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Open porous hydrophilic supported thin-film composite forward osmosis membrane via co-casting for treatment of high-salinity wastewater

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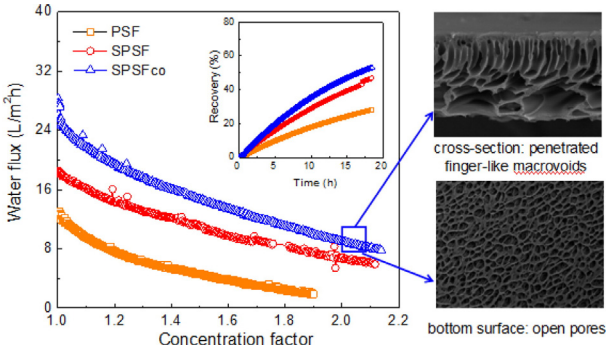
HIGHLIGHTS

- Hydrophilic substrates were prepared via single and co-casting approaches.
- Open pores were formed in the bottom surface using co-casting method.
- TFC FO membranes were prepared based on the two substrates.
- TFC FO membrane with hydrophilic support via co-casting method showed the lowest *S* value.
- Water flux was improved with TFC FO membrane in treating synthetic produced water.

GRAPHICAL ABSTRACT



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ABSTRACT

High-performance thin film composite (TFC) forward osmosis (FO) membranes with a low degree of internal concentration polarization (ICP) are critical for concentrating high-salinity wastewaters. This report focuses on the preparation of TFC FO membranes via a sacrificial approach. In order to improve the FO flux, hydrophilicity and morphology of the support membrane were mainly investigated. The hydrophilicity of the polysulfone (PSF) substrate was tuned by blending with sulfonated poly (ether ether ketone) (SPEEK), and the resulting SPEEK blended PSF membrane was denoted as SPSF substrate. The pore structure of the SPSF membrane was tailored by the application of a co-casting technique, which yielded a TFC membrane with a structure parameter (*S*) of 191 μm. In contrast, the TFC membranes based on the PSF and SPSF substrates through single layer casting showed *S* values of 527 μm and 361 μm, respectively. These results indicate that the combined hydrophilicity and open pore structure are responsible for the lowered *S* value. Further application of the hydrophilic substrate based TFC membranes in the treatment of high salinity wastewaters (10 wt%) demonstrated the higher initial water flux (28.3 L/m^2·h) with a water recovery rate of 53.2% in comparison to the TFC membrane based on the pristine PSF through the single layer casting. This new method paves a way to generate high-performing FO membranes.

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1. Introduction

Hydraulic fracturing is an effective technology in the exploration of shale gas, an important unconventional natural gas, which has been considered as an essential component of the global energy system to ensure sustainable energy supply [1–5]. However, hydraulic fracturing process discharges large amounts of high-salinity flowback and produced water with total dissolved solids (TDS) ranging up to 400,000 mg/L [6], and frequently the water contains a wide spectrum of organic compounds. Conventional physical, chemical, and biological treatment technologies are confront of large footprint and high capital and operational costs, and therefore energy and cost efficient processes are needed to be developed [7].

In contrast to pressure-driven processes, forward osmosis (FO), a diffusion based membrane process, utilizes the osmotic pressure difference as the driving force for the transport of water through the membrane. FO is characterized by its low operational pressure, low fouling tendency, easy operation, process safety and small footprint [8–10]. Desalination of high-salinity wastewater using FO processes has been demonstrated in literatures [11–14]. Similar to other membrane processes, the performance of the FO membrane is vital. However, a desired high FO flux has not been obtained during treatment of high-salinity produced water, which has been mostly attributed to the negative influence of internal concentration polarization (ICP). For example, Cath et al. investigated the FO treatment of high salinity wastewater from oil and gas exploration [15]. Further, Oasys Water reported the treatment of high-salinity brine streams and wastewater with average TDS of 73,000 ± 4200 mg/L from oil & gas exploration [16] using the FO processes. We have demonstrated the applications of FO for the treatment of shale gas drilling flowback fluids [17,18] and underground brine [19]. In particular, we have found that when a high salinity feed was used, the FO flux was much lower due to the severe dilutive ICP in the draw side, concentrative external concentration polarization (ECP) in the feed side, and reverse solute flow from the draw to the feed solution. Therefore, development of membranes with reduced ICP plays an important role in treatment of feed streams with high-salinity through FO process.

Membrane structure and property determine the degree of ICP that takes place within the porous support of a FO membrane, which cannot be mitigated by enhancing the operating conditions [20]. Membrane structure parameter is normally taken as a direct indication of the degree of ICP, which is determined by the membrane porosity, tortuosity and thickness. We have found that improving the porosity of the substrate layer via a co-casting technique can effectively reduce the membrane structure parameter [21]. Also, it has been demonstrated that membrane substrate wettability also affects FO flux in that wettability of the substrate determines the effective areas for mass transport [22]. More specifically, intrinsically hydrophilic materials can improve the wetting of membrane pores leading to enhanced effective areas for osmotic flow to take place and consequently an increased membrane flux. For instance, hydrophilic nylon 6,6 substrate was used as support for TFC membrane preparation. The resulting TFC membranes showed improved water flux due to increased wetting pores [23]. Similarly, Tang and co-workers reported reduced structure parameters of the polysulfone substrate by incorporation of porous zeolite nanoparticles, resulted from the improved surface porosity and wettability [24]. Sulfonated poly (ether ether ketone) (SPEEK) is a hydrophilic polymer, which could be utilized to control the wetting property of the substrate membrane. Chung and coworkers [25] demonstrated that addition of SPEEK to PSF improved the hydrophilicity of the substrate, and the water flux of resultant TFC FO membrane increased by 50% compared to the pristine membrane.

Co-casting has been demonstrated as an effective engineering approach to increase the porosity and pore connectivity of the substrate [26–28]. Modification of the membrane morphology has been systematically investigated and demonstrated by He et al. [26,27,29]. When a PSF/DMAC solution was co-cast above a PEI solution, during the immersion phase separation process, the PEI sublayer acts as an additional solvent reservoir and promotes formation of finger-like macrovoids to penetrate across the PSF layer [21]. After phase separation and membrane formation, the PEI delaminated from PSF layer, resulting in a PSF support membrane with an open bottom surface morphology, consequently a higher porosity. Results have shown that the structural parameter of the TFC co-cast membrane was reduced. Based on above arguments, it can be seen that the increase in the support membrane hydrophilicity and porosity separately can effectively improve the membrane performance. It would intrigue to see the effects of combined effects of improved porosity and hydrophilicity. However, application of co-casting to form hydrophilic substrate has not yet been reported for the preparation of TFC membrane.

In order to improve the FO flux when feed water salinity is high, the combination of porosity and hydrophilicity in the substrate for TFC FO membrane is investigated. TFC FO membranes were prepared using a SPEEK blended hydrophilic substrate using a co-casting approach. The single layer cast membrane was used for comparison where morphologies, porosity, and water permeability of the substrates were analyzed. TFC membranes based on these substrates were characterized, and their performance in RO and FO processes were evaluated. Finally, the FO performance in concentrating synthetic produced water was examined in order to confirm the effects of co-casting and substrate hydrophilicity.

2. Materials and methods

2.1. Materials

SPEEK with a sulfonation degree of 77% was supplied by Shanghai Erane Tech. Co. Ltd. Polysulfone (PSF, P-3500NT) was purchased from Solvay. Polyetherimide (PEI M1000) was supplied by GE. PSF and PEI particles were dried at 65 °C for 24 h in an oven before usage. *N,N*-dimethyl acetamide (DMAc), *N*-methyl pyrrolidone (NMP), *n*-hexane, polyethylene glycol (PEG 400), NaCl, KCl, $KHCO_3$, $CaCl_2$, $MgCl_2$, $BaCl_2 \cdot 2H_2O$, and $SrCl_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. *m*-phenylenediamine (MPD, purity > 99%) and trimesoyl chloride (TMC, purity 98%) were obtained from Sigma-Aldrich. All chemicals were used as received unless stated otherwise.

2.2. Membrane substrates preparation

PEI/NMP (17/83 wt%), PSF/SPEEK/PEG400/DMAC (18/0.5/8/73.5 wt%) and PSF/PEG400/DMAC (18/8/74 wt%) solutions were separately prepared in a jacketed flask at 65 °C for 24 h. After filtered and degassed, two distinguish approaches, single casting and co-casting methods, were adopted for preparation of support for FO membranes. Detailed information of the two casting protocols can be found in our previous publications [7,18,21]. Membrane substrates fabricated using the single-layer casting approach are denoted as PSF (without SPEEK) and SPSF (with SPEEK), respectively.

For the preparation of membrane support through co-casting process, the PEI/NMP mixed solution was first cast onto a dried and clean glass plate with the casting knife height of 50 μm; simultaneously the PSF solutions with SPEEK were casted on the top of the PEI solution using another casting knife of 250 μm. Then, the nascent double-layers film was swiftly transferred into a water bath with tap water at 30 ± 1 °C for phase inversion. During phase inversion, it was found that the PEI layer was automatically delaminated from the PSF layer. The left PSF layer (named as SPSFco) was rinsed thoroughly in DI water and then stored in a plastic box with DI water for further usage.

2.3. Preparation of polyamide TFC-FO membranes

The polyamide separated layer was synthesized on the top of the membrane support by interfacial polymerization [30,31]. Briefly, the support layer was tailored and fixed onto the plexiglass frame with no