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Preparation and applications of poly vinyl alcohol (PVA) modified cellulose acetate (CA) membranes for forward osmosis (FO) processes

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ABSTRACT

Polyvinyl alcohol (PVA)-coated cellulose acetate (CA)-based flat-sheet membranes have been fabricated and tested in the forward osmosis (FO) process. PVA was used as a surface modifying agent. CA membranes prepared by conventional immersion precipitation were treated in an aqueous solution of PVA and tested water flux and salt rejection. The effects of PVA concentration, treatment time on the hydrophilicity of membrane surface, water permeability, and salt retention property of the membrane were estimated. The modified membrane was characterized by X-ray photoelectron spectroscopy and contact angle measurement. A hydrophilicity of membrane surface was observed in longer modification times and the higher PVA solution concentration accounted for a attaching of the PVA chains by glutaraldehyde as cross-linking agent. The best condition of salt rejection and permeability performance was obtained by using 1 wt% PVA solution and treatment time of 2 min. In the FO process, modified CA membrane exhibited water flux 20% higher than unmodified CA membrane without salt leakage. This result indicated that PVA coating improved water flux performance for FO processes.

Keywords: Cellulose acetate; Polyvinyl alcohol; Forward osmosis; Water flux

1. Introduction

Nowadays, forward osmosis (FO) process has attracted much attention from researchers due to its lower fouling potential, simplicity, and higher recovery [1]. Potential applications of FO include desalinating seawater [2], wastewater treatment [3], pharmaceutical and juice concentration [4], and electricity generation via a derivative pressure-retarded osmosis process [5–7]. FO is defined as the net movement of water across a semi-permeable membrane from a feed solution of lower osmotic pressure to a draw solution of higher osmotic pressure. Contrary to pressure-driven membrane processes—microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)—used hydraulic pressure as the driving force for water transport through the membrane FO is energy

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effective process because of it works depending on the osmotic pressure difference between the feed solution and the draw solution instead of applying hydraulic pressure. With ever increasing cost of energy, the study of FO technology is becoming more and more important.

The first commercial FO membranes were developed by Hydration Technology Inc. (HTI) [8]. These membranes, made from cellulose triacetate (CTA) embedded with a very thin polyester mesh instead of thick nonwoven fabric support in the traditional membrane, resulted in better FO performance than typical RO/NF membranes. This work provides inspiration for later studies. Nevertheless, their water permeability and salt rejection are not sufficiently high. In addition, they can only be used in a narrow pH range [9]. Alternatively, thin-film composite (TFC) RO membranes show high salt rejection and physical properties. However, TFC RO membranes exhibit very low water flux in FO process because they are tailored for high pressure driven membrane process. Extensive efforts have been made to develop high performance FO membranes with high water flux and low salt passage, and considerable achievements have been attained. For example, Jing Wei et al. studied flat-sheet TFC FO membranes and Yip et al. reported the high performance TFC FO membrane [10,11]. Ravindra Babu et al. studied the concentration of pineapple juice through a FO process using osmotic FO membranes that consisted of a very thin semi-permeable non-porous active skin layer [12]. Sucrose, NaCl or a mixture of sucrose and NaCl were used as draw solutions. The transmembrane flux increased from 0.44 and 0.28 LMH to 1.39 and 0.58 LMH with increasing NaCl concentration from 6 to 26 wt.% and sucrose concentration from 30 to 50 wt.%, respectively. At a sucrose concentration of 30 wt.%, the transmembrane flux was increased from 0.28 to 1.13 LMH with the addition of NaCl from 0 to 16 wt.%, while the maximum leakage of NaCl was up to 1.28%.

As the barrier between draw solution and feed solution to transport water and reject solute, membrane plays an important role on the realization of FO. Extensive studies have been focused on membrane morphology and membrane module from structural aspects FO membranes have to fabricate different from RO membranes because of it has asymmetric sponge-like structure. This asymmetric structure disturbed diffusion of solute by concentration polarization. At the solution-membrane interface (external concentration polarization or ECP) was observed, which can be controlled by increasing cross-flow or using spacers. In addition, concentration polarization can occur inside the porous support layer of an FO membrane, which is known as internal concentration polarization (ICP) [13,14]. ICP, a unique problem in FO processes, arises as the water flux in FO has an opposite direction to the solute flux. Therefore, the effective driving force (i.e. the osmotic pressure difference across the active layer) can be dramatically reduced, causing a severe reduction in the available water flux [15]. The ideal membranes for the FO process are semi-permeable hydrophilic membrane allowing water to permeate through while rejecting other components.

The objective of this study is to understand the role of polyvinyl alcohol (PVA) surface modification with cellulose acetate (CA)-based flat-sheet membrane it is a reasonable low cost and readily material, and has been successfully used for the fabrication of NF and RO membranes [16–18]. No study had reported for the CA-based PVA coating membranes for FO applications. PVA chains were introduced hydrophilic moiety onto CA membrane surface with high flux as FO membranes and investigate their potential for FO applications. We characterized surface property of the newly modified CA membranes and then evaluate their water permeation flux and salt rejection performance in a FO process.

2. Materials and methods

2.1. Materials

The polymer used for the fabrication of CA (Sigma–Aldrich, USA, Mn ~30,000) flat-sheet membrane and modifying agent PVA (Sigma–Aldrich, USA, 98%, hydrolyzed) were purchased from Sigma–Aldrich Inc. The CA membrane was supported by a nonwoven fabric. The mixture of N,N–dimethylformamide (DMF) and acetone was used as a dope solution solvent. DMF (Sigma–Aldrich, USA, anhydrous, 99.8%) and acetone (Sigma–Aldrich, USA, for HPLC, 99.9%) purchased from Sigma–Aldrich, USA. Formamide (98.5%, Junsei Chemical Co., Ltd) was used as additive in the casting solution. The draw solute NaCl (SAMCHUN PURE CHEMICAL Co., Ltd., 99.5%) was used in the FO process supplied from SAMCHUN chemical. Glutaraldehyde (GradeII, 25%, Sigma–Aldrich, USA) was used as cross-linking agent in the PVA coating process. All reagents were used without further purification.

2.2. Membrane preparation and modification

The CA-based membranes were prepared via a phase inversion method using water as coagulant. The casting solution was prepared by dissolving certain amount of CA powders in the mixture of DMF, acetone, and formamide (FA) at room temperature. The weight percentages of CA, DMF, and acetone and in the dope solution were 23, 38.5, and 38.5, respectively. As additive 30% of polymer were added to the casting solution then stirred by magnetic stirrer until the solution became homogeneous and transparent. To prepare the CA membrane, the dope solutions were cast on the glass plate with a casting knife in atmosphere 60 ± 1% humidigy and at 25 ± 1˚C. The fixed thickness of the cast film was 200 μm. The cast films were then smoothly immersed into a coagulant bath where 4˚C distilled water. The membranes were then stored kept in flowing water bath to remove residual solvent and stored in distilled water. Subsequently, the prepared CA membranes were annealed in 90˚C water for 7 min.

The surface modification was performed according to the following procedure. The CA membranes coated by PVA modifying agent solution and then immersed in the 0.01% glutaraldehyde solution for cross-linking process. Fig. 1 shows the cross-linking route between the CA membrane surface and PVA. The concentrations of PVA solution studied were 1 and 2 wt% and reactions were proceed for 1, 2, 3, and 4 min. The modified membranes were then thoroughly washed with distilled water to remove excess modifier and stored in the wet state.

2.3. Surface characterization

The surfaces of the membranes were examined by X-ray photoelectron spectroscopy (XPS) was carried out with the SIGMA PROBE, U.K. instrument. Spectra were obtained with a monochromatic Al Kα X-ray source (15 kV of photons). Binding energies were calibrated by using the containment carbon (C1s = 285 eV). The hydrophilicity of membrane surface was measured by drop shape analyzer (DE/DSA 100, KRUSS, France). Two types of membranes were used to investigate the influence of PVA segments on the wetting behavior of droplets on the CA membrane. Membranes samples were dried in vacuum at room temperature for 24 h. Small water droplets were applied onto a leveled membrane surface and profiles of the water drops were captured by optical system to determine the contact angles.

2.4. Measurement of membrane intrinsic separation properties

Intrinsic separation properties of membranes were evaluated in a cross-flow filtration setup in the RO testing mode according to Tang et al. [19]. The water flux was calculated by the following Eq. (1):

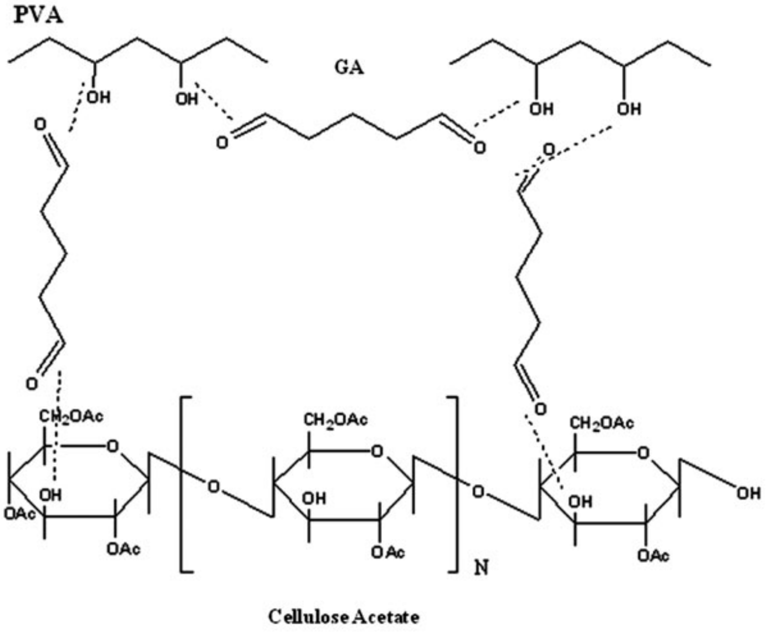

Fig. 1. Reaction scheme of cellulose acetate and PVA cross-linking.

$$J_{w1} = \frac{V}{A \times \Delta t} \tag{1}$$

where J_{w1} (L/(m^{2}h)) is the water flux, V (L) is the volume of permeated water, A (m^2) is the effective membrane area, and Δt (h) is the permeation time. Sodium chloride rejection of membrane was measured in the RO setup 225 psi, using 2000 ppm NaCl solution as feed. ECP was minimized using feed spacer and high cross-flow (3L/min). Rejection R was determined based on conductivity measurement of the feed and the following Eq. (2):

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f were the NaCl concentration of permeate and feed solutions, respectively.

2.5.2. FO performance of membrane

The FO performance was evaluated with a bench-scale circulating filtration unit, as shown in Fig. 2. The cross-flow permeation cell was a plate and frame design with a round channel on each side of the membrane. Both feed solution and draw solution were circulated at a fixed cross-flow rate of 100 ml/min which co-currently flowed through the cell channels. The temperatures of the feed and draw solutions were maintained at 22 ± 0.5 C and membrane orientation were tested with active layer-draw solution (AL-DS). Concentrated NaCl solution 1.5 M was used as draw solution and the feed solution was used DI water. The salt leakage can be calculated by measuring the conductivity in the feed solution at the end of experiment. A balance (AVG8101, OHAUS, KOREA) connected to a computer recorded down the mass of water permeating into the draw solution over a selected period of time. The water permeation flux was then calculated according to the weight change of feed water with Oahus data collect program (Balance Talk ver. 4.0) for 90 min.

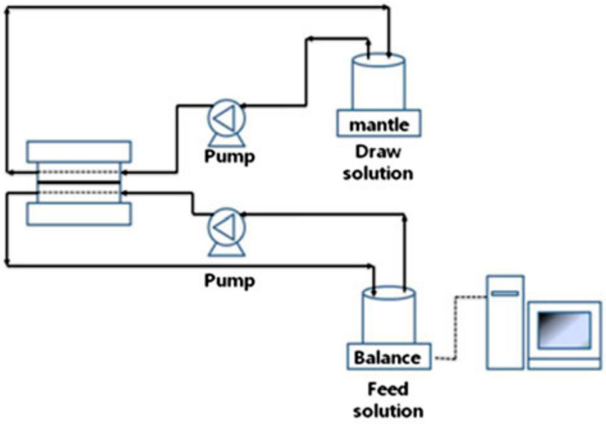

Fig. 2. Schematic diagram of laboratory-scale forward osmosis membrane process.

Table 1
Water flux and NaCl rejection of CA control, PVA1% and PVA 2% coating CA membranes: dipping time 1 min

Membrane	Water flux (LMH)	NaCl rejection (%)
CA	7.4	89.4
CA-PVA-1	8.8	89.9
CA-PVA-2	2.6	89.8

3. Results

3.1. Membrane morphology and property of PVA coated CA membranes

The water flux and NaCl rejection of modified membranes with varying concentration of the PVA

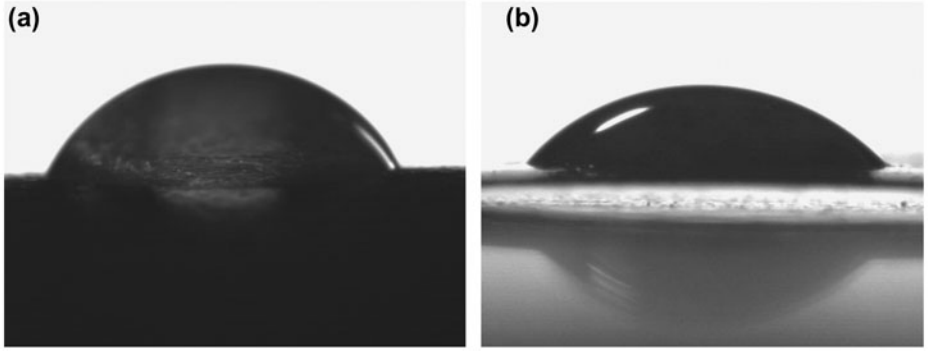

Fig. 3. Water contact angle of (a) CA control membrane and (b) CA-PVA 1% coated membrane.

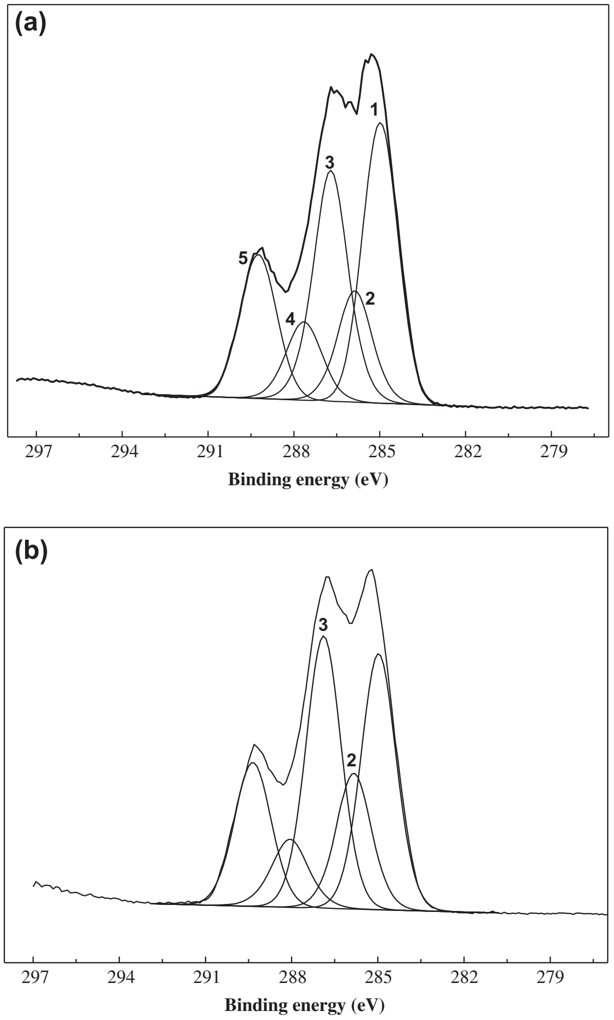

Fig. 4. XPS C1s spectrum of (a) CA control membrane and (b) PVA 1% coated CA membrane.

solutions were shown in Table 1. The water flux of modified membrane increased with 1% PVA solution in contrast the water flux of 2% PVA solution coated CA membrane decreased. It can be described the hydrophilic PVA chains increase the hydrophilcity of CA membrane surface therefore water flux significantly increased. The layer of PVA chain cross-linked with surface of CA membrane, defining an effective pore size allowing the water to permeate. The increase in the number of cross-linking site would decrease the pore size, leading to a decrease in the permeate flux. Thereby, 2% PVA solution coating membrane revealed water flux decrease. While NaCl rejections are retain high percentages with increasing concentration of PVA solutions.

3.2. Characterization of membrane surface

The simplest way to verify if the PVA chains existence on the CA membrane surface is to measure the water contact angle of the resulting membrane [20]. The water drop placed on the CA membrane in the absence of PVA coating is shown in Fig. 3(a). The observed contact angle was 39.3°. In Fig. 3(b) represent PVA-coated CA membrane. The measured contact angle is 73.5°. The water contact angle is reduced (from 73.5° to 39.3°) after coating the membrane with PVA solution. This fact could be explained by the introduction of the hydrophilic moiety on the membrane surface which was existed in the PVA chains.

Fig. 4 shows the XPS spectra of original CA membrane and 1% PVA coating CA membrane. Although all the C1s curve fit results have five peaks, they have different attribution and peak area ratio (see Table 2). The XPS peaks of C 1s(C–H peak 285 eV, C–C peak 285.8 eV, C–O–C peak 286.7 eV, C–OH peak 287.6 eV, C = O peak 289 eV) could be attributed to the presence of were shown which were composed of hydro, alkyl, ether, alcohol, and carbonyl carbon peaks. It was found that the ether and alkyl carbon peaks were increased with the degree of cross-linking of PVA with CA membrane surface. The cross-linking reaction occurred as covalent bonds are formed between CA and PVA as GA is added to the process. Indeed, Table 2 XPS result showed the increasing of alkyl and ether carbon contents in modified membrane surface.

3.3. FO performance of evaluation

Figs. 5 and 6 showed influence of concentration and dipping time of PVA solution with water flux property in FO process using 1.5 M NaCl as the draw solution and DI water as the feed solution at 25°C. The water flux increased up to about 20% and 2 min dipping time of the PVA solution after then showed a decreasing trend with water flux and salt rejection was maintained the high value without salt leakage.

Table 2
Peak area percentage of C 1s curves for CA and CA-PVA1% membranes

Membrane	C 1s peak At (%)	
	Peak2 (C–C)	Peak3 (C–O–C)
CA	8.9	18.7
CA-PVA-1	10.6	21.1

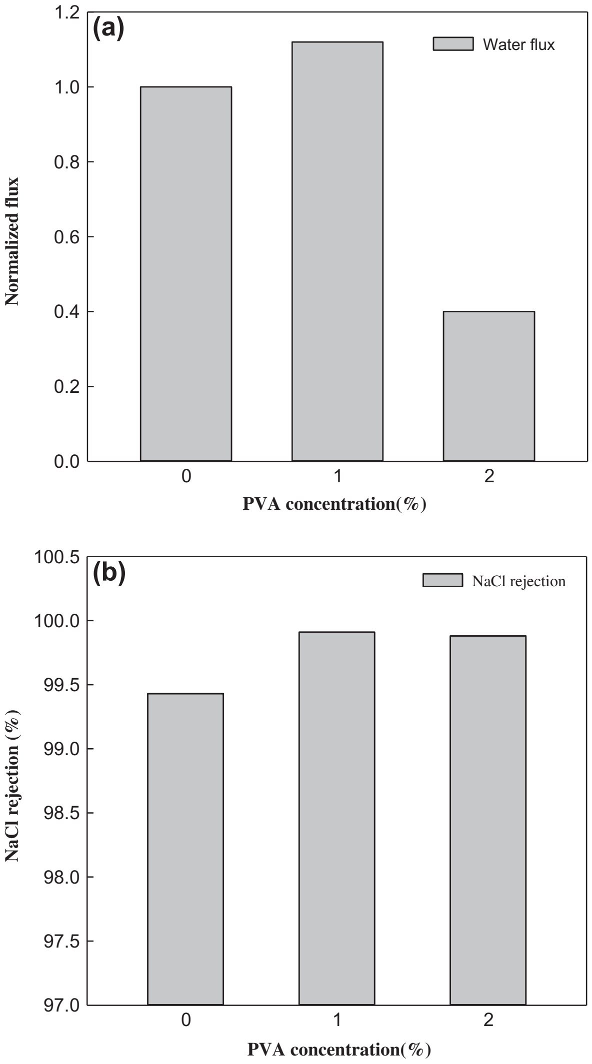

Fig. 5. FO flux results of (a) effect of concentration of PVA coating solution with flux, (b) effect of concentration of PVA coating solution with NaCl salt rejection, effect of dipping time in PVA coating solution, draw solution: 1.5 M NaCl, feed solution: DI water, temperature: 25℃, humidity: 30%.

This effect as attributed to the hydrophilicity of membrane surface by the PVA treatment, as well as an increased blocking of pores. Because of increased cross-linking site between CA membrane surface and PVA caused effective pore size decreasing to permeate water. The cross-linking between membrane surface and hydroxyl group of PVA increased with concentration of PVA and dipping time of PVA solution. It is found that the pore blocking effect exceeding the hydrophilic effect beyond 1%(concentration) and 2 min(dipping time) of PVA solution. Therefore, flux fluctuations were observed.

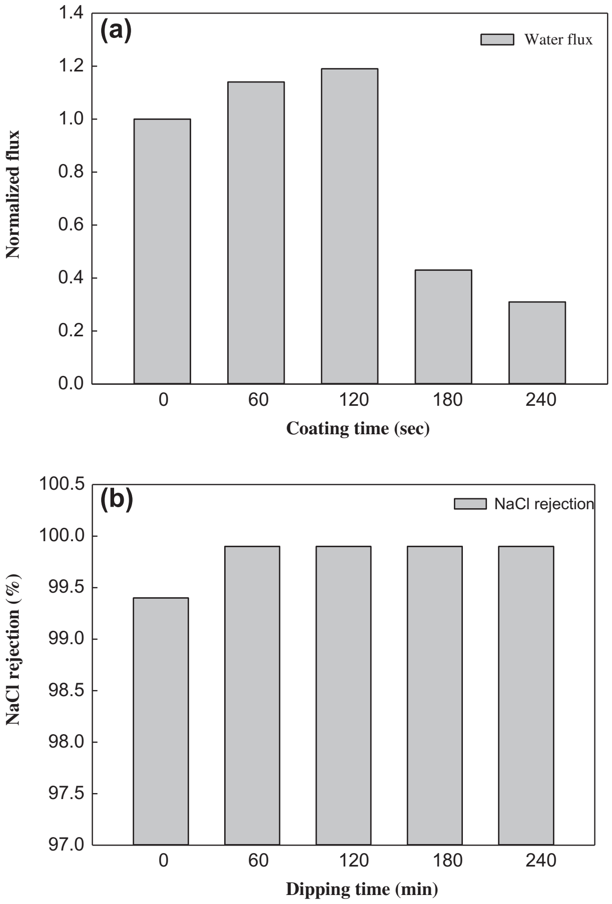

Fig. 6. FO flux results of (a) effect of dipping time of PVA coating solution with flux, (b) effect of dipping time of PVA coating solution with NaCl salt rejection, draw solution: 1.5 M NaCl, feed solution: DI water, temperature: 25℃, humidity: 30%.

4. Conclusion

The membranes fabricated in this work demonstrate that the improved water flux hydrophilic flat-sheet FO membranes can be obtained by a simple chemical treatment of PVA microporous substrates using a GA solution. Especially, when the concentration of PVA solution was not greater than 1%, the water flux of the modified CA membrane has improved about 20% compared with the unmodified CA membrane under the same operation condition. When the dipping time in PVA solution was up to 2 min, the permeation flux increased than that of unmodified CA membrane. The salt rejection was not changed after modification of CA membrane. In summary, these surface modified membranes based on CA to be potentially used in FO applications such as sea water desalination and power generation.

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References

[1] T.Y. Cath, D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: II. Combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater, J. Memb. Sci. 257 (2005) 111–119.

[2] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, J. Memb. Sci. 278 (2006) 114–123.

[3] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, Water Res. 41 (2007) 4005–4014.

[4] K.B. Petrotos, P. Quantick, H. Petropakis, A study of the direct osmotic concentration of tomato juice in tubular membrane–module configuration. I. The effect of certain basic process parameters on the process performance, J. Memb. Sci. 150 (1998) 99–110.

[5] K. Lee, R. Baker, H. Lonsdale, Membranes for power generation by pressure-retarded osmosis, J. Memb. Sci. 8 (1981) 141–171.

[6] A. Seppälä, M.J. Lampinen, Thermodynamic optimizing of pressure-retarded osmosis power generation systems, J. Memb. Sci. 161 (1999) 115–138.

[7] S. Loeb, One hundred and thirty benign and renewable megawatts from Great Salt Lake? The possibilities of hydroelectric power by pressure-retarded osmosis Desalination 141 (2001) 85–91.

[8] Y. Wang, F. Wicaksana, C.Y. Tang, A.G. Fane, Direct microscopic observation of forward osmosis membrane fouling, Environ. Sci. Technol. 44 (2010) 7102–7109.

[9] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic Pub, Dordrecht, 1996.

[10] J. Wei, C. Qiu, C.Y. Tang, R. Wang, A.G. Fane, Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes, J. Memb. Sci. 372 (2011) 292–302.

[11] 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.

[12] B.R. Babu, N. Rastogi, K. Raghavarao, Effect of process parameters on transmembrane flux during direct osmosis, J. Memb. Sci. 280 (2006) 185–194.

[13] C.Y. Tang, Q. She, W.C. 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. Memb. Sci. 354 (2010) 123–133.

[14] W.A. Phillip, J.S. Yong, M. Elimelech, Reverse draw solute permeation in forward osmosis: Modeling and experiments, Environ. Sci. Technol. 44 (2010) 5170–5176.

[15] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, J. Memb. Sci. 284 (2006) 237–247.

[16] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, J. Memb. Sci. 281 (2006) 70–87.

[17] N. Ma, J. Wei, R. Liao, C.Y. Tang, Zeolite-polyamide thin film nanocomposite membranes: Towards enhanced performance for forward osmosis, J. Memb. Sci. 405–406 (2012) 149–157.

[18] R. Haddada, E. Ferjani, M.S. Roudesli, A. Deratani, Properties of cellulose acetate nanofiltration membranes, Application to brackish water desalination, Desalination 167 (2004) 403–409.

[19] E. Ferjani, E. Ellouze, R. Ben Amar, Treatment of seafood processing wastewaters by ultrafiltration-nanofiltration cellulose acetate membranes, Desalination 177 (2005) 43–49.

[20] J.-H. Choi, K. Fukushi, K. Yamamoto, A submerged nanofiltration membrane bioreactor for domestic wastewater treatment: The performance of cellulose acetate nanofiltration membranes for long-term operation, Sep. Purif. Technol. 52 (2007) 470–477.