Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.940220

55 (2015) 2734–2740
August

Higher boron rejection with a new TFC forward osmosis membrane

R. Valladares Linares[a,b], Z.Y. Li[a,*], S. Sarp[c], Y.G. Park[c], G. Amy[a], J.S. Vrouwenvelder[a,b,d]

[a] *Water Desalination and Reuse Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia, Tel. +966 12 808 2165; email: zhenyu.li@kaust.edu.sa*
[b] *Faculty of Applied Sciences, Department of Biotechnology, Delft University of Technology, Delft, The Netherlands*
[c] *GS Engineering and Construction, Environmental Process Engineering Team, Grand Seoul building, 33, Jongno-gu, Seoul, Korea*
[d] *Wetsus, Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands*

Received 3 April 2014; Accepted 16 June 2014

ABSTRACT

Due to the stringent limits for boron in drinking and irrigation water, water treatment facilities have to incur additional treatment to remove boron down to a safe concentration. Forward osmosis (FO) is a membrane technology that may reduce the energy required to remove boron present in seawater. In *direct* FO desalination hybrid systems, fresh water is recovered from seawater using a recoverable draw solution, FO membranes are expected to show high boron rejection. This study focuses on determining the boron rejection capabilities of a new generation thin-film composite (TFC) FO membrane compared to a first generation cellulose triacetate (CTA) FO membrane. The effects of water permeate flux, membrane structure, draw solute charge, and reverse solute flux on boron rejection were determined. For TFC and CTA FO membranes, experiments showed that when similar operating conditions are applied (e.g. membrane type and draw solute type) boron rejection decreases with increase in permeate flux. Reverse draw solute flux and membrane fouling have no significant impact on boron rejection. Compared to the first generation CTA FO membrane operated at the same conditions, the TFC FO membrane showed a 40% higher boron rejection capability and a 20% higher water flux. This demonstrates the potential for boron removal for new generation TFC FO membranes.

Keywords: Forward osmosis, Boron removal, Seawater desalination, Thin-film composite, Cellulose triacetate, Draw solute interaction

1. Introduction

One of the biggest challenges in reverse osmosis (RO) desalination is boron removal, which is usually obtained with special high-boron-rejection RO membranes (with the drawback of lower water permeability) or a pretreatment step to increase pH; both involve additional cost to achieve drinking water quality standards [1]. Another solution for boron removal is using a double-pass RO system, which is more susceptible to severe scaling problems [2]. The World Health Organization lowered its boron guideline value for drinking water down to 2.4 ppm [3]; however,

---

*Corresponding author.

Presented at the Conference on Desalination for the Environment: Clean Water and Energy 11–15 May 2014, Limassol, Cyprus

most governments and environmental agencies have not applied this new value to regulations.

Boron exists as non-ionic boric acid form at the natural pH level of seawater, which is about 7–8.5 due to its high pKa (9.2). Rejection mechanisms are mostly based on size exclusion at these pH values. At a pH higher than 9.2, concentrations of borate and other ionic forms of boron become dominant compared to non-ionic forms, which are easier to remove by RO membranes due to the electrostatic repulsion mechanism. The reason of the low rejection of boric acid (non-ionic) in membrane systems is because of its ability to diffuse through the membranes in a non-ionic form in the way similar to carboxylic acids or water [4,5].

Forward osmosis (FO) has the potential to reduce the energy consumption of producing fresh water from seawater, when compared to conventional high-pressure membrane processes such as RO. FO can find a niche application as a lower energy process to achieve a high quality water [6,7], particularly if it is used in a hybrid *direct* desalination process. A FO *direct* desalination process uses saline water as the feed solution (FS), and an osmotic reagent as the draw solution (DS). The DS gets diluted with the water permeating through the membrane. This diluted solution can be converted in high quality water by an additional treatment step involving low pressure RO, enabling a robust lower cost desalination system compared to traditional high pressure seawater RO systems.

The rejection of boric acid by cellulose triacetate (CTA) FO membranes has been studied in the past with debatable results [8], and demonstrated that the rejection of boric acid was between 12 and 33%, depending on the flux conditions. Other studies with the same membrane [9–11] showed that boron rejection can be as high as 70%, depending on the DS used in the process, the pH of the feed water and the flux of water through the membrane. This highlights the importance of reverse salt diffusion in FO as one of the key mechanisms governing the boron flux. Independently, the use of non-charged draw solutes has been proposed to reduce the reverse salt diffusion through the membrane [12], but has not yet been shown to reduce the boron solute flux in a FO *direct* desalination process.

In this study, a new generation of thin-film composite (TFC) FO membranes was tested and compared to a commercially available CTA FO membrane. The study focused on determining the boron rejection of the membranes, where a deionized (DI) water and 5 mM H_3BO_3 solution was used as FS. Two solutions (0.32 M NaCl and 1 M glucose) with the same approximate osmotic pressure were used as DS independently to assess the interaction of charged solutes with the membrane in terms of reverse draw solute flux, and their role in the rejection of boron.

2. Materials and methods

2.1. FO membranes

Two FO membranes were used for this study: (i) a CTA membrane with an embedded polyester mesh and (ii) a TFC membrane with an identical embedded polyester mesh on the support layer. Both membranes were purchased from Hydration Technologies Innovation (HTI, Scottsdale, AZ, USA).

Tests were made with both membrane orientations: active layer (AL) facing the feed solution (AL-FS) and active layer facing the draw solution (AL-DS). Tests on pure water flux and DS rejection were completed in the AL-FS orientation, which has been proven to be the most effective in preventing fouling of the FO membrane [13–16].

The zeta potential (ZP) of both FO membranes was calculated with an Anton Paar Zeta Potential Analyzer (Austria). For this analysis a solution of 10 mM KCl was used as electrolyte. The ZP is measured in the pH range in which the membrane can be used safely (4 to 8 for the CTA membrane and 2 to 10 for the TFC), so the proper injection of acid (0.1 M HCl) or base (0.1 M KOH) is added in the titration process to assess the ZP.

2.2. Experimental setup and procedure

The system consisted of a cross-flow FO cell accommodating a 2 cm × 10 cm membrane coupon. Experiments were performed at a flow rate of $200\,\mathrm{mL\,min^{-1}}$, equivalent to a cross-flow velocity of $0.084\,\mathrm{m\,s^{-1}}$. One liter of feed and DS were used for each condition. This configuration has been used in previous FO studies [17].

Two FSs were used: DI water and DI water spiked with 0.002 M H_3BO_3. For the DS, two solutes were used at a concentration that could generate the same osmotic power, determined with osmolality measurements: a 0.32 M NaCl solution (corresponding to 1.8% NaCl solution), and a 1 M glucose solution. Each experiment recovered 100 mL from the FS to the DS.

Water temperature was kept constant with a heating/chilling device at 20 ± 1°C. The pH of the feed water was maintained at 7.2. No dissociation of B is expected due to the stability of boric acid at this pH [10].

Three fluxes were measured/calculated and reported in the results and discussion section: (i) water flux through the FO membrane (from FS to DS),

(ii) boron flux through the FO membrane (from FS to DS), and (iii) reverse solute flux (from DS to FS), which refers to the DS molecules being transported through the membrane in opposite direction of the water flux.

An additional experiment was run with a pre-fouled membrane to study the effect of fouling caused by natural organic matter (NOM). A SEPA CF II filtration cell (Sterlitech, Kent, WA, USA) accommodating a 139 cm membrane sheet was used in dead-end mode for 24 h at a pressure of 100 psi to foul the membrane with a solution containing 20 mg L^{-1} of Xanthan gum to simulate a fouling layer of biopolymer.

3. Results and discussion

An overview of the studies is given in Table 1.

3.1. Membrane characterization

Fig. 1 shows scanning electron microscopy (SEM) images of both CTA and TFC membranes. The CTA membrane has a smooth uniform layer on both sides, and no pores can be identified on its surface. On the other hand, the support layer of the TFC membrane (Fig. 1(f)) shows a highly porous structure, one of the reasons why the membrane presents a higher water flux due to reduced concentration polarization effect (as specified by the membrane supplier, and found as well in this study). For the TFC membrane, the polyamide thin-film layer (Fig. 1(e)) serves as the separation layer (AL). The polyester mesh filaments can be seen in the cross section for both CTA and TFC membranes (Fig. 1(a) and (d)).

The results for ZP presented in Fig. 2 were calculated using the Helmholtz-Smoluchowski equation [18]. The CTA membrane has a slight negative charge after pH 4.5, for both AL and SL. The TFC membrane has a negative charge for the AL, and a significantly stronger negative charge for the SL.

In summary, the new TFC membrane has higher water permeability than the CTA membrane. The stronger negative charge of the TFC membrane on both SL and AL is expected to have an effect on the reverse draw solute flux compared to the less negatively charged CTA membrane. Such effect is discussed further in Section 3.3 in relation with boron flux results.

3.2. Membrane performance

3.2.1. Water flux

Fig. 3 shows the water flux (permeate flux) patterns for the two membranes after the extraction of a fixed water volume (100 mL) through the FO membrane. Figure 3(a) represents the water flux obtained with DI water as FS, whereas Fig. 3(b) shows the results obtained with DI water spiked with 0.002 M H_3BO_3 as FS. There is no significant difference in the water flux when boron is added to the FS. Nevertheless, there is a clear difference between using NaCl and glucose as DS, considering that both solutions

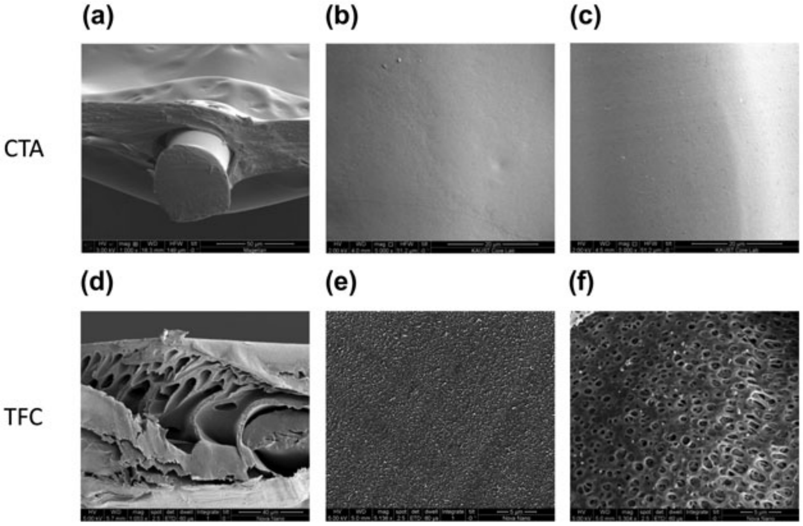

Fig. 1. SEM images showing the different structure of a CTA and a TFC FO membrane: (a) and (d) cross section (magnification 1,000×) showing the polyester embedded mesh (fibers), (b) and (e) AL (magnification 5,000×), and (c) and (f) support layer (magnification 5,000×).

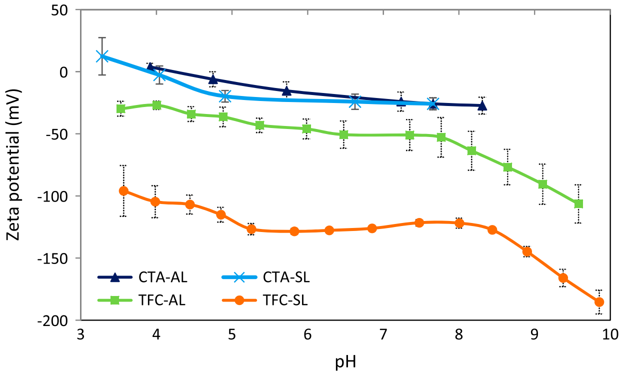

Fig. 2. ZP measured with a 10 mM KCl electrolyte for the CTA (same composition for AL and support layer (SL)) and TFC (polyamide AL and polysulfone SL) FO membranes. The TFC FO membrane has a more negatively charged surface on both sides, compared to the CTA membrane.

have similar osmotic pressure. The lower water flux obtained with glucose may be explained by a higher viscosity of the DS, which is a phenomenon known to occur with concentrated solutions of saccharides such as glucose or sucrose [19]. When comparing the performance of the two membranes, the new TFC membrane has about 20% higher water flux than the CTA membrane, regardless of the DS used under the experimental conditions in this study.

3.2.2. Draw solute rejection

The rejection percentage of DS is summarized in Table 1. The rejection for both, NaCl and glucose molecules, is equally high for both CTA and TFC membrane types. When results in Fig. 3 are compared to rejection results (Table 2), the TFC FO membrane shows to have a better performance (higher water flux at the same driving force) without compromising the low solute flux characteristic of membranes designed for osmotic processes.

Based on the results for water flux and draw solute rejection, both TFC and CTA FO membranes are suitable for desalination in terms of solute rejection for charged (NaCl) and neutral (glucose) osmotic agents, even when boron is present in the feed water, which had no impact on the water flux or reverse draw solute flux.

In conclusion, the new TFC FO membrane shows a better performance than the first generation CTA FO membrane for water permeability.

3.3. Boron flux

The boron flux in $\text{mg}\,\text{m}^{-2}\,\text{h}^{-1}$ for the different membranes and DSs used can be seen in Fig. 4(a) and (c). The interaction with a charged and non-charged molecule (NaCl and glucose, respectively) as DS does not directly impact the boron flux. This might be related to the neutral charge of boric acid at pH 7. On the other hand, the membrane orientation does play a role in boron flux, which increases when the AL-DS.

The effect of NOM membrane fouling on boron removal was studied with pre-fouled CTA and TFC membranes. The NOM fouling layer, composed of a biopolymer, does not seem to play an important role in promoting or decreasing boron transport through the membrane, as suggested by Jin et al. in previous studies [10].

Fig. 4(b) and (d) shows the reverse solute flux for both membranes under different membrane orientations. When glucose is used as DS, the reverse draw solute flux is significantly lower for both membranes in both orientations due to the larger molecule size

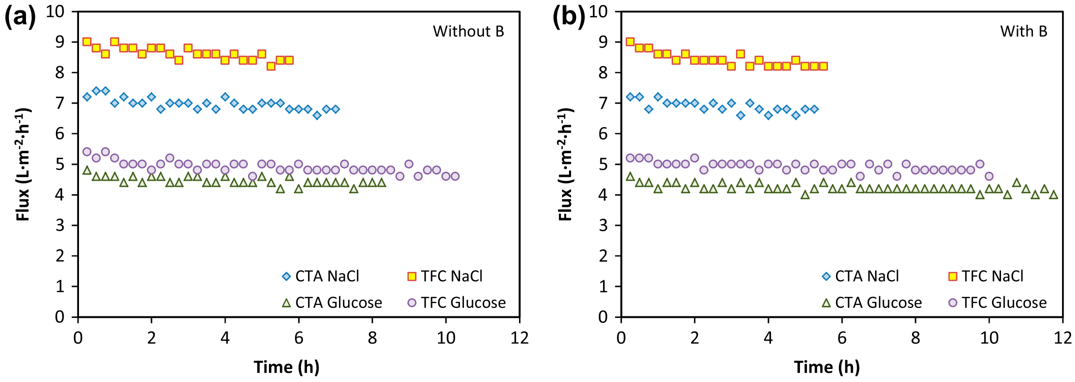

Fig. 3. Water flux patterns for different FO membranes. (a) Flux patterns for DI water as FS for both CTA and TFC membrane using different DSs (NaCl and glucose); (b) flux patterns for DI water spiked with boron as FS for both CTA and TFC membranes using different DSs. All experiments were performed in AL-FS orientation.

Table 1
Scheme of experimental studies on CTA and TFC FO membranes

Study	Figure	Table	Results section
Membrane characterization			
SEM observation	1		3.1
Zeta potential measurement	2		3.1
Membrane performance			
Water flux	3		3.2.1
Draw solute rejection		2	3.2.2
Boron flux			
Impact membrane orientation	4, 5		3.3
Impact of draw solution	4, 5		3.3
Impact fouled membrane	4, 5		3.3

Table 2
Total rejection of solutes from DS to the feed by FO membranes

	Rejection*(%)			
Membrane type	NaCl	Glucose	NaCl + B**	Glucose + B**
CTA	99.2	99.9	99.2	99.9
TFC	99.1	99.8	99.1	99.9

*Experiments conducted in AL-FS orientation.

**Boron was added as 5 mM boric acid (H_3BO_3) to the FS.

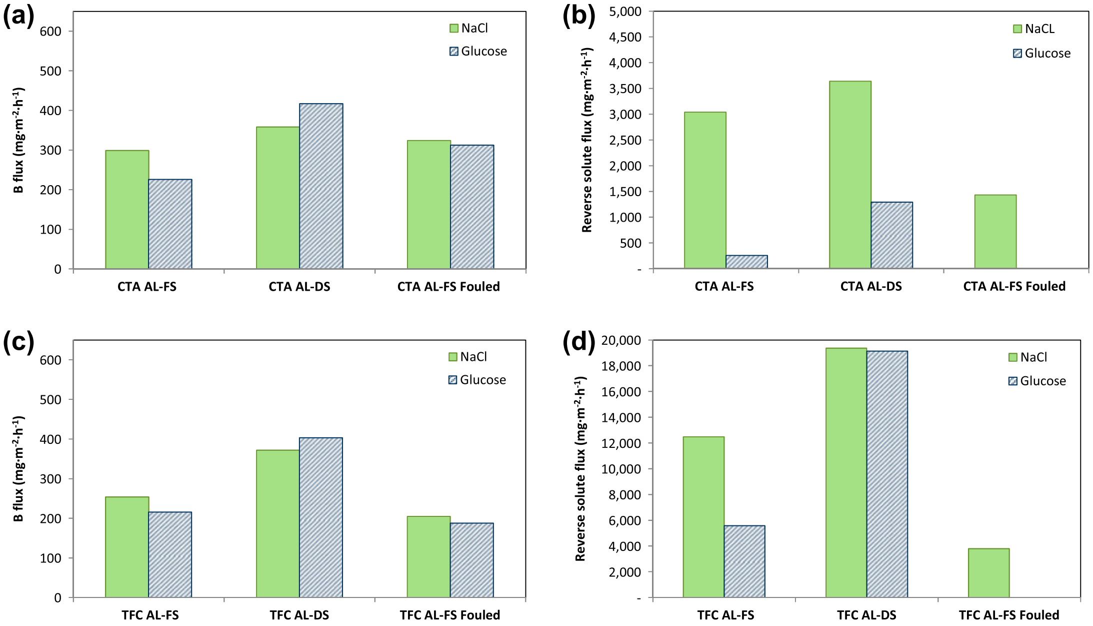

Fig. 4. Boron flux (a and c) and reverse solute flux (b and d) in mg m^{-2} h^{-1} for CTA and TFC FO membranes using NaCl and glucose as DS for three conditions: AL-FS, AL-DS, and a fouled membrane in AL-FS orientation.

compared to NaCl, except for the TFC membrane operated in AL-DS mode, which might be explained by the structure of the AL with its lower negative charge compared to the support layer, and the highly porous support which allows a higher number of solute molecules inside its structure.

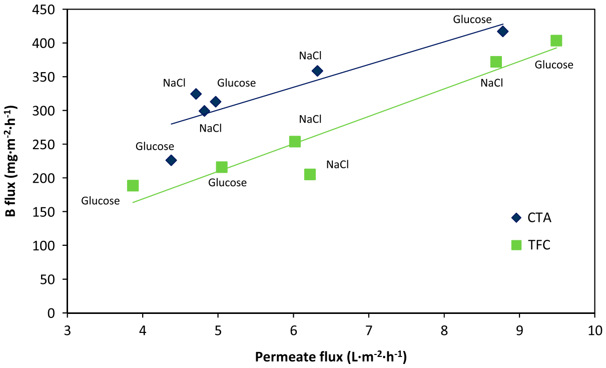

Fig. 5. Linear relation between boron flux and water permeate flux for CTA and TFC FO membrane. Independent from the draw solute used (NaCl or glucose), boron flux is directly proportional to the permeate flux. The TFC FO membrane enabled a lower boron flux than the CTA FO membrane.

A comparison between the membrane types, permeate water flux and boron flux is shown in Fig. 5. A linear positive correlation can be observed between the boron flux and the water flux (both boron and water fluxes have the same direction: from FS to DS). As the water flux increases, the boron flux increases, for both TFC and CTA membranes.

In essence, this study shows that the new generation TFC FO membrane exhibits compared to the first generation CTA membrane: (i) a 40% lower boron flux and (ii) 20% higher water flux for both types of draw solutes tested (NaCl and glucose). This demonstrates the potential for boron removal for new generation TFC FO membranes, even at high water fluxes compared to CTA FO membranes.

4. Conclusions

Experiments on boron rejection by CTA and TFC FO membranes have shown that:

- Membrane characteristics play a role in boron flux. At low and high water flux, the new generation TFC FO membranes show a lower boron flux than CTA FO membranes.
- Boron rejection is not affected by reverse draw solute flux, nor the draw solute charge.
- Natural organic matter fouling layer on the membrane has no significant impact on boron flux.

This demonstrates that the new generation TFC FO membrane is potentially suitable for *direct* desalination, particularly in terms of solute rejection and a reduced boron flux.

Acknowledgements

The authors sincerely thank Hydration Technology Innovations for the valuable contribution to providing FO membranes. The authors appreciate Mr Muhannad Abu-Ghdaib and the WDRC laboratory staff at KAUST for their great assistance.

References

[1] C. Dominguez-Tagle, V.J. Romero-Ternero, A.M. Delgado-Torres, Boron removal efficiency in small seawater Reverse Osmosis systems, Desalination 265(1–3) (2011) 43–48.
[2] D. Hasson, H. Shemer, I. Brook, I. Zaslavschi, R. Semiat, C. Bartels, M. Wilf, Scaling propensity of seawater in RO boron removal processes. J. Membr. Sci. 384(1–2) (2011) 198–204.
[3] World Health Organization, Guidelines for Drinking-water Quality, fourth ed., WHO Press, Geneva, 2011.
[4] H. Koseoglu, N. Kabay, M. Yüksel, S. Sarp, Ö. Arar, M. Kitis, Boron removal from seawater using high rejection SWRO membranes—Impact of pH, feed concentration, pressure, and cross-flow velocity, Desalination 227(1–3) (2008) 253–263.
[5] N. Nadav, Boron removal from seawater reverse osmosis permeate utilizing selective ion exchange resin, Desalination 124(1–3) (1999) 131–135.
[6] D.L. Shaffer, N.Y. Yip, J. Gilron, M. Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: Improved product water quality for potentially less energy, J. Membr. Sci. 415–416 (2012) 1–8.
[7] R. Valladares Linares, Z. Li, M. Abu-Ghdaib, C-H. Wei, G. Amy, J.S. Vrouwenvelder, Water harvesting from municipal wastewater via osmotic gradient: An evaluation of process performance, J. Membr. Sci. 447 (2013) 50–56.
[8] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, Environ. Sci. Technol. 43(17) (2009) 6769–6775.
[9] C. Kim, S. Lee, H.K. Shon, M. Elimelech, S. Hong, Boron transport in forward osmosis: Measurements, mechanisms, and comparison with reverse osmosis, J. Membr. Sci. 419–420 (2012) 42–48.
[10] 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.
[11] X. Jin, C.Y. Tang, Y. Gu, Q. She, S. Qi, Boric acid permeation in forward osmosis membrane processes: Modeling, experiments, and implications, Environ. Sci. Technol. 45(6) (2011) 2323–2330.
[12] J.S. Yong, W.A. Phillip, M. Elimelech, Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, J. Membr. Sci. 392–393 (2012) 9–17.
[13] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, J. Membr. Sci. 320(1–2) (2008) 292–302.
[14] Y. Wang, F. Wicaksana, C.Y. Tang, A.G. Fane, Direct microscopic observation of forward osmosis

membrane fouling, Environ. Sci. Technol. 44(18) (2010) 7102–7109.

[15] E.R. Cornelissen, D. Harmsen, K.F. de Korte, C.J. Ruiken, J.-J. Qin, H. Oo, L.P. Wessels, Membrane fouling and process performance of forward osmosis membranes on activated sludge, J. Membr. Sci. 319(1–2) (2008) 158–168.

[16] 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(1–2) (2011) 356–362.

[17] Z.-Y. Li, V. Yangali-Quintanilla, R. Valladares-Linares, Q. Li, T. Zhan, G. Amy, Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis, Water Res. 46(1) (2012) 195–204.

[18] R. Valladares Linares, V. Yangali-Quintanilla, Z. Li, G. Amy, Rejection of micropollutants by clean and fouled forward osmosis membrane, Water Res. 45(20) (2011) 6737–6744.

[19] E.M. Garcia-Castello, J.R. McCutcheon, M. Elimelech, Performance evaluation of sucrose concentration using forward osmosis, J. Membr. Sci. 338(1–2) (2009) 61–66.