Water flux behavior of blended solutions of ammonium bicarbonate mixed with eight salts respectively as draw solutions in forward osmosis

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HIGHLIGHTS

- Water fluxes of different NH_4HCO_3 mixed solutions in forward osmosis were studied.
- Blended solutions formed by NH_4HCO_3 and eight inorganic salts were draw solutions.
- After mixed single salt with NH_4HCO_3, the water flux increased notably.
- $NH_4Cl + NH_4HCO_3$ mixture gained the highest water flux.

ARTICLE INFO

ABSTRACT

Forward osmosis (FO) is a novel membrane technology which has huge potential in the field of desalination and wastewater reclamation. Recoverable draw solutions (DS) with high osmotic pressure are crucial to FO process. This study investigated the water flux behavior of draw solutions formed by ammonium bicarbonate and eight soluble inorganic salts (K_2SO_4, NaCl, KCl, KNO_3, NH_4Cl, NH_4NO_3, urea and $(NH_4)_2HPO_4$), respectively. A laboratory-scaled plate-and-frame FO setup with TFC FO membrane was used. The result indicated that the properties and water flux behavior of the aforementioned eight salt solutions were all enhanced after blended with NH_4HCO_3. Mixture of NH_4Cl and NH_4HCO_3 exhibited the highest water flux when deionized water or simulated brackish water was used as feed solution (FS). Meanwhile, water flux of blended solution formed by urea and NH_4HCO_3 was the lowest. However, urea gained the highest water flux increase after blending with NH_4HCO_3. The osmotic driving force generated by draw solution in each FO process has not been utilized effectively no matter which kind of feed water was used. Moreover, the performance ratio (PR, experimental water flux divided by theoretical water flux) of most salt solutions decreased slightly after blending with NH_4HCO_3.

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1. Introduction

With insufficient freshwater sources and tremendous water demands in the world, saline water, as an alternative freshwater source, has recently received worldwide attention. Membrane technology plays a vital role in the desalination of brackish water and seawater. Reverse osmosis (RO) is currently the most typical technique in the field of desalination [1,2]. However, large energy demand, severe membrane fouling as well as large costs limit the wide application of RO process [3–6]. As an emerging novel membrane separation process with lower energy consumption and membrane fouling tendency, forward osmosis (FO) has recently drawn great attention [7–9]. In FO process, water naturally permeates across a semi-permeate membrane from low concentration solution (feed solution, FS) side to concentrated solution (draw solution, DS) side driven by an osmotic pressure gradient. Therefore, pressure-generated equipment is unnecessary in a FO process. The main energy consumption step in FO desalination process is the separation and recovery of draw solute, but the energy needed is much less than traditional pressure-driven membrane process [10–12]. Loose and sparse fouling layer on FO membrane can also be removed through physical cleaning because of the lack of additional hydraulic pressure [12,13]. An ideal DS should generate high osmotic pressure and can be easily retrieved, which is crucial for FO process.

McCutcheon et al. [14] firstly applied NH_3–CO_2 as draw solution in FO process. The pure product water could be separated from diluted draw solution by low temperature distillation, as ammonium bicarbonate could be decomposed into ammonia and carbon dioxide gases when

heated at 60 °C. Since then, many researchers [3,10,11,15] have done a flurry of investigations on that FO process. Recently, Phuntsho et al. [16,17] reported a promising FO process named fertilizer drawn forward osmosis (FDFO) which avoided the need of separation and regeneration of draw solutes. The diluted draw solution after desalination could be directly used for irrigation, as an essential nutrient source for crop growth is included in it. In fact, the final concentrations of plant nutrients in the diluted draw solution much exceed the demand for crop growth. Therefore, the draw solution has to be further diluted using additional fresh water before direct irrigation, which is not desirable in the region where lacks of sufficient fresh water sources. Phuntsho et al. [4] also proposed that, using blended fertilizers as DS instead of single fertilizer, the final nutrient concentration of a particular nutrient could be significantly reduced in FDFO desalination process. However, because of the limitations offered by the osmotic equilibrium, achieving acceptable nutrient concentrations in the final FDFO product water for direct irrigation will still remain a challenge especially when high salinity feed water is used. Consequently, DS formed by blending dissolvable inorganic salts with ammonium bicarbonate could achieve lower nutrient concentrations in diluted DS as a result of multiple nutrients containing. Especially, if the ammonium bicarbonate was removed from the diluted DS through low temperature distillation, the final nutrient concentration would decrease a lot.

Phuntsho et al. [16] found that in FDFO process, the DS of KCl, NaNO₃ and KNO₃ performed best in terms of water flux, while NH₄H₂PO₄, (NH₄)₂HPO₄, Ca(NO₃)₂ and (NH₄)₂SO₄ had the lowest reverse solute fluxes. Zhao et al. [18] evaluated the influence of different ions on water flux performance of FO process and found that the salts contained K^+ and Cl^- were the optimal candidates for DS, but the Na^+ and NH_4^+ salts also have good water flux performance. According to the previous explorations and the characteristics of NH_4HCO_3 and fertilizer salts, solutions mixing eight dissolved inorganic salts (K_2SO_4, NaCl, KCl, KNO₃, NH₄Cl, NH₄NO₃, urea and $(NH_4)_2HPO_4$) with ammonium bicarbonate respectively were selected as draw solution candidates for FO process in this study. Flux behavior of the FO process to determine the suitability of blending dissolved inorganic salt with ammonium bicarbonate as draw solution was investigated in this study for further exploration of an excellent draw solution. This paper also compared the performances of the single salt solution and the blended solutions using deionized water (DI water) and simulated brackish water as feed solution respectively in terms of water flux.

2. Theoretical fundamentals

The generalized water flux of FO process is shown in Eq. (1):

$$J_w = A\sigma\left[\pi_{D,b} - \pi_{F,b}\right] \qquad (1)$$

where A is the pure water permeability coefficient of the FO membrane; σ is the reflection coefficient; and $\pi_{D,b}$ and $\pi_{F,b}$ are the osmotic pressure of the bulk draw solution and bulk feed solution respectively. Especially, when the flux of FO process is low and the feed solution is dilute extremely, the value of σ could be assumed to be 1 (i.e., complete rejection of the feed solution).

In reality, due to the asymmetric FO membrane structure, two kinds of concentration polarization (CP) effects negatively influenced the flux behavior in the FO process: concentrative external concentration polarization (ECP) happened on the membrane dense layer facing feed water and dilutive internal concentration polarization (ICP) occurred inside the membrane porous layer against draw solution. Thus, Eq. (1) should be modified as below [19]:

$$J_w = A\left[\pi_{D,b}\exp(-J_w K) - \pi_{F,b}\exp\left(\frac{J_w}{k_F}\right)\right] \qquad (2)$$

where k_F is the mass transfer coefficient of the feed, and K is the solute resistance to diffusion within the membrane support layer, and it is defined as:

$$K = \frac{t\tau}{D\varepsilon} \qquad (3)$$

where D is the diffusion coefficient of the draw solute; t, τ and ε are the thickness, tortuosity, and porosity of the support layer, respectively.

As shown in Eq. (2), when lower K value and high the k_F value are applied, the deleterious effects caused by the concentrative ECP and dilutive ICP will be negligible. That means the FO process, which treats FS with lower salinity while using the FO membrane with thinner and more porous supporting layer could achieve higher permeate pure water flux. Furthermore, when the osmotic pressure gap between DS and FS is low enough, the water flux shown in Eq. (2) can be replaced by Eq. (1) [4].

3. Materials and methods

3.1. Experimental setup

Fig. 1 describes the apparatus of laboratory-scale FO setup used in our study. The crossflow membrane cell was designed with channels on both sides of the membrane. The basic specifications and other relevant details about the different apparatus used were clearly shown in Table 1.

A TFC FO membrane (HTI Inc., USA) was used in all experiments, which was composed of a polysulfone support layer onto a thin polyester nonwoven fabric at bottom and a selective polyamide active layer on top. Fig. 4 shows the surface micrographs of the active (1a) and support layer (1b) of the TFC FO membrane. Micrographs of the membranes were obtained using a HITACHI S-520 scanning electron microscope. It had been verified that TFC membrane possessed both high water flux and salt rejection. Furthermore, its high membrane performance would not degrade after prolonged exposure to ammonium bicarbonate draw solution [20]. The working pH range (2–12) of TFC FO membrane was also wider than CTA FO membrane (pH: 4–6) [21,22]. These excellent properties enable TFC FO membrane to be more suitable for this study. All tests were operated under FO mode (i.e., the active side of membrane faced with the feed solution, while the support side of membrane was against draw solution). According to the speed of pumps and effective membrane area, the flow velocities of feed and draw solution were all at 2.775×10^{-3} m/s. Draw solution and feed water co-currently passed through the permeation rectangle channel in all tests. The co-current flow mode was adopted to minimize the strain of the suspended membrane [23]. A water bath controlled by temperature controller was used to adjust the temperature of both feed and draw solutions at 25 ± 1 °C. Each experiment was carried out for 5 h. Water flux was measured continuously by a digital mass scale connected to a computer.

3.2. Feed and draw solutions

In order to find an optimal draw solute for desalination of brackish water, nine dissolved salts (NH_4HCO_3, K_2SO_4, NaCl, KCl, KNO₃, NH₄Cl, NH₄NO₃, urea and $(NH_4)_2HPO_4$) were chosen as candidates. Previous works have verified that these salts all had excellent performance in FO process [15,16,18,24,25]. NH_4HCO_3 can blend with each and/or all of other eight salts to form stable solution without producing any prepetition or gas. In addition, the salts contained the essential nutrient element (N, P or K) for crop growth and can be divided as three groups according to that three essential elements (N-group: NH_4HCO_3, NH₄Cl, NH₄NO₃ and urea; K-group: K_2SO_4, KNO₃ and KCl; P-group: $(NH_4)_2HPO_4$). NaCl was chosen as draw solute just for comparison, as it was the optimal representative of the widely employed inorganic