Fouling and long-term durability of an integrated forward osmosis and membrane distillation system

T. Husnain, B. Mi and R. Riffat

ABSTRACT

An integrated forward osmosis (FO) and membrane distillation (MD) system has great potential for sustainable wastewater reuse. However, the fouling and long-term durability of the system remains largely unknown. This study investigates the fouling behaviour and efficiency of cleaning procedures of FO and MD membranes used for treating domestic wastewater. Results showed that a significant decline in flux of both FO and MD membranes were observed during treatment of wastewater with organic foulants. However, shear force generated by the increased cross-flow physically removed the loosely attached foulants from the FO membrane surface and resulted in 86–88% recovery of flux by cleaning with tap water. For the MD membrane, almost no flux recovery was achieved due to adsorption of organic foulants on the hydrophobic membrane surface, thus indicating significant irreversible fouling/wetting, which may not be effectively cleaned even with chemical reagents. Long-term (10 d) tests showed consistent performance of the FO membrane by rejecting the contaminants. However, organic foulants reduced the hydrophobicity of the MD membrane, caused wetting problems and allowed contaminants to pass through. The results demonstrate that combination of the FO and MD processes can effectively reduce irreversible membrane fouling and solve the wetting problem of the MD membrane.

Key words | flux recovery, forward osmosis, membrane distillation, organic fouling, wastewater reuse

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INTRODUCTION

Recently developed membrane technologies exhibit high potential to address water scarcity challenges. New membrane processes, including osmotically driven forward osmosis (FO) and thermally driven membrane distillation (MD) have demonstrated many advantages over traditional pressure-driven processes (Burgoyne & Vahdati 2000; Cath *et al.* 2006; Chen *et al.* 2009). The processes have their limitations when used as a stand-alone system, i.e. recovery of draw solution in forward osmosis, and fouling and wetting problem in membrane distillation. In an integrated forward osmosis – membrane distillation (FO-MD) system, MD is used to recover draw solutes for continuous FO operation, and FO works as a pre-treatment barrier to reduce MD fouling. Combining the systems with each other circumvent the drawbacks and achieve high rejection of contaminants, operation at ambient pressure and has the potential of using renewable low grade heat as energy source (Husnain 2014).

Membrane fouling describes the potential deposition and accumulation of constituents in the feed stream of the membrane. Fouling is a major problem for application of membrane processes. It is an important consideration in the design and operation of membrane systems as it affects pre-treatment needs, cleaning requirements, operating conditions, cost and performance (Metcalf & Eddy 2003). Numerous studies have been conducted to elucidate the mechanism governing the fouling in pressure-driven membranes, i.e. microfiltration, reverse osmosis (RO), etc. However studies investigating the mechanisms of fouling in FO are scarce. Recent research has focused on developing membranes that are more resistant to fouling (Riffat 2012). Mi & Elimelech (2008) observed a strong correlation between organic fouling in FO and intermolecular adhesion force, thus alginate fouling is more severe than fouling caused by bovine serum albumin (BSA) and humic acid. They also suggested that hydrodynamic condition and

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intermolecular adhesion have little effect after cake layer is formed. Liu & Mi (2012) observed a rapid flux decline in FO due to synergistic effect of alginate and gypsum. The organic fouling is mostly reversible and high flux recovery was achieved by simple water rinse, without any chemical cleaning reagents, thus suggesting low fouling potential, although membrane material and membrane foulants interaction plays an important role. The full-scale application of FO process has been hindered by lack of systematic mechanistic understanding of its fouling and cleaning behaviour (Mi & Elimelech 2010).

Fouling is also a major obstacle in the MD process. Municipal wastewater is rich in organic content, e.g. protein, amino sugars, polysaccharides and polyhydroxy-aromatics. For feed-water high in natural organic matter (NOM) like municipal wastewater, organic fouling appears to be the most significant factor in increasing fouling potential (Liu *et al.* 2001) by forming NOM patches around the pores on the membrane surface that eventually expand to form a continuous gel layer. The level of feed temperature significantly influences the level of fouling and severe MD membrane fouling by protein was observed by the researchers at higher temperatures (Gryta 2012). High temperature also increases the scaling problem caused by $CaCO_3$. With temperature drop, solute solubility decreases and deposit is formed as a result of temperature polarization. Deposition of organic foulants on the membrane surface is one of the major operational problems in MD (Gryta *et al.* 2008). Tun *et al.* (2005) examined the effect of high concentration of NaCl and Na_2SO_4 on the permeate flux and observed that flux gradually decreases during the MD process until feed concentration reaches the super-saturation point causing the precipitation of such sparingly soluble minerals, and flux decreases sharply to zero. The same result was obtained by Yun *et al.* (2006), who concluded that when the membrane surface concentration reaches saturation, the properties of the boundary layer will differ from the bulk solution properties. When treating seawater, scaling potential caused by gypsum and calcium carbonate is a critical problem (Curcio *et al.* 2010). Precipitation of $CaCO_3$ on the membrane surface was observed when tap water was used as feed. Khayet *et al.* (2004) demonstrated a preferential adsorption of humic acid at the surface of membrane exhibiting higher hydrophobic character with a consequential more pronounced deterioration of the trans-membrane flux.

In recent years, there has been a growing interest in FO. Recent studies have shown that FO could be of strategic importance in several applications where RO has dominated for several decades as well as in other applications such as liquid food processing and material recycling. It has the potential of lower irreversible fouling compared to pressure-driven membrane processes, because of the lack of applied hydraulic pressure, presenting an attractive approach to the area of water and wastewater treatment (Lee *et al.* 2010). The objective of this study was to investigate the fouling potential and efficiency of cleaning procedures of an integrated FO-MD system for sustainable wastewater reuse. Laboratory-scale studies were conducted to evaluate the long-term durability and performance of the integrated system.

MATERIALS AND METHODS

The FO membrane was provided by Hydration Technology Innovations (Albany, OR). It has an asymmetric structure and is made of Cellulose Triacetate (CTA) with embedded polyester screen support. According to the manufacturer, the total thickness of the membrane is approximately 50 μm, maximum operating temperature is 71 °C, the maximum trans-membrane pressure is 10 psi, and the operating pH range is 3 to 8. The MD membrane was obtained from GE Osmonics (Minnetonka, MN). It is an asymmetric polypropylene (PP) membrane with nominal pore size of 0.22 μm and thickness of 130–170 μm.

The wastewater used in this study was the secondary effluent from Blue Plains Advanced Wastewater Treatment Plant (AWTP) in Washington, DC. In order to facilitate the fouling on the membrane surface, the wastewater was spiked with organic foulants. Sodium alginate and bovine serum albumin (BSA/Fraction V) were used as the model organic foulants. Alginate has been extensively used in membrane fouling research to represent polysaccharides which constitute a major fraction of soluble microbial products in wastewater effluent. Bovine serum albumin (also known as BSA) is a serum albumin protein which is often used to represent fouling caused by protein in wastewater (Mi & Elimelech 2010). The molecular weight of BSA was 66,000 daltons (66 kDa). The solubility in water or aqueous buffers was 20 mg/mL and required up to 24 h to fully dissolve. Stock solutions of BSA and alginate (10 g/L) were prepared with deionized (DI) water, 24 h in advance for complete dissolution of foulants. The stock solutions were kept in sterilized glass bottles in a refrigerator (4 °C). The physicochemical characteristics of the wastewater used in this study are presented in Table 1.

Table 1 | Characteristics of wastewater for fouling and cleaning experiments

Parameters	Units	Feed
pH	–	7.96
Alkalinity	mg/L as $CaCO_3$	175
Turbidity	NTU	>150
TSS	mg/L	24.6
Soluble COD	mg/L	27.2
Conductivity	μS/cm	1,685
NH_3-N	mg/L	12.05
Sodium alginate	mg/L	100
BSA (Fraction V)	mg/L	100

TSS, total suspended solids; COD, chemical oxygen demand.

Bench-scale FO-MD membrane modules consisted of a custom-built cross-flow membrane cell with three channels for feed, draw and permeate. The effective area for both FO and MD membranes were 20.02 cm^2 in the membrane cell. The FO membrane was placed between feed and draw, and the MD membrane was placed between draw and permeate. For the individual FO process, feed was the wastewater, draw was 1 M NaCl solution and the permeate channel was blocked. Water was transported from feed to draw due to concentration gradient across FO membrane. For the individual MD process, feed channel was blocked, draw was the wastewater operating at a higher temperature (50 °C), and permeate was purified water. Water was transported from draw to permeate due to temperature induced vapour pressure gradient across the MD membrane. In the integrated FO-MD system, feed was the wastewater, draw was 1 M NaCl solution and permeate was purified water. The operating temperature of feed, draw and permeate were maintained at 20 °C, 50 °C and 20 °C, respectively. The schematic of bench-scale setup of the FO-MD process is shown in Figure 1.

The protocol for all fouling experiments in the FO process comprised the following steps. New membrane cells were placed in the FO system before the experiments. The feed and draw tank were filled with 2 L solutions. The temperatures of the feed and draw tanks were maintained at room temperature (20 ± 1 °C) and cross-flow rates were 0.4 L/min. The system was run for 15 min in closed loop without passing flow through the membrane cell to stabilize the temperature before the feed and draw flows were allowed into the membrane cell. The weight change in the draw tank was continuously monitored by a computer and the water flux through the FO membrane was recorded. For the MD process, the experimental protocol was similar to the FO process, except the temperatures

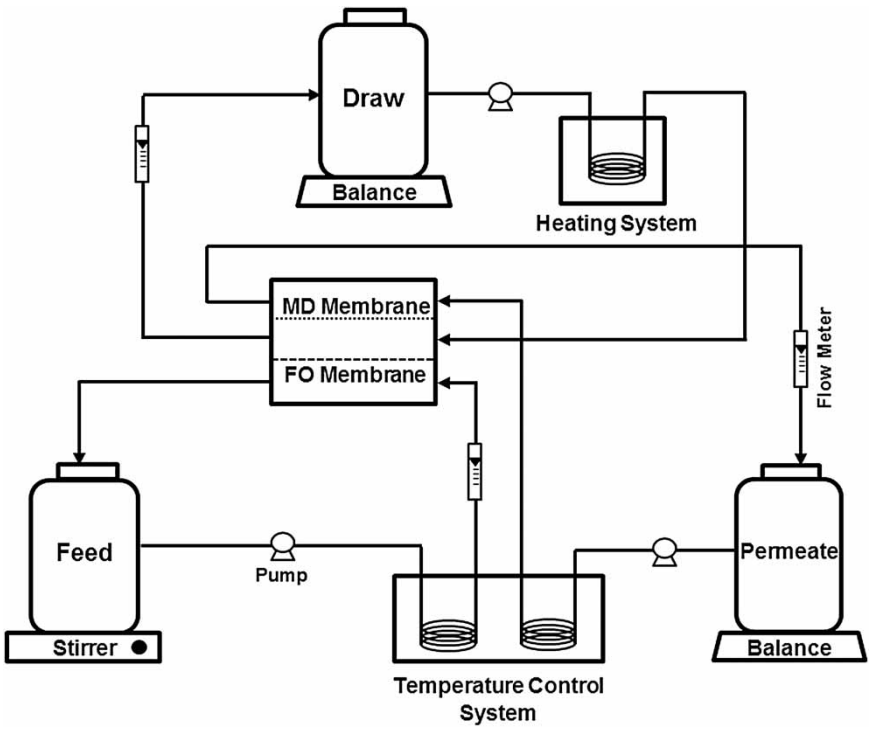

Figure 1 | Schematic diagram of the integrated FO-MD membrane system.

of the draw and permeate tanks were maintained at 50 °C and 20 °C, respectively.

The membrane cleaning was performed for 5–30 min after 48 h of continuous (day and night) fouling experiment to investigate flux recovery. The original solution tanks were switched with tap water tanks. The cross-flow rates of the channels were increased to 1.0 L/min. The system was run for 5, 15 or 30 min to allow the increased cross-flow to remove the foulants from the membrane surface.

RESULTS AND DISCUSSION

Significant decline in trans-membrane flux in the FO and MD membranes were observed while treating wastewater with organic foulants, as shown in Figure 2. For the FO membrane, the gradual decline in flux was due to dilution and fouling effect. For MD, the flux declined rapidly. The hydrophobic character of the MD membrane enhanced the adsorption of organic materials onto the membrane surface and resulted in the rapid flux decline.

Comparing the fouling effect of FO and MD, it was clear that the MD membrane was more susceptible to fouling. For FO, the flux declined gradually over time, whereas for MD, most of the flux declined in the initial 4–6 h of the experiment. Although MD had a higher initial flux of 4×10^{-6} $m^3/m^2.s$ as compared to 3.4×10^{-6} $m^3/m^2.s$ for FO, and the final flux was approximately 1.9×10^{-6} $m^3/m^2.s$ for both FO and MD membranes after 48 h, FO was able to treat 1,095 mL of water as compared to 556 mL for MD. Also, MD was affected by fouling when secondary effluent was used without any additional foulants, which is not the case for FO. Therefore, domestic wastewater which is rich in organic content is difficult to treat by the MD process alone.

The results from the cleaning experiments showed great potential for cleaning FO membranes with tap water. In Figure 3, FO flux declined from approximately 3.4×10^{-6} $m^3/m^2.s$ to less than 2×10^{-6} $m^3/m^2.s$ in all experiments. However, cleaning the membrane with tap water recovered up to 88% of the initial flux. The cleaning time played an important role on the flux recovery. Increasing cleaning time from 5 to 15 min increased the flux recovery from 74 to 86%, although cleaning for longer period did not result in improved flux.

Flux recovery in FO is generally much higher than other pressure driven membrane processes. This is due to the fact that FO is a low pressure operation. The foulants are loosely attached to the membrane surface as compared to pressure driven processes, and hence are physically removed by the shear force generated by the increased cross-flow. The low pressure operation also facilitates the use of tap water for cleaning the membrane without harmful chemicals and detergents, thus being more environmentally sustainable.

The cleaning experiments with the MD membrane showed little to no recovery of flux, as illustrated in Figure 4. The hydrophobic characteristics of the membrane attracted the organic and inorganic foulants and caused irreversible membrane fouling. Therefore, tap water was not able to remove the foulants from the membrane surface and no flux recovery was achieved. Other researchers have used chemicals, such as 5% (by wt.) solution of HCl (Gryta *et al.* 2008) and detergents to clean the membrane surface. The obtained results also suggest that tap water may not be an option for cleaning a fouled MD membrane.

The initial fluxes were consistent for the new membranes, whereas the variations in fluxes after fouling and cleaning were relatively high. We also observed that the flux decline due to membrane fouling were different even after using the

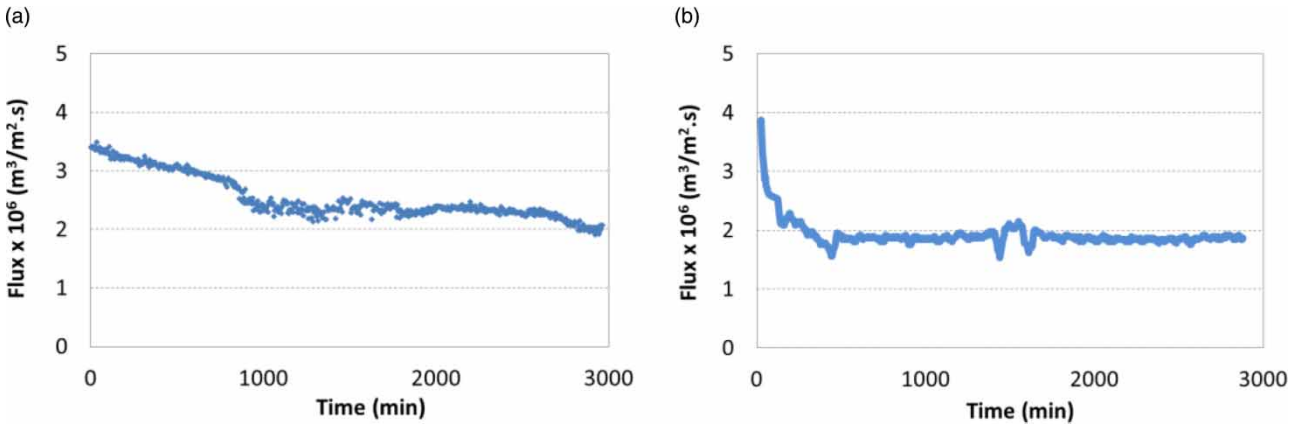

Figure 2 | Flux decline in (a) FO and (b) MD membrane systems.

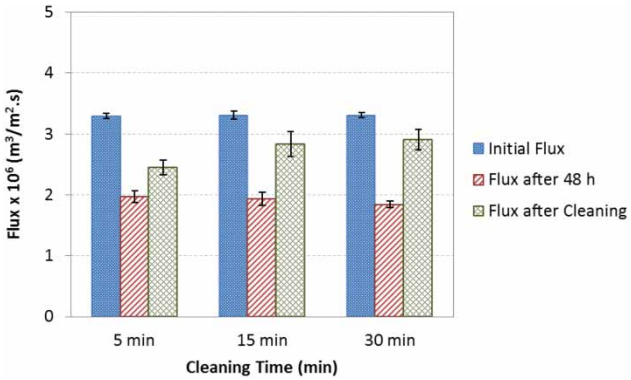

Figure 3 | Flux recoveries in FO membrane system.

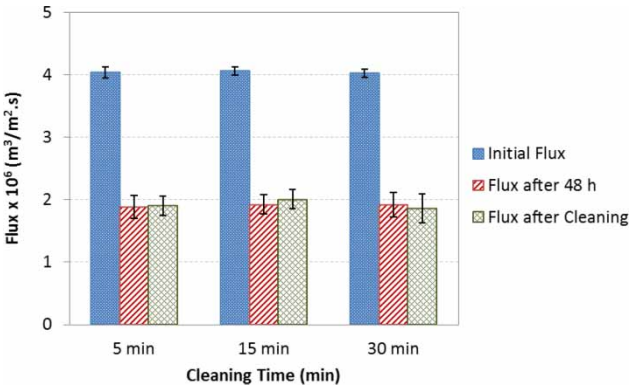

Figure 4 | Flux recoveries in MD membrane system.

same feed solution. The variations could be due to the presence of membrane defects or wastewater characteristics.

Long-term durability and performance of the FO and MD processes were conducted by running the experiments for 10 d. The durability was determined by the contaminant rejection potential. The FO membrane demonstrated excellent performance in rejecting NH_3-N with feed concentration of 12.05 mg/L for long periods, as shown in Figure 5. Although flux declined continuously due to dilution and fouling effect, the NH_3-N concentration in the draw solution was fairly constant with less than 0.3 mg/L of nitrogen after 10 d. This indicated that the FO membrane performance, in terms of contaminant rejection, did not deteriorate with time. The soluble chemical oxygen demand (COD) concentration in the draw solution was less than 10 mg/L after 10 d. Other parameters such as pH, alkalinity, turbidity and total suspended solids (TSS) were also consistent in the draw solution.

In contrast, the performance of the MD membrane deteriorated over time, as shown in Figure 6. The conductivity of the permeate was less than 50 μS/cm for the first 6 d, then

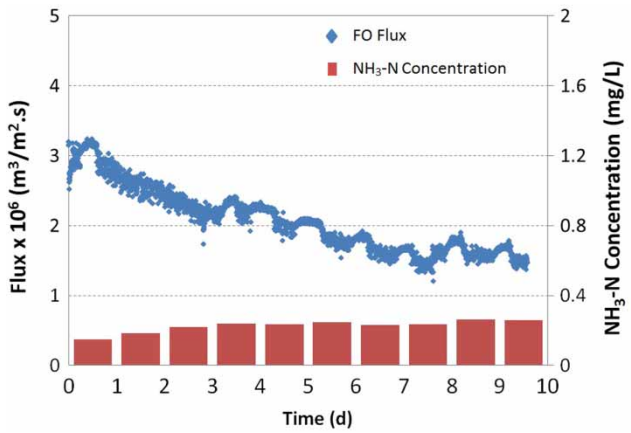

Figure 5 | Flux and NH_3-N concentrations in FO membrane durability test.

increased rapidly, indicating performance deterioration in terms of rejection. When the same experiments were conducted with pure NaCl solution (which is the draw solution for FO process), the conductivity measurements were less than 15 μS/cm, as shown in Figure 6. No sudden deterioration of membrane performance was observed here. It showed that organic materials present in the wastewater were responsible for damaging MD membrane performance. Because of the hydrophobic character of the MD membrane, the organic foulants were adsorbed on the membrane surface. This caused membrane wetting problems, reduced its hydrophobicity and allowed contaminants (measured by conductivity) to pass through the membrane.

The results demonstrate another advantage of the FO membrane as compared to the MD membrane. FO performed better than MD in rejecting contaminants for longer periods when treating wastewater with organic content. FO was able to reject most common contaminants from wastewater for at

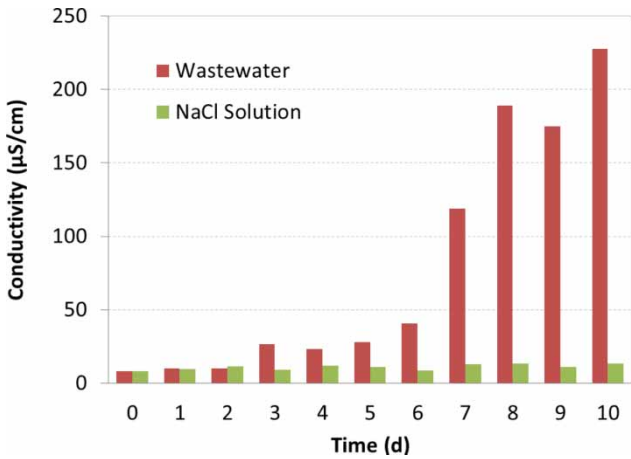

Figure 6 | Conductivity measurements in MD membrane durability test.

least 10 d. For MD, the performance was consistent when using NaCl as the feed, but organic contents of wastewater deteriorated its performance significantly. In the integrated FO-MD system, FO rejected most of the foulants from the feed solution and kept the foulants away from the draw solution, thus reducing the effect of fouling on the MD performance.

CONCLUSIONS

Overall, the FO membrane exhibited low fouling potential and high cleaning efficiency, whereas fouling and cleaning were major obstacles in the MD operation. Cleaning the FO membrane with tap water recovered up to 88% of the initial flux, which was not the case for MD. The performance of the FO membrane was also consistent in the long-term (10 d) experiments with less than 0.3 mg/L NH_3-N in the draw solution. The deterioration of MD membrane performance was observed due to the presence of organic materials in the feed solution. The synergistic effects of the FO and MD processes have the potential to reduce membrane fouling problem, because FO membrane retains foulants on the feed side, thus preventing irreversible MD membrane fouling in the integrated FO-MD system.

REFERENCES

Burgoyne, A. & Vahdati, M. 2000 Review: Direct contact membrane distillation. *Separation Science and Technology* **35** (8), 1257–1284.

Cath, T. Y., Childress, A. E. & Elimelech, M. 2006 Forward osmosis: principles, applications, and recent developments. *Journal of Membrane Science* **281** (1/2), 70–87.

Chen, T. C., Ho, C. D. & Yeh, H. M. 2009 Theoretical modeling and experimental analysis of direct contact membrane distillation. *Journal of Membrane Science* **330** (1/2), 279–287.

Curcio, E., Ji, X., Profio, G. D., Sulaiman, A. O., Fontananova, E. & Drioli, E. 2010 Membrane distillation operated at high seawater concentration factors: role of the membrane on $CaCO_3$ scaling in presence of humic acid. *Journal of Membrane Science* **346** (2), 263–269.

Gryta, M., Tomaszewska, M. & Karakulski, K. 2008 Fouling in direct contact membrane distillation process. *Journal of Membrane Science* **325**, 383–394.

Gryta, M. 2012 Effectiveness of water desalination by membrane distillation process. *Membranes* **2** (3), 415–429.

Husnain, T. 2014 *Combined Forward Osmosis and Membrane Distillation System for Wastewater Treatment and Reuse*. PhD Thesis, George Washington University, Washington, DC.

Khayet, M., Velázquez, A. & Mengual, J. I. 2004 Direct contact membrane distillation of humic acid solutions. *Journal of Membrane Science* **240** (1–2), 123–128.

Lee, S., Boo, C., Elimelech, M. & Honga, S. 2010 Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). *Journal of Membrane Science* **365**, 34–39.

Liu, C., Caothien, S., Hayes, J., Caohuy, T. & Otoyo, T. 2001 Membrane chemical cleaning: From art to science. In: *Proceedings of Membrane Technology Conference, March 4–7*, San Antonio, TX.

Liu, Y. & Mi, B. 2012 Combined fouling of forward osmosis membranes: Synergistic foulant interaction and direct observation of fouling layer formation. *Journal of Membrane Science* **407–408**, 136–144.

Metcalf & Eddy 2003 *Wastewater Engineering: Treatment and Reuse*. 4th edn, McGraw Hill, Inc., NY, USA.

Mi, B. & Elimelech, M. 2008 Chemical and physical aspects of organic fouling of forward osmosis membranes. *Journal of Membrane Science* **320** (1/2), 292–302.

Mi, B. & Elimelech, M. 2010 Organic fouling of forward osmosis membranes: fouling reversibility and cleaning without chemical reagents. *Journal of Membrane Science* **348** (1/2), 337–345.

Riffat, R. 2012 *Fundamentals of Wastewater Treatment and Engineering*. CRC Press, FL, USA.

Tun, C. M., Fane, A. G., Matheickal, J. T. & Sheikholeslami, R. 2005 Membrane distillation crystallization of concentrated salts – flux and crystal formation. *Journal of Membrane Science* **257** (1–2), 144–155.

Yun, Y., Ma, R., Zhang, W., Fane, A. G. & Li, J. 2006 Direct contact membrane distillation mechanism for high concentration NaCl solutions. *Desalination* **188** (1–3), 251–262.

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