Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21983

105 (2018) 1–10
February

The forward osmosis application: using the secondary effluent as makeup water for cooling water dilution

Chen Wang[a], Baoyu Gao[a,*], Pin Zhao[a], Qinyan Yue[a], Ho Kyong Shon[b], Shihui Yang[a]

[a]*Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan250100, China, email: wangchen_sdu@aliyun.com (C. Wang), Tel. +8653188366771, Fax +8653188364513, email: baoyugao_sdu@aliyun.com (B. Gao), wszplak@163.com (P. Zhao), qyyue58@aliyun.com (Q. Yue), ysh939596@aliyun.com (S. Yang)*

[b]*School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia, email: Hokyong.Shon-1@uts.edu.au (H.K. Shon)*

Received 22 August 2017; Accepted 5 February 2018

ABSTRACT

This study evaluated the feasibility of using the secondary effluent as makeup water for cooling water. The secondary effluent and the simulated cooling water were used as feed solution (FS) and draw solution (DS) in FO process. Ammonium bicarbonate was added into the simulated cooling water to promote the osmotic pressure. The tests were studied under different membrane orientations, temperatures and flow rates using both TFC-FO and CTA-FO membranes, and determined in terms of water flux, the permeate recovery and membrane fouling. The considerable permeate recovery (18.9% at 20 h) and reversible membrane fouling indicated that the feasibility of using FO for cooling water reuse. CTA- and TFC-PRO modes had higher initial water flux, but more significant flux decline compared to CTA- and TFC-FO modes. The optimal conditions were determined to be 25°C and 17.0 cm/s in which the water flux was highest. The results showed that water flux did not increase with the temperature when it was above than 30°C. The same situation occurred at the cross flow velocity above than 17 cm/s. The fouling of TFC membrane was serious after running 20 h, but it could be cleaned well by 1 h simple surface flushing and the water flux could restore nearly 93.8%.

Keywords: Forward osmosis; The secondary effluent; Cooling water; Water flux; Membrane fouling

1. Introduction

Power plants are among the biggest water-consuming industries. Of all systems in a power plant, cooling towers (CT) are the largest water consumers using 60–70% of the total fresh water demanded in industry [1,2]. A large amount of make-up water is used to keep the water balance and cooling water operation at a steady state because a significant amount of water is lost by evaporation, wind action, leakage and drainage. Drainage loss is called the cooling tower blowdown water which constitutes the biggest portion of the feed water loss. It varies greatly with changes in source water quality and cooling water treatment [2]. In the past, most of blowdown water was discharged directly to surface water bodies without any treatment in China leading to the waste of water resources and serious environmental pollution [3,4]. Thus, these reasons have been the primary motivations driving recent research on blow down water treatment and reuse [5].

Conventional method for the treatment of blow down water is a combination of conventional techniques such as coagulation/flocculation, biochemical treatment, and disinfection prior to desalination by ion exchange [1]. However, ion exchange technology has a number of disadvantages such as long treatment time, significant space requirements, high running cost, etc. [6,7]. Recently, two major types of technologies that are used for blow down water treatment and reuse can be classified as thermal process and membrane process. Wang et al. [1] investigated coagulation as a

---

*Corresponding author.

pretreatment of a membrane distillation system, which promoted the water flux of membrane. Zhang et al. [8] studied a pilot test of UF pretreatment before RO filtration for cooling tower blowdown water for reuse in power plants. They proved that the UF pretreatment can relieve RO fouling. Altman et al. [9] showed that a nanofiltration treatment on a side stream of reuse cooling water could decrease water usage and discharge in total. But one of main obstacles impeding these technologies is membrane fouling simply because hydraulic pressure is the driving force in these processes. The membrane fouling adversely affects operation costs, energy demand, membrane cleaning and lifespan of the membrane.

In the past decade, forward osmosis (FO) has been considered as an energy-efficient and economical technology [10–13]. FO is a technical term describing the natural phenomenon of osmosis: the transport of water molecules diffuse through a semi-permeable membrane driven by the osmotic pressure difference between the two sides of the membrane [12,14]. Theoretically, the FO membrane allows only permeation of water molecules while the solution or salts molecules are rejected [15]. Due to the absence of applied pressure and the small pore radius, FO has some potential advantages over current technologies, which can be summarized as low energy, low and reversible membrane fouling, and high retention [16,17]. FO performance enhances with the increase of temperature. It is assumed that cooling water can be a suitable draw solution. The cooling water can be diluted after the FO process, which can be reused into the cooling circle system. Moreover, the temperature of cooling water usually is high, which is beneficial to the water permeation. W. Wendong et al. [18] chose rainwater as feed solution and cooling water as draw solution in FO, and studied the effects of pH and temperature on forward osmosis membrane flux. They found that the method for cooling water makeup is feasible. The water flux increased approximately 10 times when increased the temperature of the draw solution from 3°C to 50°C .However, it may not be practicable in many areas with less rainfall.

Secondary treated municipal wastewater is a reliable and easily accessible resource [19]. Nowadays, secondary effluent is usually treated by advanced treatment such as traditional coagulation sedimentation, membrane treatment technology, advanced oxidation treatment and disinfection for agricultural irrigation, industrial water and groundwater recharging [20]. If we can use secondary effluent as the make-up water for cooling water in the FO process, it can save fresh water resource and reduce the water environmental pollution. However, there still exists a problem that the osmotic pressure of the cooling water is not high enough to drive the secondary effluent. In our work, the ammonium bicarbonate was added into the cooling water to increase the osmotic pressure of draw solution. Ammonium bicarbonate has been proved to have highly soluble and capable of generating high osmotic pressure [13]. As we all know that, the diluted ammonium bicarbonate can be easily removed by heating above 60°C [21,22]. So ammonium bicarbonate is a desirable solute because it can help to raise osmotic pressure and can be easily decomposed into gases which will not influence the composition of draw solution.

In this study, FO was applied to use the secondary effluent as makeup water for cooling water dilution. The effects of membrane orientation, temperature and cross velocity on the water fluxes were studied. The performances of two kinds of FO membranes the polyamide-based thin-film composite (TFC) FO membrane and the cellulose triacetate (CTA) FO membrane were measured and compared. Moreover, the feasibility of using FO for cooling water recycling was studied in terms of the permeate recovery and membrane scaling. Membrane autopsy was analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). It is envisioned that this study may support the fundamentals to the further development of FO in reusing cooling waste.

2. Materials and methods

2.1. Feed and draw solution

The feed solution (FS) in our study was the secondary effluent obtained from the Guangda sewage plant in Jinan, China. Detail properties of the secondary effluent are presented in Table 1. The osmotic pressure was measured by Freezing Point Osmometer (Germany loser).It can be seen that the osmotic pressure of the secondary effluent is from 0.52 atm to 0.68 atm. Its pH ranges from 7.52 to 7.75 indicating the secondary effluent is neutral. The draw solution (DS) was the simulated cooling water discharged from a power plant in Beijing which was consisted of 1.3 g NaCl, 2.5 g $MgSO_4 \cdot 7H_2O$ and 2.5 g $NaHCO_3$ adding NH_4HCO_3 (6.3 g) to raise its osmotic pressure [23]. Its basic properties including pH, osmotic pressure and viscosity were predicted using OLI Systems analyzer and are shown in Table 2. With an increase in temperature, the pH of DS ranges from 7.59 to 7.79. The recommended operational pH ranges of TFC-FO membrane and CTA-FO membrane is from 2.0 to 12.0 and 3.0 to 8.0. So both membranes will not undergo structure change in the FO processes. The osmotic pressure increases with the increased temperature. But the amplitude of the

Table 1
Characteristics of the secondary effluent

	Secondary effluent
pH	7.52~7.75
TDS (mg/L)	1023~1122
DOC (mg/L)	5.956~6.015
TN (mg/L)	7.47~7.55
TP (mg/L)	0.308~0.316
Calcium stiffness (mmol/L)	2.25~2. 43
Osmotic pressure (atm)	0.52~0.68

Table 2
Properties of DS at different temperatures

Temperature (°C)	pH	Osmotic pressure (atm)	Viscosity (mPa·s)
20	7.79507	6.48524	1.05245
25	7.72462	6.60233	0.936646
30	7.65673	6.71621	0.840056
35	7.59135	6.82702	0.758534

variation is very small, only 5.25% from 20°C to 35°C. Moreover, the viscosity of DS decreases with the increased temperature. All chemicals used in our studies were analytical grade, which were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai).

2.2. Forward osmosis membrane

Our studies used two kinds of FO membrane: the homemade TFC-FO membrane and the commercial CTA-FO membrane. The TFC-FO membrane had been verified possessing high water flux and salt rejection [24,25]. The CTA-FO membrane was provided by Hydration Technology Innovations (HTI), Albany, USA. It was made from cellulose acetate embedded in a polyester woven mesh and owned the general characteristics of asymmetric structure. To have a clear observation of the CTA- and TFC-FO membranes, micrographs of both membranes were determined using the scanning electron microscope (HITACHI S-520). The support and active layers micrographs are shown in Fig. 1. More physical and chemical properties of TFC- and CTA-FO membranes are presented in Table 3. Contact angle were measured using a contact angle goniometer (JC2000C Contact Angle Meter, Shanghai Zhongchen Experiment Equipments Co. Ltd., China).

There are two different layers of the FO membrane: a thick mechanical support layer (SL) and a thin active layer (AL). This results in two distinct membrane orientations. When the mechanical support layer faces the DS and the active layer faces the FS, the orientation is described as the

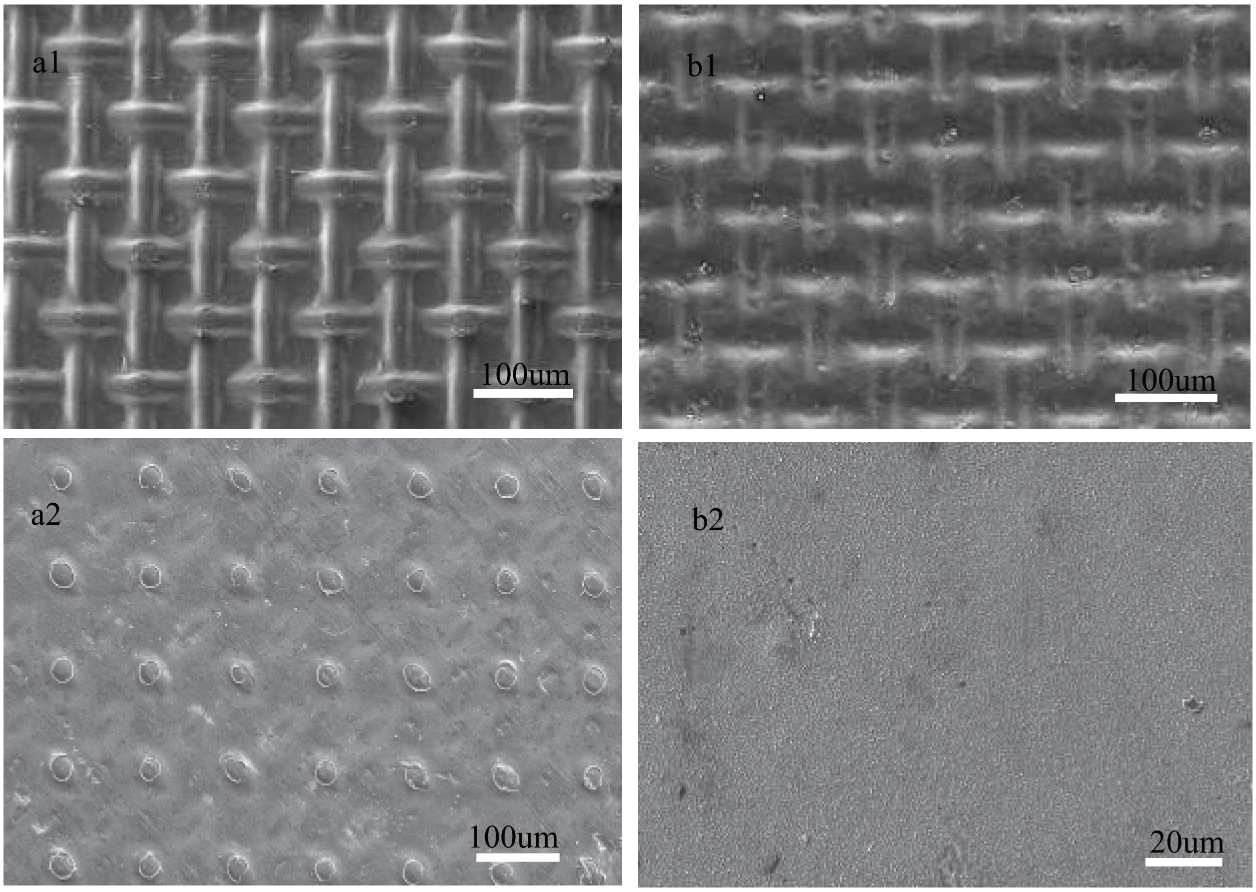

Fig. 1. SEM images of CTA- and TFC-FO membranes: (a1) support layer of CTA membrane, (a2) active layer of CTA membrane, (b1) support layer of TFC membrane, (b2) active layer of TFC membrane.

Table 3
The comparison of physical and chemical properties between TFC-FO membrane and CTA-FO membrane

Sample	Active layer material	Contact angle (°)		Zeta potential (mv) at active layer	Operating pH
		Active layer	Support layer		
TFC	Polyamide	57	65	–28.75	2–11
CTA	Cellulose triacetate	77	72	16.61	3–8

FO mode. On the contrary, when the active layer faces the DS and the mechanical support layer faces the FS, the orientation is described as the PRO mode.

2.3. Forward osmosis system

The FO system in this study was a laboratory-scale FO setup [26]. The diagrammatic sketch of the setup is shown in Fig. 2. The effective membrane area of the FO membrane unit was 20.0 cm^2 (7.7 cm length, 2.6 cm width and 0.3 cm depth). Two peristaltic pumps (BT300-2J, Baoding Longer Precision Pump CO., Ltd., China. Pump head: YZ1515x) were used to adjust FS and DS at the flow rates of 8.5, 17.0, 25.5 cm/s. A water bath controlled by temperature controller was used to adjust the temperatures of both FS and DS at 20 ± 1, 25 ± 1, 30 ± 1, 35 ± 1°C. A weight balance (Satorius weighting technology GmbH, Gottingen, Germany) was used to record the variation in the DS weight for water flux computation. Both of the original volumes of FS and DS are 1L in our studies.

2.4. Membrane characterization

2.4.1. Water flux

The water flux is calculated as:

$$J_w = \frac{\Delta m}{A \times \Delta t \times \rho} \tag{1}$$

where J_W refers to the water flux during FO process, L/(m^2 h) (LMH); A refers to the effective membrane area; Δt refers to the measuring time interval; Δm refers to the measuring weight interval of the water which permeates from feed solution to draw solution; ρ refers to the water density.

2.4.2. Reverse salt flux

The reverse salt flux is calculated as:

$$J_S = \frac{C_t \times V_t - C_0 \times V_0}{A \times \Delta t} = \frac{C_t(V_0 - J_W \times A \times \Delta t) - C_0 \times V_0}{A \times \Delta t} \tag{2}$$

where J_S refers to the reverse salt flux during FO process, g/(m^2 h) (gMH); A refers to the effective membrane area; Δt refers to the measuring time interval; V_0 and C_t refer to the initial and final volumes of feed solution, respectively; C_0 and C_t refer to the initial and final salt concentrations of feed solution, respectively.

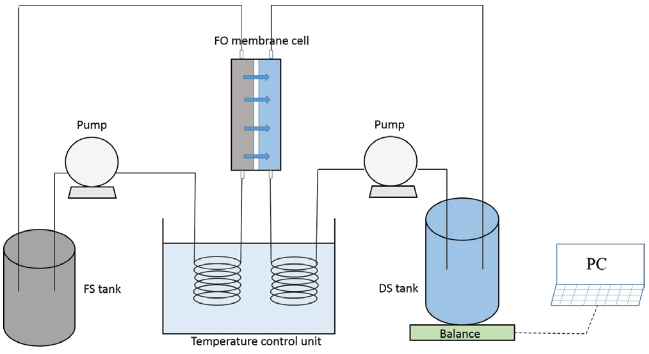

Fig. 2. The schematic diagram of the lab scale FO experimental setup.

3. Results and discussion

3.1. Basic FO performance

In order to investigate the feasibility of using cooling water as DS in the FO process, the basic FO performance including water flux and reverse solute flux were measured. The experiments were conducted in both PRO and FO modes at 25°C and 17 cm/s using TFC- and CTA-FO membranes. The FS and DS were the secondary effluent and the simulated cooling water adding ammonium bicarbonate, respectively. The experimental results are shown in Fig. 3. Figs. 3a and b represent the water flux and the reverse solute flux, respectively. The initial water fluxes on both CTA- and TFC-PRO modes (10 and 10.6 LMH) were higher than those in FO modes (5.9 and 7.88 LMH). The water flux declined about 66.9% and 47.6% of its initial level in CTA-PRO and TFC-PRO modes, respectively. While in FO mode, the water flux declined about 47.8% and 32.7% of its initial level of CTA and TFC membranes less than the flux declined in PRO mode. This results attribute to the more serious membrane fouling in PRO mode which can induce the permeation drag force leading to more rapid flux decline [27,28]. Concentration polarization (CP) is another main factor lower the flux of the process. In PRO mode, the support layer faces the feed side leading to the concentrative internal concentration polarization (CICP). In the feed side, the fouling related CICP can create an enhanced osmotic pressure in the fouling layer. So the enhanced osmotic pressure within the fouling layer reduces the driving force across the membrane, leading to the significant flux decline. In FO mode, the support layer is facing the draw side causing the dilutive internal concentration polarization (DICP). However, the fouling on the dense and smooth active layer was reversible. The shear stress on the smooth membrane surface could inhibit the foulants accumulation and reduce the external concentration polarization (ECP) [29,30]. This phenomenon expounds the lower water flux decline in FO mode than in PRO mode.

As shown in Fig. 3b, the reverse solute fluxes on both CTA- and TFC-PRO modes were higher than those in FO modes. This suggests that the reverse solute flux is directly related to the water flux. Although FO mode had lower initial water flux than PRO mode, the less significant flux decline in FO mode during the experiments cannot be ignored. Moreover, it is proven that the membrane fouling in FO mode is less serious and more reversible than that in PRO mode [31,32]. This suggests that FO mode maybe preferable for the secondary effluent desalination to PRO mode. So the FO mode is selected in our later study.

3.2. Determination of the optimal operating conditions

Water flux is an important indicator when evaluate the FO performance. So in this part, we aimed to determine the optimal operating conditions in which the water flux was relatively high. The effects of temperature and cross flow velocity were investigated in the FO process.

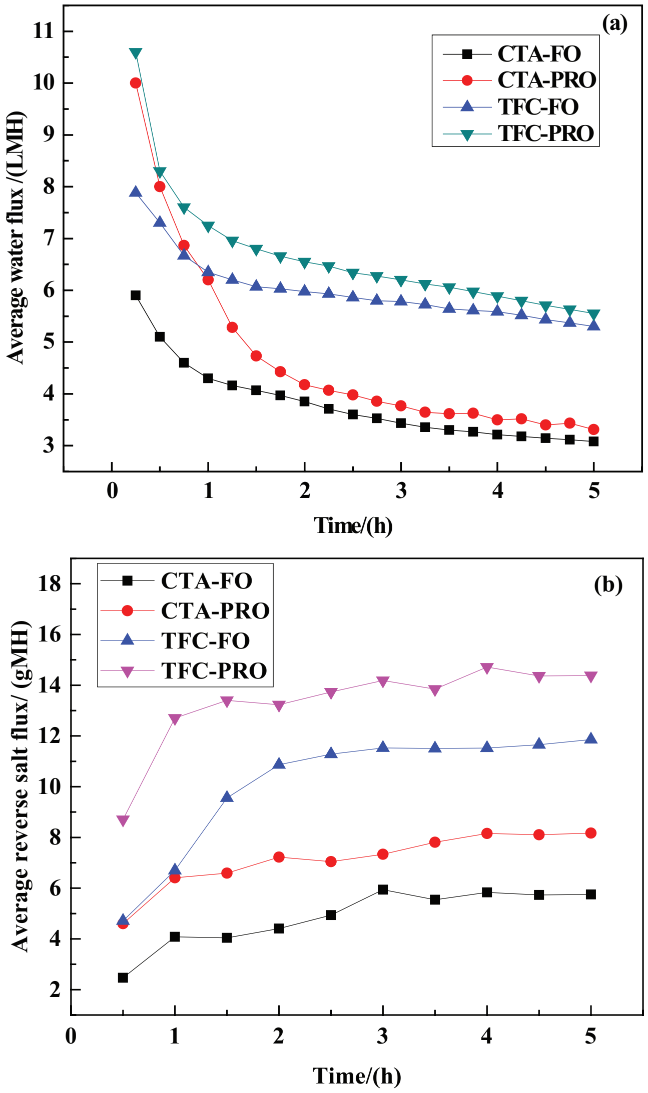

Fig. 3. Variations of water flux and reverse solute flux with time at different membrane orientation. (a) water flux and (b) reverse solute flux. The temperature: 25°C and cross flow velocity: 17 cm·s^{-1}.

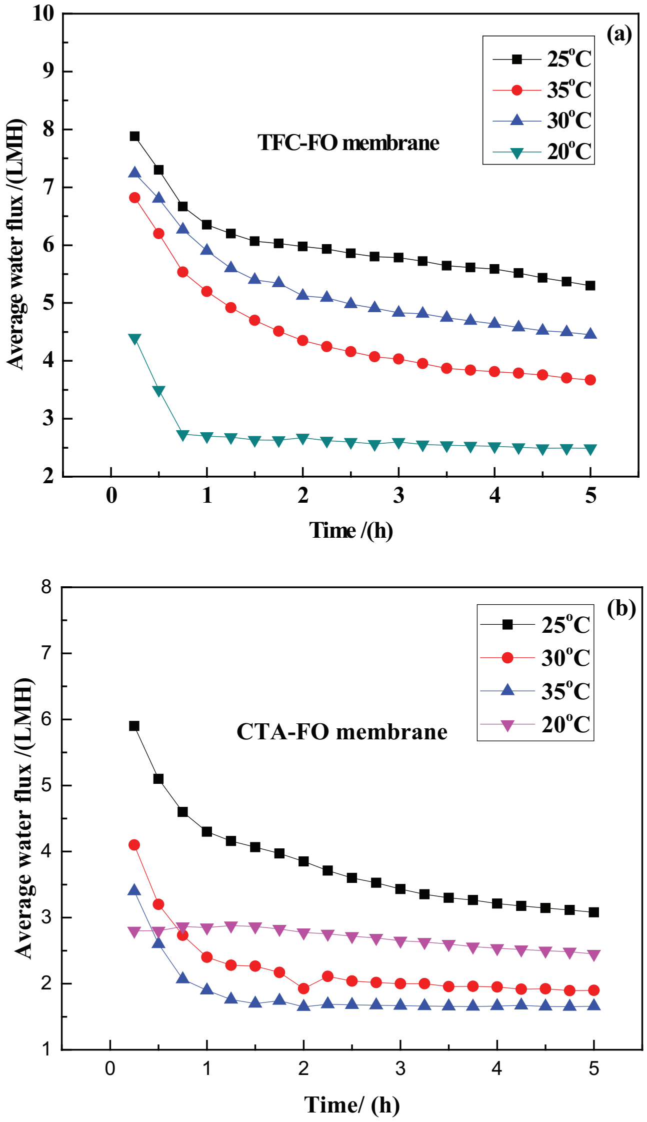

Fig. 4 Effect of temperature on the water fluxes (a) TFC-FO membrane and (b) CTA-FO membrane. The cross flow velocity: cm·s^{-1}.

3.2.1. Temperature

The influence of temperature on the water flux in the FO process was studied by using both TFC-FO and CTA-FO membrane at the cross flow velocity of 17.0 cm/s under FO mode. The variation of water flux at four temperatures (20, 25, 30 and 35°C) is shown in Fig. 4. Figs. 4a and 4b represent the use of the TFC-FO and CTA-FO membranes, respectively.

Temperature has a remarkable impact on water flux of FO process because it will influence the solution physical and chemical properties [33]. As presented in Fig. 4a, the water flux increased from 2.49 to 5.3 LMH when the temperature increased from 20 to 25°C. This is in accordance with the results of some previous papers [33,34]. It was mainly due to the increased osmotic pressure and diffusion coefficient, and decreased viscosity of used solutions at high temperature. To be specific, at the feed side, the enhanced temperature increased diffusion coefficient and at the same time decreased the viscosity (Table 2), and then resulted in the improvement of water-transporting kinetics; and at the draw side, the enhanced temperature increased osmotic pressure (Table 2) leading to the improvement of driving force. While the water flux decreased from 5.3 LMH to 4.45 and 3.67 LMH when the temperature increased from 25°C to 30 and 35°C. It may be due to the decomposition of the ammonium bicarbonate. As proven in some previous papers, ammonium bicarbonate begins to decompose when the temperature is higher than 30°C [35]. The decomposition of ammonium bicarbonate resulted in the decrease of osmosis pressure of DS which would directly affect the water flux. Since the concentration of DS (12.3 g/L) in our studies was low, the enhanced temperature had a little effect on the osmotic pressure (as shown in Table 2) and a little decomposition of ammonium bicarbonate would play a significant role. So during the FO process at high temperature, the osmotic pressure of DS reduced. However, the final osmotic pressure of DS cannot be measured by the OLI Systems analyzer. So the final osmotic pressure of DS were not provided.

Aydiner et al. [36] showed that increasing temperature to 35°C promoted the water flux but further increase to 40°C leading to the reduction of water flux, since whey was concentrated with NaCl as draw solution during the forward osmosis. Seker et al. [37] found that there was linear increase in water flux with increase of temperature to 45°C when d NaCl and KCl were as draw solution. However, increasing temperature to 30°C the water flux increased but after 30°C the water flux reduced using NH_4HCO_3 as draw solution. They concluded that effective osmotic pressure played a more significant role for water flux than the reduction of viscosity of draw solution by increased temperature. Effective osmotic pressure is osmotic pressure between the draw and feed solution. Zhao et al. [25] proved that the high temperature will lead to high reverse solute flux which hindered the water permeation.

Fig. 4b shows the variation of water flux at the temperature 20, 25, 30 and 35°C using the CTA-FO membrane. The water flux increased from 2.45 to 2.89 LMH when the temperature increased from 20 to 25°C and decreased to 1.9 and 1.66 LMH at 30 and 35°C. The variation of water flux in terms of temperature was different from that using TFC membrane. When using TFC membrane, the water at 30 and 35°C was lower than 25°C, but was higher than 20°C. While when using CTA membrane, the water flux at 35°C was lowest. The water flux at 20°C was higher than that at 30 and 35°C. It meant that the TFC membrane had a better performance at high temperature compared to CTA membrane using the cooling water as DS.

The results from experimental work proved that the water permeation was susceptible to temperature when the temperature was low (<30°C). But when the temperature reached 30°C, the enhanced temperature would have a negative influence on the water permeation due to the decomposition of ammonium bicarbonate. The water flux at 25°C was highest compared to the water flux at other temperatures. So the temperature of 25°C was selected in our following work.

3.2.2. Cross flow velocity

The impact of cross flow velocity on FO water flux was investigated at temperature 25°C under FO mode in this part. The variation of water flux with time at three cross flow velocities (8.5, 17.0 and 25.5 cm/s) is shown in Fig. 5. Figs. 5a and 5b represent the use of TFC-FO and CTA-FO membranes, respectively.

As shown in Fig. 5a, the water flux increased from 3.67 LMH to 5.3 LHM when the cross flow velocity increased from 8.5 cm/s to 17.0 cm/s. The increased water flux suggested that higher cross flow velocity would alleviate the external CP in the active layer and promote the water permeation across the membrane, which was in agreement with the study conducted by McCutcheon and Elimelech [38]. While when the cross flow velocity increased from 17.0 cm/s to 25.5 cm/s, the water flux decreased from 5.3 LMH to 3.24 LHM. This was a surprising situation. Phuntsho et al. [39] showed that the water flux increased when the cross flow rate between 8.5 and 17.1 cm/s and beyond this optimum cross flow rates the influence of cross flow is insignificant. Xu et al. [40] also convinced this opinion. They argued that varying cross flow rate alter thickness of mass transfer boundary layer at the surface of the membrane. At higher cross flow rates, the boundary layer becomes thinner leading to the higher mass transfer rate and reduced concentration polarization. Further increasing the flow rate did not promote water flux because of the reduced feed recovery rate at higher flow rate. Seker et al. [37] concluded that increasing the flow rate more than optimum cannot promote water flux mainly because the flow rates have more effect on external concentration polarization than internal concentration polarization. Due to the absences of pressure, the external concentration polarization has a little influence in the FO process.

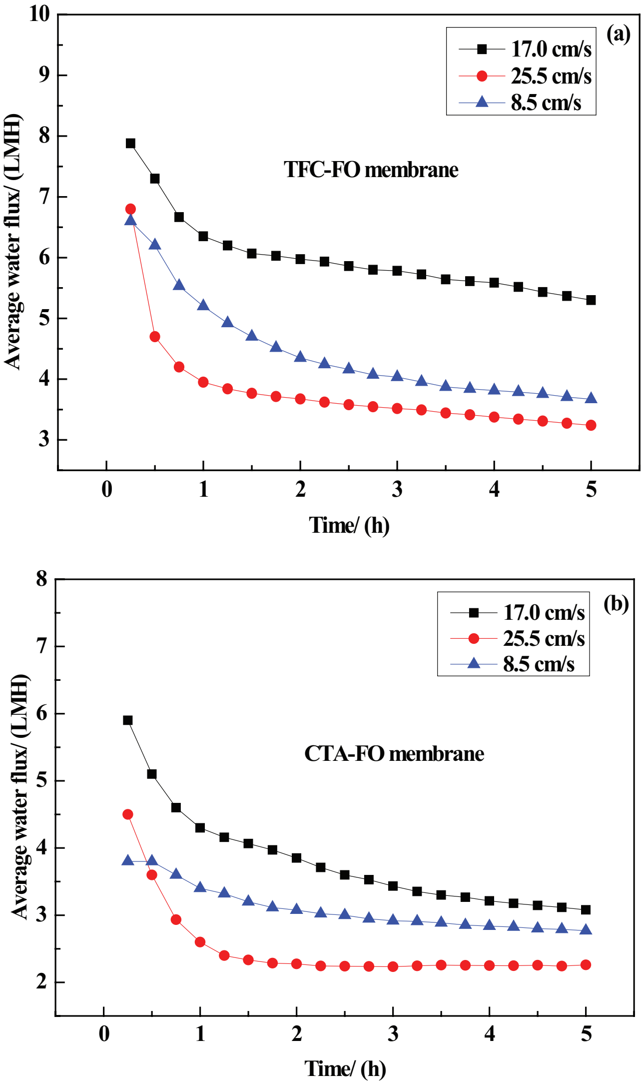

Fig. 5. Effect of cross flow velocity on the water fluxes (a) TFC-FO membrane and (b) CTA-FO membrane. The temperature: 25°C.

Fig. 5b shows the variation of water flux at the cross flow velocity 8.5, 17.0 and 25.5 cm/s using the CTA-FO membrane. The experimental results showed that water flux increased from 2.77 LMH to 3.08 LHM when the cross flow velocity increased from 8.5 cm/s to 17.0 cm/s and water flux decreased from 3.08 LMH to 2.26 LHM when the cross flow velocity increased from 17.0 cm/s to 25.5 cm/s. The water flux variation is the same as the study using TFC-FO membrane.

Results from experimental work demonstrated that, when cross flow velocity was low (8.5–17 cm/s), water flux increased with the increased cross flow velocity. However, when the cross flow velocity increased above some level (17–25.5 cm/s), water flux decreased with the increased cross flow velocity. In our study using three cross flow velocities, water flux was highest when the cross flow velocity was 17.0 cm/s. So the cross flow velocity 17.0 cm/s was our choice.

3.3 Feasibility analysis of using the secondary effluent as makeup water for cooling water

In order to further confirm the feasibility of using the secondary effluent as makeup water for cooling water in FO process. In this part, experiments were conducted in terms of the permeate recovery and membrane scaling.

3.3.1. The permeate recovery

The permeate recovery of the secondary effluent was investigated at different operating time (5, 10 and 20 h) at 25°C and 17.0 cm/s using TFC-FO membrane. A weight balance (Satorius weighting technology GmbH, Gottingen, Germany) was used to record the initial weight of FS and the amount of the increased weight in DS. The permeate recovery is calculated as:

$$R = \frac{\Delta M}{M_0} \tag{3}$$

where R is the permeate recovery; ΔM is the amount of the increased weight in DS; M_0 is the initial weight of FS.

Table 4 showed the results of the calculated permeate recovery at different operating time (5, 10 and 20 h). The permeate recovery was 5.3%, 13.1% and 18.9% at the operating time was 5, 10 and 20 h. The value of 10 h was 7.8% higher, while the value of 20 h was 13.6% higher than that of 5 h. Susan J. Altman et al. [9] studied using side-stream membrane treatment of cooling tower water to reduce water usage. The results showed that the average water recovery was 23% and the maximum savings in make-up water usage was 16%. In our test, when the operating time was 20 h, the permeate recovery can get 18.9%. So the permeate recovery was considerable compared to previous studies. Fig. 6 presents the variation of water flux at the operating time of 10 and 20 h. The water flux decreased rapidly with the increased of time in the experiments. The final water flux at 20 h was 4.725 LMH, and compared to the initial water flux 7.13 LMH it dropped 2.405 LMH. The results explained that the water flux has been decreasing with the increase of time. Thus in the actual application, adding salts to DS is necessary to ensure the systems of continuous operation.

Table 4
The permeate recovery at different operating time

Time	5 h	10 h	20 h
M_0 (g)	1000	1000	1000
ΔM (g)	53	130.6	189
R	5.3%	13.1%	18.9%

3.3.2. Membrane scaling

To further study the feasibility of using FO for cooling water recycling, membrane fouling was discussed in this section. Membrane fouling is correlated to the foulants deposition, concentration polarization and reverse solute diffusion, so it is a complex problem. Membrane fouling can reduce the permeate water flux, water recovery and permeate quality which leads to high operating cost and shortened membrane life [41]. Therefore, the research on membrane fouling is very necessary for the practical application. The original virgin and used membranes were taken out from the membrane cell and analyzed by SEM. In order to keep the fouling intact, membrane samples after FO run were instantly flash-frozen in liquid nitrogen and subsequently were dried 3–4 h in a vacuum oven. The membrane used in this test was TFC-FO membrane. The results are shown in Fig. 7. Figs. 7a1, b1 and c1 represent the active layer and 7a2, b2 and c2 represent the support layer. The membranes under operating time of 5 and 20 h were compared with the pristine membranes. Figs. 7a2, b2 and c2 show that the support layer were almost the same. In the FO process, the pure water permeated from feed to draw solution. In the FO mode, the concentration of salt in the support layer of the draw side was diluted and it would relieve the membrane scaling. So the support layers were nearly similar. Figs. 7a1, b1 and c1 clearly show that the active layer in 5 h was fouled slightly and the active layer in 20 h was fouled severely. Membrane fouling in FO mode was caused by the deposition of foulants from feed solution onto the active

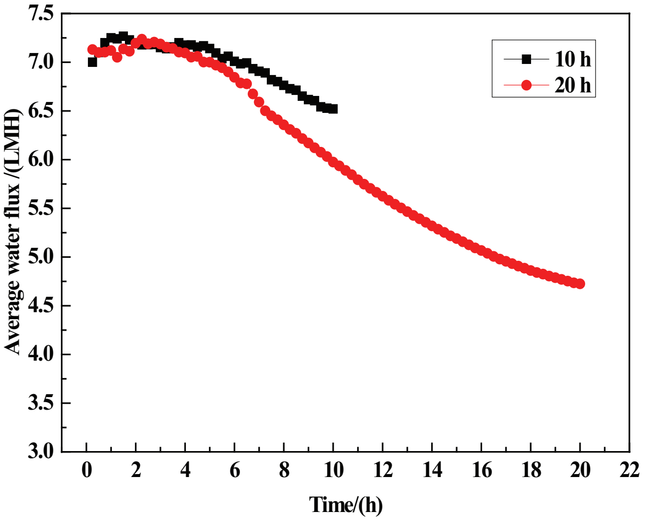

Fig. 6. Variation of water flux with time. The temperature: 25°C and cross flow.

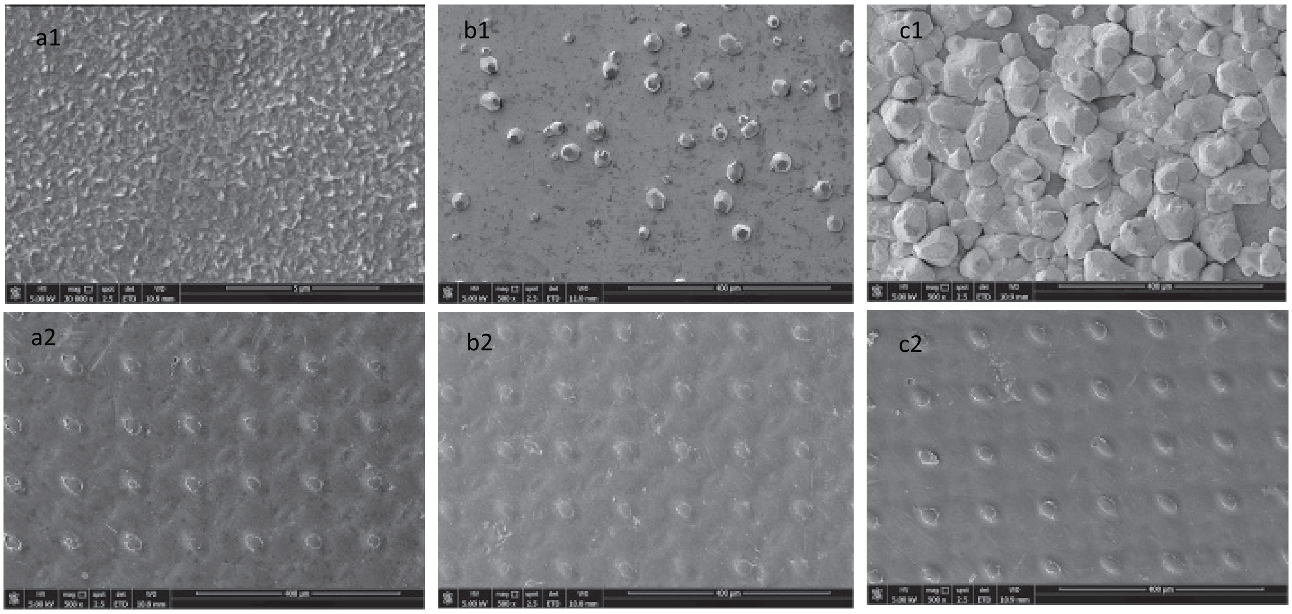

Fig. 7. SEM images of TFC-FO membrane. (a1 and a2) active layer and support layer of the pristine membrane. (b1 and b2) active layer and support layer of the membrane after operating 5 h. (c1 and c2) active layer and support layer of the membrane after operating 20 h. The temperature: 25°C and cross flow velocity: 17 cm·s^{-1}.

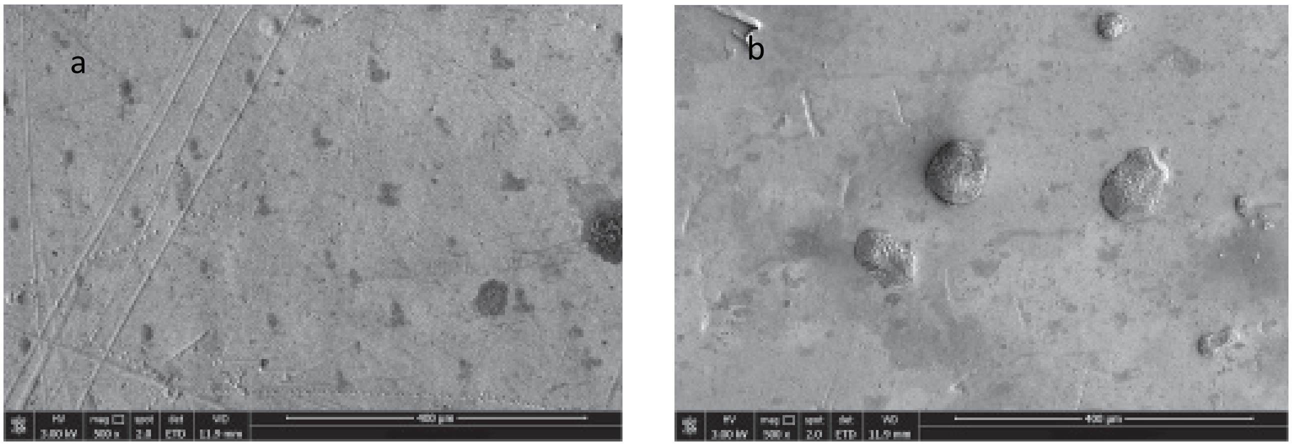

Fig. 8. SEM images of the cleaned membrane. (a) cleaned membrane with operating time of 5 h and (b) cleaned membrane with operating time of 20 h. The temperature: 25°C and cross flow velocity: 17 cm·s^{-1}.

layer surface and the subsequent formation of the "cake layer". In our tests, HCO_3^- was contained in DS and it could pass through the membrane to the FS side. In the FS, HCO_3^- and Ca^{2+} bound to $CaCO_3$ precipitation and deposited on the membrane surface. On the long term fouling behavior the fouling was governed by foulant-deposited-foulant interaction. So with the increase of time, membrane fouling will become more and more serious.

Mi and Elimelech proved that simple surface flushing could remove the deposited foulants from the fouled FO membrane and restore the water flux [42]. Thus membrane cleaning is required when the membrane fouling is severe. The fouled membranes after operating 5 and 20 h were cleaned using DI water on both the feed and draw side of the membrane at the same cross flow velocity of fouling experiment (17 cm/s) for 1 h. The results of SEM analysis are shown in Fig. 8. Figs. 8a and 8b represent the cleaned membrane with the operating time of 5 and 20 h, respectively. It can be seen that the foulants on the membrane (operating 5 h) surface were almost completely removed. There were little foulants on the membrane (operating 20 h) surface compared to Fig. 7c1. The EDS analysis results are shown in Table 5. C and O were main raw materials of the pristine membrane. The active layer of TFC membrane was fouled with $CaCO_3$. Compared to the fouled membrane, the $CaCO_3$ in cleaned membrane was almost removed. The water flux with time (20 h) using the cleaned membrane (operating 20 h) is presented in Fig. 9. It is clear that the water flux of the pristine membrane and the cleaned membrane had almost the same trend. The final water flux was 4.43 LMH using

Table 5
Atomic percentage of elemental composition of pristine, fouled and cleaned membrane surfaces by EDS analysis. The fouled membrane is operating 20 h

Membrane		C	O	S	Ca
TFC active layer (FO mode)	Pristine	83.8	12.84	3.36	–
	Fouled	69.75	21.42	2.55	6.28
	Cleaned	83.62	12.72	3.55	0.11

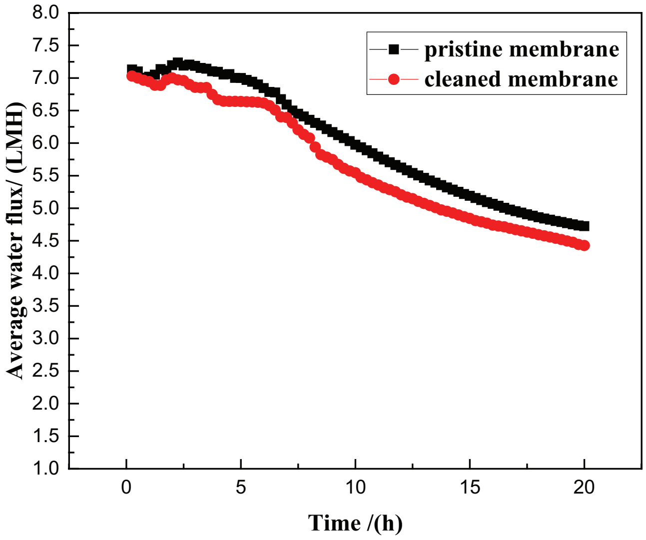

Fig. 9. Variation of water flux using the pristine membrane and the cleaned membrane (1 h flushing). The temperature: 25°C and cross flow velocity: 17 cm·s^{-1}.

the cleaned membrane, and it was 6.2% lower than the final water flux (4.73 LMH) using the pristine membrane. It meant that 1 h simple surface flushing the membrane after running 20 h could get significant effect and the water flux restored nearly 93.8%. The small differences were due to the fact that the simple flushing could remove the foulants on the membrane surface effectively, there were still some foulants in the holes of the membrane. These foulants were hard to be removed through simple flushing and hindered water going through the membrane leading to the reduced water flux [43]. These results confirmed that the membrane fouling was reversible in the FO process and simple surface flushing could remove the foulants effectively. The cleaned membrane could remain high performance efficiency.

4. Conclusion

In this study, the application of FO was investigated using the secondary effluent as makeup water for cooling water. The results showed that, the initial water fluxes on both CTA- and TFC-PRO modes (10 and 10.6 LMH) were higher than those in FO modes (5.9 and 7.88 LMH).While in FO mode, the water flux declined about 47.8% and 32.7% of its initial level of CTA and TFC membranes less than the flux declined (66.9% and 47.6%) in PRO mode. This phenomenon mainly attribute the permeation drag force as well as the concentration polarization. The water flux did not increase with the temperature when it was above than 30°C. The same situation occurred at the cross flow velocity above than 17 cm/s. The optimal conditions were determined to be 25°C and 17.0 cm/s in which the water flux was highest. When the operating time reached 20 h, the permeate recovery could get 18.9%. The fouling of TFC-FO membrane was serious after running 20 h, but it could be cleaned well by 1 h simple surface flushing. Through 1 h flushing the water flux could restore nearly 93.8%. The SEM-EDS results also confirmed the conclusion. The overall performance demonstrates that FO is feasible to recycle cooling water.

Acknowledgments

This work was supported by the Taishan Scholar Program (No. ts201511003).

References

[1] J. Wang, D. Qu, M. Tie, H. Ren, X. Peng, Z. Luan, Effect of coagulation pretreatment on membrane distillation process for desalination of recirculating cooling water, Sep. Purif. Technol., 64 (2008) 108–115.
[2] J. Zhang, H. Zeng, C. Ye, L. Chen, X. Yan, Pilot test of UF pretreatment prior to RO for cooling tower blow down reuse of power plant, Desalination, 222 (2008) 9–16.
[3] J. Zhang, L. Chen, H. Zeng, X. Yan, X. Song, H. Yang, C. Ye, Pilot testing of outside-in MF and UF modules used for cooling tower blow down pretreatment of power plants, Desalination, 214 (2007) 287–298.
[4] J. Qu, C. Yin, M. Yang, H. Liu, Development and application of innovative technologies for drinking water quality assurance in China, Front. Environ. Sci. Eng. China, 1 (2007) 257–269.
[5] F.-H. Wang, H.-T. Hao, R.-f. Sun, S.-y. Li, R.-m. Han, C. Papelis, Y. Zhang, Bench-scale and pilot-scale evaluation of coagulation pre-treatment for wastewater reused by reverse osmosis in a petrochemical circulating cooling water system, Desalination, 335 (2014) 64–69.
[6] P. Kumar, A. Pournara, K.-H. Kim, V. Bansal, S. Rapti, M.J. Manos, Metal-organic frameworks: Challenges and opportunities for ion-exchange/sorption applications, Prog. Mater Sci., 86 (2017) 25–74.
[7] N. Chitpong, S.M. Husson, High-capacity, nanofiber-based ion-exchange membranes for the selective recovery of heavy metals from impaired waters, Sep. Purif. Technol., 179 (2017) 94–103.
[8] H. Zhang, C. Dong, L. Bian, Q. Zhao, Experiment study on corrosion control using coking wastewater as circulating cooling water, Earth Sci. Front., 15 (2008) 186–189.
[9] S.J. Altman, R.P. Jensen, M.A. Cappelle, A.L. Sanchez, R.L. Everett, H.L. Anderson, L.K. McGrath, Membrane treatment of side-stream cooling tower water for reduction of water usage, Desalination, 285 (2012) 177–183.
[10] T. Cath, A. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, J. Membr. Sci., 281 (2006) 70–87.
[11] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, J. Membr. Sci., 396 (2012) 1–21.
[12] K. Lutchmiah, A.R. Verliefde, K. Roest, L.C. Rietveld, E.R. Cornelissen, Forward osmosis for application in wastewater treatment: a review, Water Res., 58 (2014) 179–197.

[13] Q. Ge, M. Ling, T.-S. Chung, Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future, J. Membr. Sci., 442 (2013) 225–237.

[14] R. Kumar, P. Pal, A novel forward osmosis-nano filtration integrated system for coke-oven wastewater reclamation, Chem. Eng. Res. Des., 100 (2015) 542–553.

[15] M. Qasim, N.A. Darwish, S. Sarp, N. Hilal, Water desalination by forward (direct) osmosis phenomenon: A comprehensive review, Desalination, 374 (2015) 47–69.

[16] 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.

[17] Y. Kim, J.H. Lee, Y.C. Kim, K.H. Lee, I.S. Park, S.-J. Park, Operation and simulation of pilot-scale forward osmosis desalination with ammonium bicarbonate, Chem. Eng. Res. Des., 94 (2015) 390–395.

[18] W. Wang, Y. Zhang, M. Esparra-Alvarado, X. Wang, H. Yang, Y. Xie, Effects of pH and temperature on forward osmosis membrane flux using rainwater as the makeup for cooling water dilution, Desalination, 351 (2014) 70–76.

[19] R.B. Theregowda, R. Vidic, A.E. Landis, D.A. Dzombak, H.S. Matthews, Integrating external costs with life cycle costs of emissions from tertiary treatment of municipal wastewater for reuse in cooling systems, J. Cleaner Prod., 112 (2016) 4733–4740.

[20] A. Subramani, M. Badruzzaman, J. Oppenheimer, J.G. Jacangelo, Energy minimization strategies and renewable energy utilization for desalination: a review, Water Res., 45 (2011) 1907–1920.

[21] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—carbon dioxide forward (direct) osmosis desalination process, Desalination, 174 (2005) 1–11.

[22] 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.

[23] F.-c. Tao, S.-h. Huo, c.-l. Wang, Optimization for recirculating cooling water concentration of fossil fuel power plant, Guangzhou Chem. Ind., 40 (2012).

[24] P. Liu, B. Gao, H.K. Shon, D. Ma, H. Rong, P. Zhao, S. Zhao, Q. Yue, Q. Li, Water flux behavior of blended solutions of ammonium bicarbonate mixed with eight salts respectively as draw solutions in forward osmosis, Desalination, 353 (2014) 39–47.

[25] P. Zhao, B. Gao, S. Xu, J. Kong, D. Ma, H.K. Shon, Q. Yue, P. Liu, Polyelectrolyte-promoted forward osmosis process for dye wastewater treatment – Exploring the feasibility of using polyacrylamide as draw solute, Chem. Eng. J., 264 (2015) 32–38.

[26] P. Zhao, B. Gao, Q. Yue, S. Liu, H.K. Shon, Effect of high salinity on the performance of forward osmosis: Water flux, membrane scaling and removal efficiency, Desalination, 378 (2016) 67–73.

[27] B.D. Coday, N. Almaraz, T.Y. Cath, Forward osmosis desalination of oil and gas wastewater: Impacts of membrane selection and operating conditions on process performance, J. Membr. Sci., 488 (2015) 40–55.

[28] S. Zhao, L. Zou, D. Mulcahy, Effects of membrane orientation on process performance in forward osmosis applications, J. Membr. Sci., 382 (2011) 308–315.

[29] Y. Wang, M. Zhang, Y. Liu, Q. Xiao, S. Xu, Quantitative evaluation of concentration polarization under different operating conditions for forward osmosis process, Desalination, 398 (2016) 106–113.

[30] W. Fang, R. Wang, S. Chou, L. Setiawan, A.G. Fane, Composite forward osmosis hollow fiber membranes: Integration of RO- and NF-like selective layers to enhance membrane properties of anti-scaling and anti-internal concentration polarization, J. Membr. Sci., 394–395 (2012) 140–150.

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

[32] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, J. Membr. Sci., 320 (2008) 292–302.

[33] 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.

[34] A.H. Hawari, N. Kamal, A. Altaee, Combined influence of temperature and flowrate of feeds on the performance of forward osmosis, Desalination, 398 (2016) 98–105.

[35] A. Deng, A. Chen, S. Wang, Y. Li, Y. Liu, X. Cheng, Z. Zhao, D. Lin, Porous nanostructured poly-l-lactide scaffolds prepared by phase inversion using supercritical CO_2 as a nonsolvent in the presence of ammonium bicarbonate particles, J. Supercrit. Fluids, 77 (2013) 110–116.

[36] C. Aydiner, S. Topcu, C. Tortop, F. Kuvvet, D. Ekinci, N. Dizge, B. Keskinler, A novel implementation of water recovery from whey:"forward–reverse osmosis" integrated membrane system, Desal. Water Treat., 51 (2013) 786–799.

[37] M. Seker, E. Buyuksari, S. Topcu, D. Sesli, D. Celebi, B. Keskinler, C. Aydiner, Effect of process parameters on flux for whey concentration with NH_3/CO_2 in forward osmosis, Food Bioprod. Process., 105 (2017) 64–76.

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

[39] 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.

[40] Y. Xu, X. Peng, C.Y. Tang, Q.S. Fu, S. Nie, Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis performance in a spiral wound module, J. Membr. Sci., 348 (2010) 298–309.

[41] Q. She, R. Wang, A.G. Fane, C.Y. Tang, Membrane fouling in osmotically driven membrane processes: A review, J. Membr. Sci., 499 (2016) 201–233.

[42] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, J. Membr. Sci., 348 (2010) 337–345.

[43] P. Xiao, J. Li, Y. Ren, X. Wang, A comprehensive study of factors affecting fouling behavior in forward osmosis, Colloids Surf., A, 499 (2016) 163–172.