PEO membrane for CO_2/N_2 separation. (d) Robinson's upper bond (2008). 1, pristine PEO membrane; 2, 30% NH_2-Co/ZIF-8 5% PEO membrane; 3, 30% NH2-Co/ZIF-8 15% PEO membrane; 4, 15% NH2-Co/ZIF-8 15% PEO membrane; 5, ZIF-8@PD-PI membrane;[6] 6, PIM-UIO-66 membrane;[7] 7, PIM-PI-EA membrane; 8, the MPCM membrane;[8] 9, PIM-1-UIO-66-NH2 membrane [9].

In this study, the Zn in ZIF-8 was substituted by Co to decrease the pore size of the nanoparticles (Co/ZIF-8) while increase its adsorption capacity for CO2. Subsequently, the dimethylimidazole in the ligand was replaced by diamino-benzimidazole (2-amBzIM) to further control the pore size of Co/ZIF-8 (NH2-Co/ZIF-8). The CO2 adsorption isotherms result indicated that the NH2-functionalization heterogeneous Co/ZIF-8 nanoparticles have an enhanced CO2 adsorption capability. Furthermore, the amino functionalization also benefits to the effective combination of organic and inorganic materials. Finally, the NH2-Co/ZIF-8 was designed and dispersed in the polymer matrix through the chelation with metal ions and the ester groups in the methacrylate-terminated PEO and the acrylate-terminated PEO. The amphiphilic interaction between the polymer and NH2-Co/ZIF-8 significantly increased the CO2 solubility resulting in the boost of both CO2 permeability and CO2/N2 selectivity. The best performance membrane exhibits a CO2 permeability of 2916 Barrer and a CO2/N2 selectivity of 47, surpassing the Robeson's upper bond (2008) by a wide margin [5].

Table 1 Gas permeability (P) of the 30% NH_2-Co/ZIF-8 (Y) PEO membranes (1 Barrer = 10^{-10} [cm^3 (STP) cm]/(cm^2 s cm Hg)).

PEO Membranes	**Permeability (Barrer)**						**Ideal Selectivity (α)**
	CO_2	**N_2**	**D[10^{-7} cm^2/s]**		**S[10^{-2} $cm^3/(cm^3cmHg)$]**		**CO_2/N_2**
			CO_2	**N_2**	**CO_2**	**N_2**	
30% NH_2-Co/ZIF-8 0%	1851	53	10.4	2.6	17.8	2.0	34.9
30% NH_2-Co/ZIF-8 2%	2442	60	11.2	2.8	21.8	2.1	40.7
30% NH_2-Co/ZIF-8 5%	2916	62	10.8	2.4	27.0	2.6	47.0
30%NH_2-Co/ZIF-8 15%	3296	86	9.6	1.8	34.3	4.8	38.3

KEYWORDS

Gas separation, PEO, MOFs, CO_2 Capture

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Tailoring Structural Properties of Microporous Materials in Mixed-Matrix Membranes for CO_2/CH_4 Separation

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ABSTRACT

Natural gas, which comprises mainly methane (CH_4) has been readily utilized as an energy resources due to its natural abundance together with its feasibility in producing cleaner energy than coal or petroleum. Nevertheless, as natural gas is not renewable, diversification of the current energy resources is required to cope with the increase in energy demand for the subsequent years. Thus, biogas which is a renewable resource provides a practical method to minimize the current shortcoming. Nevertheless, presence of substantial amount CO_2 in the biogas can lead to a decrease in the caloric value together with the potential corrosion to the transportation pipeline. In this extent, membranes generally show several merits as compared to conventional purification process (e.g. cryogenic distillation) due to its small plant footprint, high energy efficiency and ease of operation. However, in view of the trade-off limitation between permeability and selectivity in polymeric membrane as well as molecular sieve membranes that suffers poor scalability, mixed-matrix membranes (MMM) which is capable in combining the advantages of both polymer and porous materials have been a technically feasible method to circumvent these challenges.

The studies begin with the utilization of zeolite materials in MMM. In general, zeolites which is inorganic in nature show its difficulty in demonstrating good compatibility with the polymer matrix. Thus, decoration on the surface of zeolites using amine or nanowhiskers through entanglement with the polymer chains is feasible in improving the filler/polymer compatibility. Nevertheless, such incorporation tends to decrease the micropore volume of the filler, which limits the enhancement in CO_2 permeability. Thus, metal-organic frameworks (MOFs) and microporous organic polymers (MOPs) which possess organic moieties that allows an improvement in filler/polymer compatibility have been utilized.

Therefore, $Zn(pyrz)_2SiF_6$ (SIFSIX-3-Zn) which possess an optimal pore window of 3.8 Å is chosen as it allows size exclusion behavior between CO_2 and CH_4, leading to an extraordinarily high selectivity. Based on the gas permeation results, incorporation of 20 wt% $Zn(pyrz)_2(SiF_6)$ in polymeric membrane shows an improvement in both CO_2 permeability and CO_2/CH_4 selectivity, which can be verified further from the solubility-diffusivity analysis. On the other hand, incorporation of amine-impregnated MOPs which possess higher CO_2 adsorption as compared to bare MOPs have shown a clear

improvement in CO_2/CH_4 separation performance as compared to its nascent membranes, when the loading was increased to 15 wt%.

Nonetheless, based on the performance reported above, it is generally desirable to incorporate the fillers with the loading to be sufficiently high to attain such enhancement. Besides, the plausible creation of non-ideal effects can be potentially generated, leading to the creation of non-selective bypaths together with the decrease in mechanical strength. Thus, the incorporation of two-dimensional (2D) materials in polymeric membrane have been feasible in improving CO_2/CH_4 selectivity, with 43% increment with only 4 wt% loading. However, due to the plausible creation of tortuous pathway for the diffusion of gas molecules, the gas permeability can be highly sacrificed. Therefore, the combination of two different fillers (i.e. 2D and 3D fillers) in polymeric membranes which functions to improve CO_2 permeability (3D fillers) and CO_2/CH_4 selectivity (2D fillers) can be feasible in tuning the membrane performance towards the CO_2/CH_4 upper bound limit.

KEYWORDS

Mixed-matrix membrane, CO_2 separation, polyimide, nanoporous materials

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Session 11: Membrane Fouling and Characterization

Comparison of Different Membrane Assisted Biosorptions During Sorption Processes

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ABSTRACT

Membrane biosorption (MBS) which combines membrane separation and biosorption, exhibits several advantages in wastewater treatment including more efficient process and smaller footprint. In MBS, membrane can facilitate a better contact between the biosorbent and the sorbate (pollutant) resulting in an improved sorption kinetic (non-diffusive MBS). Membrane also helps to remove priority pollutant from a wastewater by providing a selective extraction and avoids the mixing between the biosorbent and wastewater (permeated MBS). In addition, membrane can remove gas pollutant from a waste gas stream and supply bubble-less aeration that improve the biological growth of the biosorbent (gas contacting MBS). However, there are several challenges that need to be addressed for MBS application, e.g. diffusion limitation in membrane and uncontrolled biofilm formation. Therefore, it is imperative to identify membranes with appropriate characteristics as well as biofilm control strategies. This paper reviews recent developments in MBS. The review focuses on features and performance of different MBS configurations. Biofilm formation, its role, and optimization in MBS application as well as challenges and strategies for future applications are also discussed.

KEYWORDS

biofilm; bioreactor; membrane; integrated process

Comparison of Thin-Film Composite (TFC) and Cellulose Acetate (CTA) Membrane in Gypsum Scaling

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ABSTRACT

Osmotically driven membrane processes (ODMPs) have gained wide interests in the recent decade. It utilizes the osmotic pressure difference ($\Delta\pi$) between a dilute feed solution (FS) and a concentrated draw solution (DS) as driving force to drive the water in the FS permeating through a semi-permeable membrane to the DS side [1]. Generally, OPMPs include forward osmosis (FO, hydraulic pressure = 0) and pressure retarded osmosis (PRO, $0 <$ hydraulic pressure $< \Delta\pi$) depending on applied hydraulic pressure in the DS. FO process has an outstanding advantage of low energy consumption compared to reverse osmosis process (RO) when the regeneration of diluted DS is not required; PRO process is a promising environmentally friendly candidate to produce clean energy from salinity gradients [2-8].

Despite the superiority and attractiveness of ODMPs, gypsum scaling is still one of the major challenges as calcium and sulphate ions are common in water sources such as industrial wastewater, brackish ground water and seawater and it will evidently decrease water flux hence shorten membrane operation life span or even damage its integrity. In this study, gypsum scaling was systematically investigated in the ODMPs using both polyamide thin-composite film (PA TFC) and cellulose acetate (CTA) membranes. In the active-layer-facing-draw-solution (AL-DS) orientation (a typical PRO operation mode), TFC membrane exhibited significant performance loss during scaling test and showed nearly no water flux recovery after DI water rinsing. Furthermore, a TFC membrane integrity loss was for the first time observed. However, in the active-layer-facing-feed-solution (AL-FS) orientation (a typical FO operation mode), TFC membrane kept its integrity in the similar experimental conditions where other researchers claimed an integrity loss was found [9, 10]. In comparison, CTA membrane had around 70% or above water flux recovery in both orientations. The results above were further confirmed by scanning electron microscopy (SEM) images as well as X-ray spectroscopy (EDS) element mappings and results reported here should have instructive implications for membrane selection and design in order to mitigate gypsum scaling in the future.

KEYWORDS

Gypsum scaling, osmotically-driven membrane processes, internal concentration polarization, membrane integrity

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Application of the Stabilized Chlorine Biofouling Control Agent in Seawater Reverse Osmosis (SWRO)

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ABSTRACT

Membrane biofouling, caused by bacterial biofilm formation, is a significant challenge for seawater reverse osmosis desalination plants. Biofouling leads to the use of higher operating pressure, more frequent chemical cleaning, and shorter membrane life [1,2].

To address this issue, KURIVERTER^{TM} IK-110 (IK-110) is introduced in this study. IK-110 is a unique on-line biofilm control agent and mainly consists of the stabilized chlorine [3,4], which can deactivate bacterial activity and reduce the adhesion of microorganism on reverse osmosis (RO) membrane. As an on-line dosing agent, the membrane deterioration effect of IK-110 is one of the main concerns for customers, even it is NSF certified chemical. To showcase the safe application of IK-110 for SWRO system, Kurita has collaborated with NEWRI and PUB to set up SWRO pilot plant to evaluate IK-110 long term performance at Tuas test bedding site, in Singapore.

Before the pilot test, the accelerated membrane deterioration tests were performed by membrane immersion test in laboratory. Upon completion of the membrane immersion in target solution for certain period, the impact of this solution on RO membrane deterioration was studied through evaluating membrane permeability, membrane rejection and membrane characterization by Fourier Transform Infrared (FTIR). The membrane performance was compared for exposure to NH2Cl and IK-110. NH2Cl exposed membranes shows higher permeability than IK-110, while membranes exposed to IK-110 show higher rejections for the elements (Na, Ca, Mg, B) in almost all the tested conditions. In addition, the impact of IK-110 on RO membrane integrity was studied with and without the presence of Br, as bromide in seawater may react with the IK-110 and the resulting bromide compound may have oxidation effect to the RO membranes. The membrane performance and FTIR results were shown to be not affected by the presence of Br when they were exposed to IK-110. All results proved that IK -110 have negligible membrane deterioration effect for RO membrane.

Furthermore, through two years SWRO pilot study, various IK-110 on-line dosing strategies were implemented in SWRO units for biofouling control, including continuous and intermittent IK-110 dosing. During this operation, feed, reject and permeate of RO trains were analyzed for system rejection evaluation, which presented the RO membrane deterioration conditions. Two RO trains achieved stable sodium rejection of >98% and calcium, magnesium rejection >99.9% for whole operation period, indicating that the IK -110 have no impact for membrane degradation in long term operation.

In summary, the pilot scale SWRO evaluation tests not only confirmed the effectiveness of IK-110 to suppress biofouling, but also proved the safety of IK-110 to be used as an on-line dosing agent with negligible RO membrane deterioration effect.

KEYWORDS

KURIVERTER^{TM} IK-110, SWRO, membrane deterioration, biofouling control

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Characterization and Preliminary Evaluation of Antifouling Performance of Composite Polymer-Metal Complex Membrane for Membrane Bioreactor Application

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ABSTRACT

One strategy to improve the antifouling characteristics of polymeric membrane is through incorporation of antimicrobial[1] component during membrane preparation and/or post treatment such as surface modification[2]. This imparts antimicrobial characteristics to the membrane particularly at the surface which inhibits fouling formation through microbial inhibition. However, these added components are loosely held in the polymer matrix particularly at the surface and leach out during subsequent use resulting to reduced efficacy in the long run[2]. In this study, a flat sheet composite membrane was prepared from a Polythiourea (PTU) solution in Dimethyl Sulfoxide (DMSO) using two distinct phase-separation processes. The dense separation layer at the surface was formed through Complexation-Induced Phase Separation[3] (CIPS) using copper acetate as a complexing agent wherein elemental copper initiates phase separation through crosslinking and subsequent formation polymer-metal complex at the interphase of the copper acetate and PTU solution both in DMSO as solvent. This results to a rigid membrane with controlled copper loading which imparts antimicrobial properties and is insoluble in the original solvent. Meanwhile, the support layer was formed through the conventional Non-Solvent Induced Phase Separation[4] (NIPS) through exposure to a non-solvent such as water. The fabricated membrane was image using Scanning Electron Microscope (SEM) wherein copper distribution were also mapped at the surface and cross-section using Electron Diffraction Spectroscopy (EDS) and/or Auger Electron Spectroscopy (AES), whereas the surface topography and surface charge distribution were determined using an Atomic Force Microscope (AFM)/Electrostatic Force Microscope (EFM)[5]. The pore size and pore size distribution of the membrane was also measured using a porometer. The antifouling performance of the membrane were also evaluated through filtration experiments using humic acid and/or sodium alginate wherein the flux recovery in terms of flux recovery ratio[6] was determined after each filtration experiments.

KEYWORDS

Membrane Bioreactor, CIPS, Fouling, Composite Membrane

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Effect of Pore Resistance and Electrolyte Concentration in Membrane Characterization by Electrochemical Impedance Spectroscopy

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ABSTRACT

Electrochemical impedance spectroscopy (EIS), as an sensitive and non-destructive technique, allows the quantitative electrical analysis of different materials in electrolytes such as nanosheets[1], coatings[2], and membranes[3]. Since the electrical properties are related to the membrane states, such as porosity and surface charges, EIS could be potentially applied as an in situ real-time method for probing the membrane state (e.g. fouling and pore shrinking) during the separation process. However, a clearer correlation between the EIS results and membrane performance and the corresponding explanations are still being explored. Herein, a simple model was proposed to explain the correlation between the EIS results and water flux of a membrane and the corresponding experiment was designed to confirm it.[4] According to this model, EIS can be promisingly used for examining the water flux of separation membranes. Besides, since EIS is based on the electrochemical relaxations related to the intrinsic properties of the membrane system, concentration of the charge, which is determined by the electrolyte concentration, was also one of the key factors influencing the EIS results. In order to obtain more reliable results, it is necessary to find an optimized concentration range of the electrolyte for evaluating the membrane by EIS. Therefore, the effects of the membrane structure and electrolyte concentration on the EIS data were studied[5], which could provide guidance for the selection of electrolyte concentration and suitable application conditions for efficient EIS analysis of membrane materials.

KEYWORDS

Membrane characterization; electrochemical impedance spectroscopy; pore resistance; electrolyte concentration

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Poster Session

A Self-standing, Support-Free Membrane for Forward Osmosis with No Internal Concentration Polarization

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ABSTRACT

Conventional asymmetric or thin-film composite forward osmosis (FO) membranes suffer from severe internal concentration polarization, which significantly hinders process performance and practical applications. Here we report the synthesis of COOH-derived polyoxadiazole copolymer for the fabrication of a self-standing selective thin film without a support layer. The thickness of the membrane was controlled at merely a few micrometers to achieve high rejection of the Na2SO4 draw solution, while maintaining acceptable water permeability. Due to the symmetric architecture, the membrane exhibited excellent and identical FO performance at both of its sides. The structural parameter of the fabricated membranes was zero due to the absence of internal concentration polarization in the symmetric FO membranes. Our results highlight the potential of support-free membranes for the further development of FO technology.

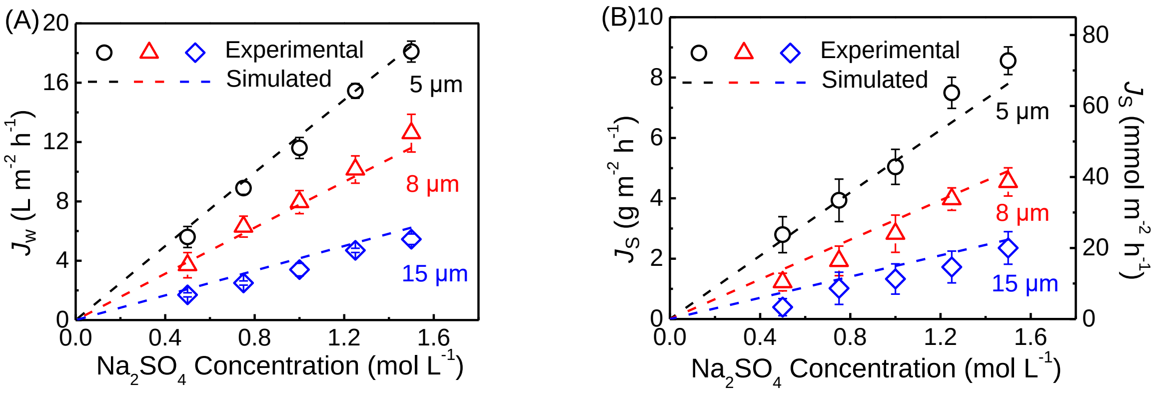

Figure 1. (A) Water flux (J_w) and (B) reverse draw salt flux (J_S) for the PTAODH-1.0 membranes with different thickness. Experiments were carried out in an FO test cell with an effective membrane area of 10 cm^2 and a crossflow velocity of 10.36 cm/s using different concentrations of Na_2SO_4 as draw solution and DI water as feed solution. At least two parallel tests were conducted at 25 °C for 2 h, and the average values and error bars are presented.

KEYWORDS

Forward osmosis membrane, Symmetric, Self-standing, No ICP

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Biofouling Prevention of Drinking Water Reverse Osmosis Membrane by Vanillin: Comparative Metagenomics

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ABSTRACT

Biofouling leads to water quality deterioration and higher maintenance cost for cleaning of membranes. Metagenome analysis of biofouled membranes revealed vanillin to be promising broad spectrum antibiofouling agent, as it inhibited prominent biofouling biota members like Proteobacteria, Acidobacteria, Actinobacteria, Bacteroidetes, Candidatus, Nitrospira and Firmicutes. To evaluate efficiency of vanillin, comparison of the lab-scale reactor metagenomic profiles (taxonomic) with real life fresh, brackish and waste water biofouled membrane community were performed.

As membrane biofouling phenomenon is a quorum sensing (QS) driven behavioural attribute, breaking such microbial linguistic signal could find promising bio-strategy to combat the issue (Lade et al. 2014, Qureshi et al 2015). Lab based experiments demonstrated the role of vanillin as antibiofouling agents. Two identical laboratory scale column feeding RO modules (drinking grade RO) were connected to tap water (chloride 10-40ppm, residual chlorine 0.2 ppm) reservoir, capacity of 40 litre. The transmembrane pressure between the membrane feed water and permeate water was monitored through digital pressure gauge (Liu et al 2003). Each module was operated continuously underneath 2 L/min flow rate using diaphragm pump. Water circulation of the untreated RO reactor (taken as control, Raw Membrane; RM) was carried out for 6 hr/day continuously, followed by overnight resting time for biofilm development. For study using vanillin spiking, another 40L reservoir containing 0.5 mg/ml vanillin in autoclaved water, was connected with RO module (considered as treated, TM) and was allowed to serve vanillin shocks for 1hr/day to the RO cartridge. Biofouling rates and also scanning electron microscopy of membrane cut pieces showed substantial difference in biofilm formation rates upon vanillin treatment.

A significant level of pressure change (first pressure drop) in untreated raw membrane (RM) was observed at 27 day and continued to increase intermediately; which revealed the starting of biofilm formation and subsequent pore blockage. An intermediate 42 days static pressure drop plateau was observed (second pressure drop, RM) which strongly recommended presence of stable biofilm that was unable to be washed off from membrane surface. Third pressure drop was observed at 67 day.

Interestingly when vanillin shock was given to RO module, film formation rates were reduced. First pressure drop of TM, occurred 17 days delayed than RM and furthermore in the continuous runs of reactor, the biofouling rate was unstable which implied loosely bound biofilm associated with module. Even after 95 days operation also, pressure drop of vanillin spiked membrane did not meet the pressure gap of untreated module.

Metagenomic DNA of RM and TM were extracted for high throughput sequencing, and quantitative PCR analysis. Trueseq illumina sequencing was performed followed by the *de novo* assembly by metaSPAdes. Taxonomic annotation was classified using Kaiju, MG-RAST (Menzel et al 2016) and COGNIZER was used for annotating functional capabilities of microbial communities. After normalization,

abundance of Proteobacteria was lowered 0.3% to 0.1% upon giving vanillin shock. In RM metagenome community the second highest biofilm forming group i.e Acidobacteria was found majorly removed by vanillin in TM community. Proteobacteria employ sphingolipid to remain attached with membrane surface (Ashhab et al 2014, Chew and Yang 2017, Pal et al 2018) and played major role in signalling. The enriched biofilm population of Proteobacteria, Acidobacteria, Acnitobacteria, Bacteroidetes, Candidatus, Nitrospira and Firmicutes in Raw membrane declined in abundance when module was spiked with vanillin and primarily non biofilm or loose film former such as Planctomycetes and Verrucomicrobea have been arising (Feng et al 2017). In functional annotation, “biofilm and quorum sensing” as well as “cell signalling” proteins got ~15,13 and 32 fold decreased in TM respectively. QscR (quorum-sensing repressor) was found to exclusively present in TM and for RM; YspR QS activator, AI2 ABC transport, QS transcriptional activator and LuxR were uniquely present. In qPCR, relative fold change pattern primarily indicated lower copy number of all targeted biofouling genes (ica, pgaC, sol and lasI). The results revealed significant decrease in amplification of biofilm genes, representing destabilized biofilm profile in treated RO module (You et al 2018, Pal et al 2016).

For understanding the probable broad spectrum efficiency of vanillin as an antibiofouling biomolecule, real life membrane biofilms were collected from water treatment systems (petroleum plant discarded RO membrane used for the brackish water treatment-**PRO**; household RO used for fresh water treatment-**DRO**). In addition of that, one reference biofouled RO metagenome (**OUT**) was selected from MG-RAST server, cited by Ashaheb et al 2014 (used to treat waste water). JVenn analysis revealed that the lab scale simulation was quite successful because it enriched almost 48% of 0.1% abundant genus of real life biofouling community in lab designed RO module. At the same time Venn plotting indicated that major biofouling groups could be removed by vanillin treatment as the vanillin spiked community share very less biofouling biota with others (Table 1).

The study thus demonstrated the broad spectrum application strategy of using vanillin to prevent membrane biofouling in RO water purification systems. The application of a biomolecule (vanillin) could help in scrubbing and destabilizing biofilms of drinking water Reverse Osmosis membrane module.

Sample	**Common Genus**	**Name of the Genus (0.1% cut off)**	**Significance**
RM Vs TM	19	Bradyrhizobium, Sphingomonas, Methylibium, Novosphingobium, Mesorhizobium, Variovorax, Gemmatimonas, Afipia, Bryobacter, Zavarzinella etc.	1. Majority of biofilm Genus were restricted. 2. 70.3% higher abundant biofouling population was removed
RM Vs DRO	11	Pseudomonas, Mycobacterium, Rhodococcus, Enterobacter, Acinetobacter, Sphingobacterium, Sphingomonas, Nocardia, Serratia, Streptomyces, Nitrospira etc	1. Lab scale Simulation was successful. 2. 48.1% similar biofouling population of domestic RO was localized in lab reactor
TM Vs DRO	0	-	1. None of the biofouling genus was detected at common OUT Zone. 2. Vanillin treatment could be effective to treat Domestic Drinking water RO (12 month used) module.
DRO Vs PRO	14	Sinorhizobium, Nocardioides, Exiguobacterium, Saccharopolyspora, Halobacillus, Synechococcus, Clostridium, Sphaerobacter, Pseudonocardia, Piper, Enterobacter, Pseudomonas etc	1. Irrespective of salt stress these genus could be common target for anti-biofouling strategy.
PRO Vs DRO Vs TM	0	-	1. Target potent biofouling genus could be removed by vanillin
PRO s DRO Vs RM Vs Out	1	Nocardia	1. Highly probable biofouling genus that could be found irrespective of membrane niches 2. Nocardia can be removed by vanillin

Table 1: Taxonomic comparison of five biofouled membrane metagenomes where TM-treated membrane (labscale), RM- raw membrane (labscale), DRO- Drinking water RO

(household), PRO- Plant RO, (brackish water petrochemical industry), Out- outsource RO (waste water treatment plant Ashhab 2014)

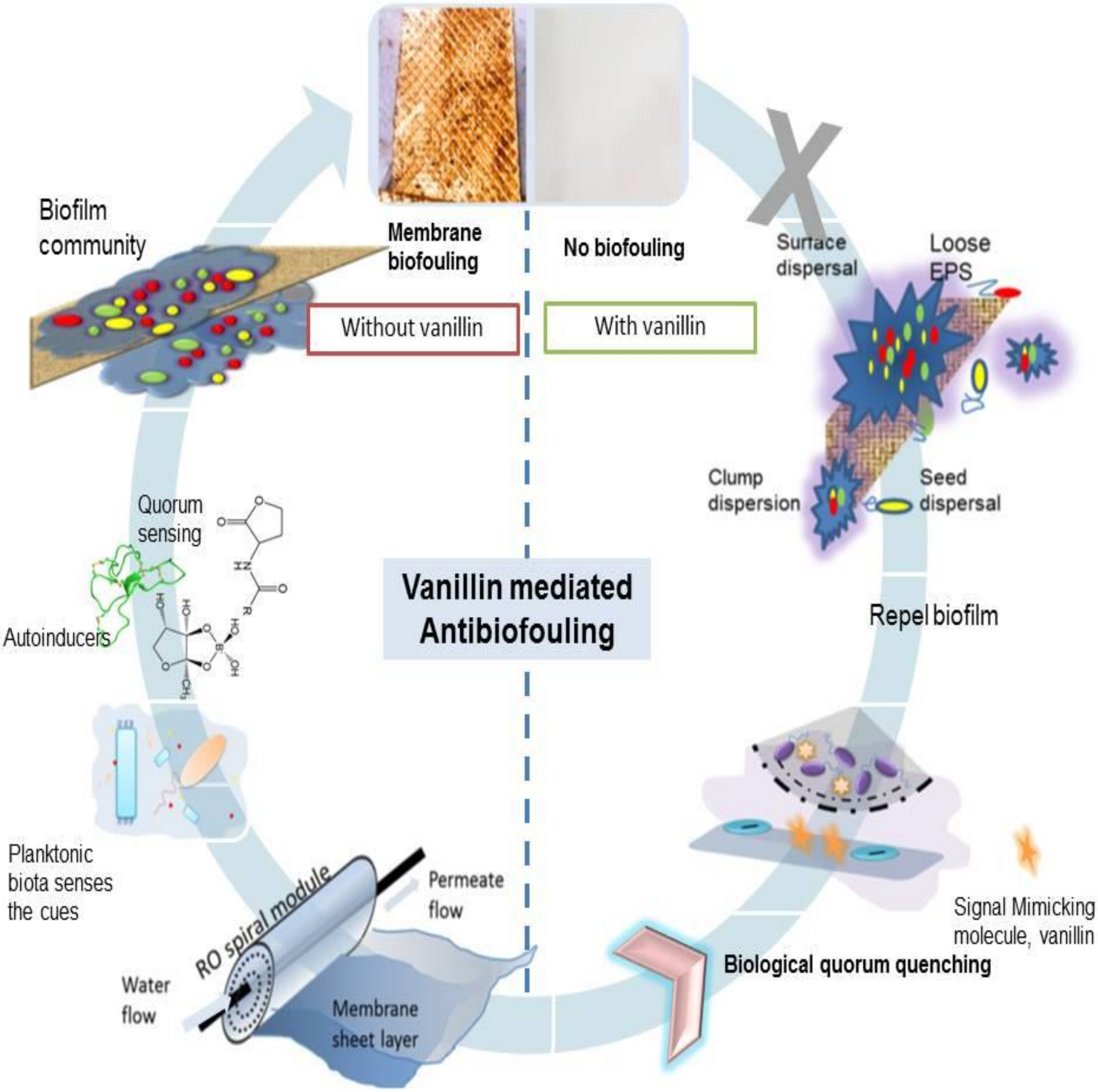

Figure 1: Graphical representation showing Vanillin mediated antibiofouling mode of action on RO membrane

KEYWORDS

membrane biofouling, vanillin, Reverse Osmosis membrane reactor, metagenome

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Preparation and Performance of Nonwoven Fabric Reinforced PVDF/GR Hollow Fiber Composite Microfiltration Membrane

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ABSTRACT

In membrane bioreactor (MBR) system, high mechanical strength and antifouling property are very important for application of hollow fiber membrane. Nowadays, the most popularly used hollow fiber membranes are prepared by wet-spinning method [1, 2, 3].These hollow fiber membranes have high permeability but low tensile strength and are easily damaged or broken in the state of serviceability. Reinforcement threads such as PET (Poly (ethylene terephthalate)) can be incorporated in the support layer of hollow fiber membrane for the purpose of improving the mechanical properties [4].Polyvinylidene Fluoride (PVDF) is an ideal separation membrane, with excellent thermal and chemical stability, acid-base resistance and mechanical properties [5, 6, 7], which is an important part of membrane bioreactors. Graphene, a truly two - dimensional material with high specific surface area and excellent thermal optical and mechanical properties, as well as exceptional hydrophobicity/superhydrophilicity, has great potential in the fields of adsorption and separations[8, 9, 10, 11].

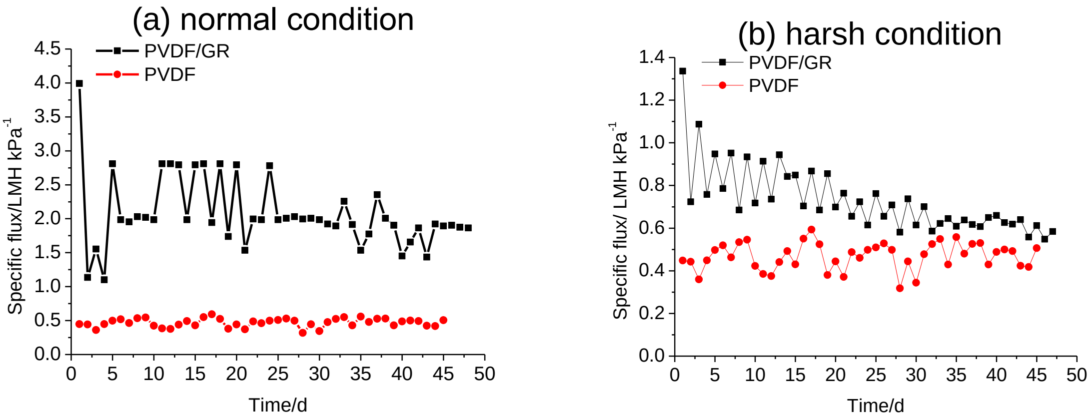
In this paper, PET fiber reinforced PVDF/graphene composite hollow fiber MF membrane was prepared by the non-solvent induced phase separation (NIPS) and coating method with different contents of graphene dispersed uniformly in the PVDF casting solution. The crystal structure of graphene was characterized by X ray diffraction (XRD), scanning electron microscope (SEM) and Raman spectrum. The structure of the membranes was characterized by scanning electron microscope (SEM) and Raman spectrum. The results indicate that the pure water flux of the modified membrane was 2900 LMH, when the addition content of graphene was 2%.

Oil resistant experiments show that PVDF/GR membrane has better oil resistance. In 5%, 10%, 20% soybean emulsified oil solutions, PVDF/GR membrane has higher membrane flux and lower flux decline factor than that of pure PVDF membrane (Table 1).

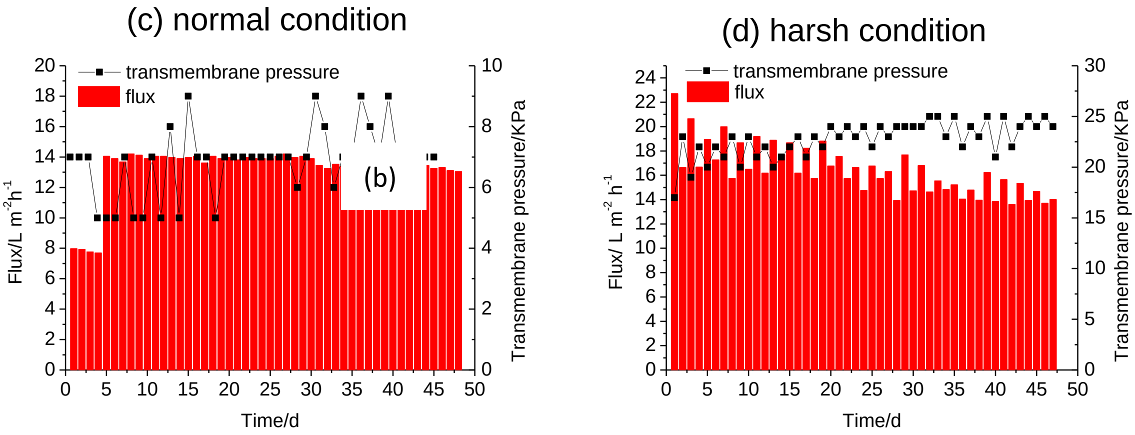
Normal long-term stability experiments (Aeration is 5 m^3/h, the suction to the stay ratio is 8.5 min to 3.5 min) in a MBR system indicate that PVDF/GR membrane has stable flux and transmembrane pressure, and shows higher specific flux than PVDF membrane. Reducing aeration to one-third and running in harsh condition (Aeration is 1.6 m^3/h, the suction to the stay ratio is 8.5 min to 3.5 min) , PVDF/GR membrane has a water flux over 10 LMH and transmembrane pressure within 30 kPa, which shows higher specific flux than that of in normal conditions (Figure 1).

Table 1 Oil resistant experiments

Oil content	PVDF membrane			PVDF/GR membrane		
	Original flux/LMH	After 42d flux/LMH	flux decline factor/%	Original flux/LMH	After 42d flux/LMH	flux decline factor/%
5%	2246	739	67.10	2584	1113	56.93
10%	2229	726	67.43	2917	1358	53.45
20%	2408	835	65.32	2868	1612	53.79


(a) normal condition

(b) harsh condition


(c) normal condition

(d) harsh condition

Figure 1 Long-term stability experiments

Specific flux in normal conditions (a) and in harsh condition (b);

Flux and transmembrane pressure in normal condition (c) and in harsh condition (d)

KEYWORDS

Polyvinylidene Fluoride; Graphene; hollow fiber; oil resistant;

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Improved Rejection Ability of Interfacially Synthesized Polyester Thin-Film Composite Membrane by Surface Cross-Linking

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ABSTRACT

In this work, polyester thin-film composite (TFC) nanofiltration membrane was firstly prepared by the interfacial polymerization (IP) of triethanolamine (TEOA) and trimesyl chloride on porous polysulfone support and then performed with surface cross-linking via using poly(acrylic acid) (PAA) for improved rejection ability. The preparation procedure is schematically illustrated in Fig. 1. FTIR and XPS analyses confirmed that surface cross-linking was implemented through the esterification reaction between the carboxyl group of PAA and the residual hydroxyl group of TEOA/TMC layer. The rejection performance of the TEOA/TMC composite membrane could be effectively improved at a sacrifice of membrane flux via forming a relative dense skin on the top of the selective layer of TEOA/TMC. The performance of the surface cross-linked TEOA/TMC membrane could be tuned via varying the cross-linking conditions including PAA content, curing time and temperature. The performance advantage of the surface cross-linked TEOA/TMC membrane was illustrated in Table 1. After surface cross-linking with PAA, the mean pore radius decrease evidently from 1.32 to .096 nm and the PWP declines significantly from 24.6 to 9.7 l/m^2.h.bar, indicating the formation of dense skin. The pure water permeability of the surface cross-linked loose TEOA/TMC membrane is higher by 115.6% compared to the dense TEOA/TMC TFC membrane with nearly the same pore size, indicating the asymmetric structure of the selective layer of the surface cross-linked loose TEOA/TMC membrane. The surface cross-linked TEOA/TMC membrane shows the salt rejections following the order of R(Na_2SO_4) > R($MgSO_4$) > R(NaCl) > R($MgCl_2$) and the dye removals in the order of Reactive red (99.8%) > Methyl blue (99.2%) > Congo red (98.2%) > Sunset yellow (97.1%) >Neutral red (64.5%). The results demonstrate that the construction of asymmetric separation layer via surface cross-linking is a possible route to tune the perm-selectivity of TFC membrane.

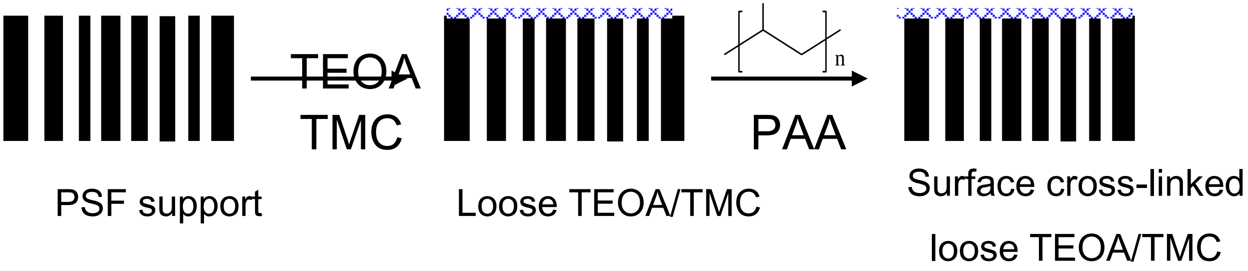

Fig.1 Schematic for the preparation of TFC membrane via IP followed by surface cross-linking.

Table 1 Mean pore size (r_p), molecular weight cut-off (MWCO) and pure water permeability (PWP) of the prepared membranes

Membrane	r_p (nm)	MWCO (Da)	PWP (l/m^2.h.bar)
Loose TEOA/TMC	1.32	3500	24.6
Surface cross-linked loose TEOA/TMC	0.96	1680	9.7
Dense TEOA/TMC	0.98	1730	4.5

KEYWORDS

Nanofiltration; Surface cross-linking; Polyester TFC membrane; Improved rejection ability

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Triblock Copolymer Polymersomes Incorporating Aquaporin Z Proteins for Biomimetic Membranes

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ABSTRACT

Facing a rising problem with the water scarcity and water quality, development of membranes with improved performance for water treatment applications is increasingly important. Biomimetic membranes can be an efficient alternative to traditional membranes, due to their improved water permeability and selectivity. The biomimetic membranes active layer is doped with active transmembrane protein facilitating water transport. Such proteins which govern selective water transport are bacterial isoform Aquaporin Z (AqpZ) [1,2]. However, in order to incorporate such proteins in the active layer of the membrane, stabilization of them is required, to protect them from degradation and ensure their functionality. Transmembrane proteins are usually stabilized in liposomes or polymersomes [3,4]. The latter are preferable due to the increased physical and chemical stability of polymersomes over liposomes [5]. Moreover, use of polymersomes allows introduction of the active groups which can participate in covalent bonding of the polymersomes to the active layer of the membrane [6].

Here, we propose stabilization of AqpZ in the polymersomes made of poly(methyloxazoline)-poly(dimethylsiloxane)-poly(methyloxazoline) (PMOXA-PDMSPMOXA), blended with NH_2 active groups – which through the reaction with trimesoyl chloride (TMC) covalently bond with the polyamide active layer of the membrane.

Polymersomes were prepared by self-assembly bulk rehydration method in aqueous solution according to the procedure described in the patent by Aquaporin A/S [7]. The size and concentration of polymersomes was evaluated with Nanoparticle Tracking Analyzer (NTA), Nanosight NS300 (Malvern Panalytical, UK). ζ-potential was measured with Dynamic Light Scattering (DLS), Zetasizer Nano ZS (Malvern Panalytical, UK). The activity of AqpZ in polymersomes is evaluated with Stopped-Flow Light Scattering (SFLS), Bio-Logic SFM 300 (Bio-Logic, France), using a monochromator at 517 nm and a cut-off filter at 530 nm. During the SFLS experiment, 38 μL of polymersomes solution is rapidly mixed with 38 μL of 0.3 M NaCl solution having higher osmolarity than the buffer solution of polymersomes – polymersomes exposed to high osmolarity gradient shrink, as there is water efflux from polymersomes to the osmolyte. The rate of shrinkage is expressed by the light scattering change. The higher the water efflux through polymersomes – the fastest is the change of light scattering. The change of light scattering over time is fitted to the exponential growth equation (Eq. 1) and the rate of change expressed in exponential coefficient k_i, which is directly proportional to the water flux through the polymersomes [8].

$$Y = \sum_{i=1}^{N} c_i \, e^{-k_i t} \qquad \textit{Equation 1.}$$

Where Y is light scattering, N is number of exponential terms, t is time (s), c_i is relative amplitude and k_i is the exponential coefficient (s^{-1}). The osmotic water permeability through polymersomes P_f was calculated with use of Eq. 2 [9].

$$P_f = \frac{k}{\frac{S_A}{V_0}} V_w \Delta_{osm} \qquad \textit{Equation 2.}$$

Where P_f is osmotic water permeability (μm/s), k is the exponential coefficient (s^{-1}),S_A is vesicle surface area (μm^2), V_0 is initial vesicle volume (μm3), V_w is molar volume of water (0.018 $Lmol^{-1}$) and Δ_{osm} is the osmolarity difference that drives the polymersome shrinkage ($osmolL^{-1}$).

Summary of characteristics of the polymersomes are presented in the Table 1.

Table 1. Polymersome characteristics – size distribution, concentration of particles, zeta-potential and osmotic water permeability. D10, D50 and D90 are particle size distribution intercepts of 10 %, 50 % and 90 %.

Sample	Mean size [nm]	D10 [nm]	D50 [nm]	D90 [nm]	Conc. of particles [particles/mL]	ζ-potential [mV]	pH	P_f [μm/s]
AQP-1	187 ± 2	123 ± 2	173 ± 3	255 ± 3	$1.8 \times 10^{11} \pm 5.6 \times 10^{9}$	+ 0.87	8.03	2180
AQP-0	167 ± 1	94 ± 1	148 ± 2	232 ± 5	$1.7 \times 10^{11} \pm 4.8 \times 10^{9}$	+ 0.35	8.10	1660

Polymersomes having AqpZ functionally reconstituted in the matrix (AQP-1) resulted in 30% increased water efflux – 2180 μm/s, compared to the polymersomes without AqpZ proteins – 1660 μm/s (AQP-0). The polymersomes size distribution, concentration, ζ-potential and pH are comparable when AqpZ are reconstituted or not.

Such polymersomes were integrated into the active polyamide layer of the flat sheet membrane via in-situ interfacial polymerization on polysulfone support (Aquaporin A/S, Denmark) between the aqueous solution of m-phenylenediamine (MPD), ecaprolactam, and organic solution of trimesoyl chloride (TMC) (all reagents grade is >99% for synthesis and are obtained from Merck KGaA, Germany) and Isopar E (Brenntag Nordic, Denmark). The resulting membranes were tested in the lowpressure reverse osmosis mode at 5 bars applied pressure with 10 mM NaCl as feed solution, at 25°C and feed flow of 60 Lh^{-1}. The membranes reconstituting AQP-0 resulted in 20% improved water permeability, while the membranes reconstituting AQP-1 resulted in 50% improved water permeability in comparison to the control membranes which composed of polyamide layer without polymersomes. The rejection of NaCl was maintained at the range of 92-93% for all the membranes (Figure 1).

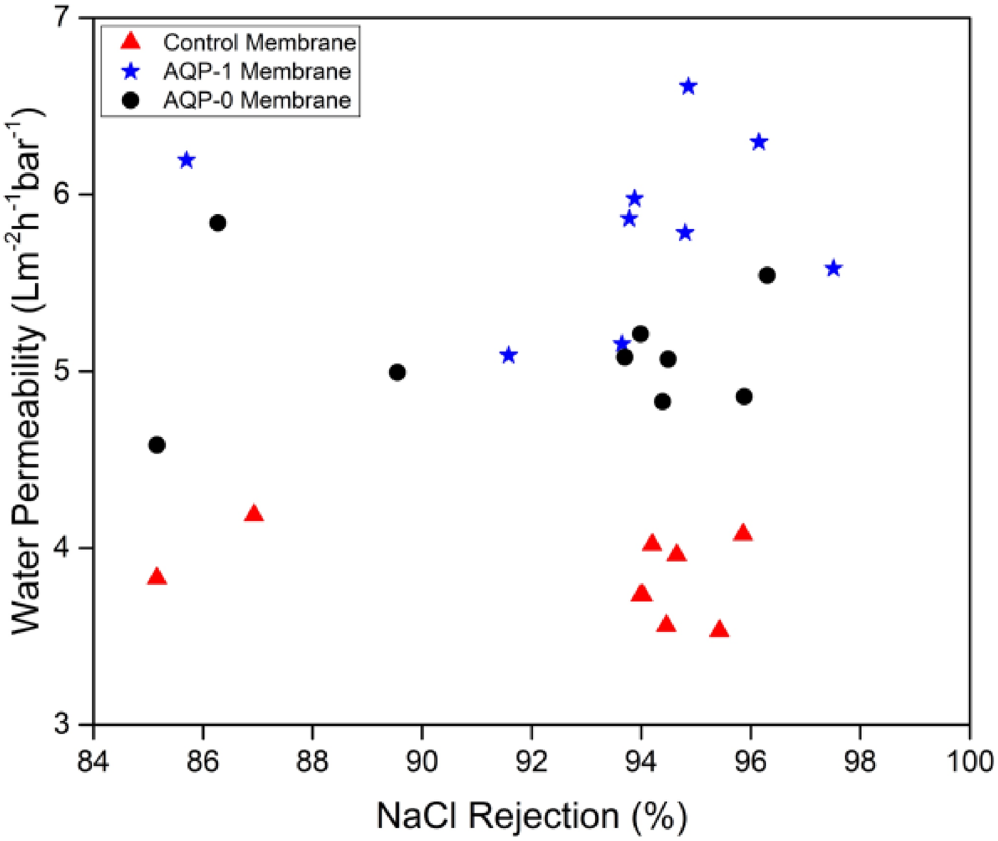

Figure 1. Comparison of the performance of membrane samples – water permeability and NaCl rejection. The membranes were tested at 5 bars with 10mM NaCl as feed solution, at 25°C and feed flow of 60 Lh^{-1}.

Incorporation of amino-functionalized polymersomes reconstituting Aquaporin Z into polyamide layer of the thin film composite membranes resulted in significant increase of water permeability without sacrificing the NaCl rejection in reverse osmosis experiment.

KEYWORDS

Biomimetic polyamide membranes; Triblock copolymers; Polymersomes; Aquaporin; Reverse osmosis

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Design and Fabrication of Hierarchical Porous Membrane for Flow-through Removal of Aqueous Micropollutants

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ABSTRACT

The global occurrence of micropollutants in various aqueous environment has attracted increasing attention due to their potential hazard on aquatic ecosystems and human health. Adsorption has risen as a fast and efficient technology for micropollutants removal. Current adsorptive membranes can be prepared by introducing functional groups via surface grafting, which enjoy good sorption capacity but have limited transport efficiency. In order to ease the trade-off relationship between sorption capacity and transport efficiency, we report a series hierarchical porous polymer materials possessing multiscale pores containing macro-, meso- and microporous structures. The obtained hierarchical porous structure should possess both high capacity brought about by numerous micropores and high transport efficiency from mesoporous and macroporous transport channels. 1) A commercial regenerated cellulose (RC) membrane was used as a starting material for the synthesis of hierarchical porous membrane considering its large pore diameter. The SiO_2 nanoparticles with thiol groups (SiO_2-SH) were introduced onto the RC membrane to increase its adsorption capacity. A series of adsorptive membranes were synthesized by post-modification of the thiol groups and demonstrated desirable adsorption property for Hg^{2+}, Pd^{2+} and Cd^{2+}, and boron. 2) The polymer of intrinsic microporosity PIM-1 was fabricated into microfiber membranes by electrospinning for carbendazim and phenol adsorption. The electrospun PIM-1 membrane was demonstrated to have hierarchical porous structure with high surface area. The equilibrium adsorption capacity for carbendazim and phenol was 0.084 mmol/g and 0.804 mmol/g, respectively. Both the sorption capacity and kinetic coefficients are high when comparing with other sorbents for either carbendazim or phenol. 3) A hierarchical porous poly-melamine-formaldehyde (PMF) filled metal mesh was prepared by thermosetting a high internal phase emulsion of melamine and formaldehyde monomers. The obtained PMF filled metal mesh show excellent adsorption properties for heavy metal ions. Incorporating mesopores or macropores into the space of microporous structure as additional low resistance transport pathways is an efficient material synthesis strategy to enhance mass transport.

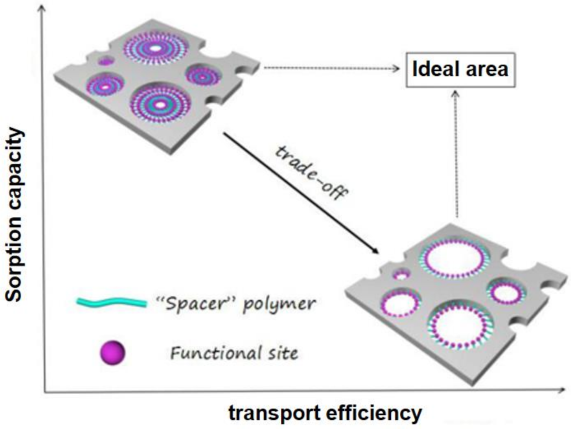

Fig.1 The trade-off relationship between sorption capacity and transport efficiency

KEYWORDS

Hierarchical porous structure; Adsorption; Micropollutants

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Synthesis of Thin Film Composite Polyamide Membranes: Effect of Chemical Additives in Aqueous and Organic Phases on Membrane Morphology and Performance

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ABSTRACT

The aromatic polyamide thin film composite (TFC) membrane is currently the mainstream reverse osmosis (RO) membrane. A variety of approaches have been explored to control the thin film forming dynamics to achieve enhanced membrane performance. Additive approach provides a simple, yet very effective way of improving the performance of thin film composite membrane. However, there is a lack of correlation between physical and chemical properties of a wide range of additives and the membrane properties. In our article, a variety of additives were used to prepare RO membranes. The objective is 1) to establish fundamental mechanistic understanding of membrane performance improvement by additives, 2) to establish correlation between the properties of the additives and the membrane morphology and separation performance, and 3) to provide guidelines of selecting effective additives. The adding of DMSO, formamide, acetamide into the aqueous solution, or cyclohexanone into the organic phase, which showed approximately 2 times higher water permeance with no significant salt rejection decrease compared to control polyamide membranes. The mass of thin polyamide film was measured using a quartz crystal microbalance (QCM). The results show that greater film mass correlates with increased permeance.

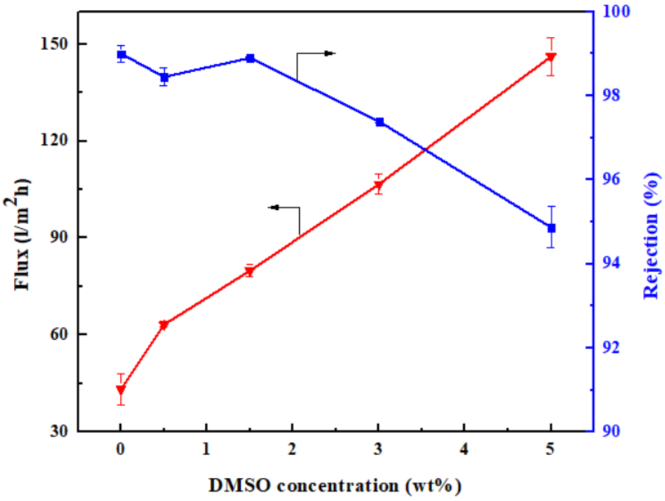

Fig.1 Effects of DMSO concentration in aqueous solution on membrane desalination performance

KEYWORDS

Reverse osmosis; Polyamide; Additive

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Effect of UV Treatment and PEG Grafting on Polysulfone Membrane Surface to Improve Hydrophilicity for Wastewater Treatment

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ABSTRACT

The Earth's surface is concealed by water of about 361 million square kilometres, nearly 70.8% of all. However, the fresh water is only 2.5% of the whole water. So it is necessary to prepare more fresh water for drinking and other purposes (Zwane et al. 2018). Several methods have been used to purify wastewater. Among those methods, Membrane separation technology have obtained more interested in the treatment of wastewater, seawater desalination, water purification and others. This is due to their many advantages such as low energy consumption, high efficiency and no need of chemical requirements (Pan et al. 2019). Polysulfone (PSF) is one of the top polymers for flat sheet membrane production due to their many excellent properties such as high chemical, thermal and mechanical resistance and easy for film-forming. Furthermore, the properties of separation and plasticization are in an acceptable level (Chittrakarn et al. 2016). However, PSF in nature is a high hydrophobicity and low surface energy that cause low antifouling ability and low permeability of PSF membranes. These drawbacks become main challenges in their practical application. Many works reported the increase of water flux and hydrophilicity properties of PSF membrane after UV irradiation treatment. But the drawback of this technique is a very short lifetime effect that show hydrophobicity recovery within hours. (Nyström and Järvinen 1991, Konruang et al. 2015, Xing et al. 2018). UV grafting technique had been used to modify membrane surface in some research group. The starting radicals was generated by UV irradiation on membrane surface that advances the covalent bonding of desired chains onto the membrane surface for graft polymerization (Akbari et al. 2016, Basri, Ismail and Aziz 2011). Poly(ethylene glycol, PEG) is the most usually used to improve hydrophilicity property of membrane surface due to its hydrophilicity, low toxicity, good biocompatibility, and low cost (Vatanpour et al. 2019, Abu Seman et al. 2010). Thus, PSF membrane surface in this work was modified by UV grafting technique. PSF membrane surface was irradiated by UV-ray at 312 nm wavelength and then, was grafted by PEG in order to increase hydrophilicity. The scanning electron microscope (SEM) was used to verify the top, bottom and cross-section of PSF membrane as shown in Figure.1 A, B and C, respectively. These results show that the top side of membrane surface carried out much smaller pore size than that of the bottom side due to the formation of skin layer induced by phase inversion process. The water contact angle (WCA) of the treated membrane decrease while the surface energy (SE) of the treated PSF membrane increase when compare to the untreated PSF membrane (PSF-Untreated). Furthermore, PSF membrane which was treated by UV ray and was grafted with PEG (PSF-UV-PEG) had the lowest WCA and had the highest SE as shown in Table.1. The atomic force microscope (AFM) was used to

verify surface roughness of the untreated, UV-treated and UV-grafted PSF membrane surface and gave the result as shown in Figure.1 D, E and F, respectively. The RMS value of untreated, UV-treated and UV-grafted membrane were 45.45 nm, 112.61 nm, and 134.32 nm, respectively. These results support the WCA and SE results due to Wenzel's equation. In this case, the introduction of surface roughness will also enhance the surface wettability of membrane (Wang et al. 2012). So this work gives a strategy for the surface design and construction of wastewater separation membrane for practical use.

Table.1 The water contact angle and surface energy of membranes.

Sample	Water contact angle (degree)	Surface energy (mJ/m^2)
PSF-Untreated	82.48±2.62	24.44±0.28
PSF-UV	66.13±0.80	40.36±1.16
PSF-UV-PEG	57.47±4.29	43.87±0.31

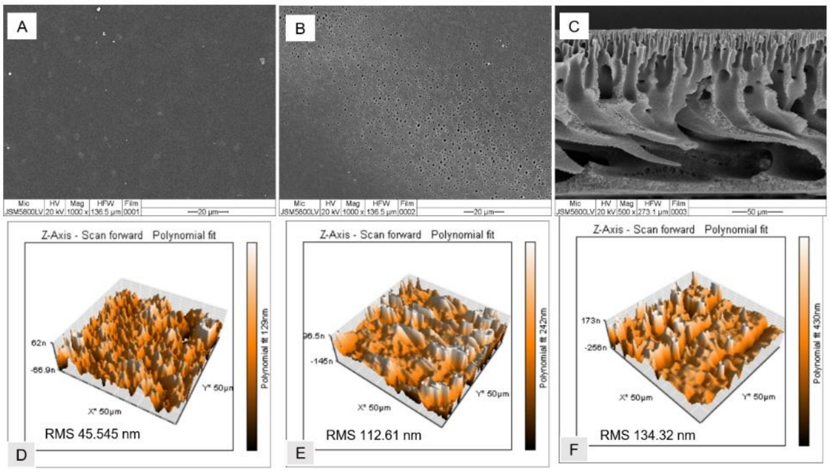

Figure.1 The SEM figure of top (A), bottom (B) and cross-section (C) and the roughness of PSF-Untreated (D), PSF-UV (E) and PSF-UV-PEG (F).

KEYWORDS

Surface modification, hydrophilicity membrane, UV treatment, PEG-grafting, wastewater treatment.

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Dye Sensitizer of Chlorophyll as Mixed with TiO_2 Nanoparticle in Photocatalytic for Enhancing the Hydrogen Production

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ABSTRACT

Development of photocatalytic titanium dioxide (TiO_2) nanoparticles has been widely use in semiconductor material because its chemical stability, great capacity oxidation, non-toxic and low cost [1]. TiO_2 contains energy gap of 3.2 eV, in which UV light can excite the electron from the valence to the conduction band. Current, TiO_2 have been develop for enhancing the performance of recombination electron hole (e-, h+). Many methods to improving TiO_2 based photocatalytic including noble metal doping, surface modification and co-catalyst heterojunction [2]. Dye sensitizer is natural dye pigment such as anthocyanins, betalains, carotenes and chlorophyll has been studied by coating on TiO_2 for enhancing the efficiency of water splitting under visible light and increasing hydrogen production [3]. This project aims to study the effect of Dye Sensitizer of Chlorophyll Mixed with TiO_2 nanoparticle in photocatalytic for enhancing the hydrogen production [4]. Pandan leaves plant are extracted for chlorophyll and mixed with anatase TiO_2 that has been stimulated by burning at different ratios. The experiment was performed in order to study the efficiency of the separation of water molecules by light acceleration and measuring the capacitance voltage of the capacitor that is collected from the experiment set. It was found that the average voltage potential of TiO_2 was stimulated but not mixed with chlorophyll extract can harvest the potential difference of 0.002 volts. But when mixed with chlorophyll extracted with volume of 10, 20 and 30 cubic centimeters. Can harvest an average potential difference of 0.027, 0.032 and 0.034 volts, respectively. Results shows that chlorophyll can be used as an enhancing agent for the production of hydrogen via water splitting by light-accelerating reactions with a positive improvement. Further result will be presented later.

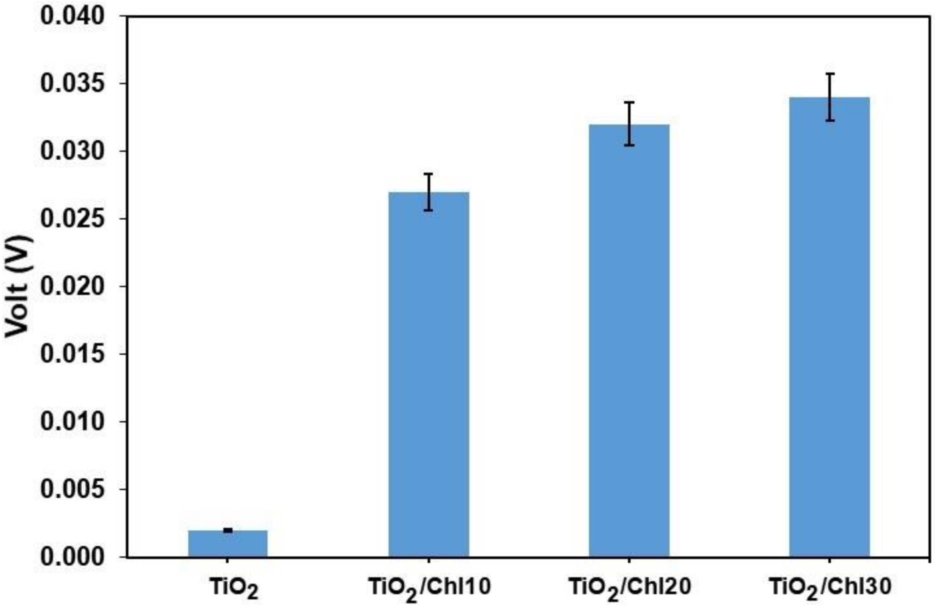

Figure 1 Present the obtained harvesting voltage from pure TiO_2 comparing with different concentration of chlorophyll (10, 20, 30%) mixed with TiO_2: TiO_2:Chl10, TiO_2:Chl20 TiO_2:Chl30, respectively.

KEYWORDS

Dye Sensitizer, chlorophyll, hydrogen and photocatalytic

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Tailoring the Characteristics of Graphene Oxide Membranes for Gas Separation and Water Purification

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ABSTRACT

In recent years, graphene oxide membranes emerged as a promising and versatile tool for existing and new membrane technology. The potential of graphene oxide membranes was shown in studies on its water purification and gas separation properties. To fully exploit the potential, further research must be conducted to precisely control the characteristics of these novel membranes. Here, we present our recent findings in tailoring the membranes porosity, which is crucial for gas separation and water purification, by vacuum heat treatment and hydrothermal reduction. Additionally, we show that the intercalation of transition metal ions leads to an improvement of the selectivity in separating gas mixtures with graphene oxide membranes.

Versatile Through-Hole Membranes with Ordered and Tuneable Pore Geometry

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ABSTRACT

Membranes with spatially ordered, monodisperse pores are attracting growing interests from many fields of research and development. While such ordered porous membranes pave the way for a myriad of greater membrane functions not easily achieved through conventional membranes, their unique membrane morphologies demand the utilisation of costly instrumentations or elaborate post-processing steps. In this talk, we will present facile and scalable methods for the fabrication of such membranes as well as the governing parameters that serve as predictive design guidelines to accurately engineer the dimensions of membrane pore features. We employ extensively mold-based advanced lithographic techniques and tools but we also develop platforms of our own. We will introduce a pilot scale Roll-to-Roll (R2R) production platform that not only provides significantly improved membrane production throughput and reproducibility but also has the capability to creating structures with various customised architectures and surface textures that are not easily attainable by conventional techniques. The R2R platform provides promising avenues for designing, prototyping and manufacturing membrane products in which forms and functions are fully integrated.

KEYWORDS

Deterministic pore architectures; predictive design; nanofabrication; hierarchical membranes; roll-to-roll production.

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