



## Influence of different ion types and membrane orientations on the forward osmosis performance



Pin Zhao<sup>a</sup>, Qinyan Yue<sup>a,\*</sup>, Baoyu Gao<sup>a</sup>, Jiaojiao Kong<sup>a</sup>, Hongyan Rong<sup>a</sup>, Pan Liu<sup>a</sup>, Ho Kyong Shon<sup>b</sup>, Qian Li<sup>a</sup>

<sup>a</sup> Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

<sup>b</sup> School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia

### HIGHLIGHTS

- Effects of different ions on FO performance were studied.
- Cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$  and  $\text{NO}_3^-$ ) were chosen.
- Comparing with FO mode, PRO mode had higher water flux, which declined faster yet.
- $\text{K}^+$  and  $\text{Cl}^-$  were the optimal candidates of cation and anion, respectively.

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### ABSTRACT

This study investigated the influence of different ions on forward osmosis (FO) performance in terms of water flux.  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  were selected as representatives of draw solutions (DSs). Data were obtained from laboratory-scale experiments under well controlled conditions in both membrane orientations operated in FO mode pressure retarded osmosis (PRO) mode. The basic properties of DS (osmotic potential, viscosity, diffusion coefficient) changed the water and reverse salt transmission. The results indicated that the performance of one solution in different modes was different. The behavior of  $\text{Na}^+$  and  $\text{K}^+$  salts was quite satisfactory in the PRO mode; specifically  $\text{NaCl}$  had the greatest water flux ( $16.96 \text{ L}/(\text{m}^2 \text{ h})$ ), and the following largest was  $\text{KCl}$  ( $16.55 \text{ L}/(\text{m}^2 \text{ h})$ ).  $\text{K}^+$  salts had the highest water flux among all the selected positive ions in the FO mode which was  $\text{KCl}$  ( $10.30 \text{ L}/(\text{m}^2 \text{ h})$ ). To the negative ions,  $\text{Cl}^-$  salts showed higher water flux than nitrates in both PRO and FO modes, such as the water flux of  $\text{NaNO}_3$  was  $7.96 \text{ L}/(\text{m}^2 \text{ h})$ , while that of  $\text{NaCl}$  was  $8.86 \text{ L}/(\text{m}^2 \text{ h})$  in the FO mode. Overall,  $\text{K}^+$  and  $\text{Cl}^-$  were regarded as optimal candidates of cation and anion, respectively.

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### 1. Introduction

FO is a sustainable alternative technology in membrane-based desalination and wastewater reuse and has aroused great attention of the world. It utilizes a highly concentrated draw solution (DS) to induce the driving force for separation, leading pure water from feed solution (low concentration) to DS (high concentration) under the concentration gradient across the semi-permeable membrane. Unlike reverse osmosis (typical pressure-driven membrane processes), FO occurs spontaneously in the absence of hydraulic pressure, which makes FO not only minimize the system energy consumption, but also lower membrane fouling [1–7].

However, FO is still facing some barriers, such as suitable membrane and DS. Ideal FO membrane should be thin but have good mechanical strength, high water permeability and salt rejection at the same time.

Although the current flat sheet FO membranes, which are made of cellulose triacetate (CTA) produced by Hydration Technologies Inc., have been used for broad commercial purposes, they have relatively low water permeability and salt rejection especially for osmotic seawater desalination [8,9]. The draw solutes should ideally be inert, near neutral pH, non-toxic and have high osmotic potential. Furthermore, it should be recovered and regenerated easily. However, this is not an easy task, which requires an additional processing unit and thus consumes extra energy [10,11].

Some studies have demonstrated that solution of highly soluble gases—ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ), satisfied the criteria of DS due to their properties, such as high solubility in water, a low molecular weight and easily being separated and recycled [12,13]. McCutcheon et al. [14] investigated the relationships among the DS concentration, feed water salinity and permeate flux behavior in the ammonia–carbon dioxide FO process. They found that the experimental water fluxes were far lower than those expected based on available bulk osmotic pressure gap and membrane pure water permeability data. Moreover,

\* Corresponding author. Tel.: +86 531 88365258; fax: +86 531 88364513.  
E-mail address: [qyyue58@aliyun.com](mailto:qyyue58@aliyun.com) (Q. Yue).

internal concentration polarization was thought to be the major cause. However, the ammonium draw solutes decompose into ammonia and carbon dioxide gases that can be separated by standard means through moderate heating (near 60 °C) [15]. Recently, Phuntsho et al. [16,17] put forward a new concept of FO, in which fertilizer was used as DS and it was called fertilizer-drawn forward osmosis (FDFO) desalination. The novelty of this particular FO process is that the diluted DS after desalination can be directly used for fertilization without separation and recovery. Phuntsho et al. [18] also evaluated the performances of the commonly used chemical fertilizers as DS. They concluded that the DS of KCl, NaNO<sub>3</sub> and KNO<sub>3</sub> performed best in terms of water flux, while NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> had the lowest reverse solute fluxes.

It was well known that the selection of an optimal draw solution was one key component for successful development of FO technologies. Achilli et al. [10] had developed a protocol for the selection of optimal draw solutions for FO applications which could be used to determine the most appropriate draw solutions for specific FO applications. Nonetheless, researches about the influence of different kinds of ions on the FO performance are still relatively few.

In our study, the permeation performance which varied with the different kinds of ions was investigated using the PA-based thin-film composite (TFC) membrane. The main aim of this paper was to evaluate the performance of some chemical fertilizers when they were used as DS in FO process. More specifically, the objectives were (1) to evaluate FO process performance by using different positive ions as well as the different negative ions in DS; (2) to compare the FO performance of the different ions in PRO and FO modes; and (3) to choose the best candidates from the selected chemicals as the DS for PRO and FO modes, respectively.

## 2. Materials and methods

### 2.1. Feed and draw solutions

Several kinds of salts (NaCl, NaNO<sub>3</sub>, KCl, KNO<sub>3</sub>, NH<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub>, CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>) were selected as representatives to prepare the DS. They were all analytically pure. In order to maintain single variable, the concentrations of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in different DSs were consistent and all maintained at 0.5 M. Since Ca<sup>2+</sup> was divalent ions which was different from Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, the concentration of Ca<sup>2+</sup> was 0.25 M, while the concentrations of Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> were 0.5 M, when the concentrations of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> were 0.5 M. 0.5 M CaCl<sub>2</sub> and 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub> were studied as well to compare with 0.25 M CaCl<sub>2</sub> and 0.25 M Ca(NO<sub>3</sub>)<sub>2</sub>. The feed solution (FS) used in this study was de-ionized water. Solution characteristics such as viscosity, pH, and osmotic pressure were predicted using OLI Systems analyzer. The concentration of DS was 0.5 M unless there were special notes.

### 2.2. Forward osmosis membrane

The membrane used in our study was the PA-based thin-film composite (TFC) membrane, whose source was withheld for commercial interest at behest of the supplier. It had been studied by the previous papers and was different from both the TFC membrane used widely for reverse osmosis (RO) and CTA-FO membrane which had broad applications in FO system. The membrane exhibited more advantages in

terms of FO performance such as the higher water permeability, more decent salt rejection, improved selectivity and superior separation properties [19]. Physical and chemical properties of membranes as provided by the manufacturer for TFC FO membranes and from various literatures for CTA membrane were compared and presented in Table 1 [20].

Micrographs of the membranes were obtained utilizing using a HITACHI S-520 scanning electron microscope. In order to keep the fouling intact, wet membrane samples were flash-frozen in liquid nitrogen and subsequently were dried overnight in a vacuum oven. Fig. 1 shows the SEM images of the surface of TFC FO membrane. Fig. 1(a) represents the top view of the active layer, which appears continuous with a ridge-and-valley morphology. This appearance indicated that the membrane possessed potential of good selectivity property. The support layer SEM micrographs show numerous holes of varying sizes whose diameters ranged from to 1 μm to 5 μm.

### 2.3. Forward osmosis system

The FO experimental setup used in this study consisted of a cross flow membrane cell, two peristaltic pumps (BT300-2J) to circulate DS and FS in corresponding closed loop, water bath controlled by heater/chiller to adjust the temperatures of the DS and FS, solution tanks and a weighing balance (Sartorius weighing technology GmbH, Gottingen, Germany) to record the variation in the DS weight for water flux computation and two glass rotameters to maintain the cross-flow velocities of the DS and FS. The bench-scale FO unit set up had two channels on both sides of the membrane. It laid flat over a test bed. The channels were same with each other, which provided an effective membrane area of 20.0 cm<sup>2</sup> (7.7 cm length × 2.6 cm width × 0.3 cm depth). They allowed the DS and FS to flow through separately on both sides of the membrane, with FS in the upper side and DS in the lower side in this experiment. Both DS and FS flowed in the same direction, whose velocities were maintained at 19.65 cm/s. The temperature of the DS and FS was kept at 25 ± 1 °C. The initial volumes of DS and FS were 500 mL and 1000 mL, respectively. As water diffused through the membrane, the volume of DS slowly increased while that of FS decreased.

### 2.4. Membrane orientation

There are two modes of membrane orientation in FO process. Specifically, the first one is porous layer facing the FS and the dense layer facing the DS. The orientation has been used in previous studies on PRO desalination, since the porous support layer is required to resist the pressurization of the permeate stream [21]. Therefore it is referred to as the PRO mode. To the other one, the DS is placed against the support layer and the dilute feed is on the active layer, which is the typical orientation described in previous studies in FO process [12,14]. So it is referred to as the FO mode.

### 2.5. Theoretical water flux

In an optimal situation, water flux is given by the following equation:

$$J_w = A\sigma[\pi_D - \pi_F] = A\sigma\Delta\pi \quad (1)$$

**Table 1**  
The comparison of physical and chemical properties between TFC-FO membrane and CTA-FO membrane.

Sample	Active layer material	Contact angle (°)		Zeta potential at pH 6 (mV) Active layer	Operating pH	Membrane thickness (mm)	Ref.
		Active layer	Support layer				
CTA	Cellulose triacetate	76.6	81.8	-2.1	3–8	93	[20]
TFC	Polyamide	45	45	86	2–12	116 ± 1	

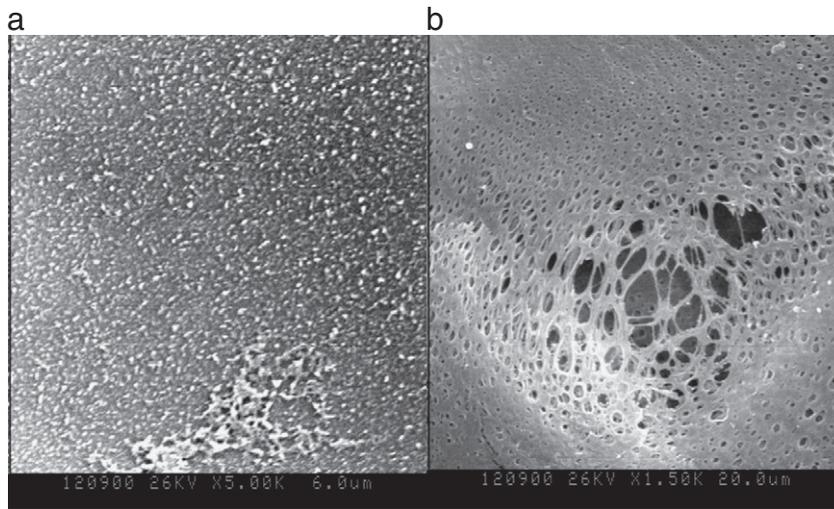


Fig. 1. SEM images of the clean TFC FO membranes displaying (a) the active layer (b) the support layer.

where  $J_w$  is the water flux through FO membrane which is symmetric;  $A$  is the membrane permeability coefficient;  $\sigma$  is the reflection coefficient;  $\pi_D$  and  $\pi_F$  are the osmotic pressures of the DS and FS, respectively, and  $\Delta\pi$  is the net osmotic gradient.

However, all the FO membranes used were asymmetric, they contained thick mechanical support layer which made the value of  $\sigma$  lower. This membrane structure led severe CP effect which hampered the performance of the FO process. In the PRO mode, pure water was used as FS; water diffused from feed side to draw side due to osmotic pressure gradient across the membrane, which resulted in the external concentration polarization (dilutive) in the active layer. At the same time, salt diffused from the draw to the feed side leading to internal concentration polarization (concentrative) in the porous support layer. In the FO mode, internal concentration polarization (dilutive) and external concentration polarization (concentrative) occurred on the porous support layer and active layer, respectively [22–24].

Considering negative effects of concentration polarization on the actual water flux, Eq. (1) can be modified to the form of Eq. (2) [6,26].

$$J_w = A\sigma[\pi_{D,m} - \pi_{F,m}] = A\sigma\left[\pi_D \exp(-J_w k) - \pi_F \exp\left(\frac{J_w}{k_f}\right)\right] \quad (2)$$

where  $\pi_{D,m}$  and  $\pi_{F,m}$  are the osmotic pressures of the DS and FS at the membrane surfaces, respectively.  $k$  is the solute resistance to diffusion within the DS side and  $k_f$  is individual mass transfer coefficients on the feed.

### 3. Results and discussion

#### 3.1. Characteristic of draw solution

Based on the basic properties such as pH, solubility and osmotic potential, the previous studies screened nine different fertilizers which were commonly used in the world for crop production. They were  $\text{NaNO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , respectively [18]. It can be clearly seen that the common negative ions used in the FO system were  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  and the common positive ones were  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ .

In this study, the eight kinds of chemicals ( $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$ ) were chosen as DS. The two sets ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$  and  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ) were conducted to investigate the effect of various cations on permeation under the condition of the same anion, while  $\text{KCl}$  &  $\text{KNO}_3$

and  $\text{CaCl}_2$  &  $\text{Ca}(\text{NO}_3)_2$  were selected to investigate the effect of the two anions ( $\text{Cl}^-$  and  $\text{NO}_3^-$ ) on permeation.

The basic properties of DS such as pH, osmotic potential and viscosity were determined using OLI Stream Analyzer 3.1 (OLI Systems Inc., Morris Plains, NJ, USA). This software used thermodynamic modeling based on published experimental data to predict properties of solutions over a wide range of concentrations and temperatures [6,14]. The results in Table 2 indicated that pH of all the solutions were between 4 and 7. More specifically, they were between 6 and 7 except for the pH of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$  which were 4.94 and 5.05, respectively. All the DSs were neutral or near neutral which met the requirements of the membrane. Osmotic pressure was a key property of DS to predict the water flux. In general, the greater the osmotic pressure, the better the potential of osmotic effect. To the solutions of 0.5 M, solute of divalent cation had the greater osmotic pressure than that of monovalent cation. It resulted mainly from more negative ions. The osmotic pressure was a function of solution concentration. To the same solution, higher concentration it had, more osmotic pressure it possessed. Taking  $\text{CaCl}_2$  for example, the osmotic pressure increased from 16.40 atm to 34.98 atm when its concentration increased from 0.25 M to 0.5 M. The osmotic pressures of  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  in 0.5 M were 34.98 atm, 26.49 atm, respectively, while the osmotic pressures of 0.5 M monovalent cation salt solutions were all below than 23 atm. To all the solutions, the salt of  $\text{Cl}^-$  had larger osmotic pressure than that of  $\text{NO}_3^-$ . In the case of the same ion concentration, the  $\text{Na}^+$  solutions showed the highest osmotic pressure followed by  $\text{K}^+$  and  $\text{NH}_4^+$  solutions. The last line of Table 2 shows the viscosity of different DSs. Similar to the situation of osmotic pressure, the viscosity of  $\text{Cl}^-$  salt was greater than that of  $\text{NO}_3^-$  salt in the same concentration. The viscosity decreased with the concentration, but the change was slight. Among all the DSs in 0.5 M, the  $\text{CaCl}_2$

Table 2  
Properties of draw solution.

Molarity	Draw solution	pH	Osmotic pressures (atm)	Viscosity ( $\text{m}^2/\text{s}$ )	
0.5 M	NaCl	6.99	22.772	9.2E–05	
	NaNO <sub>3</sub>	7.00	21.300	8.9E–05	
	NH <sub>4</sub> Cl	4.94	21.881	8.8E–05	
	NH <sub>4</sub> NO <sub>3</sub>	5.05	17.764	8.6E–05	
	KCl	6.98	22.021	8.8E–05	
	KNO <sub>3</sub>	6.99	20.125	8.5E–05	
	CaCl <sub>2</sub>	6.75	34.983	9.9E–05	
	Ca(NO <sub>3</sub> ) <sub>2</sub>	6.85	26.491	9.2E–05	
	0.25 M	CaCl <sub>2</sub>	6.84	16.397	9.4E–05
		Ca(NO <sub>3</sub> ) <sub>2</sub>	6.89	13.674	9.1E–05

had the highest viscosity followed by  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{NaCl}$  and  $\text{NaNO}_3$ , while  $\text{NH}_4^+$  and  $\text{K}^+$  solutions showed the lowest viscosity. The change regulation of viscosity was similar to the osmotic pressure, excluding disproportion to the concentration. The basic properties would provide theoretical support for the following analysis of water flux.

### 3.2. Effects of positive ions on water flux

To evaluate the influence of positive ion type of DS on water flux through the FO membrane, two groups of salts ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{CaCl}_2$ ;  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ ) were used as DS. All the experiments were carried out at the same water flux and temperature in both PRO and FO modes. 0.5 M  $\text{NaCl}$ , 0.5 M  $\text{KCl}$ , 0.5 M  $\text{NH}_4\text{Cl}$  and 0.25 M  $\text{CaCl}_2$  were selected as a team to remove anionic effect on experimental results. However, the cation concentration of 0.25 M  $\text{CaCl}_2$  was lower than that of 0.5 M  $\text{NaCl}$ , 0.5 M  $\text{KCl}$  or 0.5 M  $\text{NH}_4\text{Cl}$ . In order to examine the effect of cation concentration on the water flux, the water flux of 0.5 M  $\text{CaCl}_2$  was investigated for comprehensive analysis.

The operating steps to the  $\text{NO}_3^-$  salts were as the same as the  $\text{Cl}^-$  salts.

#### 3.2.1. Effects of positive ions on water flux in the PRO mode

The water flux decline profiles of various DSs in the PRO mode were shown in Fig. 2. The sets of  $\text{Cl}^-$  salts (0.5 M  $\text{NaCl}$ , 0.5 M  $\text{KCl}$ , 0.5 M  $\text{NH}_4\text{Cl}$ , 0.25 M  $\text{CaCl}_2$  and 0.5 M  $\text{CaCl}_2$ ) and  $\text{NO}_3^-$  salts (0.5 M  $\text{NaNO}_3$ , 0.5 M  $\text{KNO}_3$ , 0.5 M  $\text{NH}_4\text{NO}_3$ , 0.25 M  $\text{Ca}(\text{NO}_3)_2$  and 0.5 M  $\text{Ca}(\text{NO}_3)_2$ ) are presented in Fig. 2(a) and (b), respectively.

It was clear from Fig. 2(a) that  $\text{NaCl}$  and  $\text{KCl}$  had higher water flux among all the DSs. Then the sequence decreasingly was 0.5 M  $\text{CaCl}_2$ ,  $\text{NH}_4\text{Cl}$  and 0.25 M  $\text{CaCl}_2$ . For example, the average water fluxes of  $\text{NaCl}$  ranged from 18.68  $\text{L}/(\text{m}^2 \text{h})$  to 16.96  $\text{L}/(\text{m}^2 \text{h})$ , and these of  $\text{KCl}$  were

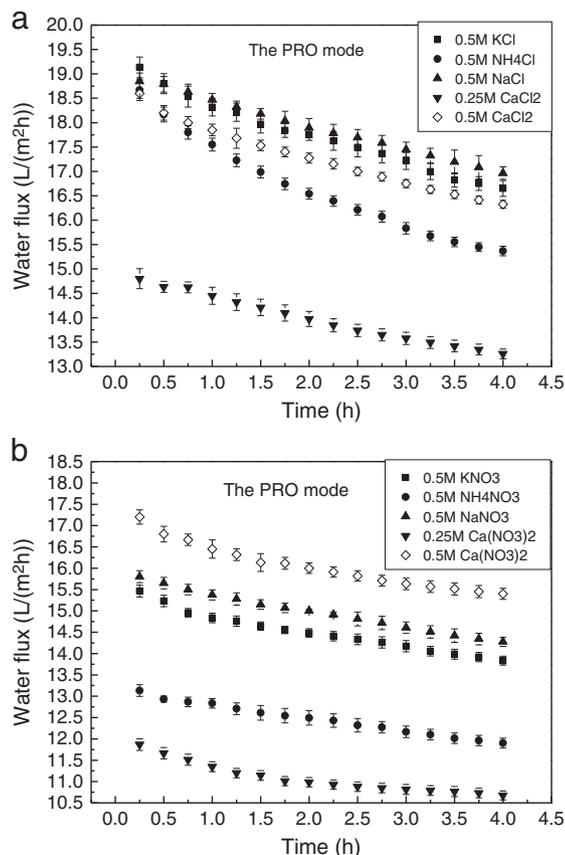


Fig. 2. Variation of FO water fluxes with time to different draw solutions in the PRO mode using (a) chloride salts as DS and (b) nitrates as DS.

between 19.15  $\text{L}/(\text{m}^2 \text{h})$  and 16.56  $\text{L}/(\text{m}^2 \text{h})$ . The lowest water flux was obtained by  $\text{CaCl}_2$  of 0.25 M, with the range of 14.79  $\text{L}/(\text{m}^2 \text{h})$  to 13.25  $\text{L}/(\text{m}^2 \text{h})$ . The result of the set of  $\text{NO}_3^-$  salts was similar to that of  $\text{Cl}^-$  salts, excluding that the water flux of  $\text{NH}_4\text{NO}_3$  was very low, which was from 13.14  $\text{L}/(\text{m}^2 \text{h})$  to 11.88  $\text{L}/(\text{m}^2 \text{h})$ . This was mainly due to its special properties that  $\text{NH}_4\text{NO}_3$  did not dissociate fully in water (data not mentioned).

However, the result in Fig. 2 indicated that the high osmotic pressure and low viscosity promoted the effect of FO. The osmotic pressure and viscosity of the draw solutions were taken from Table 2 and their correlation with the water flux was plotted in Fig. 3. Among all the above DSs except 0.5 M  $\text{Ca}(\text{NO}_3)_2$  and 0.5 M  $\text{CaCl}_2$ ,  $\text{Na}^+$  salt solution had the highest osmotic pressure as well as rather high viscosity. While  $\text{K}^+$  salt solution had the lowest viscosity and the osmotic pressure which was only lower than  $\text{Na}^+$  salt solution. Thus both FO performances of  $\text{Na}^+$  and  $\text{K}^+$  salt solutions were pretty satisfactory. It is important to notice that the water fluxes of 0.5 M  $\text{Ca}(\text{NO}_3)_2$  and 0.5 M  $\text{CaCl}_2$  were comparatively lower in spite of the higher osmotic pressure.  $\text{Ca}(\text{NO}_3)_2$  with the highest molecular weight among the selected draw solution was probably affected more severely by ICP. The rate of diffusion is inversely proportional to molecular mass. The viscosity of  $\text{CaCl}_2$  was greater, which would hinder the pure water permeation. The hypothesis was reported by previous researches that the higher viscosity and low diffusion coefficient of DS impeded water through the membrane support layer thereby aggravating the ICP effects which would lead to lessening water flux, but there is still not unanimous agreement on it [25,26]. Although net osmotic gradient between the two sides of membrane was a measure of osmotic effect, its non-linearity with the actual flux indicated that the other basic properties such as viscosity, diffusion coefficient and reverse solute flux (RSF) had combined effects on the flux [27,28].

#### 3.2.2. Effects of positive ions on water flux in the FO mode

To evaluate the influence of positive ion types in DS on water flux, a set of FO performance of 0.5 M  $\text{NaCl}$ , 0.5 M  $\text{KCl}$ , 0.5 M  $\text{NH}_4\text{Cl}$ , 0.25 M  $\text{CaCl}_2$  and 0.5 M  $\text{CaCl}_2$  was tested. Moreover, the performances of  $\text{NO}_3^-$  salts (0.5 M  $\text{NaNO}_3$ , 0.5 M  $\text{KNO}_3$ , 0.5 M  $\text{NH}_4\text{NO}_3$ , 0.25 M  $\text{Ca}(\text{NO}_3)_2$  and 0.5 M  $\text{Ca}(\text{NO}_3)_2$ ) were studied at the same situation. The result can be seen in Fig. 4. As shown in Fig. 4(a), in the FO mode, the average fluxes of the five kinds of DS (0.5 M  $\text{KCl}$ , 0.5 M  $\text{NH}_4\text{Cl}$ , 0.5 M  $\text{NaCl}$ , 0.25 M  $\text{CaCl}_2$  and 0.5 M  $\text{CaCl}_2$ ) in the total 4 h were 10.30  $\text{L}/(\text{m}^2 \text{h})$ , 9.87  $\text{L}/(\text{m}^2 \text{h})$ , 8.86  $\text{L}/(\text{m}^2 \text{h})$ , 6.48  $\text{L}/(\text{m}^2 \text{h})$  and 8.80  $\text{L}/(\text{m}^2 \text{h})$ , respectively. The results indicated that  $\text{KCl}$  had the highest water flux and then orderly followed by  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ , 0.5 M  $\text{CaCl}_2$  and 0.25 M  $\text{CaCl}_2$ . As to  $\text{NaCl}$  solution, the pure water permeability was relatively low, which was different from the situation

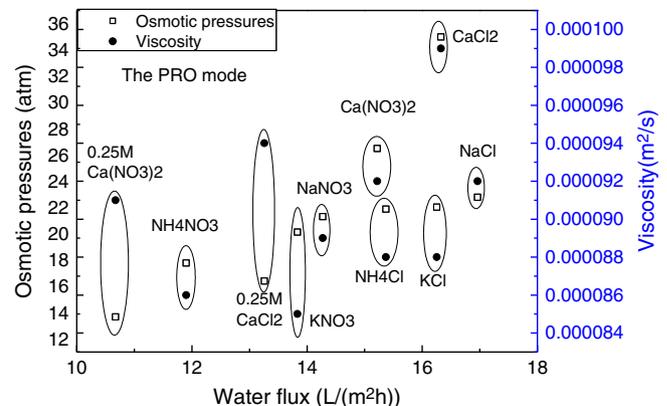


Fig. 3. Water flux of each draw solution as a function of osmotic pressure and viscosity at 0.5 M and 0.25 M in the PRO mode.

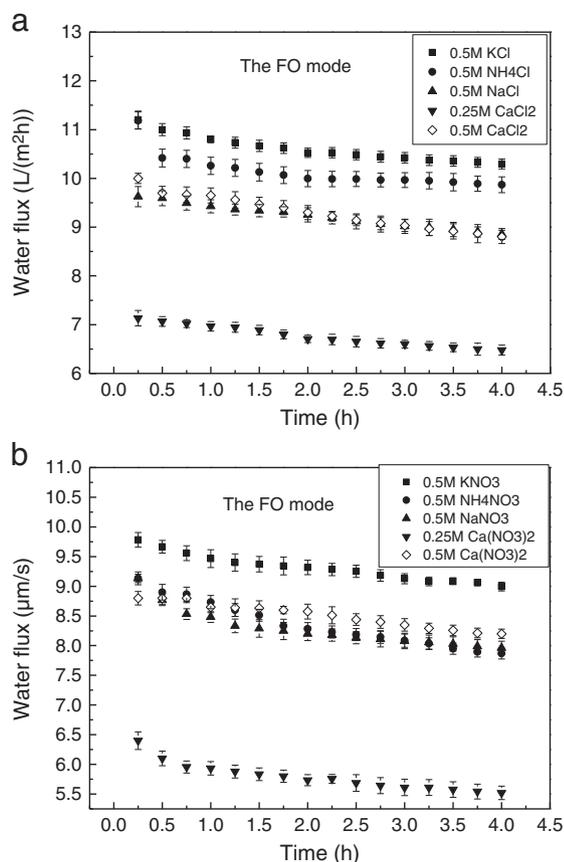


Fig. 4. Variation of FO water fluxes with time to different draw solutions in the FO mode using (a) chloride salts as DS and (b) nitrates as DS.

of the PRO mode. The unsatisfactory performance of NaCl in the FO mode would result from the greater adverse effect of viscosity and diffusion coefficient on the water permeability. This indicated that the effects of positive ions on water flux were various in different modes of membrane orientation.

The correlation of the water flux with the osmotic pressure and viscosity of the draw solutions was plotted in Fig. 5. Although the osmotic pressure of 0.5 M CaCl<sub>2</sub> was much higher than that of 0.5 M NaCl, they showed the same flux. One acceptable explanation was that the viscosity of 0.5 M CaCl was much higher than that of 0.5 M NaCl and this would hinder the water transmission through the membrane. The basic properties of mean

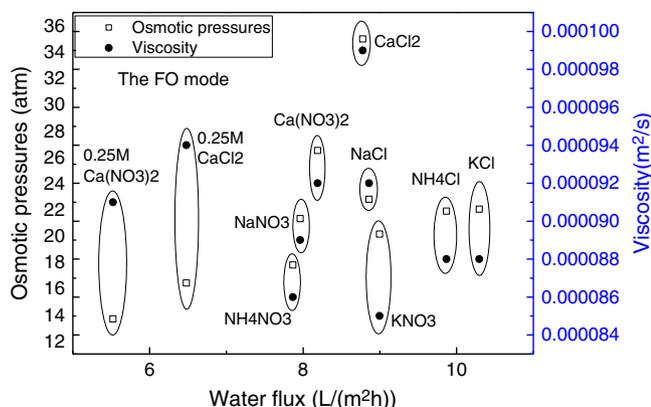


Fig. 5. Water flux of each draw solution as a function of osmotic pressure and viscosity at 0.5 M and 0.25 M in the FO mode.

surface may not be sufficient to predict the effect of positive ions on actual water flux. Further investigation is necessary to understand such effects.

### 3.3. Effects of negative ions

Three sets of DS (KCl&KNO<sub>3</sub>, NH<sub>4</sub>Cl&NH<sub>4</sub>NO<sub>3</sub>, CaCl<sub>2</sub>&Ca(NO<sub>3</sub>)<sub>2</sub>) were conducted in order to examine the effect of negative ions type (Cl<sup>-</sup> & NO<sub>3</sub><sup>-</sup>) of DS on FO performance based on sustainable flux. The experimental conditions were identical to those in Section 3.2.

The flux-decline curves obtained during the runs of both PRO and FO modes are depicted in Fig. 4. It was evident that the water flux of Cl<sup>-</sup> was larger than that of NO<sub>3</sub><sup>-</sup>. The poor performance of NO<sub>3</sub><sup>-</sup> salt in terms of water flux was partially attributed to the low osmotic pressure of NO<sub>3</sub><sup>-</sup> salt solution. However, the RSF of Cl<sup>-</sup> was probably larger than that of NO<sub>3</sub><sup>-</sup>, because the order of hydrated ion radius was Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup>. Furthermore, it has also been reported that the rejection order to the RO membrane operated under a high pressure was NO<sub>3</sub><sup>-</sup> < Cl<sup>-</sup> [11].

### 3.4. Comparison on effects of draw solutions on water flux between the PRO and FO modes

To examine the different effects of positive and negative ions on transmembrane flux between the PRO mode and FO mode, the two membrane orientations were tested at all the same conditions. From Figs. 2 and 4, it was obviously seen that, to the same DS, the situation of water flux was different between the PRO and FO modes. For instance, to PRO mode, as KCl, NH<sub>4</sub>Cl and NaCl solution are concerned, the average water fluxes were 19.58 L/(m<sup>2</sup> h), 19.40 L/(m<sup>2</sup> h) and 18.40 L/(m<sup>2</sup> h) during the first 0.25 h and 17.11 L/(m<sup>2</sup> h), 15.70 L/(m<sup>2</sup> h) and 16.00 L/(m<sup>2</sup> h) during the total 4 h. The reductions were 2.49 L/(m<sup>2</sup> h), 3.70 L/(m<sup>2</sup> h) and 2.41 L/(m<sup>2</sup> h), respectively. In the first 1.25 h, the water flux of NH<sub>4</sub>Cl was larger than that of NaCl; however, the water flux of NaCl was greater than that of NH<sub>4</sub>Cl in the later time. Both the value level and change slope of the water flux versus time curves were diverse.

#### 3.4.1. Different effects of draw solutions on final water flux between the PRO and FO modes

The influence of DS types on final water flux was investigated and compared in FO and RO modes. The average water fluxes in the total 4 h of 0.5 M KCl, 0.5 M NH<sub>4</sub>Cl, 0.5 M NaCl, 0.25 M CaCl<sub>2</sub> and 0.5 M CaCl<sub>2</sub> in both PRO and FO modes can be summarized from Figs. 2 and 4. To all the selected DSs, the water flux was higher in PRO mode than that in FO mode. The case that the concentrative ICP phenomenon occurring in the PRO mode was less severe (hence less impedance to flux) than the dilutive ICP occurring in the FO mode was one reason for the situation.

One of the interesting observations from the data of average water fluxes was that, to the different DSs, the gaps of water flux between the PRO and FO modes were various. For example, the largest one was 0.5 M NaCl, 8.10 L/(m<sup>2</sup> h), while the lowest one was 0.5 M NH<sub>4</sub>NO<sub>3</sub>, 4.03 L/(m<sup>2</sup> h).

The gaps of water flux between the PRO and FO modes to different salts can also be calculated. The first observation was that the gaps of water flux between the PRO and FO modes had the regularity that the gap to the NO<sub>3</sub><sup>-</sup> salt was smaller than that of Cl<sup>-</sup> salt. For example, the gaps of KCl, NH<sub>4</sub>Cl and NaCl were 5.98 L/(m<sup>2</sup> h), 5.51 L/(m<sup>2</sup> h) and 7.99 L/(m<sup>2</sup> h), respectively, while the gaps of KNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub> and NaNO<sub>3</sub> were 4.82 L/(m<sup>2</sup> h), 4.03 L/(m<sup>2</sup> h) and 6.31 L/(m<sup>2</sup> h), respectively. The next observation was that the gap of water flux between the PRO and FO modes was higher to the DS of high concentration than that to the DS of low concentration, the gaps of 0.25 M CaCl<sub>2</sub> and 0.5 M CaCl<sub>2</sub> were 6.77 L/(m<sup>2</sup> h) and 7.56 L/(m<sup>2</sup> h), respectively. At the same time, the gaps of 0.25 M Ca(NO<sub>3</sub>)<sub>2</sub> and 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub> were 5.15 L/(m<sup>2</sup> h) and 7.2 L/(m<sup>2</sup> h), respectively.

### 3.4.2. Different effects of draw solutions on change of water flux between the PRO and FO modes

In order to determine the diverse changing trends of water flux to different DSs in different modes, the change of average water flux in the special time intervals was calculated. The drop rates of water flux were compared between different DSs and different modes. The reduction was the gap between water flux of the first 0.25 h and that of the total 4 h, which can be calculated from Figs. 2 and 4. In the PRO mode, 0.25 M  $\text{Ca}(\text{NO}_3)_2$  showed the lowest degree of reduction which was as low as 1.19 L/(m<sup>2</sup> h) and  $\text{NH}_4\text{NO}_3$  had the second lowest degree of reduction which was 1.23 L/(m<sup>2</sup> h);  $\text{NH}_4\text{Cl}$  showed the highest degree of reduction among the selected DS which was 3.30 L/(m<sup>2</sup> h) and then was KCl (2.48 L/(m<sup>2</sup> h)). In the FO mode,  $\text{NH}_4\text{Cl}$  showed the highest degree of reduction as large as 1.33 L/(m<sup>2</sup> h), while the smallest reduction in the FO mode belonged to 0.5 M  $\text{CaCl}_2$  and it was 0.42 L/(m<sup>2</sup> h). It can be clearly seen that, to all the selected  $\text{Cl}^-$  salts, the reduction rate of water flux was larger than that of  $\text{NO}_3^-$  salts.

As we all know that the lessened water flux indicates that the speed of the water through the membrane reduces with the increasing running time. The osmotic pressure of solution is proportional to its concentration. When the DS has greater water flux, it would be diluted faster and thus its water flux rate would reduce faster. As mentioned above,  $\text{Cl}^-$  salts showed greater water flux than  $\text{NO}_3^-$  salt. Like the result of KCl, its water flux reduced fastest only except for  $\text{NH}_4\text{Cl}$  in the FO mode. The result of  $\text{NH}_4\text{Cl}$  was partly due to the high water flux. However, the crucial factor could attribute to RSF.  $\text{NH}_4^+$  possessed much smaller hydrated ion and could easily diffuse through the membrane. This resulted in more severe RSF which lessened the osmotic pressure difference between the two layers of FO membrane [29,30].  $\text{CaCl}_2$  had the highest viscosity and lowest diffusion coefficient at the beginning which blocked water through the membrane, but with the solution diluted, their viscosity decreased and diffusion coefficient increased which was beneficial to pass water. Moreover,  $\text{Ca}^{2+}$  as divalent ions had much lower reverse permeation rate than monovalent ions [31]. The membrane fouling was also one of the reasons for water flux reduction; however, this influence was slight and negligible for a short time.

There was other important regularity that the reduction in the PRO mode was greater than in the FO mode dramatically. This mainly attributed to larger trans-membrane flux and more severe RSF.

## 4. Conclusions

In this study, the influences of various types of cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$  and  $\text{NO}_3^-$ ) on the FO performance (water flux) in PRO mode (the porous layer facing the FS) and FO mode (the porous layer facing the DS) were studied and compared systematically using the TFC FO membrane using deionized water as FS. The following conclusions have been drawn from this study.

1. Different types of positive ions in DS played a remarkable role in determining the water flux.  $\text{Na}^+$  and  $\text{K}^+$  salts were the optimal candidates as DS. They showed rather satisfactory FO performance, whose water fluxes in both PRO and FO modes were high and the reduction rates were low at the same time.  $\text{NH}_4^+$  salts were suitable for DS as well.  $\text{NH}_4^+$  salts had high flux in the beginning time but declined by rather fast rate mainly due to the high reverse solute flux (RSF).
2. Different types of negative ions significantly affected the FO performance. For the most part, the  $\text{Cl}^-$  salts showed much higher trans-membrane flux and reduction rate than  $\text{NO}_3^-$  salts to both PRO and FO modes. Moreover, the  $\text{Cl}^-$  salts revealed greater gap of water flux in the PRO and FO modes than  $\text{NO}_3^-$  salts.
3. To the same DS, the water flux of PRO mode was higher than that of FO mode. At the same time, the flux in PRO mode declined faster than that in FO mode. However, one of the reasons was that the concentrative ICP phenomenon occurring in the PRO mode was less severe than

the dilutive ICP occurring in the FO mode. On the other hand, the gaps of water fluxes between the PRO and FO modes were various to the different DSs.

## References

- [1] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments, *J. Membr. Sci.* 281 (2006) 70–87.
- [2] H.Y. Ng, W. Tang, W.S. Wong, Performance of forward (direct) osmosis process: membrane structure and transport phenomenon, *Environ. Sci. Technol.* 40 (2006) 2408–2413.
- [3] L.A. Hoover, W.A. Phillip, A. Tiraferri, N.Y. Yip, M. Elimelech, Forward with osmosis: emerging applications for greater sustainability, *Environ. Sci. Technol.* 45 (2011) 9824–9830.
- [4] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: opportunities and challenges, *J. Membr. Sci.* 396 (2012) 1–21.
- [5] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (2011) 712–717.
- [6] 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 (2012) 734–744.
- [7] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), *J. Membr. Sci.* 365 (2010) 34–39.
- [8] 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.
- [9] 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.
- [10] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *J. Membr. Sci.* 364 (2010) 233–241.
- [11] S. Kim, H. Ozaki, J. Kim, Effect of pH on the rejection of inorganic salts and organic compound using nanofiltration membrane, *Korean J. Chem. Eng.* 23 (2006) 28–33.
- [12] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia-carbon dioxide forward (direct) osmosis desalination process, *Desalination* 174 (2005) 1–11.
- [13] R.L. McGinnis, J.R. McCutcheon, M. Elimelech, A novel ammonia-carbon dioxide osmotic heat engine for power generation, *J. Membr. Sci.* 305 (2007) 13–19.
- [14] 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.
- [15] M. Tryppuc, U. Kielkowska, Solubility in the  $\text{NH}_4\text{HCO}_3^+$   $\text{NaHCO}_3^+$   $\text{H}_2\text{O}$  system, *J. Chem. Eng. Data* 43 (1998) 201–204.
- [16] S. Phuntsho, H.K. Shon, T. Majeed, I. El Saliby, S. Vigneswaran, J. Kandasamy, S. Hong, S. Lee, Blended fertilizers as draw solutions for fertilizer-drawn forward osmosis desalination, *Environ. Sci. Technol.* 46 (2012) 4567–4575.
- [17] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, J. Kandasamy, Fertiliser drawn forward osmosis desalination: the concept, performance and limitations for fertigation, *Rev. Environ. Sci. Biotechnol.* 11 (2012) 147–168.
- [18] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: evaluating the performance of fertilizer draw solutions, *J. Membr. Sci.* 375 (2011) 172–181.
- [19] W. Fam, S. Phuntsho, J.H. Lee, H.K. Shon, Performance comparison of thin-film composite forward osmosis membranes, *Desalin. Water Treat.* 51 (2013) 6274–6280.
- [20] 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.
- [21] K.L. Lee, R.W. Baker, H.K. Lonsdale, Membranes for power-generation by pressure-retarded osmosis, *J. Membr. Sci.* 8 (1981) 141–171.
- [22] B. Chanukya, S. Patil, N.K. Rastogi, Influence of concentration polarization on flux behavior in forward osmosis during desalination using ammonium bicarbonate, *Desalination* 312 (2013) 39–44.
- [23] C.H. Tan, H.Y. Ng, Modified models to predict flux behavior in forward osmosis in consideration of external and internal concentration polarizations, *J. Membr. Sci.* 324 (2008) 209–219.
- [24] 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.
- [25] J.R. McCutcheon, M. Elimelech, Modelling water flux in forward osmosis: implications for improved membrane design, *AIChE* 53 (7) (2007) 1736–1744.
- [26] C.Y. Tang, Q. She, W.C. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, *J. Membr. Sci.* 354 (2010) 123–133.
- [27] S. Zhao, L. Zou, Effects of working temperature on separation performance, membrane scaling and cleaning in forward osmosis desalination, *Desalination* 278 (2011) 157–164.
- [28] 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.
- [29] B. Wishaw, R. Stokes, The diffusion coefficients and conductances of some concentrated electrolyte solutions at 25, *J. Am. Chem. Soc.* 76 (1954) 2065–2071.
- [30] C. Boo, S. Lee, M. Elimelech, Z. Meng, S. Hong, Colloidal fouling in forward osmosis: role of reverse salt diffusion, *J. Membr. Sci.* 390 (2012) 277–284.
- [31] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, *Environ. Sci. Technol.* 43 (2009) 6769–6775.