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Thin-film nanofibrous composite reverse osmosis membranes for desalination
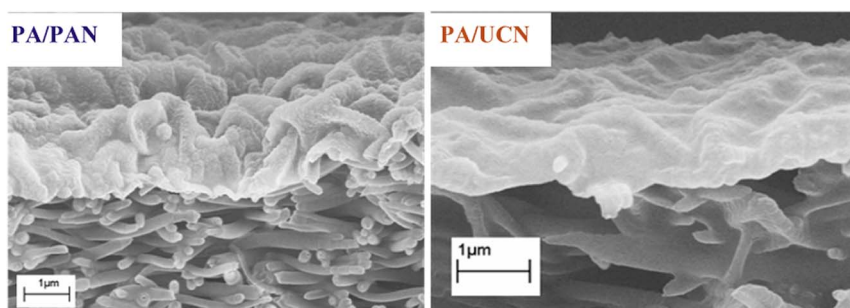
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GRAPHICAL ABSTRACT

ABSTRACT

Interfacial polymerization of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) was carried out on top of the highly permeable nanofibrous ultrafiltration (UF) membrane substrates to create thin-film nanofibrous composite (TFNC) reverse osmosis (RO) membranes for desalination. The UF substrates contained distinct fibrous layers: poly(ethylene terephthalate) (PET) non-woven mat as the mechanical support, electrospun polyacrylonitrile (PAN) nanofibrous scaffold as the mid-layer or barrier layer, and ultra-fine cellulose nanofibers (CNs) as the barrier layer. An aliphatic co-monomer, piperazine (PIP) and different additives (e.g. an ionic liquid 1-octyl-3-methylimidazolium chloride, OMIC) were included in interfacial polymerization to improve the permeation flux for RO operations. To further increase the membrane permeability, a spray coating method was also used to control the barrier layer thickness by adjusting the load of the aqueous solution in polymerization. The optimized RO membrane exhibited a rejection ratio of 96.5% against NaCl (500 ppm) and a flux of 28.6 L/m^2 h at 0.7 MPa, approaching the performance of a high-flux commercial RO membrane (DOW FILMTEC™ XLE). We believe higher permeation flux can be achieved using nanocomposite barrier layer with the CN-based UF substrate, while still maintaining high salt rejection ratio.

1. Introduction

Reverse osmosis (RO) is a separation technology, which is widely used for desalination of seawater and brackish water. The separation process requires the use of sufficient pressure (0.7–5.5 MPa) to overcome the osmosis pressure of the salt solution [1]. Currently, the state-of-the-art RO membranes employ the thin-film nanocomposite (TFC) format [2], which contains a thin densely cross-linked barrier layer on

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top of the porous polymeric substrate. Materials of the barrier layer are typically made of highly cross-linked polyamides prepared by interfacial polymerization, in which the structure and composition of the barrier layer are directly related to the performance of salt retention and energy consumption. The porous substrate usually contains a sponge-like polymer layer, made by the phase inversion method, supported by the non-woven fibrous mat. Functions of this composite substrate is to provide (1) mechanical strength, and (2) small pore structure to support the thin and dense barrier layer to reduce the resistance of the permeate flow.

The polyamide top layer is formed by condensation polymerization of two immiscible phases at the interface: an aqueous solution, containing multifunctional amine, and an organic solution containing acryl chloride. In the past four decades, many monomers have been demonstrated [1,3–9] for this reaction, in which m-phenylenediamine (MPD) and trimesoyl chloride (TMC) were widely used as two effective monomers to produce high performance RO barrier layers. To improve the permeability but without sacrificing the rejection capability of the barrier layer, non-active additives were often introduced into the polyamide layer. For example, nanoparticles, such as zeolites [10–12], silver nanoparticles [13], silica nanoparticles [14] and titanium dioxide (TiO$_2$) nanoparticles [15] have been embedded into polyamide to enhance the permeability or the salt rejection. Small organic molecules, such as acetone [16], isopropyl alcohol [17,18], phenol [18] and n-propanol [17] have been added into the aqueous phase to improve the permeability. Other additives, such as anionic surfactant [19,20], ionic liquid [21], organic acid and amine [7,22] have also been used to adjust the membrane permeability. It is clear that there is a delicate balance between the permeability and salt rejection ratio for each approach, where the effect of additives also depends on the membrane fabrication process [23].

Though the substrate seems to have only indirect effect on the RO performance, recent studies indicated that the morphology of the substrates might play a more important role in formation of the barrier layer than we expected. For example, interfacial polymerization was carried out on a series of polyethersulfone (PES) substrates with varying pore size and surface hydrophobicity by Hoek's group. They found that the substrate with larger pore size and more hydrophilic surface could facilitate the production of more permeable RO membranes by forming a comparatively thin barrier layer [24]. In another study, a new type of porous nanofibrous substrate was used to replace the conventional substrate (made by phase inversion) to produce nanofiltration (NF)/RO membranes. This substrate was created by electrospinning of polymer nanofibers (diameter: 100–300 nm) on the non-woven mat [25]. The pore size of the final nanofibrous substrate was in microfiltration (MF) scale, which was generally larger than those substrates made by phase-inversion having pore size in ultrafiltration (UF) scale. A new format of thin-film nanofibrous composite (TFNC) membrane, suitable for NF applications, was prepared by interfacial polymerization on the electrospun MF substrate, which exhibited higher permeability than the TFC membranes with comparable salt selectivity [21,26,27]. However, we noticed that the relatively larger pore size (sub-microns) from the electrospun nanofibrous scaffold often led to higher defect density in resulting NF membranes. This motivated us to explore the use of finer nanofibrous scaffold to support the interfacially polymerized barrier layer. The general relationship between the TFNC membrane performance and nanofiber diameter has been studied systematically by Ramakrishna's group [28], where the diameter of electrospun fiber (50–500 nm) could be controlled by polymer solution concentration. They found that when the fiber diameter decreased, the substrate pore size became smaller and the resulting TFNC membranes tended to yield higher salt rejection but lower permeability.

In this study, ultra-fine cellulose nanofibers (CNs) extracted from biomass using the combined chemical and physical means was employed to prepare the top nanofibrous support for interfacial polymerization. The average cross-sectional dimension of CNs was around

5 nm, where these fibers could form a thin top layer (thickness of ~100 nm) on top of the electrospun scaffold. This composite structure resulted in a UF membrane having mean pore size around 20 nm [27,29]. Because of the high porosity (> 70%) in both supporting layer and barrier layer, this novel class of UF membranes could exhibit up to10-fold higher permeability than commercial UF membranes for separation of water and oil emulsion (rejection ratio > 99.5%) [29]. In our previous studies, interfacial polymerization was carried out within the CN layer and resulted in nanocomposite barrier layers, containing a portion of interconnected CNs imbedded in the polyamide matrix. In was found that naturally occurring surface between water impenetrable CN and polymer matrix acted as directed water channels to improve the permeation flux in NF operations [30–32]. It was also seen that the position of the aqueous and organic interface in interfacial polymerization could directly determine the content of CN embedded in the barrier layer.

To determine only the substrate effect on the performance of RO membrane, the aqueous and organic interface in interfacial polymerization was purposely positioned above the nanofibrous substrate in this work. We expected that there should be distinct differences between to the CN substrate (smaller fiber diameter, smaller pore size and smoother substrate surface) and the electrospun substrate (larger fiber diameter, larger pore size and rougher substrate surface).To achieve this goal, interfacial polymerizations were carried out on two fibrous substrates (i.e., electrospun polyacrylonitrile (PAN) nanofibrous scaffold and CNs). Scanning electron microscopy (SEM) was used to examine the surface morphology of both substrates and resulting RO membranes. A large range of hydraulic pressure (0.7 MPa–5.5 MPa) was applied onto the RO membrane to first determine the mechanical strengths of the substrates, especially the CN-based UF substrate. To fabricate RO membranes with high permeation flux for the treatment of brackish water (500 ppm NaCl), co-monomers and additives (e.g. 1-octyl-3-methylimidazolium chloride that is an ionic liquid) in the aqueous phase were used to fine-tune the permeability of the barrier layer, and their concentrations for interfacial polymerization were optimized. Finally, permeation fluxes of the RO membranes were further improved by loading the controlled aqueous solution through a spray coating technique, where the results were found to approach those of commercial membranes fabricated by using the slot-die approach.

2. Experimental

2.1. Materials and reagents

In this study, polyacrylonitrile (PAN) (M$_w$ = 1.5 × 10^5 Da) was purchased from Polysciences, Inc.; polyethylene terephthalate (PET) non-woven cloth was provided by Junyaku Co., Ltd. (Japan); wood pulps (Biofloc 96) were provide by Tembec Tartas Factory in France. The chemicals used to prepare ultra-fine cellulose nanofibers were 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) from Acros Organics, sodium bromide (NaBr) from Fisher Scientific Company, 10–15% of sodium hypochlorite (NaClO) aqueous solution and sodium hydroxide (NaOH) from Sigma-Aldrich. Monomers trimesoyl chloride (TMC), m-phenylenediamine (MPD), and co-monomer piperazine (PIP) were employed to prepare the barrier layer of the RO membranes through interfacial polymerization, where triethylamine (TEA), 1-octyl-3-methylimidazolium chloride (OMIC), camphor-10-sulfonic acid (CSA), isopropyl alcohol (IPA), and o-aminobenzoic acid (o-ABA) were used as additives to improve the permeability of the barrier layer. All abovementioned chemicals were purchased from Sigma-Aldrich and used without further purification.

2.2. Preparation of electrospun PAN substrate

To obtain a 10 wt% homogenous solution, PAN was dissolved in DMF for 2 days at 60 °C and the solution was electrospun onto the PET