Dual-skinned polyamide/poly(vinylidene fluoride)/cellulose acetate membranes with embedded woven

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Abstract

We propose multilayer membranes including (i) a thin selective polyamide (PA) layer prepared via interfacial polymerization, (ii) a poly (vinylidene fluoride) (PVDF) asymmetric porous support with high adhesion to the PA layer and high mechanical strength, (iii) a strong woven fabric, and (iv) fouling resistant porous cellulose acetate (CA) layer. The PA layer rejects solutes of the draw solution. The PVDF/woven fabric/CA (PVDF/CA) integrated layer performs as a mechanical support with unique properties for forward osmosis (FO) applications. It consists of a modified PVDF top layer suitable for the deposition of a PA layer and a highly hydrophilic bottom layer (CA) with a tunable pore size to minimize foulant deposition and intrusion onto and into the support. The experimental results using bovine serum albumin (BSA) as a model foulant show that the presence of the CA layer at the bottom of the FO membrane (PA/PVDF/CA) reduces 75 % fouling propensity compared to the simple FO membrane made of PVDF, woven fabric and PA (PA/PVDF). Fouling tests with 2000 ppm oily feed faced the bottom of the FO membranes further indicate the superiority of the PA/PVDF/CA membrane compared to the PA/PVDF membrane. Moreover, the bottom CA layer can be adjusted with a flexible range of pore size, varied from sub-micron to sub-nanometer depending on the feed composition. The newly developed multilayer FO membrane has comparable performance to the state-of-the-art membrane with added tailored fouling resistance for specific wastewater feeds.

Keywords

Dual-skinned membrane, multilayer membrane, forward osmosis, fouling resistance

Introduction

The success of separation processes such as microfiltration (MF) [1], ultrafiltration (UF) [2-4], nanofiltration [5-7], reverse osmosis (RO) [8, 9] highly depends on the chemistry of the applied membranes and strict morphology control. Membranes for these processes are mostly asymmetric. The optimal performance is hardly obtained with a single material. In most cases membranes consist of multilayers of different materials with a combination of hydrophobicity, chemical and mechanical stability and porosity gradient. A variety of commercial asymmetric membranes are available and well established in different applications, with decades of optimization. Previously available membranes developed for reverse osmosis were the starting choice for emerging applications for wastewater treatment and water reuse, such as forward osmosis (FO) and pressure retarded osmosis (PRO). However this and other emerging processes have different driving forces and operation conditions than pressure driven processes. It is expected that more optimization would be required to guarantee the full potential of the technology. Optimization could be achieved by the development of new synthesized materials or the combination of commercially available polymers in an innovative construction, tailoring pore size, hydrophilic-hydrophobic balance, adhesion between layers and embedding of mechanical supports [10-15]. In this form water permeance, selectivity, fouling and mechanical resistance could be tuned. We demonstrate here a multilayer membrane constituted by polyamide/poly(vinylidene fluoride/cellulose acetate (PA/PVDF/CA), which was specifically tailored to optimize all membrane properties required for forward and pressure retarded osmosis. We combine the use of embedded woven with strong mechanical strength and the concept of dual skin membrane in the same membrane to target maximal performance and fouling resistance. Each of these strategies has been used before separately, but not all together in a

membrane with multi-material layers. Challenges are (i) how to provide acceptable adhesion between layers of different compositions, and (ii) how to co-cast different solutions to form the final membrane, mastering pore morphology control in each layer. By succeeding, we can profit from the best advantages of each of the composing polymeric material, which are known to contribute in different ways to membrane properties:

Selectivity. Polyamide (PA), prepared by interfacial polymerization is regularly used as dense selective skin for reverse osmosis membranes, because it is possible to obtain with extremely thin thickness and high salt rejection [16-18]. This secures selectivity without compromising water permeance. PA is chosen as top selective layer in this work.

Mechanical Strength. Polyester or polypropylene woven is used to strengthen the mechanical stability of a membrane. The integration is done as a bottom layer for UF or an embedded grid in FO membranes [17, 19]. . The most known case is the commercial HTI cellulose triacetate (CTA). In this work a woven is used embedded in the interface between the CA and PVDF layer. The additional challenge in this step, when using layers of different composition, in comparison to embedding in a pure CTA membrane, is how to avoid delamination.

Pore tuning and adhesion. CA has been successfully used as membrane material for decades, with low cost, high hydrophilicity and good processability. It has advantages to reduce fouling too and was chosen as the bottom layer of the membrane in this work as described bellow. The drawbacks and reasons for not choosing a fully integral asymmetric CA membrane are the following. Although CA membrane coated with a thin PA layer would be good FO membrane, the formation of PA layer onto the hydrophilic CA support is not trivial because of their easy delamination from each other and weak mechanical properties [18, 20]. Therefore, a PVDF layer was designed in this study to enhance even more mechanical strength and to strongly link the PA

layer and the CA layers. Although CA and PVDF have different properties, such as large differences of hydrophilicity, the miscibility of the two polymer solutions and their similar precipitation rates when immersed in water lead to the good adhesion between CA and PVDF layers. While PVDF is stronger than CA and has a better adhesion with PA, having a full PVDF substrate (without the CA layer) would not be the best choice, since the fouling resistance would not be satisfactory as discussed below.

Fouling. This is an important issue in practically all membrane-based water treatment processes. The effect on separation performance is strongly dependent on the membrane orientation during operation. This is clearly seen in FO/PRO. In PRO mode, where the active layer faces the draw solution, fouling may occur on and inside the porous support, facing the feed. In addition, the feed concentration may become higher inside the porous support than in the feed (outside the membrane). This phenomenon is referred to as concentrative internal concentration polarization (ICP). In the FO mode, where the active skin faces the feed solution, fouling may occur on the dense selective layer and the draw solution is diluted inside the porous layer by the permeated water that creates a dilutive ICP. Extensive research has confirmed that the PRO mode induces a higher water flux than the FO mode due to the less severe ICP [21, 22]. However, membranes operated under the PRO mode have larger fouling propensity because foulants from the feed solution can easily intrude the porous support (internal fouling) that reduces flow channels and enhances ICP [23, 24]. As a result, flux drops significantly over time and fouling is more difficult to be removed under the PRO mode than the FO mode. Today, most practical FO applications are operated under the FO mode.

Figure 1. Schematic illustration of membrane fouling propensity in FO processes using single-skinned membrane under (a) FO mode and (b) PRO mode, and dual-skinned membrane under PRO mode.

Different approaches have been conducted to eliminate fouling and its impact on FO and PRO processes such as changing operation conditions, cleaning methods, embedding nanoparticles [25], changing material choices [26-29] and chemically modifying membrane surfaces [30]. Most studies focus on developing membranes with a fouling-resistant *selective* layer. FO membranes with fouling-resistant *support* layers are still less developed. Such membranes are urgently needed so that one can use various brine as draw solutions (i.e., seawater reverse osmosis brine) and explore FO/RO integration for higher water production [13, 31]. In this work a fouling-resistant support layer is added based on CA. An interesting approach to reduce fouling in FO/PRO membranes was originally proposed by Wang et al. [32], and subsequently explored by other groups in the field. They introduced a *dual-skinned membrane* as shown in Fig. 1. Dual-skinned FO membranes consist of a dense selective skin facing the draw solution

and a loose dense skin facing the feed side could prevent the reverse diffusion of draw solutes and at the same time prevent the foulant intrusion into the porous support. The idea is simple and has been demonstrated in a few reports using integral asymmetric membranes prepared by phase inversion [32, 33], surface coating using layer-by-layer (LbL) deposition [34, 35], interfacial polymerization [36], or combined interfacial polymerization and surface coating [37]. However there is still a need for optimization of the method and this is one of the goals of this work. The disadvantage of using CA phase inversion to provide both the selective skin and the fouling-resistant skin is that the selective skin prepared in this way has relatively low water permeance, compared to thin PA layers prepared by interfacial polymerization. Poor FO performance is then achieved. This is the reason why the PA selective layer was chosen in this work. On the other hand CA is very effective as secondary skin layer to minimize fouling. For this layer CA is more effective and versatile than the other approaches using dense coatings. It is looser than in other cases, addressing better the requirements appointed in previous mathematical dual-skinned FO membrane studies [38]. Compared to other coatings CA gives more flexibility to adjust the pore sizes of the secondary skin, when working with foulants of different size, without unnecessary loss of water permeance.

In summary the membranes proposed in this work profit from the selectivity and high water permeance of PA thin layers, low delamination and mechanical strength provided by the PVDF layer, further stability added by the embedded woven and fouling resistance given by the CA layer.

Materials

Commercially available poly(vinylidene fluoride) (PVDF, Kynar® HSV 900) was supplied by Arkema. Poly(methyl methacrylate) (PMMA, $M_w \sim 350,000$) and cellulose acetate (CA, $M_n \sim 50,000$) were purchased from Sigma-Aldrich. PVDF, PMMA and CA were dried in a vacuum oven at 60°C overnight prior to use as the membrane materials. Trimesoyl chloride (TMC), m-phenylene diamine (MPD), lithium chloride (LiCl), n-hexane, isopropanol (IPA), N-methyl-2-pyrrolidone (NMP), ethyl acetate, tween-80 and soybean oil were ordered from Sigma-Aldrich. Sodium chloride (NaCl) and acetone were obtained from Merck. Fluorescein isocyanate conjugated bovine serum albumin (BSA-FITC) was acquired from Invitrogen. Polyester woven fabric sheet (WS0050) was supplied by Industrial Netting. The woven has a nominal hole size of 50 μm and a thickness of 60 μm .

Experimental

Casting of flat-sheet membrane supports

Before casting the PVDF/woven fabric substrate, the woven fabric was attached onto a glass plate by using a waterproof adhesive tape. A 150 μm gap casting knife was used to spread the PVDF solution over the woven fabric, followed by immersion in a water coagulant bath at room temperature. After complete coagulation, the as-cast membranes were kept in water overnight for complete solvent removal.

PVDF/CA supports were fabricated with 3 layers including: (i) a top PVDF asymmetric porous layer, (ii) an embedded woven fabric layer, and (iii) a bottom CA asymmetric porous layer. Two methods were adopted to fabricate the PVDF/CA supports as illustrated in Fig. 2.

Figure 2. Fabrication steps of membrane supports by Methods (a) 1 and (b) 2 and their FESEM images.

Although the two methods were based on non-solvent induced phase separation, their casting procedures were different:

- (i) In method 1 (Fig. 2a), a thin layer of CA solution was cast with a casting knife (step 1) on a glass plate. A PVDF solution layer was cast onto a NMP pre-wetted woven fabric immobilized on another glass plate (step 2). Immediately after casting the PVDF solution, the resulting PVDF solution/woven bilayer was detached from the glass plate and attached onto the previously as-cast CA solution layer, so that the PVDF solution was placed as the top layer while the woven fabric was embedded between the PVDF and CA layers as the reinforcement (step 3). Afterwards, the multilayer set was immersed in a water coagulant bath (step 4).

- (ii) In method 2 (Fig. 2b), after casting the CA solution onto a glass plate (step 1), a woven fabric was placed on its top (step 2). A PVDF solution was then cast immediately over the woven fabric (step 3), followed by immersing the entire membrane set in a water coagulant bath (step 4).

CA supports with polymer concentrations of 8.0 wt% and 12.0 wt% were fabricated by spreading the polymer solutions onto glass plates using a 150 μm gap casting knife, followed by placing a woven fabric on top of the as-cast layer. After the phase inversion process using water as the coagulant, CA membranes with the active layers formed on the glass plate were obtained.

Interfacial polymerization of flat-sheet FO membranes

A thin PA layer was synthesized on the top of the as-prepared PVDF/woven fabric and PVDF//woven fabric/CA supports by interfacial polymerization using MPD and TMC as monomers. The support was placed in a frame so that its surface was in contact with a 3.4 wt% MPD monomer aqueous solution for 5 min. After the excess MPD solution was removed, the support surface was exposed to a 0.1% (w/v) TMC solution in hexane containing 3 wt% ethyl acetate for 1.5 min, followed by 3 min in an IPA/water (50/50, v/v) solution. The freshly prepared thin film composite membranes were dried in open air at room temperature for 1.5 min and then rinsed with DI water several times to remove unreacted monomers. The resultant membranes were stored in DI water prior to further use.

FO performance

The FO membrane performance was evaluated on a lab-scale cross-flow FO set-up. NaCl solutions of various concentrations were used as draw solutions while DI was used as the feed. The experiments were carried out at 23 ± 1 °C with feed and draw solutions flowing counter-currently on each side of the membrane. Water flux (J_v , $\text{Lm}^{-2}\text{h}^{-1}$, abbreviated as LMH) and reverse salt flux (J_s , $\text{gm}^{-2}\text{h}^{-1}$, abbreviated as gMH) were measured using the following equations:

$$J_v = \frac{\Delta V}{A_{\text{eff}} \Delta t} \quad (1)$$

and

$$J_s = \frac{\Delta(C_t V_t)}{A_{\text{eff}} \Delta t} \quad (2)$$

where ΔV (L) is the volume of water that has permeated across the membrane in a predetermined time Δt (h) during the tests. A_{eff} is the effective membrane surface area (m^2). C_t and V_t are the salt concentration (g/L) and the volume of the feed (L) at the end of the tests, respectively. The feed conductivity was measured by a ProfiLine Cond 3310 conductometer (WTW, Germany).

Protein adhesion test

Bovine serum albumin (BSA) was used as a model organic foulant in this study. The foulant adsorption propensity on PVDF, PA and CA surfaces was evaluated by measuring the fluorescence intensity of the support surfaces after exposing them to a BSA-FITC solution (0.5 mg/mL) for 1 h and imaged by an epifluorescence optical microscope (Olympus BX61) with a filter for 495/520 nm. The images were analyzed using ImageJ software.

Organic fouling test

The organic fouling tests were performed with a lab-scale system as described in the previous FO performance section at a cross-flow velocity of 10 cm/s. An oily feed solution was used as a feed model containing with high propensity organic foulant. The oily feed solution was prepared by emulsifying soybean oil and tween 80 in 1000 ppm NaCl solution to form 2000 ppm oil in water (OiW) emulsion [39]. Besides fouling experiments, baseline experiments were conducted using the same method as fouling experiments except that DI water was used as the feed solution. The extent of the flux decline associated with oil particle adsorption was evaluated by normalizing the fouling data to the baseline data.

Results and discussion

Fig. 2 compares the morphologies of supports prepared by the two casting methods. Our aim is to obtain multilayer and robust PVDF/woven/CA (referred to as PVDF/CA) supports for thin-film composite FO membranes. As aforementioned, the PVDF asymmetric porous layer is for the formation of the polyamide layer by interfacial polymerization, the woven fabric acts as a mechanical support and the CA layer rejects foulants. The porous support prepared by Method 1 has a thick woven embedded PVDF layer and a thin CA bottom layer. No much interactions and interpenetration can be observed between the two layers. The porous support prepared by Method 2 shows better interpenetration between these two materials because the casting step 3B helps link the two layers together. As a result, the support has a thicker CA bottom layer and a thinner PVDF top layer. Since CA is more hydrophilic than PVDF, the resultant support may exhibits lower water resistance and would improve water flux and reduce ICP in the PVDF/CA supported FO membrane. Therefore, all subsequent studies were based on the PVDF/CA supports fabricated by Method 2.

Figure 3. FESEM images of PVDF/CA (12%) membranes before and after the interfacial polymerization process.

The PVDF/woven fabric/CA support was prepared using a 12.0 wt% CA casting solution. The casting knife was set with gaps of 80 μm and 200 μm when casting the CA and PVDF layers, respectively. Fig. 3 shows its surface and cross-section morphologies and the corresponding PA composite membrane. The total thickness of the PVDF/woven fabric/CA support is approximately 105 μm with PVDF and CA layers of about 35 μm and 70 μm , respectively. The high magnification cross-section image shows very strong adhesion between the PVDF and CA layers without any delamination. The inner structure of the PVDF/CA support is fully porous and asymmetric with inter-connecting pores. While the PVDF layer has a finger-like macrovoid structure, the CA layer has a macrovoid-free and fully sponge-like structure. The

macrovoid-free structure of the CA layer is formed due to its well-known hydrophilic nature that promotes a slower demixing during the phase inversion process. The PVDF surface is porous with small pores of < 100 nm in diameter. The pure water permeance of the multilayer support is $1236 \text{ Lm}^{-2}\text{h}^{-1}/\text{bar}$ (Table S1). After the interfacial polymerization the surface is fully covered by a thin polyamide with rough ridge-valley and globular structures. While a fully porous structure is seen in the bulk of the CA layer, a relatively dense skin is observed on the bottom surface. The skin is formed during the phase inversion due to the strong interaction between CA and the glass plate.[33]

Figure 4. FESEM cross-section (top) and bottom surface (bottom) images of (a) PVDF and (b) PVDF/CA (8%) porous supports.

Three types of supports were prepared with the same total casting knife gap of 200 μm : (i) PVDF/woven fabric (referred to as PVDF); (ii) PVDF//woven fabric/CA prepared using 8.0 and 12 wt% CA solutions (referred to as PVDF/CA(8%) and PVDF/CA(12%), respectively). The cross-section and bottom surface morphologies of all substrates are presented in Fig. 3 and 4. Although the same gap height of casting knife was used during casting, the PVDF support has a thickness of $\sim 125 \mu\text{m}$, while the PVDF/CA one has a thickness of $\sim 105 \mu\text{m}$. The water contact angles of the PVDF and CA layers are 87 and 56, respectively, as shown in Table S1, indicating the PVDF layer is more hydrophobic than the CA layer.

Table S1 compares their water permeances measured by filtration in dead-end cells. Due to the high hydrophilicity and large pore size (Fig. 4) of the CA(8%) support, it has almost 4 times higher pure water permeance than the PVDF support (Table S1). However, the CA(12%) support has a lower permeance than the PVDF support.

Table 1. Comparison transport properties and structural parameters of single-skinned and dual-skinned FO membranes.

Membrane ID	Water permeance ^a A ($\text{Lm}^{-2}\text{h}^{-1} \text{ bar}^{-1}$)	Salt rejection ^b R_s (%)	Salt flux ^b B ($\text{Lm}^{-2}\text{h}^{-1}$)	Structural parameter S ^c (μm)
PA/PVDF	1.178	91.4	0.370	463
PA/PVDF/CA(8%)	1.208	91.1	0.395	391
PA/PVDF/CA(12%)	1.109	91.3	0.351	549

^aTested using DI water as feed.

^bTested using 2000 ppm NaCl as feed; nanofiltration mode operation at 5 bar.

^cStructural parameters were calculated based on experiments under PRO mode using 2 M NaCl as draw solution and DI water as feed.

After the interfacial polymerization, Table 1 shows the transport properties and structural parameter (S) of the final membranes while Fig. 5 and 6 display their FO performance under FO and PRO modes, respectively. The PA/PVDF/CA(8%)- membrane has better FO and PRO performance than the PA/PVDF- membrane with draw solution concentrations ranging from 0.5 to 2 M (Fig. 5 and 6) because of lower ICP. While the water permeances and salt rejections of membranes with different supports were comparable, a lower S value (391 μm) was measured from the PVDF/CA(8%) support (Table 1). Therefore, the PA/PVDF/CA(8%)- membrane gives an overall better FO and PRO performance among these 3 membranes, as confirmed in Fig. 5 and 6, respectively.

Figure 5. Water fluxes (J_v) and reverse salt fluxes (J_s) as a function of draw solution concentration. Results for PA/PVDF, PA/PVDF/CA(8%), and PA/PVDF/CA(12%) membranes under the FO mode.

Figure 6. Water fluxes (J_v) and reverse salt fluxes (J_s) as a function of draw solution concentration. Results for PA/PVDF and PA/PVDF/CA(8%) membranes under the PRO mode.

When the support was prepared from a 12 % CA solution, the bottom surface of the CA layer was relatively dense without any visible pores (Fig. 3). Hence, the PA/PVDF/CA(12%) membrane has two skins including a selective polyamide top skin for solute rejection and a looser CA bottom skin for foulant rejection. As compared in Fig. 6, the PA/PVDF/CA(12%) membrane has the lowest water flux under the PRO mode because (1) it has the lowest A value (Table 1), (2) its substrate has the highest S parameter (Table 1) and (3) the lowest water permeance (Table S1). This is due to the fact that the dual-skinned membrane has an additional transport resistance from the CA skin. The PA/PVDF/CA(12%) membrane must be further optimized to have high FO performance.

Figure 7. Comparison between water fluxes (PRO mode) and reverse salt fluxes of PA/PVDF/CA(12%) membranes with different substrate casting gaps. DI water was used as feed; 2.0 M NaCl was used as draw solution.

To optimize the dual-skinned PA/PVDF/CA(12%) membrane's performance, the thickness of the PVDF layer on the PVDF/CA(12%) support was reduced by changing the casting knife gap. Fig. 7 illustrates the resultant cross-section and surface morphologies. By reducing the casting knife gap from 200 to 120 μm, the final support thickness drops from ~ 105 to 75 μm. The top surface morphology of the supports remains unchanged when reducing the casting gap from 200 to 150 μm. Since a thinner support thickness reduces ICP, Fig. 7 shows that the water flux increases from 39 at the casting gap of 200 μm to 53 LMH at the casting gap of 150 μm. However, a further decrease in casting gap to 120 μm results in membranes with

defects. The reverse salt flux increases but without improving the water flux. As a result, the PA/PVDF/CA(12%) membrane has the best results with a 150 μm casting gap. This dual-skinned PA/PVDF/CA(12%) membrane has good transport properties, as shown in Table 1. It has a S parameter of 380 μm , which is lower than that (~ 533 μm) of commercially available woven-embedded thin film composite membranes [17]. The newly developed dual-skinned membrane design is promising for FO and PRO applications.

Figure 8. The BSA protein attachment on the PVDF, CA and PA surfaces after 1 h exposure to BSA-FITC solutions.

To mimic the real deposition and accumulation of foulant molecules on membranes, Fig. 8 compares the BSA protein adsorption propensity onto various membrane surfaces. A labeled protein, BSA-FITC, was used to quantitatively compare the amounts of adsorbed protein

on different membrane surfaces. The relative protein attachment (%) was determined from the fluorescence signal of the FITC dye in the attached BSA-FITC molecules.

In single-skinned FO membranes, foulant deposition and accumulation occur on the surface of the active layer as well as within the porous structure of the membranes. Fouling on the supports may significantly affect the performance and cleaning efficiency. Fig. 8 indicates that the protein attachment on the CA surface is much lower than that on the PVDF surface. This is due to the effects of CA hydrophilicity and repulsive forces between the acetyl and hydroxyl groups of CA and the negatively charged BSA.

Figure 9. Morphology, roughness and contact angles of PA/PVDF/CA(12%) membrane; (a) top and (b) bottom layer.

Fig. 9 shows that the morphology of the top polyamide surface is much rougher than that of the bottom CA(12%) layer. The surface roughness was quantitatively analyzed and presented by the mean roughness (R_a) and root-mean-squared roughness (R_q) values. The polyamide layer has a significantly higher surface roughness (R_a : 66.0, R_q : 85.1) higher than the CA(12%) layer (R_a : 12.1, R_q : 16.1). In addition, the CA layer is more hydrophilic with a lower water contact angle (θ) of 56° than the polyamide layer with a contact angle of 74° . The increase of surface hydrophilicity and the decrease of surface roughness have been reported as contributing factors for reducing fouling properties [40]. Therefore, the CA layer would have less fouling than the polyamide or PVDF layers, as indicated by the protein attachment data shown in Fig. 8.

Figure 10. Effect of the second skin (CA, 12%) of the FO membranes on organic fouling under the PRO mode when the feed contains 2,000 ppm oil-water emulsion.

The contribution of the CA layer to the high fouling resistance of PA/PVDF/CA membranes was demonstrated by using 2000 ppm OiW and 1000 ppm NaCl feed solutions and NaCl draw solutions in PRO mode. The flux decline of PA/PVDF and PA/PVDF/CA(12%) membranes caused by oil particles was compared with the initial water flux of approximately 17 ± 0.5 LMH. Similarly, the baseline tests were performed under the similar conditions as the fouling tests using DI water as the feed. To represent the effect of oil particle fouling without the effect of the diluted draw solution and decreased osmotic driving force during the fouling tests, the flux decline curves in Fig. 10 were obtained after the normalization of the fouling curves to the baseline curves. A severe flux decline due to the oil particle fouling is observed when PA/PVDF membrane was used. In contrast, no significant flux decline can be seen during the fouling test using PA/PVDF/CA(12%) membrane. PA/PVDF/CA(12%) membrane has a rather non-porous, smooth and hydrophilic CA bottom skin (Fig. 3 and 9), which is expected to completely avoid the penetration of oil particles into the bulk of the porous support and to eliminate the deposition of the foulant onto the bottom surface of the membrane. The results demonstrate that the CA(12%) layer in the PA/PVDF/CA(12%) membrane has capability of providing fouling resistance to produce better performance membrane.

Conclusion

We propose multilayer and mechanical robust FO membranes (PA/PVDF/CA) comprising a polyamide selective layer on PVDF/woven/CA porous support. A good adhesion without any delamination of PVDF/woven/CA support has been observed. The bottom surface pore size of PA/PVDF/CA membranes can be changed from sub-micron to sub-nano by increasing the CA concentration in the casting solution from 8% to 12%, respectively. The performance and fouling

resistance of the PA/PVDF/CA membranes were demonstrated and compared to analogous membranes without the CA layer.

PA/PVDF/CA membrane fabricated from 8% CA solution has a hydrophilic CA bottom layer with high porosity and sub-micron surface pores (Fig. 4). Therefore, this membrane has higher water fluxes under FO and PRO modes compared to PA/PVDF membrane (Fig. 5 and 6). The hydrophilicity and high porosity of CA layer may lead to the low foulant deposition and the easy removal of accumulated foulants.

When using 12% CA solution for the bottom layer, a dual-skinned FO membrane having a primary dense polyamide skin on top and a second loose CA skin on the support is formed. The loose dense surface, high hydrophilicity and less surface roughness of the CA skin can prevent the penetration of foulants into the bulk of the porous support and reduce the deposition of foulants onto the support surface. Compared to PA/PVDF membrane under the PRO mode, the dual-skinned PA/PVDF/CA membrane has high fouling resistance to emulsified oil particles (Fig. 10) because of less surface and internal fouling propensity. Hence, the dual-skinned PA/PVDF/CA membrane is suitable to be used under PRO mode, in which the CA skin would be exposed to the feed solution containing foulants.

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References

- [1] I.C. Escobar, B. Van Der Bruggen, Microfiltration and ultrafiltration membrane science and technology, *J. Appl. Polym. Sci.*, 132 (2015).
- [2] M. Birkner, M. Ulbricht, Ultrafiltration membranes with markedly different pH- and ion-responsivity by photografted zwitterionic polysulfobetain or polycarbobetain, *J. Membr. Sci.*, 494 (2015) 57-67.
- [3] A.L. Zydney, Membrane technology for purification of therapeutic proteins, *Biotechnol. Bioeng.*, 103 (2009) 227-230.
- [4] Y. Xie, R. Tayouo, S.P. Nunes, Low fouling polysulfone ultrafiltration membrane via click chemistry, *J. Appl. Polym. Sci.*, 132 (2015).
- [5] S.P. Sun, K.Y. Wang, N. Peng, T.A. Hatton, T.S. Chung, Novel polyamide-imide/cellulose acetate dual-layer hollow fiber membranes for nanofiltration, *J. Membr. Sci.*, 363 (2010) 232-242.
- [6] D. Menne, J. Kamp, J. Erik Wong, M. Wessling, Precise tuning of salt retention of backwashable polyelectrolyte multilayer hollow fiber nanofiltration membranes, *J. Membr. Sci.*, 499 (2016) 396-405.
- [7] S. Livazovic, Z. Li, A.R. Behzad, K.V. Peinemann, S.P. Nunes, Cellulose multilayer membranes manufacture with ionic liquid, *J. Membr. Sci.*, 490 (2015) 282-293.
- [8] M. Elimelech, W.A. Phillip, The future of seawater desalination: Energy, technology, and the environment, *Science*, 333 (2011) 712-717.
- [9] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination-Development to date and future potential, *J. Membr. Sci.*, 370 (2011) 1-22.

- [10] N.L. Le, N.M.S. Bettahalli, S.P. Nunes, T.S. Chung, Outer-selective thin film composite (TFC) hollow fiber membranes for osmotic power generation, *J. Membr. Sci.*, 505 (2016) 157-166.
- [11] S.P. Sun, T.S. Chung, Outer-selective pressure-retarded osmosis hollow fiber membranes from vacuum-assisted interfacial polymerization for osmotic power generation, *Environ. Sci. Technol.*, 47 (2013) 13167-13174.
- [12] L. Shen, S. Xiong, Y. Wang, Graphene oxide incorporated thin-film composite membranes for forward osmosis applications, *Chem. Eng. Sci.*, 143 (2016) 194-205.
- [13] T.S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, Forward osmosis processes: yesterday, today and tomorrow, *Desalination*, 287 (2012) 78-81.
- [14] N. Widjojo, T.S. Chung, M. Weber, C. Maletzko, V. Warzelhan, The role of sulphonated polymer and macrovoid-free structure in the support layer for thin-film composite (TFC) forward osmosis (FO) membranes, *J. Membr. Sci.*, 383 (2011) 214-223.
- [15] N.N. Bui, J.R. McCutcheon, Hydrophilic nanofibers as new supports for thin film composite membranes for engineered osmosis, *Environ. Sci. Technol.*, 47 (2013) 1761-1769.
- [16] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, *Environ. Sci. Technol.*, 44 (2010) 3812-3818.
- [17] J. Ren, J.R. McCutcheon, A new commercial thin film composite membrane for forward osmosis, *Desalination*, 343 (2014) 187-193.
- [18] R.C. Ong, T.S. Chung, J.S. de Wit, B.J. Helmer, Novel cellulose ester substrates for high performance flat-sheet thin-film composite (TFC) forward osmosis (FO) membranes, *J. Membr. Sci.*, 473 (2015) 63-71.

- [19] J.R. McCutcheon, M. Elimelech, Influence of membrane support layer hydrophobicity on water flux in osmotically driven membrane processes, *J. Membr. Sci.*, 318 (2008) 458-466.
- [20] I.L. Alsvik, M.B. Hägg, Pressure retarded osmosis and forward osmosis membranes: Materials and methods, *Polymers*, 5 (2013) 303-327.
- [21] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, *J. Membr. Sci.*, 284 (2006) 237-247.
- [22] J.J. Qin, S. Chen, M.H. Oo, K.A. Kekre, E.R. Cornelissen, C.J. Ruiken, Experimental studies and modeling on concentration polarization in forward osmosis, *Water Sci. Technol.*, 61 (2010) 2897-2904.
- [23] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, *J. Membr. Sci.*, 354 (2010) 123-133.
- [24] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, *J. Membr. Sci.*, 320 (2008) 292-302.
- [25] N. Ma, J. Wei, R. Liao, C.Y. Tang, Zeolite-polyamide thin film nanocomposite membranes: Towards enhanced performance for forward osmosis, *J. Membr. Sci.*, 405–406 (2012) 149-157.
- [26] P. Li, S.S. Lim, J.G. Neo, R.C. Ong, M. Weber, C. Staudt, N. Widjojo, C. Maletzko, T.S. Chung, Short- and Long-Term Performance of the Thin-Film Composite Forward Osmosis (TFC-FO) Hollow Fiber Membranes for Oily Wastewater Purification, *Ind. Eng. Chem. Res.*, 53 (2014) 14056-14064.

- [27] P.H. Duong, S. Chisca, P.Y. Hong, H. Cheng, S.P. Nunes, T.S. Chung, Hydroxyl Functionalized Polytriazole-co-polyoxadiazole as Substrates for Forward Osmosis Membranes, *ACS Appl. Mater. Interfaces*, 7 (2015) 3960-3973.
- [28] G. Han, J.S. de Wit, T.S. Chung, Water reclamation from emulsified oily wastewater via effective forward osmosis hollow fiber membranes under the PRO mode, *Water Res.*, 81 (2015) 54-63.
- [29] M.F. Flanagan, I.C. Escobar, Novel charged and hydrophilized polybenzimidazole (PBI) membranes for forward osmosis, *J. Membr. Sci.*, 434 (2013) 85-92.
- [30] K. Lutchmiah, A.R.D. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: A review, *Water Res.*, 58 (2014) 179-197.
- [31] C. Klaysom, T.Y. Cath, T. Depuydt, I.F.J. Vankelecom, Forward and pressure retarded osmosis: potential solutions for global challenges in energy and water supply, *Chem. Soc. Rev.*, 42 (2013) 6959-6989.
- [32] K.Y. Wang, R.C. Ong, T.S. Chung, Double-skinned forward osmosis membranes for reducing internal concentration polarization within the porous sublayer, *Ind. Eng. Chem. Res.*, 49 (2010) 4824-4831.
- [33] S. Zhang, K.Y. Wang, T.S. Chung, H. Chen, Y.C. Jean, G. Amy, Well-constructed cellulose acetate membranes for forward osmosis: Minimized internal concentration polarization with an ultra-thin selective layer, *J. Membr. Sci.*, 360 (2010) 522-535.
- [34] S. Qi, C.Q. Qiu, Y. Zhao, C.Y. Tang, Double-skinned forward osmosis membranes based on layer-by-layer assembly-FO performance and fouling behavior, *J. Membr. Sci.*, 405-406 (2012) 20-29.

- [35] S. Wang, J. Cai, W. Ding, Z. Xu, Z. Wang, Bio-inspired aquaporins containing double-skinned forward osmosis membrane synthesized through layer-by-layer assembly, *Membranes*, 5 (2015) 369-384.
- [36] X. Song, L. Wang, C.Y. Tang, Z. Wang, C. Gao, Fabrication of carbon nanotubes incorporated double-skinned thin film nanocomposite membranes for enhanced separation performance and antifouling capability in forward osmosis process, *Desalination*, 369 (2015) 1-9.
- [37] P.H.H. Duong, T.S. Chung, S. Wei, L. Irish, Highly permeable double-skinned forward osmosis membranes for anti-fouling in the emulsified oil-water separation process, *Environ. Sci. Technol.*, 48 (2014) 4537-4545.
- [38] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, R. Field, A.G. Fane, Modeling double-skinned FO membranes, *Desalination*, 283 (2011) 178-186.
- [39] P.H.H. Duong, T.S. Chung, Application of thin film composite membranes with forward osmosis technology for the separation of emulsified oil-water, *J. Membr. Sci.*, 452 (2014) 117-126.
- [40] Y. Gu, Y.N. Wang, J. Wei, C.Y. Tang, Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules, *Water Res.*, 47 (2013) 1867-1874.