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

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HIGHLIGHTS

- Effects of different ions on FO performance were studied.
- Cations (Na^+, K^+, NH_4^+ and Ca^{2+}) and anions (Cl^- and NO_3^-) were chosen.
- Comparing with FO mode, PRO mode had higher water flux, which declined faster yet.
- K^+ and 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. NaCl, $NaNO_3$, KCl, KNO_3, NH_4Cl, NH_4NO_3, $CaCl_2$ and $Ca(NO_3)_2$ 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 Na^+ and K^+ salts was quite satisfactory in the PRO mode; specifically NaCl had the greatest water flux (16.96 L/(m^2 h)), and the following largest was KCl (16.55 L/(m^2 h)). K^+ salts had the highest water flux among all the selected positive ions in the FO mode which was KCl (10.30 L/(m^2 h)). To the negative ions, Cl^- salts showed higher water flux than nitrates in both PRO and FO modes, such as the water flux of $NaNO_3$ was 7.96 L/(m^2 h), while that of NaCl was 8.86 L/(m^2 h) in the FO mode. Overall, K^+ and Cl^- were regarded as optimal candidates of cation and anion, respectively.

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 (NH_3) and carbon dioxide (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,

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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, $NaNO_3$ and KNO_3 performed best in terms of water flux, while $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ 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, $NaNO_3$, KCl, KNO_3, NH_4Cl, NH_4NO_3, $CaCl_2$ and $Ca(NO_3)_2$) were selected as representatives to prepare the DS. They were all analytically pure. In order to maintain single variable, the concentrations of Cl^- and NO_3^- in different DSs were consistent and all maintained at 0.5 M. Since Ca^{2+} was divalent ions which was different from Na^+, K^+ and NH_4^+, the concentration of Ca^{2+} was 0.25 M, while the concentrations of Na^+, K^+ and NH_4^+ were 0.5 M, when the concentrations of Cl^- and NO_3^- were 0.5 M. 0.5 M $CaCl_2$ and 0.5 M $Ca(NO_3)_2$ were studied as well to compare with 0.25 M $CaCl_2$ and 0.25 M $Ca(NO_3)_2$. The feed solution (FS) used in this study was deionized 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^2 (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	