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Aromatic solvent-assisted interfacial polymerization to prepare high performance thin film composite reverse osmosis membranes based on hydrophilic supports

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ABSTRACT

We report an aromatic solvent-assisted interfacial polymerization (IP) method to prepare high performance thin film composite reverse osmosis (RO) membranes based on a polyacrylonitrile support. The use of toluene and xylene as an organic solvent phase led to excellent water flux and unprecedentedly high NaCl rejection (~99.9%), exceeding both the control membrane prepared using a conventional aliphatic solvent (*n*-hexane) and commercial RO membranes. The membrane prepared using *n*-hexane had a thick and moderately dense PA layer, due to the limited amine monomer diffusion, accounting for its relatively low performance. In contrast, the membranes fabricated using toluene/xylene had roof-like structures covering a thin and highly dense basal PA layer, which was formed by increased amine diffusion and an expanded miscible interface zone resulting from the enhanced miscibility of toluene/xylene with water. The excellent membrane performance achieved using toluene/xylene can be attributed to the thin and highly cross-linked basal PA layer.

1. Introduction

Polyamide (PA) thin film composite (TFC) membranes are the most commonly used reverse osmosis (RO) membranes for water treatment and seawater desalination due to their high permselectivity [1,2]. TFC RO membranes are conventionally prepared *via* interfacial polymerization (IP) of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers dissolved in aqueous and organic phases, respectively, to produce an ultrathin PA permselective layer on top of a porous support [3,4]. Practically, the porous support is first impregnated with an MPD aqueous solution and then placed in contact with a TMC solution in an organic solvent (typically aliphatic hydrocarbon solvents such as hexane, heptane, octane and decane) to induce the IP reaction [3].

Although the conventional IP method has been highly refined, there are still some technical limitations. Specifically, the structure and performance of the IP-assembled TFC membranes are affected by the structure (*i.e.*, pore size, pore distribution and porosity) and chemical properties (*i.e.*, chemistry and hydrophilicity) of the support used [3–10]. This imposes constraints on the selection of viable supports, restricting the application of TFC membranes to a narrow range of environments. This is related with the fact that most commercial RO membranes are fabricated exclusively using relatively hydrophobic polysulfone (PSF) and polyethersulfone (PES) supports [6,9]. These supports have low organic solvent resistance, so the TFC membranes are unsuitable for environments that contain organic solvents [11]. In addition, although hydrophilic supports are beneficial for osmotic pressure-driven separation processes such as forward osmosis and pressure-retarded osmosis, fabricating a high rejection selective layer on a hydrophilic support is challenging [8,12–15]. Klaysom and colleagues have made extensive efforts to improve RO performance based on hydrophilic polyacrylonitrile (PAN) supports by optimizing the IP process, but the maximum attainable NaCl rejection was still far below acceptable RO rejection levels [16].

In the IP process, MPD impregnated in the support pores

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diffuses toward the organic solvent phase to react with TMC due to its reasonable solubility in the organic phase, leading to the formation of an incipient PA layer though which MPD subsequently migrates, causing the layer to grow [17]. Thus, the formation and structure of the PA layer are governed by the MPD diffusion behavior, which is in turn determined by interfacial tension and MPD solubility in the organic solvent [18–25]. When a hydrophilic support is used, its strong affinity with MPD retards MPD migration toward the organic phase [6,17,26], while the low MPD solubility and high interfacial tension with water for conventional aliphatic organic solvents also limit the MPD diffusion rate, making it very difficult to produce defect-free, highly-selective PA layers [16,17,26]. Previous research has sought to enhance membrane performance by adding solvent additives such as acetone, ethyl acetate, diethyl ether and dimethyl sulfoxide into the aliphatic hydrocarbon solvent during the IP process in order to reduce interfacial tension and enhance MPD solubility in the organic phase [22–25]. Although this can greatly enhanced water permeability, salt rejection was often sacrificed with showing the flux-rejection trade-off [22–25]. As a result, establishing an alternative organic solvent system that enables the fabrication of high performance RO membranes based on hydrophilic supports is of fundamental and practical importance.

Aromatic hydrocarbon solvents such as toluene and xylene have lower interfacial tension with water and greater MPD solubility than conventional aliphatic hydrocarbons, which can facilitate MPD diffusion and thus promote the IP reaction, possibly resulting in high membrane performance. Despite these potential advantages, aromatic hydrocarbon solvents have not yet been employed to fabricate TFC RO membranes, mainly due to the fact that conventional PSF and PES supports have poor solvent resistance.

In this study, we employed for the first time aromatic hydrocarbon solvents (toluene and xylene) to fabricate highly permselective RO membranes using a PAN support. Although it is difficult to fabricate highly selective PAN-supported RO membranes [16], PAN was chosen owing to its high hydrophilicity, which is beneficial for osmosis-driven applications, and its excellent organic solvent resistance, which enables toluene and xylene to be used in the IP process and the prepared TFC membranes to be employed in chemically harsh conditions containing organic solvents. It was shown that the PAN-supported membranes prepared using toluene or xylene exhibited excellent water flux and remarkably high NaCl rejection (~99.9%), exceeding the performance of both a control membrane prepared using a conventional aliphatic hydrocarbon solvent (*n*-hexane) and commercial RO membranes. The MPD diffusion behavior toward the organic phase was examined using liquid chromatography for the aliphatic and aromatic hydrocarbon solvents. In addition, the structure and physico-chemical properties of the membranes were comprehensively characterized to correlate them to membrane performance and elucidate the IP mechanism involved in the use of the particular organic solvent type.

2. Experimental

2.1. Materials

The following chemicals were uses as purchased: *m*-phenylenediamine (MPD, 99.0%, Tokyo Chemical Industry), trimesoyl chloride (TMC, 98.0%, Tokyo Chemical Industry), sodium chloride (NaCl, 99.0%, Samchun Chemical), *n*-hexane (95.0%, Daejung Chemical), toluene (99.8%, Daejung Chemical), xylene (98.5% sum of *o*-, *m*-, *p*-xylene, Daejung Chemical). Deionized (DI) water was supplied using a purification system (Millipore Milli-Q). Polyacrylonitrile (PAN) ultrafiltration membranes (PAN50) were obtained from Sepro Membranes Inc. Two commercial RO membranes, SWC4+ and SW30HR, were purchased from Hydranautics/Nitto Denko and Dow Filmtec, respectively.

2.2. Membrane preparation

The TFC RO membranes were prepared using PAN supports *via* the conventional IP method with three different organic solvents (*n*-hexane, toluene and xylene). Table 1 presents the properties of the organic solvents used in the IP process. Compared to *n*-hexane, both toluene and xylene have solubility parameters closer to water, a lower interfacial tension with water and higher solubility in water, indicating their greater affinity (miscibility) with water. To prepare the TFC membrane, a PAN support was first soaked into an MPD (1.0–7.0 w/v. %) aqueous solution for 10 min and the excess MPD solution was removed with an air knife. The support was then brought into contact with a TMC (0.125–4.0 w/v. %) solution in the predetermined organic solvent (*n*-hexane, toluene or xylene) for 3–60 s to create a PA selective layer. The prepared TFC membrane was washed with a pure organic solvent to remove the residual TMC and then dried at 70 °C for 5 min. The TFC membranes prepared with *n*-hexane, toluene and xylene are hereafter referred to as TFC-hexane, TFC-toluene and TFC-xylene, respectively.

2.3. Diffusion behavior of MPD monomers

The diffusion dynamics and solubility of MPD toward the organic solvents were characterized by monitoring the MPD concentration over time in the organic phase which had been contacted with the MPD aqueous solution, as proposed in the literature [21]. First, an MPD (4.0 w/v. %) aqueous solution of 20 mL was added into a 50 mL beaker, and then the organic solvent (*n*-hexane, toluene or xylene) of 20 mL was carefully added by pouring it along the side of the beaker. The organic solution samples were collected at set time intervals and their MPD concentrations were determined using high performance liquid chromatography (HPLC, Agilent Technologies 1200 series). The diffusion dynamics was characterized by the ratio of the MPD concentration in the organic phase ($C_{organic}$) to that in the aqueous phase ($C_{aqueous}$) as a function of time.

2.4. Membrane characterization

The surface morphology of the membrane was examined with scanning electron microscopy (SEM, Hitachi S-4800). The cross-section morphology of the membrane was characterized with transmission electron microscopy (TEM, FEI Titan TM 80–300) with an accelerating voltage of 300 kV. The membrane was embedded in EPON™ resin (Polybed 812), followed by curing at 60 °C for 24 h. An ultramicrotome was then employed to obtain thinly sliced samples (~60 nm in thickness). The chemical structure and atomic composition of the membrane were analyzed with Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS), respectively. FT-IR was performed on a Nicolet IS10 spectrometer (ThermoFischer Scientific) with an attenuated total reflectance unit, while XPS analysis was performed on a PHI-5000 Versaprobe spectrometer. The surface charge and water wettability of the membrane were analyzed using the zeta potential and water contact angle measurements, respectively. The surface zeta potential of the membrane was measured with an electrophoretic measurement apparatus (ELSZ, Otsuka Electronics) in a NaCl (10 mM) aqueous solution at pH 5.8. The water contact angle of the membrane was measured using a contact angle measurement apparatus (Pheonix-300, SEO Corporation).