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Fabrication of thin film composite forward osmosis membrane using electrospun polysulfone/polyacrylonitrile blend nanofibers as porous substrate

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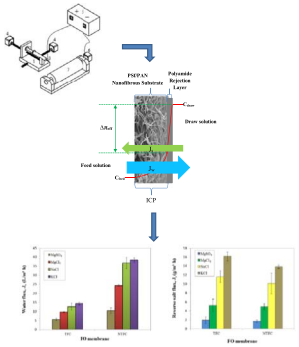
GRAPHICAL ABSTRACT



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ABSTRACT

This work investigated the influence of a new polymeric blend of polysulfone/polyacrylonitrile (PSf/PAN) nanofibers prepared via the electrospinning process as substrate to produce thin film composite forward osmosis (TFC-FO) membrane. The solvents in the electrospinning process were optimized. A polyamide (PA) thin layer was successfully fabricated on the electrospun nanofibrous substrate via interfacial polymerization. The performance of the nanofiber-based thin film composite (NTFC) membranes was compared with the in-house-made (PSf/PAN) TFC membrane, in which its substrate was fabricated by phase inversion. The NTFC membrane demonstrated significant improvement in hydrophilicity and water permeability, and the reverse salt flux (RSF) was reduced. In addition, the structural parameter (S) value of the fabricated NTFC decreased considerably which represented the reduction of internal concentration polarization (ICP) during the FO process. These achieved results were due to nanofiber structural characteristics such as high porosity and interconnected open pore structure. The effects of different salts as draw solutions (NaCl, KCl, $MgCl_2$, $MgSO_4$) on the osmotic performance of the NTFC and TFC membranes were evaluated. Among the tested draw solutions with the same osmotic pressure, the NTFC membrane exhibited higher water flux (38.3 LMH) than that of the TFC membrane (14.3 LMH) for KCl draw solution.

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1. Introduction

Considering the shortage of natural sweet water sources as well as an increased in demand for fresh water due to global population growth, the development of alternative water sources such as treated seawater and wastewater has been enhanced [1–4]. Forward osmosis (FO) is a developing technology that has recently attracted much attention because of its potential application in the production of clean water. FO enjoys lower energy consumption compared to pressure-based membrane processes such as reverse osmosis (RO) and nanofiltration (NF) [5–8]. Forward osmosis is a membrane process wherein water passes across semi-permeable membrane due to the osmotic pressure difference between draw solution (DS) which has a higher osmotic pressure and the feed solution (FS) with a lower osmotic pressure without any need for hydraulic pressure [7–9]. Generally, the FO process offers numerous advantages over other membrane processes including: lower energy consumption [10], higher recovery [11] and lower fouling tendency that results in reduced cleaning [12,13].

A desired membrane for the FO process must have the following characteristics: high water permeability, excellent solute rejection, low internal concentration polarization (ICP) and appropriate mechanical strength [14,15]. Despite the various advantages of the FO process, one of its major drawbacks is the unfavorable ICP phenomenon generated in the membrane substrate which leads to a considerable reduction in the effective osmotic driving force [16–18]. Thus, the reduction of water flux in the FO process can be attributed to the ICP [17,19], in which up to more than an 80% decrease in the water flux is reported [4,20]. The ICP is an unavoidable phenomenon in osmotically-based membrane processes that occurs within the support layer of the membrane [4,21]. Based on previous studies, the ICP can be decreased by tuning the substrate membrane structure [22–25]. Generally, in addition to having an active layer with high water permeability and high selectivity, the substrate of the FO membrane also should be thin (thickness, L) as well as possessing a high porosity (ε) and low tortuosity (τ) (i.e., the structural parameter should be small, $S = L.\tau/\varepsilon$) in order to increase the mass transfer and decrease the ICP [26,27].

Early in FO processes the cellulose triacetate (CTA) and cellulose acetate (CA) commercial asymmetric membranes were used. The support layer of the foresaid membranes were made using the phase inversion method [28,29]. However, a sponge-like structure of the support layer created a drastic internal concentration polarization that caused a low osmotic water flux. Further studies have focused on the development of commercial and lab-made thin film composite forward osmosis membranes which included a very thin polyamide layer that was fabricated via interfacial polymerization in the top surface of the polymeric substrate prepared by the phase inversion method [26,30,31]. These membranes showed a relatively higher water flux and salt rejection compared to the cellulosic membranes [30]. The FO performance was strongly limited due to ICP in the substrate membrane that arose from the tortuous morphology [32]. Therefore, new substrates are needed that provide minimal tortuosity and thickness coupled with high porosity. This can be accomplished by replacing the substrate casted with an electrospun nanofibrous substrate which fulfills the above mentioned criteria with its interconnected open pore, and high special surface area [33]. These unique specifications led to the efficient use of the nanofiber mats as TFC-FO membrane substrate.

Recently, achievements have been reported in the use of the nanofibrous substrates produced via the electrospinning process in order to fabricate nanofiber-based thin film composite (NTFC) membranes [32]. Bui et al. reported that NTFC membranes prepared onto PSf and polyethersulfone (PES) nanofibrous substrates exhibited 2 to 5 times higher water flux than commercial FO membrane [34]. Polyvinylidene fluoride (PVDF) nanofibers was used as substrate with different pore sizes for making FO membrane and the results revealed that a denser and low permeable polyamide layer was formed onto a electrospun substrate with smaller pore size. They concluded that the cross-linking degrees during interfacial polymerization was associated with the substrate morphology [35]. Nylon 6,6 was used by Huang et al. (2014) to fabricate nanofibrous substrate due to its natural hydrophilicity and excellent strength. They demonstrated that the structural parameter of the synthesized substrate was half of the commercial FO membrane. As a result, the water flux was almost doubled without a considerable reduction in salt rejection [36].

Generally, the polymeric solution used in the substrate synthesis should be optimized to achieve a suitable hydrophilicity, chemical stability and mechanical strength [33]. In order to decrease ICP, using various approaches to enhance the hydrophilicity of the substrate of FO membranes. These methods include the use of carboxylated [37] and sulfonated polymers [38,39], polydopamine coating on the substrate surface [40], copolymerization process [30] and use of hydrophilic nanoparticles [24,25,41,42]. The Blending of polymers is also an efficient method to achieve new properties of the polymeric solution with less complexity [43]. Blending not only improves the properties of membrane fabricated from single polymer but also enhances the water flux of the membrane by the reducing ICP [44]. Actually, these membranes show better permeability than the membrane composed from the single polymer [45,46].

The main purpose of this study is the synthesis of a new NTFC membrane in order to decrease ICP and improve membrane performance during the FO process. Polysulfone (PSf) is an ideal polymer in the membranous industry because of its excellent properties such as mechanical, chemical and thermal resistance, as well as its low price. Nonetheless, polysulfone is a hydrophobic polymer, which should be modified by appropriate methods. The blending of PSf and a polymer with higher hydrophilicity and spinnability (i.e. polyacrylonitrile, PAN) was used to decrease ICP. Ai-Lian and Qing reported that these two polymers are partly miscible and showed good performance in ultrafiltration membrane fabricated by casting method [47]. A PSf/PAN blend of nanofibrous substrate was synthesized. Followed by fabrication of a polyamide ultrathin layer. The polymeric solvents were optimized by changing the volumetric ratio of 1-methyl-2-pyrrolidone (DMF) and *N*,*N*-dimethylformamide (NMP). The performance of the NTFC membrane was compared to a in-house-made TFC membrane. The morphology and membranes structure were characterized using scanning electron microscopy (SEM) images, contact angle analysis, porosity measurements, and mechanical properties testing machine. We also investigated the influence of different draw solutions (KCl, NaCl, $MgCl_2$, $MgSO_4$) on the forward osmosis performance in terms of the water flux and salt rejection in the constant osmotic pressure for both the NTFC and TFC membranes.

2. Materials and methods

2.1. Materials

Polysulfone (PSf, Ultrason S 601, M_w = 60,000 g mol^{-1}, BASF) and polyacrylonitrile (PAN, M_w = 150,000 g mol^{-1}, Aldrich) were used as received without further purification to prepare the electrospun nanofibrous mats. 1-methyl-2-pyrrolidone (NMP, 99.5%, Daejung) and *N*,*N*-dimethylformamide (DMF, 99.5%, Merck) were used as solvents in the polymeric solution. *M*-phenylenediamine (MPD, ≥99%, Acros organics) and 1,3,5-benzenetricarbonyl chloride (TMC, Aldrich) and n-hexane (> 95%, Daejung) were employed to fabricate the polyamide rejection layer via interfacial polymerization. The salts of sodium chloride (NaCl, 99.9%, Pars Namak Co.), potassium chloride (KCl, ≥99.0%, Sinchem), magnesium chloride ($MgCl_2$, > 98.0%, Daejung), and magnesium sulfate ($MgSO_4$, > 98.0%, Chemsworth) were used for the forward osmosis tests.