Novel draw solutes of iron complexes easier recovery in forward osmosis process

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ABSTRACT

Forward osmotic (FO) membrane is a new process for producing fresh water from salt water. The study of draw solute is essential in the development and application of FO technology; draw solution should be good at drawing water and easy at recovery. In this paper, three complex draw solutes such as ammonium iron (II) sulfate, ammonium iron (III) sulfate and ammonium iron (III) citrate with different concentrations were studied. The physical properties such as pH, conductivity and total dissolved solids (TDS) have simultaneously been investigated. The pH of most ammonium complexes was decreased whereas TDS increased with increasing of draw solution concentrations. We found that high water flux of these iron complexes was reported in the range of 8.88–11.24 LMH which was higher than the ammonium bicarbonate draw solution. In addition, more than 90% iron complexes draw solutions were recovered by NF-90 membrane, which plays an important role in the FO process to produce fresh water. This study provides direct evidence for the ability of permeate water from feed solution to draw solution, which shows the potential applications of iron complexes in FO process to produce fresh water from sea-, brackish or river water.

Key words | FO membrane, iron complex, nanofiltration (NF), reserve salt flux, water flux

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INTRODUCTION

Along with the rise in sea levels, the status of salinity is occurring in many countries in the world including Vietnam, which seriously impacts on agricultural production and life in these areas. As a result, many people will lack clean water to use in their daily life. To cope with these issues, seawater desalination technologies have been found by scientists worldwide. Desalination can be defined as any process that removes salt from water. At present, two types of technologies that are widely used around the world for desalination can be broadly classified as either thermal technology or membrane technology. These technologies need energy to operate and produce fresh water.

According to Zheng et al. (2015), membrane technology is commonly applied for industrial wastewater treatment in China with around 6.7 million m^3 of wastewater per day (2.4 billion m^3 per year) treatment capacity applying membrane technology. Han (2013) used a reverse osmosis (RO) membrane filtering system for seawater desalination in the first phase of the Hongyanhe Nuclear Power Plant in China. The system has a maximum capacity of 16,000 m^3/day and purifies some 5.8 million m^3 of seawater per annum for power generation and domestic water. Forward osmosis (FO) membrane is a valuable technology which drives clean water permeates from feed solution to draw solution by the osmotic pressure difference across a semipermeable membrane. With a low operation cost, the FO membrane technology has been widely applied in wastewater treatment (Achilli et al. 2009), brackish water and

seawater desalination (McCutcheon *et al.* 2006), food processing (Petrotos & Lazarides 2001; Garcia-Castello *et al.* 2009), and power generation (Seppala & Lampinen 1999; Achilli *et al.* 2009). According to Phuntsho *et al.* (2013), the major factors affecting the performance of FO include membrane properties, draw solution properties, feed solution properties and the operating conditions. Determining the suitable draw solutes becomes particularly crucial for the FO process. Ge *et al.* (2013) and Klaysom *et al.* (2013) indicated that the ideal draw solute should include the principal traits such as: high solubility, minimal reverse draw solute leakage, easy regeneration, non-toxicity, low cost, and compatibility with membrane.

Inorganic salts were investigated as draw solutions in the FO process in previous studies due to their low cost and high osmotic pressure potential which creates a high flux (Achilli *et al.* 2010; Alnaizy *et al.* 2013). According to Kiriukhin & Collins (2002), the low charge and small hydrated radius of monovalent and divalent ions in the draw solution can result in a high reverse flux of salts, such as 0.6 M NaCl (7.2 GMH), 0.6 M NH_4HCO_3 (18.2 GMH) when deionized (DI) water was used as the feed solution. On the other hand, a high amount of energy as a driving force was required by the RO membrane to produce freshwater and recover these draw solutions (Zhao *et al.* 2012). In the past few decades, many studies have reported on the development of suitable draw solutions for an FO process; and a few reviews on draw solutions have been published to date (Chekli *et al.* 2012; Ge *et al.* 2013). Draw solutions can be generally classified as volatile compounds, organic compounds, inorganic compounds and novel synthetic compounds, including MNPs and polymer hydrogel. Some draw solutions showed justifiable water flux such as: 2-methylimidazole-based organic compounds (Yen *et al.* 2010), switchable polarity solvents (Stone *et al.* 2013), ferric and cobaltous hydro acid complexes (Ge *et al.* 2014) and poly (sodium 4-styrenesulfonate) (Tian *et al.* 2015). However, high reverse salt flux and relatively energy-intensive regeneration make them impractical in FO desalination. Therefore, identifying novel draw solutes with characteristics of high water flux, low reverse salt flux, and easy recovery is necessary in the FO process.

Thus, in this study, a series of ammonium complexes were investigated as draw solutes in the FO process on parameters such as water flux, reserve flux, solute rejection, and the results of the FO process after a 1-hour experiment. Exploration of suitable draw solutes plays an important role in developing the further advancement of FO processing and even commercialization of an FO membrane (Ren & McCutcheon 2014; Shaffer *et al.* 2015).

METHODS

Materials

Laboratory-grade chemical reagents were purchased from Sigma-Aldrich Corporation, Germany. The properties of these complexes are shown in Table 1. De-ionized water was produced by an ultrapure water system (Purelabflex-3, ELGA, UK). The pressure of these iron complexes were calculated as the most suitable concentration of each complex following the formula:

$$P = R.T.C \text{(bar)}$$

where P = pressure (bar), $R = 0.082$, $T = 273 + t(^\circ C)$, C (M) is the concentration of complex as 0.1, 0.4, 1.0 and 1.5 M were the most suitable concentrations of ammonium iron (II) sulfate, ammonium iron (III) citrate, ammonium iron (III) sulfate and ammonium bicarbonate complexes in FO and nanofiltration (NF) processes, respectively.

Characterizations of iron complexes

The pH value, total dissolved solids (TDS) and electrical conductivity of the iron complexes solutions were determined by pH, TDS and conductivity sensors (LAQUA pH/Ion/Cond Meter F-74BW, HORIBA, Japan) at different concentrations: as 0.05, 0.10, 0.15 and 0.20 M (A2S), as 0.05, 0.10, 0.15, 0.20, 0.40, 0.50 and 1.00 M (A3S) and 0.05, 0.10, 0.15, 0.20 and 0.40 M (A3C), respectively.

Experimental setup

The experimental setup is shown in Figure 1. The active layer of FO membrane was oriented to face the feed solution in order to reduce internal concentration polarization and thus obtain high water flux, with the support layer facing

Table 1 │ The properties of complexes used in FO process

Complex	Ammonium iron (II) sulfate (A2S)	Ammonium iron (III) sulfate (A3S)	Ammonium iron (III) citrate (A3C)	Ammonium bicarbonate (AB)
Formula	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	$NH_4Fe(SO_4)_2 \cdot 12\,H_2O$, or $NH_4[Fe(H_2O)_6](SO_4)_2 \cdot 6\,H_2O$	$(NH_4)_5Fe(C_6H_4O_7)_2$	NH_4HCO_3
Chemical formula	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	$FeNH_4(SO_4)_2$	$C_6H_8O_7.xFe^{3+}yNH_3$	NH_4HCO_3
Molar mass	284.05 g/mol (anhydrous) 392.13 g/mol (hexahydrous)	482.25 g/mol (dodecahydrate)	262.97	79.056 g/mol
Cations	Fe^{2+} and NH_4^+	Fe^{3+} and NH_4^+	Fe^{3+}	NH_4^+
Solubility in water	269 g/L (hexahydrate)	1,240 g/L	Very soluble in water	11.9 g/100 mL (0 °C) 21.6 g/100 mL (20 °C) 36.6 g/100 mL (40 °C)
Density	1.86 g/cm³	1.71 g/cm³	n.i	1.586 g/cm³
Pressure	2.44 (bar)	9.77 (bar)	24.44 (bar)	36.65 (bar)

the draw solution. The total membrane surface area was 32 cm². During experiments, the feed and draw solutions on both sides of the FO membranes were re-circulated by using two separate pumps with the same flow rate of 1.2 L/min, respectively. The system was operated at laboratory conditions. Each treatment was repeated three times over 1 hour at room temperature (around 25 ± 5 °C). pH, TDS and conductivity sensors (LAQUA pH/Ion/Cond Meter F-74BW, HORIBA, Japan) were used to monitor any changes in the containers of feed and draw solutions periodically every 15 min during experiments. The initial volume of draw solution was 0.2 L, and a 0.2 L feed solution glass was placed on a digital scale balance (Sartorius, Goettingen, Germany) to monitor the weight and volume changes at specified time intervals (Figure 1(a)). After the FO test, the diluted draw solution was recovered for reuse through an NF-90 membrane by using a cross flow module at room temperature (see Figure 1(b)). The NF-90 (DOWN) membrane was made from polyamide materials which can be used in pH ranging from 2 to 11 with 6.68 LMH/bar of pure water permeability. The filtration experiments were repeated three times using fresh membranes. The selection of the most appropriate experimental concentration for each complex is made before comparing test results between complexes.

Water flux, reserve flux and solute rejection were determined according to Hau *et al.* (2014) and Tian *et al.* (2015) as shown below.

The water flux (Jw) across the FO membrane was calculated from the volume change of feed solution using the following equation:
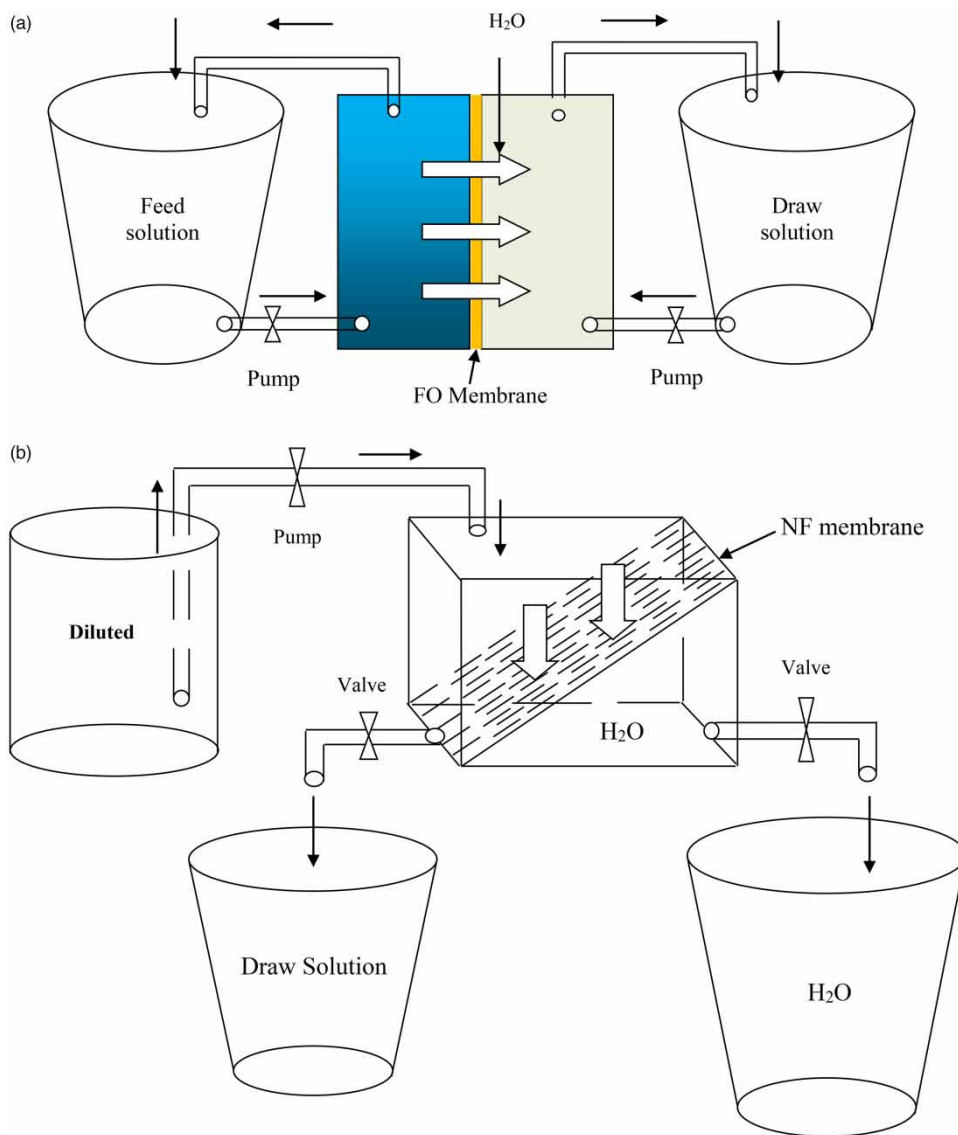
$$Jw = \frac{\Delta V}{A \Delta t}$$

where ΔV (L) is the volume of water permeated from the feed solution to the draw solution over a predetermined time Δt (h) during FO tests, A (m²) is the effective FO membrane area.

Iron complexes salts contain ion cations which were dissociated and conductive in their draw solution, some ions from draw solutions will permeate to feed solution through FO membrane. The conductivities measured from the feed solution were converted in the range of the standard curve which was built from a series of single solutions and indicated the relationship of conductivity and concentration. The concentration of draw solution transporting to the feed solution through FO membrane was thereafter obtained directly from the standard curve. The reserve salt flux (GMH) was determined by the following equation:

$$Js = \frac{Ct.Vt - Co.Vo}{Am.\Delta t}$$

where Co and Ct (mol.L⁻¹) are the initial concentration and the concentration of feed solution measured at the time t,

Figure 1 │ Re-cycle system using FO membrane in desalination.

respectively, Vo and Vt (L) are the initial volume and the volume of feed solution measured at the time t, respectively.
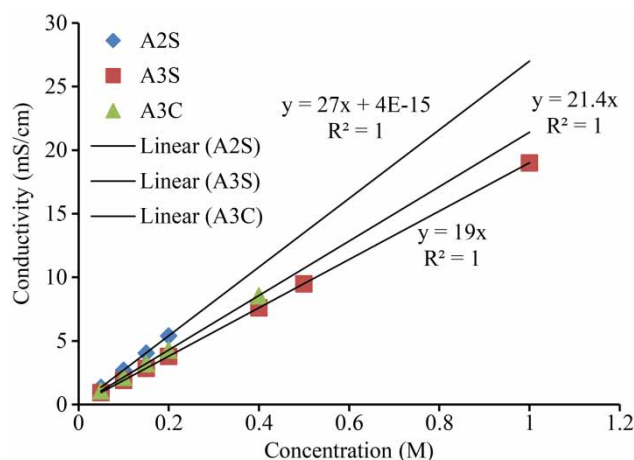
RESULTS AND DISCUSSION

Properties and characterization of iron complexes

Two different cations such as Fe^{+2} and NH_4^+ were found in these iron complexes. A2S is classified as a double salt of ferrous sulfate and ammonium sulfate. It forms monoclinic

crystals, and is soluble in water at approximately 269 g/L. About 1,240 g/L of solubility in water and the weakly violet and octahedrical crystals were noted in A3S complex whereas A3C appeared in yellow crystals and was very soluble in water.

The solution properties of various iron complexes with different concentrations were characterized and are shown in Figure 2, and this played an important role to further check whether iron complexes could act as draw solutes. There is little effect on concentrations on the pH of various iron complexes. pH of different concentrations of A3S ranged from 1.96 to 2.53, then was higher in A2S
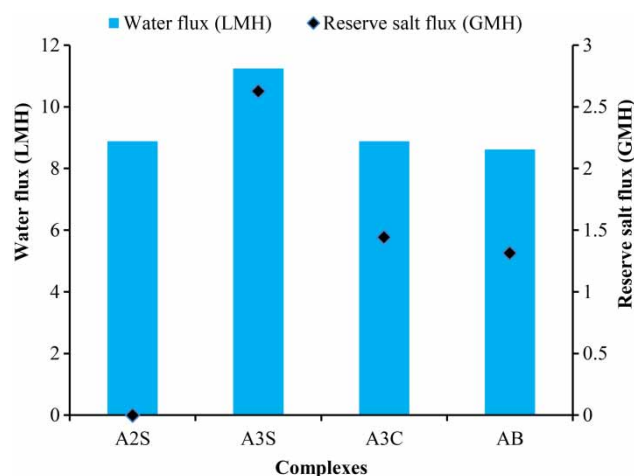
Figure 2 │ Conductivity of different concentrations of various iron complexes as draw solutes in FO process.

(3.79–3.88) and was maximum in A3C at 7.26–7.56. The recommended operational pH ranges of the current commercial thin film composite FO membrane is from 2.0 to 12.0. Therefore, the FO membrane will not undergo hydrolysis and structure change when it is tested in the draw solutions of the iron complexes, which can ensure the consistent FO performance. As shown as Figure 2, the solution conductivity was increased with increasing concentrations of various iron complexes. This is in contrast with the studies of Zhao *et al.* (2016) where the solution conductivity of four EDTA complexes was not directly proportional to that of the increment concentration, and appeared to approach plateaus or even decrease slightly after an initial increase. In addition, the difference existed in conductivity for the studied iron complexes following the order of A2S > A3C > A3S. According to Ge *et al.* (2012), the higher conductivity may lead to higher osmotic pressure. The electrical conductivity in the iron complexes solution mainly derives from two sources including the dissociation of iron ion and ligand which is affected by the property of iron ion and external conditions. Therefore, the measured conductivity of ion complexes solution results from the joint effects.

Effect of iron complexes on reserve salt flux and water flux in FO process

The results showed that 0.1, 0.4 and 1.0 M were the most suitable concentrations of ammonium iron (II) sulfate, ammonium iron (III) citrate and ammonium iron (III)

sulfate complexes in FO process, respectively. A comparison between the concentrations of these complexes was performed to select the potential draw solute for an FO process. The iron complexes as draw solutes were evaluated by quantifying reserve salt flux and water flux in FO tests, which is shown in Figure 3. In addition, NH_4HCO_3 was chosen as a benchmark for comparison with iron complexes group. The results in Figure 3 show that the experimental water flux and reserve salt flux is a function of molar concentration in FO mode where de-ionized water is employed as the feed solution. We found that the water flux of A3S (11.24 LMH) was obviously higher than A2S (8.88 LMH), A3C (8.88 LMH) and the control group (NH_4HCO_3) (8.62 LMH). This is directly related to the fact that high water flux can generate a greater osmotic driving force for water transport through the membrane. The results report that 36.0 mL of water volume was found in A3S which was obviously higher than A2S (28.4 mL), A3C (28.4 mL) and the control group AB (27.6 mL). However, the highest reserve salt flux was 2.62700 (GMH) in A3S solution, followed by A3C (1.44450 GMH), the control group (1.31415 GMH), and the lowest at A2S (0.00143 GMH). This indicated that the molecular sizes of complexes were ranged in the order: A3S < A3C < AB < A2S. Hence, molecular size leads to draw solutes permeating back to the feed solution through the FO membrane, which may affect the next stages of fresh water production. Both water flux and water volume of both A2S and A3C were higher than

Figure 3 │ The comparison of reserve salt flux, water flux and water volume between iron complexes and NH_4HCO_3.

AB. On the other hand, the reserve salt flux of A2S was obviously lower than A3C and AB. According to Kiriukhin & Collins (2002), the reserve flux of salts were 7.2 GMH in 0.6 M NaCl, 18.2 GMH in 0.6 M NH_4HCO_3, 5.6 GMH in 0.5 M $MgCl_2$ when DI water was used as the feed solution. In the studies of Hau *et al.* (2014), the results showed that the lowest reverse salt flux of 0.067 GMH was observed when 0.1 M EDTA-2Na was coupled with 15 mM. NP7 was used as a draw solution and DI water was used as a feed solution in FO mode (active layer facing with the feed solution). These results were much higher in comparision to the reserve flux of ammonium iron (II) sulfate in this study. This demonstrated that only a few ammonium iron (II) sulfate salts permeated back to the feed solution from the draw solution through the FO membrane. This indicated that A2S may be the potential draw solute in an FO process.

Recovery test of iron complexes draw solution via NF membrane

The draw solution is diluted after the FO process, thus the recovery of draw solution is necessary and represents one of the challenges in FO processing (Zhao *et al.* 2014). The large molecular weight and size of iron complexes might be separated from draw solution by a membrane with a larger pore size than that of RO. The recovery convenience of iron complex draw solution was studied through a pressure-driven NF-90 process. Table 2 shows the variation in the TDS permeate and removal efficiencies obtained using various draw solutions as A2S, A3S and A3C in comparison with AB at operation of 8 bars. Over 90% of draw solutes did not permeate through NF-90 membrane, in which 90.96% and 93.14% removal efficiencies were reported in A2S and A3C draw solution, respectively; and 95.52% of A3S was the maximum removal efficiency. In

previous studies, Hau *et al.* (2014) indicated that the NF recovery (pressure of 5.5 bar) of EDTA sodium salts exhibiting high charged compounds performed well, and had a high salt rejection of 93%. NF membrane was used by Ge & Chung (2013) to regenerate hydroacid complexes after FO, which had expanded configurations and charged groups. According to Hau *et al.* (2014), the recovery of 0.05 M EDTA-2Na coupled with 15 mM NP7 was approximately 95%, which is significantly higher than the A2S and A3S draw solutions, but a little less than the A3C draw solution. These results demonstrated that a series of iron complex draw solutions can be easily recovered using NF-90 membrane, which plays an important role in the FO process to produce fresh water using iron complexes as draw solutes substitute AB.

CONCLUSIONS

In summary, various iron complexes were investigated as draw solutes in an FO process. The results showed that high water flux of these iron complexes was reported in the range 8.88–11.24 LMH which was higher than the AB draw solution. In addition, more than 90% iron complexes draw solutions were recovered by NF-90 membrane, which plays an important role in the FO process to produce a fresh water substitute AB.

ACKNOWLEDGEMENT

Table 2 | Recovery efficient of draw solution using NF-90 membrane

Draw solution	TDS input (mg/L)	TDS output (mg/L)	Removal efficiency (%)
A2S	12,700	1,148	90.96
A3S	44,600	1,998	95.52
A3C	31,300	2,147	93.14

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