Hydrophilic polyvinyl alcohol coating on hydrophobic electrospun nanofiber membrane for high performance thin film composite forward osmosis membrane

Myoung Jun Park[a], Ralph Rolly Gonzales[a], Ahmed Abdel-Wahab[b], Sherub Phuntsho[a],*, Ho Kyong Shon[a],*

[a] Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney (UTS), P.O. Box 123, 15 Broadway, NSW 2007, Australia
[b] Chemical Engineering Program, Texas A & M University at Qatar, PO Box 23874, Doha, Qatar

GRAPHICAL ABSTRACT
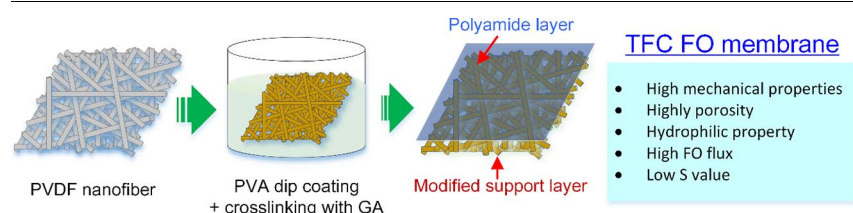
ARTICLE INFO

ABSTRACT

In this study, the hydrophilic property of polyvinyl alcohol (PVA) was utilized to improve the hydrophilicity and mechanical strength of electrospun polyvinylidene fluoride (PVDF)-supported thin film composite (TFC) forward osmosis (FO) membranes. The PVDF nanofiber support was modified with PVA via dip coating and acid-catalyzed crosslinking with glutaraldehyde prior to formation of polyamide active layer on the support via interfacial polymerization. The influence of PVA modification on the morphology and physical properties of PVDF support was evaluated through several characterization techniques while the flux performance was assessed using lab-scale FO membrane unit. The fabricated PVA-modified TFC FO membranes exhibited high hydrophilicity, porosity, and mechanical strength. FO performance tests reveal excellent flux performance (34.2 LMH using 1 M NaCl and DI water as draw and feed solution, respectively) and low structural parameters (154 μm) of the PVA-modified TFC FO membrane. Dip coating of the nanofiber support in PVA is therefore a simple and effective method for the improvement of PVDF support hydrophilicity to fabricate high performance TFC FO membranes.

1. Introduction

Rapid population growth and continuous economic development have resulted in significant increase for the demand and accessibility to clean water. To address the water scarcity crises, seawater desalination and wastewater reuse are the most adopted solutions for providing fresh and clean water supplies to the general populace [1–6]. Reverse osmosis (RO) process is the most prevalent membrane-based separation process for seawater desalination. However, RO technology faces major challenges due to its high energy cost and frequent membrane scaling and fouling problems [7]. Forward osmosis (FO) is an alternative membrane-based separation process that relies on the osmotic pressure gradient driving force which is generated by the difference in salt concentrations between the feed and draw solutions. This osmotic

---

* Corresponding authors.
    E-mail addresses: Sherub.Phuntsho@uts.edu.au (S. Phuntsho), Hokyong.Shon-1@uts.edu.au (H.K. Shon).

pressure difference drives water passage across a semi-permeable membrane while retaining contaminants and unwanted elements in the feed solution.

Unlike the hydraulic pressure-driven RO process, FO requires a relatively lower energy consumption and has a lower propensity to fouling [8,9]. Apart from seawater desalination and water treatment, FO process is a relatively new technology which can be used for various applications such as osmotic power generation [3,10–12], pharmaceutical industry [13], food processing [14], concentrating underground brine [15] and direct irrigation [16]. But for all of these applications, the efficiency and success of the FO process heavily rely on the performance of the FO membrane.

Polymeric membranes for FO processes can be fabricated through a variety of methods, which include phase inversion, electrospinning, and hollow fiber spinning [17,18]. A FO membrane is typically made of a thin film composite (TFC). A TFC FO membrane has a porous membrane support layer which facilitates convenient water transport and a thin active layer (i.e. polyamide) responsible for high salt rejection [19–25]. Due to their higher water permeability and lower reverse solute permeability as compared to the commercial cellulose triacetate (CTA), TFC membranes have been the subject of current researches on FO membrane fabrication (Hydration Technology Innovations, Inc. USA) [24,26].

Nanofibers utilization in various membrane technology applications for water and wastewater treatment has gained growing interest during the last decade. This is due to their high stability and high chemical resistance [27]. A number of previous studies on the use of nanofibrous membranes in separation processes such as membrane distillation, ultrafiltration, nanofiltration, and reverse osmosis have been performed. Electrospinning is a practical and inexpensive method for manufacturing nanofibers with high porosity, small diameter, high strength to weight ratio, and high surface to volume ratio [25,28–31]. In addition, nanofibers fabricated using electrospun technique are known to exhibit low tortuosity as a function of the interconnected void space [28]. These properties make nanofibers a suitable substrate for interfacial polymerization for fabrication of TFC membranes. The mechanical and chemical properties of electrospun nanofibers can further be improved through treatment condition optimization, selection of suitable materials, and post-treatment.

While TFC FO membranes are known to have better performance than conventional FO membranes, structural modification of the TFC support layer could further improve its mechanical strength and water flux, thereby improving the overall membrane performance. A number of previous studies focused on modifying the TFC membrane support layer via incorporation of hydrophilic nanomaterials such as titanium dioxide (TiO_2) [19,32], graphene oxide or modified graphene oxide [21,33,34], modified carbon nanotubes [35], silica nanoparticles [36,37], and porous zeolite nanoparticles [38]. The use of these materials was found to effectively reduce the structural parameter (S) and increase the porosity of the membranes. Moreover, using hydrophilic polymers in the support layers of TFC FO membranes improved the water flux and reduced the internal concentration polarization (ICP) during FO operation [22,26,29,39–45]. The results of these studies strongly indicate that hydrophilic modification of the TFC support is an effective approach to enhance the performance of the FO membranes.

A faster way towards producing commercial high-performance FO membranes is to adapt practical approaches during membrane fabrication. A simple hydrophilization technique can be conducted by using suitable hydrophilic polymers like polyvinyl alcohol (PVA). PVA is a well-known material that is highly soluble in water, environmentally safe and it has been used in a number of membrane fabrication studies [26,46]. It is polyhydroxy (i.e. −OH groups which are good sites for further reactions) and it has good chemical resistance as well as film-forming properties. But to render it stable in aqueous phase, PVA must be cross-linked by another material that can reduce its water solubility (e.g., glutaraldehyde). Cross-linking PVA with glutaraldehyde not only

reduces PVA water solubility but also improves the mechanical strength of the TFC support.

Recently, electrospun nanofiber supports were applied as a membrane substrate for TFC-FO membrane. Several studies introduced fabrication of the TFC-FO membrane support layer using hydrophilic polymers [22,26,29,47] and these hydrophilic FO membranes showed high performance. However, one major issue pointed out was the low mechanical stability of hydrophilic nanofiber support layers due to membrane swelling when it is exposed to liquids [42,48]. To address this problem, in this study a hydrophobic polyvinylidene fluoride (PVDF) was used to prepare the nanofiber substrate for TFC-FO membrane. PVDF is a well-known membrane material that is characterized by its high mechanical and chemical stabilities. Nevertheless, the hydrophobicity of PVDF may not be suitable for FO membrane because the presence of the hydrophobic support layer of the FO membrane induces the solvent transport and membrane wettability [45,49]. In addition, membrane dehydration easily occurs especially when high salinity water is used as draw solution (DS), which reduces the effective diffusion area thus increasing ICP and reducing FO flux [50]. Therefore, the hydrophilic property of PVA was exploited to improve the wettability and mechanical properties of the TFC FO membrane that was prepared using PVDF nanofiber support. The PVDF nanofiber support mat prepared via electrospinning, was modified with PVA via dip coating and crosslinking methods prior to formation of polyamide active layer on it via interfacial polymerization. The influence of PVA coating on the PVDF nanofibers was assessed through a number of characterization methods. FO bench-scale experiments were also performed to assess the performance of the TFC membrane with PVA-coated support layer as a suitable semi-permeable layer for FO process.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF, Kynar® 761, MW = 441,000 g/mol) provided by Arkema Inc., Australia, was used as the electrospinning polymer. Polyvinylalcohol (PVA, 96% hydrolyzed, Mw 85,000–124,000) and glutaraldehyde (GA, 25% aqueous solution) from Sigma-Aldrich and hydrochloric acid (HCl, 32%) from RCI Labscan Limited, Thailand were used for nanofiber membrane coating. *N,N*-dimethylacetamide (DMAc, ReagentPlus®, 99%) and acetone (analytical reagent, 99%) were purchased from Sigma-Aldrich and Chem-Supply Pty. Ltd., respectively, and used as organic solvents. 1,3-Phenylenediamine (MPD, 99%), trimesoyl chloride (TMC, 98%) and heptane (anhydrous, 99%) from Sigma-Aldrich were used for polyamide layer formation. 2-Propanol (isopropanol, IPA, Merck) and sodium chloride (NaCl, Chem Supply) were used as membrane wetting agent and draw solution, respectively.

2.2. Preparation PVDF nanofiber support

PVDF nanofiber supports were prepared via electrospinning technique with high voltage supply of 21–23 kV. PVDF (15 w/v%) was first dissolved in DMAc/acetone (5:5 v/v ratio) at constant stirring speed of 300 rpm and temperature of 60 °C for 12 h, then the solution was cooled down prior to electrospinning. The polymer solution was transferred into a plastic syringe, and then delivered at (2 mL h^{-1}) by a syringe pump (G21, ID 0.51 mm). The nanofibers were produced over a period of 3 h and during this period, they were being collected aluminum foil cover on a drum which was 180 mm apart from the needle. Temperature and humidity conditions inside the electrospinning chamber were 22–25 °C and 35–55%, respectively. The as-spun nanofiber mats were peeled off from the aluminum foil and then dried in a dry oven at 50 °C for 24 h to remove the residual solvents from the fibers. Afterwards, the PVDF nanofiber mats were heat-treated using a heat-press machine (Digital Combo, Geo Knight & Co Inc., USA) for 10 s