



Influence of the process parameters on hollow fiber-forward osmosis membrane performances

Tahir Majeed^a, Sherub Phuntsho^a, Soleyman Sahebi^a, Jung Eun Kim^a, Joon Khee Yoon^b, Kwonil Kim^b, Ho Kyong Shon^{a,*}

^aFaculty of Engineering and Information Technology, School of Civil and Environmental Engineering, University of Technology Sydney (UTS), PO Box 123, Broadway 15, Sydney 2007, Australia, Tel. +61 2 95142673; email: tahir.majeed@student.uts.edu.au (T. Majeed), Tel. +61 2 95142528; email: sherub.phuntsho@uts.edu.au (S. Phuntsho), Tel. +61 2 95142528; email: solisahebi@yahoo.com.au (S. Sahebi), Tel. +61 2 95142659; email: Jungeun.Kim@student.uts.edu.au (J.E. Kim), Tel. +61 2 95142629; email: Hokyong.shon-1@uts.edu.au (H.K. Shon)

^bSamsung Cheil Industries Inc., 332-2, Gocheon-Dong, Uiwang-Si, Gyeonggi-Do 437-711, Republic of Korea, Tel. +82 31 5963408; email: jjoon76.yoon@samsung.com (J.K. Yoon), Tel. +82 31 5963408; email: kwonil1.kim@samsung.com (K. Kim)

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ABSTRACT

Continued efforts are made in improving the performance of the low-cost forward osmosis (FO) membrane process which utilizes naturally available osmotic pressure of the draw solution (DS) as the driving force. Selection of a suitable DS and development of a better performing membrane remained the main research focus. In this study, the performance of a hollow fiber forward osmosis (HFFO) membrane was evaluated with respect to various operating conditions such as different cross-flow directions, membrane orientation, solution properties, and solution flow rates (Reynolds number). The study observed that operating parameters significantly affect the performance of the FO process. FO comparatively showed better performance at counter-current orientation. NaCl, KCl, and NH₄Cl were evaluated as DS carrying common anion. Properties of the anionic part of the DS were found important for flux outcome, whereas reverse solute flux (RSF) was largely influenced by the properties of DS cationic part. FO was operated at different DS and feed solution (FS) flow rates and FO outcome was assessed for varying DS and FS Reynolds number ratio. FO showed better flux outcome as Re ratio for DS and FS decreases and vice versa. Results indicated that by adjusting FO processes conditions, HFFO membrane could achieve significantly lower specific RSF and higher water flux outcome. It was observed that using 2 M NaCl as DS and deionized water as FS, HFFO successfully delivered flux of 62.9 LMH which is significantly high compared to many FO membranes reported in the literature under the active layer-DS membrane orientation mode.

Keywords: Hollow fiber-forward osmosis (FO) membrane; Reverse salt flux; Boundary layer effects; Draw solution; Operating parameter

*Corresponding author.

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1. Introduction

Recently, forward osmosis (FO) process has been investigated for its potential application for water purification including desalination [1–4]. Using the osmotic pressure of a draw solution (DS), it is gaining popularity as an alternative over the established desalination technologies such as thermal- and membrane-based desalination processes which consume extensive energy. For that reason, in a very short span of time, the low-cost FO process has been studied for various useful applications [5–9]. The rapid evaluation of FO process for such high number of applications indicates that the low-energy FO desalination concept is being overwhelmingly welcomed by the research community and industry [10–12].

Membrane and DS characteristics mainly affect the FO performances because they directly influence the transport of water molecules through the semi-permeable membrane. In many earlier FO studies, low performance ratio (a ratio of actual water flux to the theoretical water flux) has highlighted some serious issues in FO process which are closely linked with the suitable DS selection and FO membrane characteristics [10,13–17]. A wide range of both inorganic and organic DS have been evaluated for FO process which indicated varied performance outcome in terms of water flux and reverse solute flux (RSF) [18–22]. RSF is the movement of valuable DS molecules across the membrane to feed solution (FS) side. However, in selecting a suitable DS, DS separation and its recovery from the permeated water are still considered as the most challenging issue for the FO process. DS separation and permeate recovery from the diluted DS are complex and energy intensive and hence are critical to the FO process.

On the other side, asymmetric polymeric membranes are used for FO applications. These membranes are developed by casting a very fine active layer (AL) on a thick porous support layer (SL). These membranes are grouped into two main types, i.e. flat sheet and hollow fiber. Their asymmetric membrane structure usually results in two unique types of internal and external concentration polarization (CP) effects both at the membrane AL and SL. CP causes lowering of the net osmotic pressure gradient available for osmosis which results in lower permeate flux and low performance ratio during the FO process. Internal concentration polarization (ICP) is considered as the most critical barrier in getting better performances for different FO applications [2,22,23]. To overcome RSF and FO performance ratio issues, which seem directly linked to the FO membrane characteristics, various research groups mainly focused their attention to develop a very thin membrane AL on a highly porous SL [24–27].

Following Hydration Technology Innovations (HTI) work, who initially produced their commercial flat sheet membrane, some other companies also introduced their flat sheet membranes and used them for various applications [28–31]. Yip et al. [32] reported TFC-FO flat sheet membrane using polysulfone support. Most of the AL of flat sheet membranes were initially prepared using cellulose acetate (CA) and cellulose triacetate (CTA) followed by polyamide (PA) thin-film composite (TFC) materials [33], for hollow fiber membranes, most of the attempts were made with PA while few also used CTA AL. Some of their work was focused on AL improvement [15] while the others aimed their activities to improve FO outcome through SL modification [27,34–36].

Along with flat sheet FO membrane development activities, later, various other research groups also endeavored to fabricate a suitable FO membrane with better operational performances. Some other unique and distinctive proliferation membranes, carbon nanotubes [37], aquaporin membranes [38] are also used for FO applications. FO performance was evaluated for new kinds of FO membranes as hollow fiber forward osmosis (HFFO) membrane [39], polybenzimidazole nanofiltration membrane [40], cross-linked layer-by-layer (xLbL) FO membrane [26], layer-by-layer polyelectrolyte applied on a poly ether sulfone hollow fiber substrate [41], high flux FO membranes by chemically xLbL polyelectrolytes [33], novel poly (amide-imide) FO hollow fiber membranes with a positively charged selective layer [25], TFC-FO membrane for PRO [42], FO membrane with sulfonated polyphenylenesulfone as the supporting substrate [43], CA nanofiltration hollow fiber membranes for FO [44], CA membranes for FO with an ultra-thin selective layer [45], and others [35,46–48].

On the whole, results have shown that HFFO membranes mostly showed far better results for water flux for FO operations. To evaluate the difference in the performances of these two main types of membranes, HFFO membrane and flat sheet HTI's CTA membrane were evaluated under the same conditions for different fertilizer DS and the resultant outcome was compared [49]. The study showed that although HFFO membrane demonstrated comparatively better results, the outcome was not on par with other published work showed with HFFO membranes [24,42,44,50].

For enhanced FO performances, along with continued efforts to select a suitable DS [49] and improve membrane characteristics, effect of various FO operating parameters such as temperature [51,52], flow direction, membrane orientation [23,53,54], flow rate or velocity [14,55,56], and viscosity [57] has also been

evaluated in some earlier studies and many results demonstrated the room for improved FO performances. Varying FO performances directed that along with the membrane characteristics and DS properties, specific operating conditions also exhibit very important roles in delivering improved performances with flat sheet and HFFO membranes.

To get insight to better membrane performances, it is important to understand how the water and solute molecules transport across AL and SL of the membrane is affected. Understanding of water transport mechanisms within the membrane and SL structure may provide solution to flux, RSF, and CP issues. The water transport phenomenon is directly linked with the DS and FS properties and membrane characteristics as well. Both these affect each other during the process of osmotic movement of water molecules through membrane pores.

The purpose of this study is therefore to evaluate how some of the process parameters influence the performances of the FO process using a HFFO membrane. Parameters including membrane orientation DS properties, cross-flow directions, and cross-flow rates were evaluated. The HFFO module performance was measured using water flux and RSF as the main indicators.

2. Materials and methods

The bench-scale FO system, similar to one used in a previous study [49,58], was used to evaluate performance of HFFO membrane (Samsung Cheil Industries, Korea). HFFO membrane was made up of a PA-based thin-film composite TFC membrane with AL facing the lumen side of the fiber. The HFFO lumens carried inner diameter of 0.9 mm and outer diameter of 1.2 mm. All experiments were conducted using 28 cm-long HFFO membrane module carrying 50 fibers with a total membrane area of 396 cm². NaCl was used as a primary DS for most experiments while two other monovalent compounds such as KCl and NH₄Cl were also used for comparative studies (all chemicals were of reagent grade supplied by Chem-Supply, Australia). Since this investigation mainly involved comparative studies between each parameter so to avoid the interference of external CP on the FO performances, deionized water (DI) was used as a FS. Water flux was determined by recording the changes in the mass of the DS tank in unit time using a mass balance connected to PC for data logging. The temperatures of the DS and FS were all maintained at 25 ± 0.5 °C using a water bath linked with a temperature controller.

Two variable speed peristaltic pumps were used to transport DS and FS separately through lumen and shell sides of the module, respectively. Varying flow

rates, ranging from 0.2 to 1.2 L/min were used for different test.

HFFO operations were performed to assess the influence of three major parameters that affect its performances such as membrane orientation, cross-flow directions, cross-flow rates, and the DS properties. HFFO flux performances were evaluated for different DS and FS cross-flow arrangements. In the co-current flow arrangement, DS and FS enter and exit the FO module from the same sides with similar flow directions. In the counter-current flow arrangements, however, DS and FS enter and exit the FO module from opposite ends of the module, thereby creating an opposite flow directions as shown in Fig. 1. Initially, the study is carried out using DS and FS flow rates that were set at 1 L/min, representing Reynolds number (Re) of 1,300 and 500, respectively (laminar flows). To evaluate the effects of cross-flow, FO was only operated under active layer facing FS (AL-FS) membrane orientation.

For AL-FS membrane orientation, FS flowed inside the hollow fiber or lumen side of the fiber while the DS flowed within the shell outside the fiber. For the AL-DS membrane orientation, DS flowed inside the lumen side of the fiber while FS flowed through the outside shell area of the fibers. HFFO was operated under both co-current and counter-crossflow directions. RSF was measured by recording the change in the electrical conductivity of the FS using HACH conductivity meter (model H270G-BNDL).

FO was further evaluated for varying cross-flow arrangements with Re representing lumen side flow of 100–3,750 and shell side flow of 300–1,800. This showed that lumen side was evaluated for both laminar and transition flow zones whereas shell side was operated under laminar flow zone only. For various experiments, lumen and shell sides carried either DS or FS based on FO operation at either AL-FS or AL-DS orientation.

3. Results and discussion

3.1. Effect of cross-flow direction on FO performance

Fig. 2 compares flux outcomes under co-current and counter-current cross-flow directions. FO membrane showed only slightly higher flux under counter-current flow arrangements than the co-current cross-flow direction. Jung et al. [55] also showed that cross-flow direction slightly effected FO flux performance for a flat-sheet FO membrane along its module length. It is likely because the net driving force is higher at the DS inlet than at the outlet point of the FO module under the counter-current arrangement. Although the initial water flux under counter-current cross-flow mode is slightly higher than co-current

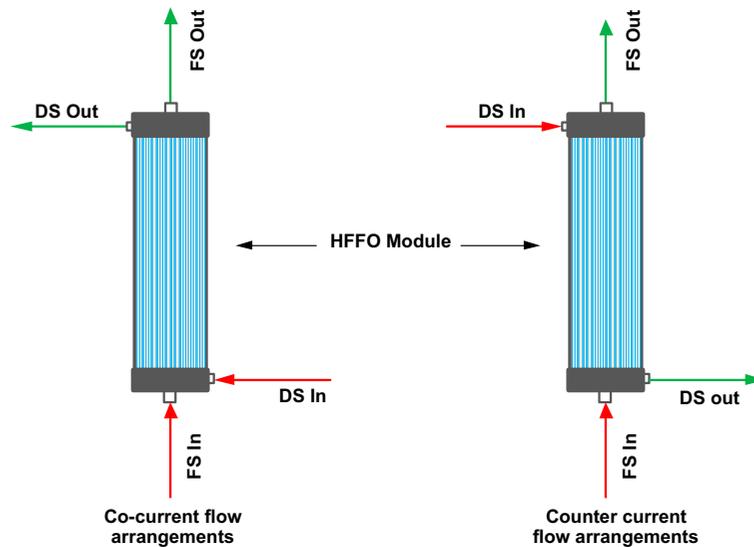


Fig. 1. HFFO membrane (in AL-FS orientation) module showing the DS and FS flow directions under the co-current and counter-current arrangement for FO experiments.

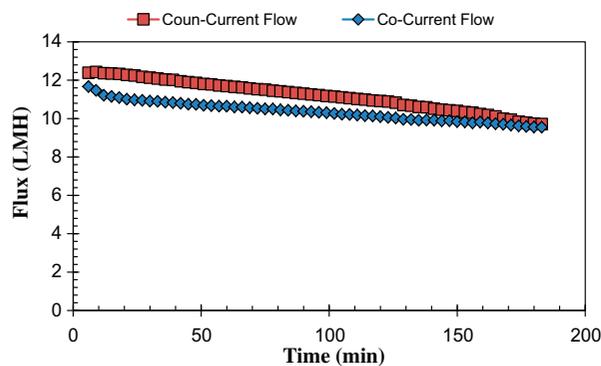


Fig. 2. FO performance in terms of water flux under different cross-flow directions. Other operating conditions include AL-FS membrane orientation, DS: 2 M NaCl, FS: DI, Re for DS: 1,300, Re for FS: 500.

cross-flow arrangement, however, it was noticed that after a longer run of about 185 min, both set of flow arrangements nearly showed similar water flux.

3.2. Effect of membrane orientation on FO performance

Fig. 3 displays water flux outcome when HFFO membrane module was operated under two different membrane orientations, i.e. AL-FS and AL-DS. Under the AL-FS mode, PA rejection layer was facing FS whereas for AL-DS mode, membrane PA AL was facing DS. FO was operated using different DS concentrations (1, 2 and 3 M NaCl) against DI water as FS. Cross-flow rate showed Re 500 and 1,300 for lumen

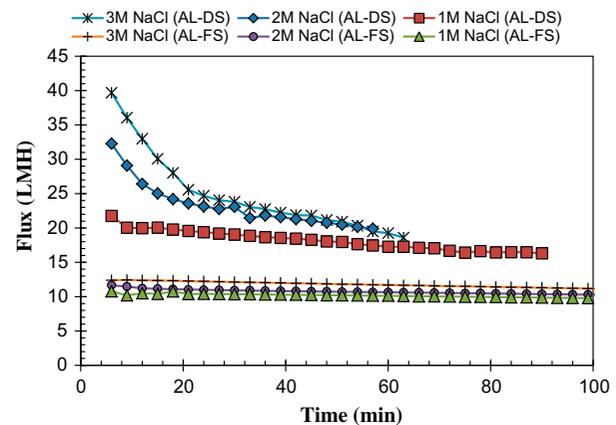


Fig. 3. Effect of DS concentration and membrane orientation on flux outcome, DI water is used as FS whereas for varying experiments, DS was used in 1–3 M NaCl, DS and FS showed Re (AL-FS) of 1,300 and 500 and for Re (AL-DS) of 500 and 1,300, respectively.

and shell side, respectively. FO results indicated a significant increase in flux outcome under the AL-DS membrane orientation. Compared to AL-FS mode, HFFO membrane under AL-DS mode delivered up to 202, 293, and 340% higher flux for 1, 2, and 3 M NaCl DS, respectively.

Water flux did not vary significantly under the AL-FS orientation for changes in DS concentration as it only showed an increase of 8% in FO flux when DS concentration was changed from 1 to 3 M. However, under the AL-DS mode, the flux was increased by 82% when the DS concentration for the similar

changes in DS concentrations. By increasing DS concentration, the flux showed more under AL-DS than AL-FS membrane orientation although this increase was not linear at higher DS concentrations. These differences in flux between AL-DS and AL-FS membrane orientation reveal that under the AL-FS orientation, ICP builds quickly in the membrane SL, reduces the available osmotic pressure difference at the membrane interface thus reducing the water flux [23,48,59,60]. Chou et al. [39] further revealed that compared to flat sheet FO, HFFO membrane takes little more time to build-up salt concentration within the substrate and to develop steady ICP. HF membrane flux, therefore, declines sharply at the initial stages of the test run. When a steady ICP is developed in the substrate, HFFO membrane then starts showing steady flux with a gradual flux decline.

Under the AL-DS membrane orientation, water flux declines distinctly initially and then the decline becomes gradual. This sharp flux drop does not follow the usual flux decline pattern observed with the flat sheet FO experiments [22,23,61,62]. No such sharp decline was also observed with the HF under the AL-FS orientation (Fig. 2). This sharp flux decline could be due to two possible reasons. Firstly, as the membrane used in these experiments had much higher area (0.04 m^2), about 20 times higher than the membrane areas used in most of the flat sheet FO studies, more volume of water was permeated in unit time which quickly diluted the DS and caused a rapid reduction in the osmotic pressure difference and ultimately resulted sharp flux decline. Later, as the flux decreased with time, the rate of DS dilution also slowed down, hence the flux decline gradually slowed in the later stages of these experiments.

3.3. Effect of membrane orientation on RSF

RSF for two types of membrane orientations was evaluated for 1 M NaCl as DS and DI water as FS. These experiments were carried out for cross-flow rate representing Re 500 and 1,300 for lumen and shell side, respectively. FS conductivity was regularly monitored using a bench-scale conductivity meter which recorded FS conductivity after a fixed time intervals. Fig. 4(a) shows FS conductivity rise due to RSF for two types of membrane orientations. It was observed that in comparison to FO operation at AL-FS orientation, conductivity of the FS rises more quickly in AL-DS orientation and HF membrane showed high-reverse salt passage in AL-DS orientation. RSF for HF membrane was observed as 3.6 and $8.88 \text{ g/m}^2/\text{h}$ for AL-FS and AL-DS orientation, respectively (Fig. 4(b)).

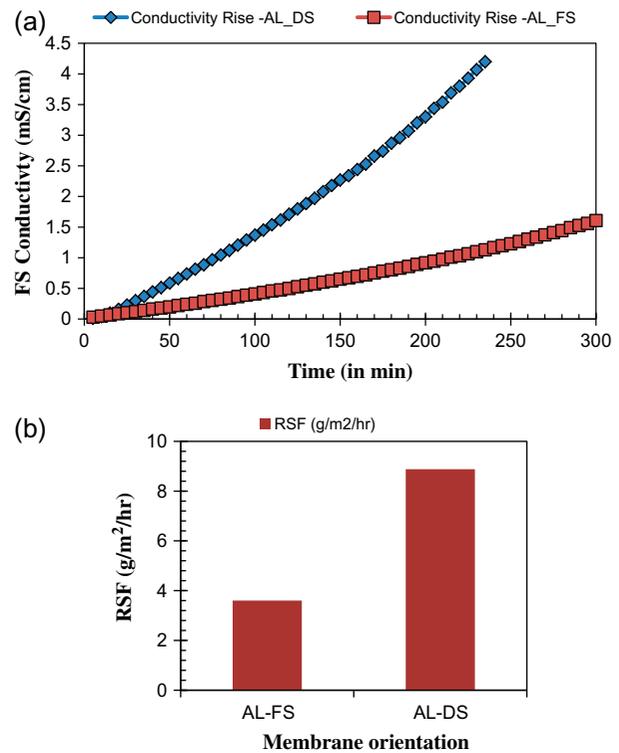


Fig. 4. (a) Effect of membrane orientation on FS conductivity rise and (b) Effect of membrane orientation of RSF, DS: 1 M NaCl and FS: DI water.

Compared to AL-FS, under the AL-DS mode, higher concentration difference between the DS and FS at the AL interface resulted higher RSF [63]. On the other hand, under the AL-DS mode, HFFO also showed higher water flux (Fig. 3). Due to the high RSF, salt concentration in the FS increased rapidly and caused lowering of the net osmotic pressure which quickly decreases flux with time in AL-DS membrane orientation [64].

In the FO process, water permeation and reverse salt diffusion take place simultaneously but in opposite directions. Water molecules move from FS side to DS side whereas draw solute movement is from DS side to FS side. It might appear that due to this opposite flow directions of water and solutes, water flux and RSF movement should apparently influence each other, probably resist other movement stream and cause slowing down of their movement. Earlier studies have indicated that the increase in DS concentration simultaneously increases flux and RSF for FO process [65]. This study also shows similar trends and it was observed that RSF increases as the water flux increases in AL-DS orientation. These indicate that water flux and RSF uses different pores and routes for their flow, independent of each other, hence rising

flow of one stream do not affect the other. For this reason, HFFO gives simultaneous rise to both flux and RSF for AL-DS membrane orientation.

3.4. Performance of HFFO membrane in terms of specific reverse solute flux

Specific reverse solute flux (SRSF) was evaluated for 3 M NaCl DS under both the AL-FS and AL-DS membrane orientation and the results were compared with the earlier published work (Fig. 5). DI water was used as FS for these evaluations and FO was operated for lumen and shell side Re of 500 and 1,300, respectively. SRSF is the ratio of RSF to water flux, which indicates the quantity of draw solutes lost by reverse diffusion per unit volume of water extracted from the FS [66]. Although some of the other's work was evaluated at varying operating conditions using different DS concentrations, the comparison indicate that operating conditions play an important role for SRSF. Compared to available results with lower DS

concentration (0.5 M NaCl), FO showed lowest value for SRSF for 3 M NaCl DS beside the fact that FO delivers higher RSF at high DS concentrations [65,67]. The comparison shows that with some adjustments in the FO process conditions, HFFO membrane could show the lowest SRSF even when operated at higher DS concentration for both AL-FS and AL-DS membrane orientation.

3.5. Effect of DS type on FO performance

Three different types of draw solutes (NaCl, NH_4Cl , and KCl) were used to evaluate effect of various DS carrying common anion but different cations on the water flux and the RSF. The results indicate the combined effects of DS properties and the AL and SL characteristics on the water flux and the RSF outcome. Fig. 6 shows flux and RSF outcome for HFFO using 1 M NaCl, NH_4Cl , and KCl as DS and with DI water FS. It shows that for these DS, the water flux and the RSF increase when the membrane orientation was

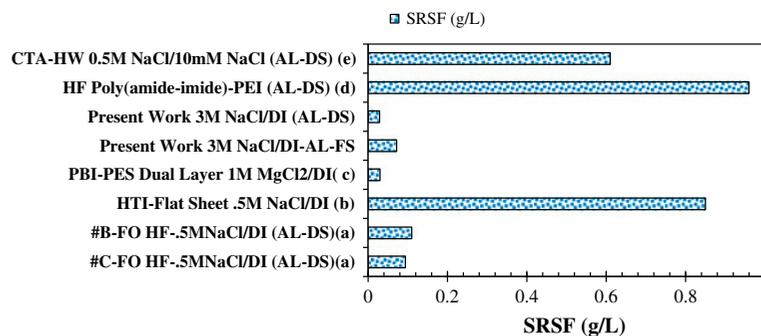


Fig. 5. Comparison of the present work SRSF outcome work with the literature data (a) [39], (b) [60], (c) [50], (d) [25], (e) [68].

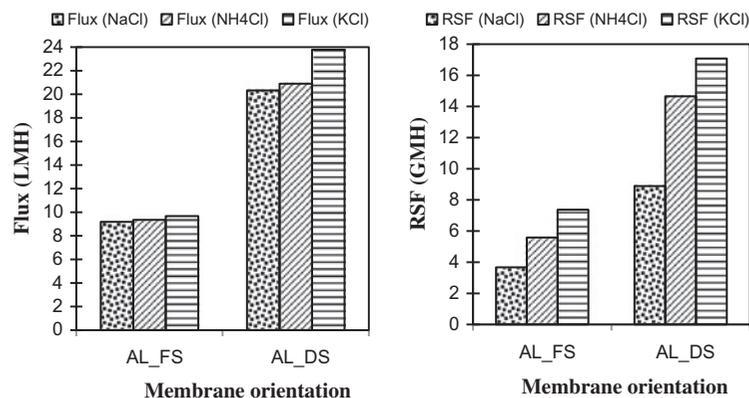


Fig. 6. FO performances using three DS carrying same anionic part (Cl^-). (a) Flux and (b) RSF. NaCl, NH_4Cl , and KCl DS were used in 1 M concentration, DI water was used as feed.

changed from AL-FS to AL-DS. Flux did not change significantly under the AL-FS membrane orientation. Amongst the three DS, KCl showed comparatively highest water flux under the AL-DS orientation.

The three DS also showed markedly difference in terms of RSF under both AL-FS and AL-DS orientation. Salt transport through the membrane is influenced by ionic/hydrated radii, charge, and size [69]. For RSF, Na^+ with higher hydrated radii showed lower RSF than K^+ and NH_4^+ . K^+ and NH_4^+ , besides having similarly close hydrated radii, showed fluctuating RSF under both membrane orientation and these results indicate that hydrated radii alone may not influence the RSF in the FO process. These results indicate that for FO process using PA membrane, anionic properties of the DS play an important role for the water flux outcome whereas RSF is largely effected by the properties of the cationic part of the DS.

Similar outcomes for various DS carrying similar cation and anion groups have already been reported elsewhere but they were not evaluated for the role of their cationic and anionic parts [65,70]. Properties of the cationic and anionic hydrated radii affect the isoelectric point of both membrane surface and these radii radicals which changes membrane surface to form a double layer [71]. Varying effects for these DS further indicate that similar undisclosed properties of the membranes and DS are used for the transport of water and solute molecules. The DS properties, such as the ionic size of the cationic part, mostly affect the diffusion resistivity to diffusion with the SL [65].

3.6. Effect of cross-flow rate on the HFFO performance

FO was operated under varying FS and DS cross-flow rates to evaluate effects of flow velocity or the Re. These experiments were carried out under both AL-FS and AL-DS membrane orientations. DS concentration was varied from 1 to 5 M NaCl whereas DI water was used as FS throughout. Two cross-flow rates representing Re 200/500 and 600/1,600 were selected for the tests. First number of the fraction represents the Re for DS and the other represents Re for the FS.

Fig. 7 presents the influence of flow rates on the water flux outcome for HFFO membrane. The results indicate better flux outcome when Re was changed from 200/500 to 600/1,600 under both AL-FS and AL-DS membrane orientations. Under the AL-FS membrane orientation, the water flux increased by 22, 18.46, and 28.8% for 1, 3, and 5 M DS concentrations, respectively, as shown in Fig. 7(a). Similarly, under AL-DS, HFFO membrane showed 37.56, 31.71, and

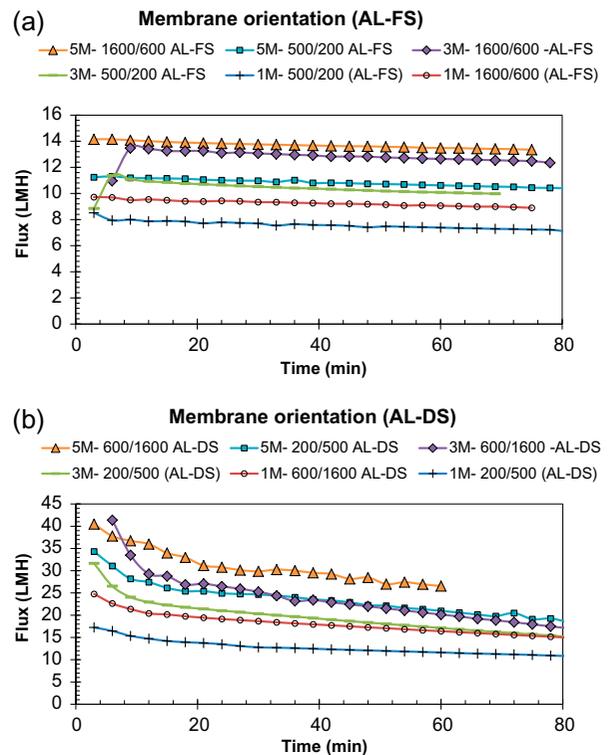


Fig. 7. Effect of changing DS/FS cross-flow rate on HFFO membrane water flux. (a) AL-FS orientation, and (b) AL-DS orientation, 1, 3, and 5 M NaCl DS were evaluated DI water FS. Fraction in legends shows Re for DS and FS, respectively. For legends, the first term of the fraction represents Re for DS and other Re for FS.

17.98% higher flux for 1 M, 3 M, and 5 M DS concentration for the above set of Re values (Fig. 7(b)).

FO was further evaluated to find which of the solutions, DS or FS flow rate, has greater impact on water flux. Experiment was started with a specific set of initial flow rates and after short test run, the flow rate of either FS or DS was changed to reflect a new set of Re values for that stream. After short test run at revised Re, both DS and FS flow rates were restored to the initial values. Fig. 8 shows flux outcome when HFFO membrane was initially operated at the Re of 600/1,600 using 1 M NaCl as DS and DI as FS. After about 20 min, FS flow rate was reduced to reflect Re no of 650 while still maintaining the same Re for DS. It was observed that reducing the FS flow rate only, the water flux decreased sharply. Overall about 60% of the flux decline was observed by reducing FS Re from 1,600 to 650. After 20 min, when the flow rate of FS was again increased to restore to its initial Re, the water flux was restored back to its normal rate.

HFFO membrane was further evaluated using 3 M NaCl as DS and DI as FS. FO test was initially started

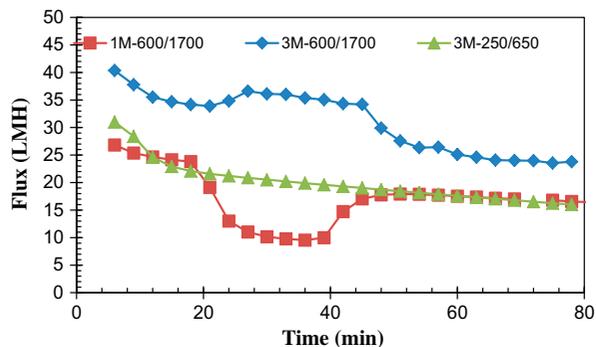


Fig. 8. Effect of changing cross-flow rate of only one stream (either DS or FS) on FO flux. These tests were performed at AL-DS membrane orientation. 1 and 3 M NaCl DS were used with DI water FS.

at Re pair of 600/1,600. Contrary to the earlier experiment, this time the flow rate of the DS was reduced to represent a lower Re of 250 while FS flow rate was kept same to maintain the uniform Re for FS and the result is displayed in Fig. 8. It was noticed that by reducing the DS flow rate, FO flux increased quickly by 8%. However, after 20 min when the flow rate was reduced to its initial value, the water flux reduced by 20.2% and followed the initial slope of the line. The results indicate that the HFFO membrane comparatively gives high flux outcome when DS flow rate is reduced. On the other hand, the resultant flux decreases when the FS flow rate is lowered.

To confirm this, FO was further evaluated for 3 M NaCl DS at comparatively lower Re pair 250/650 and the water flux outcome was compared with the earlier results (Fig. 8). Jung et al. [55] emphasized the role of flow rate affecting the mass transfer within the external CP layer to optimize FO operations in terms of energy consumption and production recovery. It was noticed that 1 M NaCl DS at higher Re pair 600/1,600 showed better flux outcome than the 3 M NaCl DS at lower Re pair 250/650. These results are important as most of the earlier studies observed that the flux did not vary noticeably by changing DS and FS flow rates using flat sheet FO membranes [24,35,42,43,55]. This suggests that the changes in the cross-flow rate bring various appropriate modifications in the HFFO membrane pore structures which results improved performances for FO processes. The hydrodynamic conditions leave very little positive influence on the flat sheet FO membrane which may affect the FO flux outcome.

Following the results from Figs. 7 and 8, FO was further operated under AL-DS membrane orientation by varying DS/FS Re pair and results are summarized in Fig. 9. It was found that HFFO gave better result at DS/FS Re values of 200/1,600 for both 1 and 3 M DS.

It was also noticed that the water flux increases with the decrease in ratio of DS/FS Re pair. Fig. 9(a) shows that for 1 M NaCl DS, flux is increased by 41% whereas Fig. 9(b) shows that for 3 M NaCl DS, flux increases by 37% when the DS/FS Re pair was increased from 200/500 to 200/1,600, which reflect reduction of DS/FS Re pair ratio from 0.4 to 0.125.

Membrane forms a boundary layer with liquids streams in contact with and these boundary layers on either side of the FO membrane induce significant resistance for water permeation and salt diffusion. The transport resistance of this boundary layer may be a function of many factors such as shape of the interface, wettability of the surface to the liquid, hydrophobicity or hydrophilicity, velocity of the liquid at the interface [72]. Boundary layer resistance is hardly affected within the SL. The water molecules penetrating into the pores of the membrane and its SL are barely affected by stirring of the bulk water or turbulence due to water flow. Therefore, in AL-DS mode, dilutive CP is not affected much with cross-flow effects. Resultant flux changes are mostly linked to the changes in the properties of the inner and outer layers of the membrane AL.

SEM images of the outer layer of polyamide AL have indicated that it carries a typical ridge valley structure [34,68]. The PA membrane surface shows irregular top surface with non-uniform pore geometry (Fig. 10). From the fluctuating flux results for HFFO under AL-DS orientation at different DS/FS Re pairs, we deduce that each DS/FS Re pair develops some pressure or stresses on the polyamide AL of the hollow fiber membrane. These probably results in stretching of the polymeric membrane that could modify the membrane pores ultimately affecting the water flux outcome. We suggest that the variation in the cross-flow rates brings similar nature of changes in the membrane structure which are developed during the cross-linkage of polymer structure which enhances flux outcome. Higher cross-linkage makes the membrane surface more hydrophilic, more smoother, and compact which enhances membrane performances [73]. Irregular shaped pores are changed to uniform size pores which allow water molecules easily pass through the membrane and thus high fluxes are obtained. We conclude that with the new pore shape arrangements, the pore structures also becomes align with each other, symmetrical throughout the membrane.

By repeating these experiments at varying DS FS flow rates, it was observed that there is a particular set of DS and FS flow rate values which help getting highest flux through the FO membrane. Other higher or lower DS and FS flow rates showed comparatively lower flux. From this we may deduce that membrane

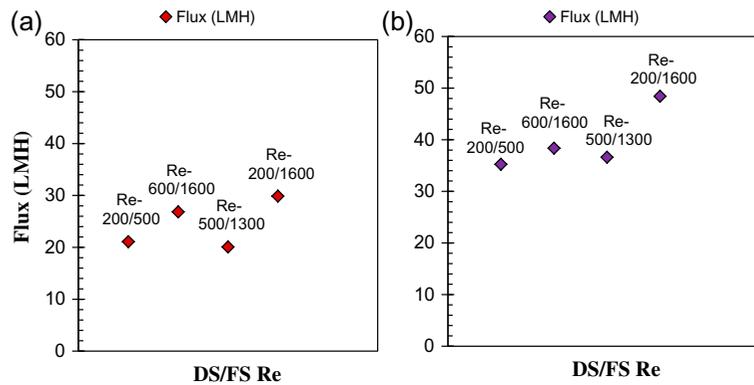


Fig. 9. Effect of changing DS and FS flow rates on FO flux performance with (a) 1 M NaCl DS and (b) 3 M NaCl DS, DI water was used as feed. Flux was evaluated at AL-DS membrane orientation.

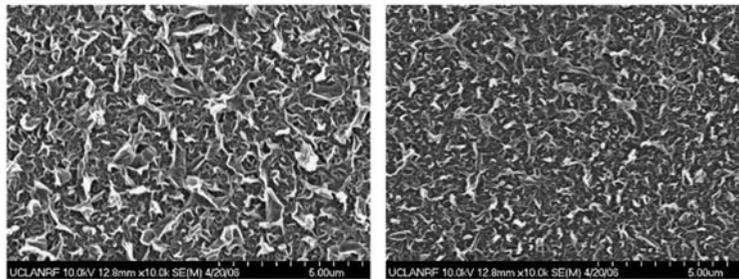


Fig. 10. SEM images of polyamide membrane AL showing irregular shape membrane structure pores (Adapted from [34]).

pores, being made of an elastomeric properties material, change shapes with pressure and flow and at some specific values of these process parameters, they form good arrangement of the pore shapes which facilitates both water and solute flux. By changing operating parameters from these optimum values, the pores again changes back to their disordered structure and which do not show the same enhanced performance. This further confirms the importance of interfacial polymerization process of the membrane making step where the polymeric material develops various pore sizes, structures, and arrangements of the membrane pores.

3.7. Combined effects of process conditions

FO membrane was further evaluated at various other DS and FS flow rates. FO membrane flux outcome for 2 M NaCl DS against DI water FS was evaluated for two different operating conditions i.e. for Re no 200/500 at AL-FS membrane orientation and Re no 3,750/1,500 at AL-DS membrane orientation and results are presented in Fig. 11. FO membrane in

AL-DS orientation showed remarkably high flux of 62.9 LMH when operated at Re 3,750/1,500. It

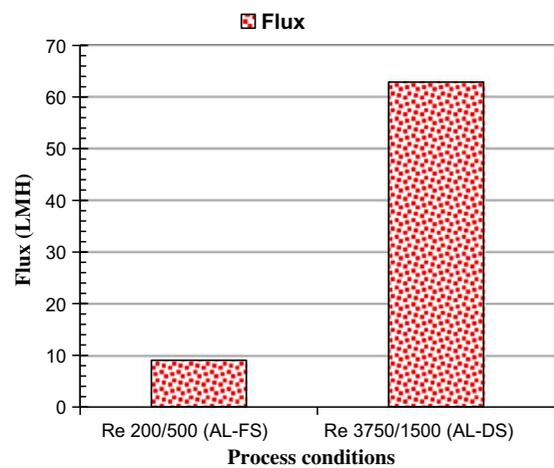


Fig. 11. Flux outcome showing effect of operating conditions for the same membrane. Condition set # 1 (AL-FS orientation, DS Re 200, FS Re 500), condition set # 2 (AL-DS orientation, DS Re 3,750, FS Re 1,500), DS: 2 M NaCl, and FS: DI water.

indicates a flux increase of about 511% for a set of two operating conditions for the same FO membrane. Along with the effect of operating conditions on CP development phenomena, for a better flux outcome, they also help transform membrane pore structure, facilitate DS come closer to membrane, reduce the boundary layer effects, and expedite water molecule transport through the membrane AL and SL pores. The variation in these FO flux performances is reflected mainly due to the changes in the membrane characteristics.

4. Conclusions

HFFO membrane was evaluated to assess the effects of some of the operating conditions in terms of water flux and RSF. Parameters including membrane orientation, DS properties, cross-flow directions, and cross-flow rates were evaluated. It was observed that operating parameters significantly affect the performance of the FO process. Main findings are summarized as follows:

- (1) Properties of the anionic part of the DS were found important for flux outcome whereas RSF was largely influenced by the properties of DS cationic part.
- (2) Results indicated that by adjusting FO processes conditions, HFFO membrane achieve significantly lower specific RSF and higher water flux outcome.
- (3) FO operation at varying DS and FS Re ratio showed better flux outcome as Re ratio for DS and FS decreases and vice versa.
- (4) FO operation under the AL-DS orientation at varying DS and FS cross-flow rates markedly showed enhanced performance outcome. It was observed that using 2 M NaCl as DS and DI water as FS, HFFO successfully delivered water flux of 62.9 LMH at DS/FS Re of 3,750/1,500.

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References

- [1] M. Elimelech, Yale constructs forward osmosis desalination pilot plant, *Membr. Technol.* 2007 (2007) 7–8.
- [2] M. Elimelech, S. Bhattacharjee, A novel approach for modeling concentration polarization in crossflow membrane filtration based on the equivalence of osmotic pressure model and filtration theory, *J. Membr. Sci.* 145 (1998) 223–241.
- [3] J.O. Kessler, C.D. Moody, Drinking water from sea water by forward osmosis, *Desalination* 18 (1976) 297–306.
- [4] O. Bamaga, A. Yokochi, E. Beaudry, Application of forward osmosis in pretreatment of seawater for small reverse osmosis desalination units, *Desalin. Water Treat.* 5 (2009) 183–191.
- [5] S. Zou, Y. Gu, D. Xiao, C.Y. Tang, The role of physical and chemical parameters on forward osmosis membrane fouling during algae separation, *J. Membr. Sci.* 366 (2011) 356–362.
- [6] J. Warczok, M. Gierszewska, W. Kujawski, C. Guell, Application of osmotic membrane distillation for reconcentration of sugar solutions from osmotic dehydration, *Sep. Purif. Technol.* 57 (2007) 425–429.
- [7] 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.
- [8] X. Jin, J. Shan, C. Wang, J. Wei, C.Y. Tang, Rejection of pharmaceuticals by forward osmosis membranes, *J. Hazard. Mater.* 227–228 (2012) 55–61.
- [9] S. Phuntsho, H.K. Shon, S. Vigneswaran, J. Cho, Assessing membrane fouling potential of humic acid using flow field-flow fractionation, *J. Membr. Sci.* 373 (2011) 64–73.
- [10] E. Cornelissen, D. Harmsen, K. De Korte, C. Ruiken, J.-J. Qin, H. Oo, L. Wessels, Membrane fouling and process performance of forward osmosis membranes on activated sludge, *J. Membr. Sci.* 319 (2008) 158–168.
- [11] T.-S. Chung, X. Li, R.C. Ong, Q. Ge, H. Wang, G. Han, Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications, *Curr. Opin. Chem. Eng.* 1 (2012) 246–257.
- [12] X. Jin, Q. She, X. Ang, C.Y. Tang, Removal of boron and arsenic by forward osmosis membrane: Influence of membrane orientation and organic fouling, *J. Membr. Sci.* 389 (2012) 182–187.
- [13] J.W. Costerton, Introduction to biofilm, *Int. J. Antimicrob. Agents* 11 (1999) 217–221.
- [14] 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.
- [15] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *J. Membr. Sci.* 188 (2001) 115–128.
- [16] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, *J. Membr. Sci.* 281 (2006) 70–87.
- [17] S. Phuntsho, S. Sahebi, T. Majeed, F. Lotfi, J.E. Kim, H.K. Shon, Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process, *Chem. Eng. J.* 231 (2013) 484–496.

- [18] C. Liu, S. Caothien, J. Hayes, T. Caothuy, T. Otoyoy, T. Ogawa, Membrane Chemical Cleaning: From Art to Science, Pall Corporation, Port Washington, NY, 2001.
- [19] A.E. Jaffer, The application of a novel chemical treatment program to mitigate scaling and fouling in reverse osmosis units, *Desalination* 96 (1994) 71–79.
- [20] A.E. Contreras, A. Kim, Q. Li, Combined fouling of nanofiltration membranes: Mechanisms and effect of organic matter, *J. Membr. Sci.* 327 (2009) 87–95.
- [21] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, *Bioresour. Technol.* 122 (2012) 207–216.
- [22] S. Zhao, L. Zou, Relating solution physicochemical properties to internal concentration polarization in forward osmosis, *J. Membr. Sci.* 379 (2011) 459–467.
- [23] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: Role of membrane orientation, *Desalination* 197 (2006) 1–8.
- [24] R. Wang, L. Shi, C.Y. Tang, S. Chou, C. Qiu, A.G. Fane, Characterization of novel forward osmosis hollow fiber membranes, *J. Membr. Sci.* 355 (2010) 158–167.
- [25] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication of novel poly(amide–imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, *J. Membr. Sci.* 369 (2011) 196–205.
- [26] Q. Saren, C.Q. Qiu, C.Y. Tang, Synthesis and characterization of novel forward osmosis membranes based on layer-by-layer assembly, *Environ. Sci. Technol.* 45 (2011) 5201–5208.
- [27] 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.
- [28] Hydration Technology Innovations, LLC. Available from: <http://www.htiwater.com/divisions/oil-gas/index.html>, March 05, 2013.
- [29] Modern Water Plc. Available from: <http://www.modernwater.com/membrane-processes/membrane-desalination>, February 19, 2013.
- [30] Statkraft AS. Available from: <http://www.statkraft.com/energy-sources/osmotic-power/prototype/>, January 14, 2013.
- [31] R.L. McGinnis, N.T. Hancock, M.S. Nowosielski-Slepown, G.D. McGurgan, Pilot demonstration of the NH₃/CO₂ forward osmosis desalination process on high salinity brines, *Desalination* 312 (2013) 67–74.
- [32] 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.
- [33] K.Y. Wang, T.S. Chung, G. Amy, Developing thin-film-composite forward osmosis membranes on the PES/SPSf substrate through interfacial polymerization, *J. Am. Chem. Soc.* 58 (2012) 770–781.
- [34] A.K. Ghosh, E.M.V. Hoek, Impacts of support membrane structure and chemistry on polyamide–polysulfone interfacial composite membranes, *J. Membr. Sci.* 336 (2009) 140–148.
- [35] 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.
- [36] A. Tiraferri, N.Y. Yip, W.A. Phillip, J.D. Schiffman, M. Elimelech, Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure, *J. Membr. Sci.* 367 (2011) 340–352.
- [37] Y.-X. Jia, H.-L. Li, M. Wang, L.-Y. Wu, Y.-D. Hu, Carbon nanotube: Possible candidate for forward osmosis, *Sep. Purif. Technol.* 75 (2010) 55–60.
- [38] M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, Highly permeable polymeric membranes based on the incorporation of the functional water channel protein Aquaporin Z, *Proc. Nat. Acad. Sci. USA.* 104 (2007) 20719–20724.
- [39] S. Chou, L. Shi, R. Wang, C.Y. Tang, C. Qiu, A.G. Fane, Characteristics and potential applications of a novel forward osmosis hollow fiber membrane, *Desalination* 261 (2010) 365–372.
- [40] K.Y. Wang, T.-S. Chung, J.-J. Qin, Polybenzimidazole (PBI) nanofiltration hollow fiber membranes applied in forward osmosis process, *J. Membr. Sci.* 300 (2007) 6–12.
- [41] C. Liu, W. Fang, S. Chou, L. Shi, A.G. Fane, R. Wang, Fabrication of layer-by-layer assembled FO hollow fiber membranes and their performances using low concentration draw solutions, *Desalination* 308 (2013) 147–153.
- [42] S. Chou, R. Wang, L. Shi, Q. She, C. Tang, A.G. Fane, Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density, *J. Membr. Sci.* 389 (2012) 25–33.
- [43] N. Widjojo, T.-S. Chung, M. Weber, C. Maletzko, V. Warzelhan, A sulfonated polyphenylenesulfone (sPPSU) as the supporting substrate in thin film composite (TFC) membranes with enhanced performance for forward osmosis (FO), *Chem. Eng. J.* 220 (2013) 15–23.
- [44] J. Su, Q. Yang, J.F. Teo, T.-S. Chung, Cellulose acetate nanofiltration hollow fiber membranes for forward osmosis processes, *J. Membr. Sci.* 355 (2010) 36–44.
- [45] S. Zhang, K.Y. Wang, T.-S. Chung, H. Chen, Y. 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.
- [46] 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.
- [47] 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.
- [48] X. Song, Z. Liu, D.D. Sun, Nano gives the answer: Breaking the bottleneck of internal concentration polarization with a nanofiber composite forward osmosis membrane for a high water production rate, *Adv. Mater.* 23 (2011) 3256–3260.
- [49] G. Chen, Y. Lu, W.B. Krantz, R. Wang, A.G. Fane, Optimization of operating conditions for a continuous membrane distillation crystallization process with zero salty water discharge, *J. Membr. Sci.* 450 (2014) 1–11.

- [50] Q. Yang, K.Y. Wang, T.-S. Chung, Dual-layer hollow fibers with enhanced flux as novel forward osmosis membranes for water production, *Environ. Sci. Technol.* 43 (2009) 2800–2805.
- [51] S.-J. You, X.-H. Wang, M. Zhong, Y.-J. Zhong, C. Yu, N.-Q. Ren, Temperature as a factor affecting transmembrane water flux in forward osmosis: Steady-state modeling and experimental validation, *Chem. Eng. J.* 198–199 (2012) 52–60.
- [52] S. Phuntsho, S. Vigneswaran, J. Kandasamy, S. Hong, S. Lee, H.K. Shon, Influence of temperature and temperature difference in the performance of forward osmosis desalination process, *J. Membr. Sci.* 415–416 (2012) 734–744.
- [53] S. Zhao, L. Zou, D. Mulcahy, Effects of membrane orientation on process performance in forward osmosis applications, *J. Membr. Sci.* 382 (2011) 308–315.
- [54] V. Parida, H.Y. Ng, Forward osmosis organic fouling: Effects of organic loading, calcium and membrane orientation, *Desalination* 312 (2013) 88–98.
- [55] D.H. Jung, J. Lee, D.Y. Kim, Y.G. Lee, M. Park, S. Lee, D.R. Yang, J.H. Kim, Simulation of forward osmosis membrane process: Effect of membrane orientation and flow direction of feed and draw solutions, *Desalination* 277 (2011) 83–91.
- [56] M.F. Gruber, C.J. Johnson, C.Y. Tang, M.H. Jensen, L. Yde, C. Hélix-Nielsen, Computational fluid dynamics simulations of flow and concentration polarization in forward osmosis membrane systems, *J. Membr. Sci.* 379 (2011) 488–495.
- [57] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, N.Y. Yip, Standard methodology for evaluating membrane performance in osmotically driven membrane processes, *Desalination* 312 (2013) 31–38.
- [58] T. Majeed, F. Lotfi, S. Phuntsho, J.K. Yoon, K. Kim, H.K. Shon, Performances of PA hollow fiber membrane with the CTA flat sheet membrane for forward osmosis process, *Desalin. Water Treat.* (2013) 1–11.
- [59] Y. Gao, W. Li, W.C.L. Lay, H.G.L. Coster, A.G. Fane, C.Y. Tang, Characterization of forward osmosis membranes by electrochemical impedance spectroscopy, *Desalination* 312 (2013) 45–51.
- [60] 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.
- [61] 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. Membr. Sci.* 278 (2006) 114–123.
- [62] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, *J. Membr. Sci.* 320 (2008) 292–302.
- [63] 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.
- [64] T. Majeed, F. Lotfi, S. Sahebi, J.E. Kim, S. Phuntsho, H.K. Shon, Fertilizer drawn forward osmosis (FDFO) for fertigation: Application to tomato, *Desalin. Water Treat.* (2014).
- [65] A. Achilli, T. Cath, A. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *J. Membr. Sci.* 364 (2010) 233–241.
- [66] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, *Environ. Sci. Technol.* 43 (2009) 6769–6775.
- [67] A. Tiraferri, N.Y. Yip, A.P. Straub, S. Romero-Vargas Castrillon, M. Elimelech, A method for the simultaneous determination of transport and structural parameters of forward osmosis membranes, *J. Membr. Sci.* 444 (2013) 523–538.
- [68] 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. Membr. Sci.* 372 (2011) 292–302.
- [69] J. Schaep, B. Van der Bruggen, C. Vandecasteele, D. Wilms, Influence of ion size and charge in nanofiltration, *Sep. Purif. Technol.* 14 (1998) 155–162.
- [70] L. Chekli, S. Phuntsho, H.K. Shon, S. Vigneswaran, J. Kandasamy, A. Chanan, A review of draw solutes in forward osmosis process and their use in modern applications, *Desalin. Water Treat.* 43 (2012) 167–184.
- [71] A.E. Childress, M. Elimelech, Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, *J. Membr. Sci.* 119 (1996) 253–268.
- [72] H. Yasuda, C.E. Lamaze, Transfer of gas to dissolved oxygen in water via porous and nonporous polymer membranes, *J. Appl. Polym. Sci.* 16 (1972) 595–601.
- [73] C. Feng, J. Xu, M. Li, Y. Tang, C. Gao, Studies on a novel nanofiltration membrane prepared by cross-linking of polyethyleneimine on polyacrylonitrile substrate, *J. Membr. Sci.* 451 (2014) 103–110.