Forward osmosis–membrane distillation hybrid system for desalination using mixed trivalent draw solution

Nguyen Cong Nguyen[a] , Hung Cong Duong[b], Hau Thi Nguyen[a], Shiao-Shing Chen[c*], Huy Quang Le[a,c], Huu Hao Ngo[d*], Wenshan Guo[d], Chinh Cong Duong[c,e], Ngoc Chung Le[a], Xuan Thanh Bui[f],

[a]Faculty of Chemistry and Environment, Dalat University, Dalat, Vietnam

[b]Le Quy Don Technical University, 236 Hoang Quoc Viet, Bac Tu Liem, Hanoi, Vietnam

[c]Institute of Environmental Engineering and Management, National Taipei University of Technology, No.1, Sec. 3, Chung –Hsiao E. Rd, Taipei 106, Taiwan, Republic of China

[d]Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Sydney, Broadway, NSW 2007, Australia

[e]Southern Institute of Water Resources Research, Ho Chi Ming City, Viet Nam

[f]Faculty of Environment and Natural Resources, University of Technology, Vietnam National University – Ho Chi Minh, Vietnam

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* Corresponding author:

Shiao-Shing Chen: Email: f10919@ntut.edu.tw; Tel:886-2-27712171#41 and Huu Hao Ngo; Email: h.ngo@uts.edu.au; Tel: +61 2 9514 2745

Abstract

Finding suitable draw solutions is still a major problem when developing FO technologies. This study represents the first time a mixed trivalent draw solution containing of EDTA–2Na and Na_3PO_4 was systemically studied for FO performance. The objective here was to achieve simultaneously low reverse salt flux and high water flux. The FO results showed that the mixed trivalent draw solution-based 0.3 M EDTA–2Na and 0.55 M Na_3PO_4 underwent higher water flux (J_w= 9.17 L/m^2·h) than that of pure 0.85 M EDTA-2Na (J_w= 7.02 L/m^2·h) due to its lower viscosity. Additionally, the specific reverse salt flux caused by mixing 0.3 M EDTA–2Na with 0.55 M Na_3PO_4 draw solution was only 0.053 g/L using DI water as the feed solution. Donnan equilibrium force and formed complexation of $[EDTANa]^{3-}$, $[HPO_4Na]^-$ with the FO membrane are believed to constitute the main mechanism for minimizing salt leakage from the mixed draw solution. Moreover, the FO desalination process utilizing the mixed trivalent draw solution achieved water fluxes of 6.12 L/m^2·h with brackish water (TDS = 5,000 mg/L) and 3.10 L/m^2·h with seawater (TDS = 35,000 mg/L) as the feed solution. Lastly, diluted mixed trivalent draw solution following the FO process was effectively separated using the MD process with salt rejection >99.99% at a mild feed temperature of 55 °C.

Keywords: forward osmosis; membrane distillation; draw solution regeneration; reverse salt flux; low-carbon desalination.

1. Introduction

Currently, forward osmosis (FO) has proved to have much potential for solving water scarcity through what is known as the green desalination process [1-6]. Unlike pressure-driven membrane processes, FO uses natural osmosis as a driving force for separation, and therefore is expected to be: (1) have minimal energy requirements for operation; (2) experience less membrane fouling; and (3) have a high potential recovery rate [7]. Hence it is compatible with challenging saline water feeds such as RO brine [8], digested sludge centrate, oil/gas drilling flow-back fluid [9, 10], and even human urine [11]. In order to further develop the FO process, suitable draw solution and good FO membrane are two important factors [12, 13]. To date, the FO membrane has been continuously refined [14, 15]and is now very much commercialized, however, exploring appropriate draw solutions is still a major obstacle in FO technology [1-3, 16]. An ideal FO draw

solution is required to possess particular characteristics including high solubility and osmotic pressure for sufficient process water flux, minimal reverse solute flux, ease of regeneration, low cost, and nontoxicity [17-20].

In recent years, various draw solutions including inorganic salts (e.g. KOH, NaCl, $MgCl_2$, NH_4Cl, and $CuSO_4$) and organic solutes (e.g. glucose, fructose, and sucrose) have been used for FO desalination applications [18, 21-25]. These inorganic salts and organic solutes are low-cost draw solutions offering relatively high FO water flux and can be regenerated using RO desalination. However, the FO process using these draw solutions suffers from two major technical issues: severe reverse solute flux and intensive energy consumed during the regeneration of the draw solutions. Reverse solute flux inevitably leads to the depletion and eventual replenishment of the draw solutions, hence increasing the chemical cost of the FO process. On the other hand, energy-intensive draw solution regeneration hinders the realization of FO as an energy-saving alternative to the RO desalination process. Several novel synthetic draw solutions have been explored to address the issues with reverse solute flux and regeneration of draw solutions. Notable examples are the synthetic 2-methylimidazole based compounds, polyelectrolytes, polymer hydrogels, magnetic nanoparticles, and hexavalent phosphazene salts [26-28]. These synthetic draw solutions have great potential with respect to minimal reverse solute flux and energy-reduced draw solution regeneration [26-28]. However, most of these synthetic draw solutions offer lower water flux compared to the above conventional inorganic salts. A hydro-acid complex has also been tested for the FO process to alleviate the issue with reverse salt flux [29, 30]. Compared to NaCl, the hydro-acid complex exhibits a higher water flux and significantly lower reverse solute flux given its expanded structure [29, 30]. However, the synthesis process of this hydro-acid entails several complicated stages, thus preventing its practical application in FO desalination. In 2018, Wang's group explored sodium phytate (PA-Na) as a novel draw solute for brackish water desalination with water flux of 2.78 L/m^2.h and the diluted PA-Na draw solution after FO may be used in food production [31]. However, the diffusion of NaCl (synthetic brackish water) from feed solution to PA-Na draw solution caused the problem of how to reuse diluted PA-Na draw solution in food production processes. In our previous study, highly charged ethylene diamine tetra-acetic disodium (EDTA–2Na) has been proposed for improved water flux and reduced reverse solute flux in the FO process [32, 33]. Compared to NaCl, EDTA–2Na has a higher charge and larger molecule size, thereby offering greater osmotic pressure and the resultant water flux; yet the reverse solute flux is noticeably

lower. Moreover, although the diluted EDTA–2Na draw solution can be effectively regenerated using the nanofiltration (NF) and MD process [32, 34-36], EDTA–2Na exhibits considerably low solubility but high viscosity. This problem stymies the use of EDTA–2Na at high concentration in the FO process with feed waters of high salinity proving to be a major challenge.

In this study, a mixed trivalent draw solution-based high charge of Na_3PO_4 and EDTA-2Na salt in the FO process was employed for the first time. Given the high charge of PO_4^{3-}, the addition of Na_3PO_4 to EDTA–2Na helps increase the osmotic pressure and hence water flux while maintaining the low reverse salt flux of the FO process. Adding Na_3PO_4 also makes possible the use of the draw solution at a higher concentration due to the higher solubility, but it lowers the viscosity of Na_3PO_4 compared to EDTA–2Na. The most benefit of adding Na_3PO_4 into EDTA-2Na is that it enables one to automatically adjust pH of the mixed draw solution to pH 8. Moreover, at the same osmotic pressure, Na_3PO_4 salt (0.0021 USD/atm) is cheaper than EDTA-Na salt (0.0066 USD/atm). The performance of the FO process with reference to water flux and reverse salt flux with the combined EDTA–2Na/Na_3PO_4 draw solution at various compositions was systematically investigated using DI water, synthetic brackish water and seawater feeds. Furthermore, the regeneration of the diluted EDTA–2Na/Na_3PO_4 draw solution via an MD desalination process confirmed the feasibility of the EDTA–2Na/Na_3PO_4 mixture as a draw solution for the FO desalination process.

2. Materials and methods

2.1. Materials

2.1.1. The lab-scale FO and MD setups

Lab-scale FO and MD setups were used in this study. The FO setup (i.e. provided by Sterlitech, USA) consisted of a custom-built membrane module and feed and draw solution tanks (Fig. 1). The membrane module was composed of a flat-sheet cellulose triacetate (CTA) membrane coupon sandwiched between two semi-cells, each of which was engraved to form a rectangular flow channel with length × width × height of 9.2 × 4.5 × 0.2 cm, respectively. The flat-sheet FO membrane was supplied by Hydration Technology Innovations (HTIs OsMem™ CTA Membrane, Albany, OR, USA), and its characteristics are presented in Table 1. The feed and draw solutions were circulated through the FO membrane module using two pumps at fixed

circulation rates of 0.5 L/min. The temperatures of the feed and draw solutions were maintained at 25 ± 0.5 °C using two water baths. In the FO membrane module, due to the osmotic pressure gradient across the membrane, water was transferred from the feed to the draw solution, leading to the concentration of the feed and at the same time the draw solution being diluted. The feed tank was placed on a digital scale (BW12KH, Shimadzu, Japan) connected to a computer in order to calculate the FO process water flux (Fig. 1).
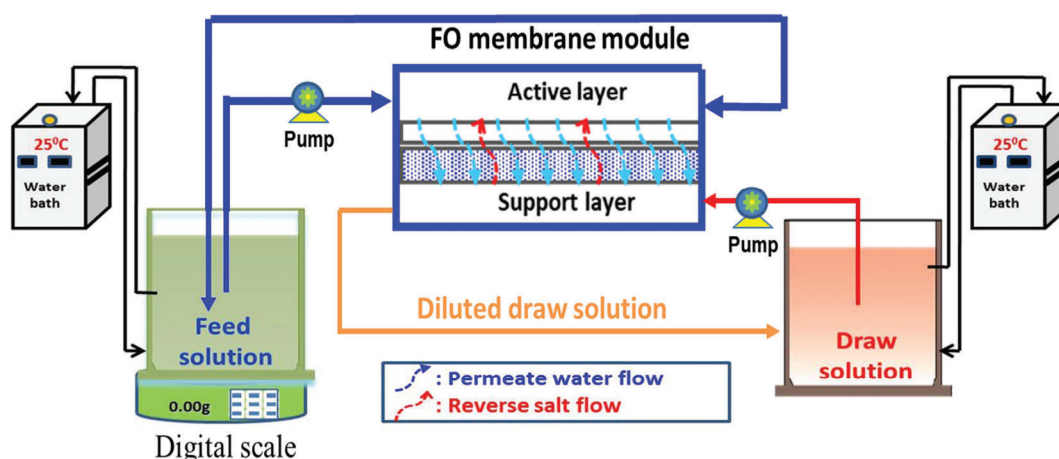

Fig. 1. Schematic diagram of the lab-scale FO setup.

Table 1. Characteristics of the FO and MD membranes.

Characteristics	FO membrane	MD membrane
Material	CTA	PTFE
Pore size	0.37 nm	0.45 μm
Thickness (μm)	50	200
Porosity (%)	–	80
Contact angle (°)	80 ± 7	114 ± 4
pH range	2–9	–

The MD setup (Fig. 2) was used to regenerate the diluted FO draw solution. It consisted of a direct contact membrane distillation (DCMD) membrane module consisting of two acrylic semi-cells and a microporous polytetrafluoroethylene (PTFE) membrane coupon inserted between them to form the feed and distillate channels. The depth, width, and length were 0.3, 10, and 10 cm, respectively. The specifications of the PTFE membrane are provided in Table 1. Plastic

spacers with a thickness of 0.1 cm were used in both feed and distillate channels to promote the fluid turbulence. A peristaltic double-head pump (Baoding Longer Precision Pump Co., Ltd., Taiwan) served to circulate the feed and distillate through the MD membrane module at flow rates of 1.5 L/min. The temperatures of the feed and distillate were controlled using two water baths equipped with thermostats. In the MD membrane module, as the diluted draw solution feed travelled along the feed side of the membrane, water evaporated and was transported through the membrane to the distillate channel, thus concentrating the feed. The concentrated feed leaving the membrane module was then returned to the feed tank for its continuous regeneration. On the distillate side, deionized (DI) water functioned as the initial distillate to condense the water vapour transferred from the feed. During the MD operation, excess distillate from the distillate tank was collected in a beaker placed on a digital balance. The weight of the beaker with excess distillate was recorded to calculate the MD process water flux.
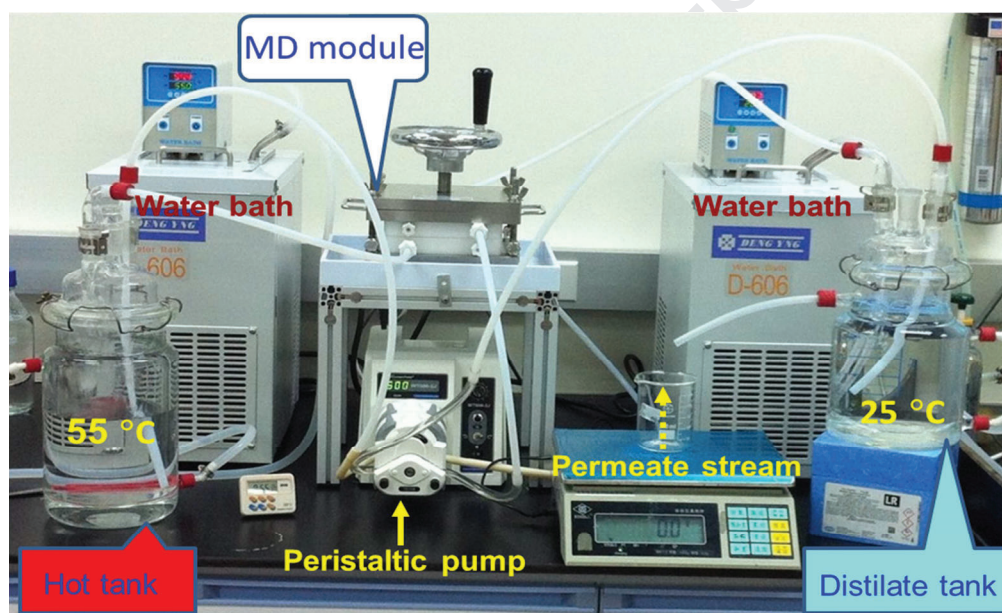

Fig. 2. Illustration of the lab-scale MD setup.

2.1.2. Draw solution and synthetic brackish waters and seawater

In this study, two draw solutions including single EDTA–2Na and mixed EDTA–2Na/Na$_3$PO$_4$ were investigated. The single EDTA–2Na draw solutions at concentrations of 0.31, 0.40, 0.50, 0.55, 0.85, and 1.05 M were prepared from laboratory-grade EDTA–2Na.2H$_2$O (99.0% purity; Sigma-Aldrich Co., Ltd., Germany). The mixed EDTA–2Na/Na$_3$PO$_4$ was prepared by combining

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0.3 M EDTA-2Na with Na₃PO₄.12H₂O (from Merck Co., Ltd., Germany) at concentrations of 0.01, 0.10, 0.20, 0.25, 0.55, and 0.75 M. The synthetic brackish waters and seawater were prepared using laboratory-grade NaCl (Taiwan). The total dissolved solids (TDS) concentration, viscosity, and osmotic pressure of the prepared synthetic brackish waters and seawater are summarized in Table 2.

Table 2. Properties of the synthetic brackish waters and seawater

FO feed solutions	TDS (mg/L)	Viscosity (cP)	Osmotic pressure (atm)
Low-salinity brackish water	5,000	0.96	4.02
Medium-salinity brackish water	15,000	1.09	13.25
High-salinity brackish water	25,000	1.11	18.34
Seawater	35,000	1.14	27.78

2.2. Analytical and calculation methods

The conductivity of the MD distillate was measured using a conductivity meter (Sension156, Hach, China), while its Na^+ and PO_4^{3-} concentrations were analysed using ion chromatography (DionexICS-90) and a UV–Vis spectrophotometer (HACH Model DR-4000, Japan). The total organic content (TOC) of the distillate was monitored using a TOC analyser (ASI-5000A, Shimadzu, Japan). The contact angle of the FO and MD membranes was measured using CAM 100 (Opto-Mechatronics P Ltd., India). DI water was used as the reference liquid. Osmotic pressure (π) of the FO draw and feed solutions was calculated using the Morse equation as follows:

$$\pi = (\Sigma\phi.n.C).R.T \tag{1}$$

where ($\Sigma\phi.n.C$) represents the total osmolality of the solution, R is the universal gas constant (i.e. 0.083 L.bar/K.mol), and T is the absolute temperature (298K). The solution's osmolality was measured using an Osmometer (Model 3320, Advanced Instruments, Inc., USA) based on the freezing-point depression method. The measured osmolality of the solutions was then converted to osmotic pressure by using the Morse equation. The viscosity of the draw solutions was measured using a Vibro Viscometer (AD Company, Japan).

The FO process water (J_w) was calculated as follows:

$$J_w = \frac{\Delta V}{A.\Delta t} \tag{2}$$

where J_w is in L/m^2·h, ΔV is the volume (L) of the distillate obtained in a time interval Δt (h), and A is the effective FO membrane area (m^2).

The reverse salt flux (J_s) of the FO process was determined from the amount of salt accumulated in the feed tank using the equation below:

$$J_s = \frac{V_t.C_t - V_0.C_0}{A.t} \tag{3}$$

where J_s is in g/m^2·h, C_t and V_t are the concentration and volume of the feed solution measured at time t, respectively, and C_0 and V_0 are the initial concentration and volume of the feed solution, respectively.

The specific reverse salt flux of the FO process was calculated from the measured water flux and reverse salt flux. It is defined as the ratio of the reverse salt flux to the water flux (J_s/J_w) and is measured in g/L. The specific reverse salt flux indicates the amount of draw solute lost per volume unit of the water produced during the FO process. The MD process water flux was also measured in L/m^2·h, and its calculation was similar to that of the FO process water flux (i.e. Eq. 2). The salt rejection of the MD process was calculated using the electrical conductivity of the feed (EC$_{feed}$) and distillate (EC$_{dis}$) as written below:

$$Rejection\ (\%) = 100 * \left(\frac{EC_{feed} - EC_{dis}}{EC_{feed}}\right) \tag{4}$$

2.3. Experimental protocols

The performance of the FO draw solutions was examined in the FO experiments with DI water feed. In these experiments, DI water was fed to the feed side (i.e. active layer side of the FO membrane) while the draw solution was fed to the membrane support layer side at the circulation rate of 0.5 L/min. The initial volume of the DI feed and the draw solution was 1 L. The FO process with DI water feed using difference draw solutions was stabilized for 1 hour, then the weight of the feed tank and the conductivity of the feed were measured three times every

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five minutes. This was done to calculate the FO process water flux, reverse salt flux, and specific reverse salt flux.

The FO process with the synthetic brackish water and seawater feeds using the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution at optimal concentrations was operated under the same conditions to the FO experiments with DI water feed. The process water flux was also measured after 1 hour of stabilization. Furthermore, an extended FO desalination process with the synthetic low-salinity brackish water feed was conducted until the feed was concentrated two-fold. The diluted mixed EDTA-2Na/Na$_3$PO$_4$ draw solution following this FO process was subsequently regenerated using the MD process.

The MD regeneration process of the diluted mixed draw solution was conducted at feed and distillate temperature of 55 and 25 °C, respectively, and at circulation rates of 1.5 L/min. The initial TDS concentration of the diluted mixed draw solution was 21,050 mg/L. During the MD regeneration process, the diluted draw solution feed was circulated through the MD membrane module and then back to the feed tank; thus, its concentration increased with the operating time. The MD process water flux together with salt rejection and the distillate TOC, Na$^+$, PO$_4^{3-}$ concentrations were measured and analysed at every hour. The MD process was terminated after the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution had been regenerated to its initial conditions, i.e. at optimal concentrations.

3. Results and discussions

3.1. The performance of the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution

Sodium phosphate (Na$_3$PO$_4$) has a lower viscosity but a higher osmotic pressure than EDTA-2Na at the same molar concentration. As a result, adding Na$_3$PO$_4$ (inorganic salt) into the EDTA-2Na (C$_{10}$H$_{14}$N$_2$Na$_2$O$_8$: organic salt) solution helps reducing the viscosity while increasing the draw solution's osmotic pressure. Indeed, the experimentally measured viscosity of the mixed EDTA-2Na/Na$_3$PO$_4$ solution was lower while its osmotic pressure was higher than those of the single EDTA-2Na solution at the same concentrations (Fig. 3). It is also worth noting that the discrepancies in viscosity and osmotic pressure between the mixed EDTA-2Na/Na$_3$PO$_4$ and the single EDTA-2Na solutions become larger when the Na$_3$PO$_4$ concentration in the mixed solution

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increased (Fig. 3). The low viscosity and high osmotic pressure of the mixed EDTA-2Na/Na$_3$PO$_4$ solution might render it a favourable draw solution for the FO process regarding the water flux.
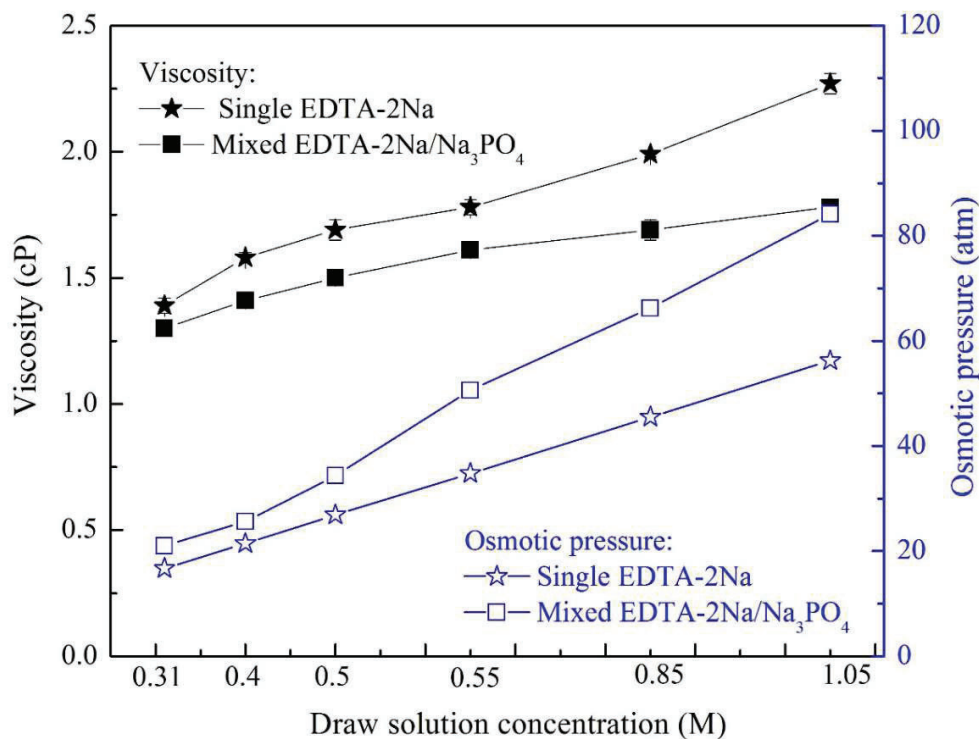

Fig. 3. Viscosity and osmotic pressure of the mixed EDTA-2Na/Na$_3$PO$_4$ and the single EDTA-2Na draw solutions at different salt concentrations. The mixed draw solutions were composed of 0.3 M EDTA-2Na and added Na$_3$PO$_4$ at various concentrations (0.01, 0.10, 0.20, 0.25, 0.55, and 0.75 M). The osmotic pressure was calculated using the Osmometer instrument, while the viscosity was measured using the viscosity meter. Error bars represent the standard variations of triple measurements.

The FO experiments with DI water feed demonstrated the advantages of the mixed EDTA-2Na/Na$_3$PO$_4$ compared to the single EDTA-2Na draw solution. The FO process using the mixed EDTA-2Na/Na$_3$PO$_4$ achieved noticeably higher water flux than the process using the single EDTA-2Na (Fig. 4). For example, at the draw solution concentration of 0.31 M, the FO process with the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution achieved a water flux of 6.32 L/m^2·h, which was 23% higher than that achieved by the process with the single EDTA-2Na draw solution. Moreover, the increase in water flux in the FO process using the mixed EDTA-

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2Na/Na$_3$PO$_4$ draw solution compared to the single EDTA-2Na draw solution was elevated at higher salt concentrations (Fig. 4).
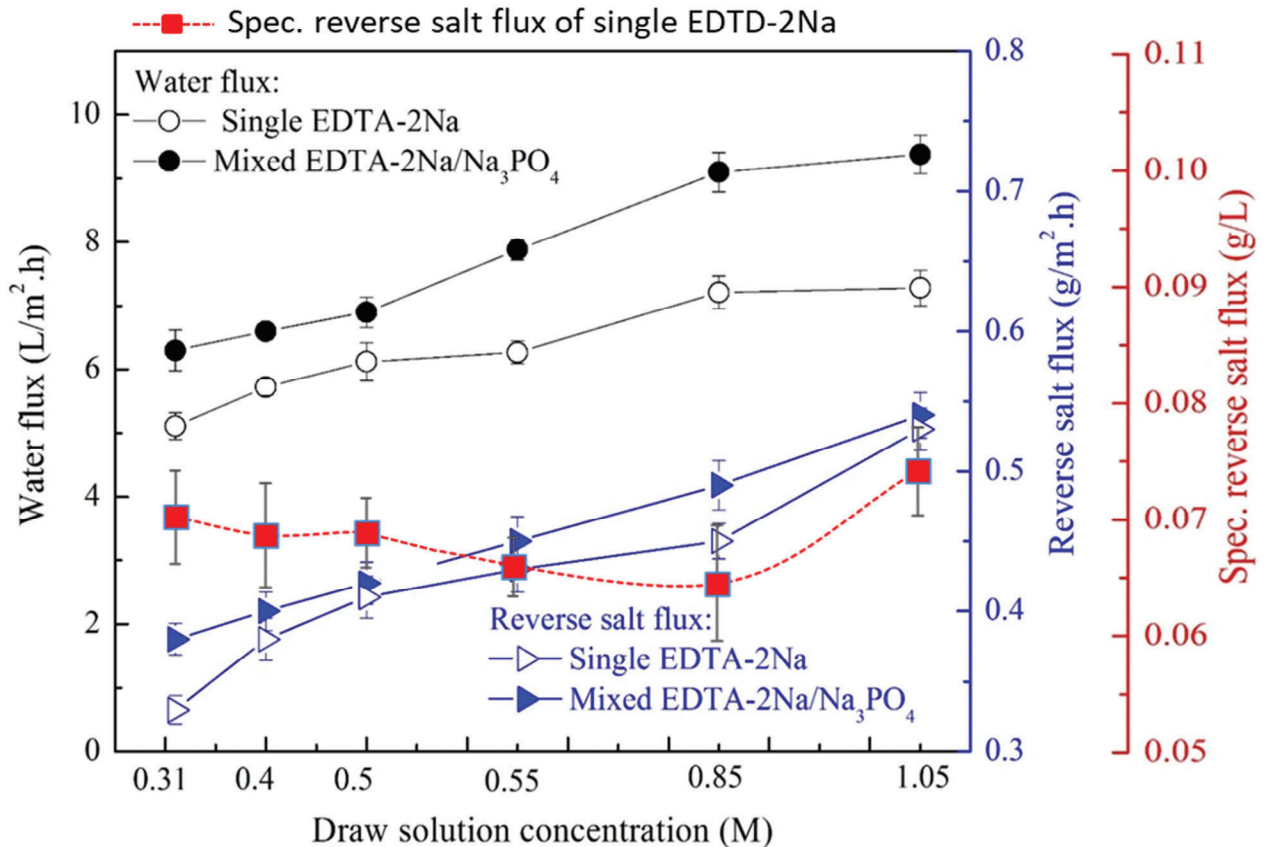

Fig. 4. Water flux, reverse salt flux and specific reverse salt flux of the FO process using the mixed EDTA-2Na/Na$_3$PO$_4$ and the single EDTA-2Na draw solutions at different salt concentrations. The mixed draw solutions were composed of 0.3 M EDTA-2Na and added Na$_3$PO$_4$ at various concentrations (0.01, 0.10, 0.20, 0.25, 0.55, and 0.75 M). DI water was used as the feed to the FO process. The FO process was operated at feed and draw circulation rates of 500 mL/min. Error bars represent the standard variations of triple experiments.

The increase in the FO water flux of the mixed EDTA-2Na/Na$_3$PO$_4$ compared to the single EDTA-2Na draw solution was consistent with the discrepancies in their osmotic pressure and viscosity. In fact, water transport in the FO process is driven by the osmotic pressure gradient across the membrane. Thus, the draw solution's osmotic pressure directly regulates the FO water

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flux. Conversely, draw solution viscosity profoundly affects the internal concentration polarization (ICP), which is an intrinsic drawback of the FO process [23]. ICP creates a smaller salt concentration (i.e. and hence osmotic pressure) inside the pores of the FO membrane support layer compared to the bulk draw solution, therefore reducing the FO process water flux [37]. Higher draw solution viscosity leads to aggravated ICP and hence reduced water flux. As a result, together with its higher osmotic pressure, the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution's lower viscosity (i.e. particularly at high concentration) favoured the increased FO water flux compared to the single EDTA-2Na draw solution (Fig. 4).

The FO process using the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution exhibited slightly higher salt reverse flux than that with the single EDTA-2Na draw solution at the same concentrations. In addition, for either the mixed EDTA-2Na/Na$_3$PO$_4$ or the single EDTA-2Na draw solution, the increased water flux resulted from elevating the draw solution concentration was associated with the aggravated reverse salt flux (Fig. 4). It is worth stating here that the transportation of salts from the draw solution to the feed solution during the FO process depends on not only the membrane properties but also the characteristics of the draw solutes, including their charge and hydraulic radius. Compared to EDTA-2Na, Na$_3$PO$_4$ has a lower charge and smaller hydraulic radius; therefore, it can penetrate through the FO membrane at a higher rate, leading to the higher reverse salt flux of the FO process with the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution. There was a trade-off between water flux and reverse salt flux in the FO process with the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution. The elevated water flux when increasing the Na$_3$PO$_4$ concentration in the mixed draw solution always correlated with a linear increase in reverse salt flux (Fig. 5). However, an optimum ratio existed between Na$_3$PO$_4$ and EDTA-2Na in the mixed draw solution with respect to specific reverse salt flux. Fig. 5 demonstrates that why mixed draw solution of 0.3 M EDTA-2Na and 0.55 M Na$_3$PO$_4$ was selected as an optimum condition in FO process as follows: (i) the mixed draw solution containing 0.3 M EDTA-2Na and 0.55 M Na$_3$PO$_4$ exhibited the minimum specific reverse salt flux (Js/Jw=0.053 g/L); (ii) the mixed draw solution was automatically adjusted to pH 8 by adding 0.55 M Na$_3$PO$_4$ (pH =12) into 0.3 M EDTA-2Na (pH=4.5) without adding pH control solution. At pH 8, mixed draw solution of 0.3 M EDTA-Na and 0.55 M Na$_3$PO$_4$ formed complexation of 27.3% [EDTANa]$^{3-}$ and 11.2% [HPO$_4$Na]$^{-}$ as shown in Fig S1 (complex formation is determined by Mineql+ software based on the chemical equilibrium model from the thermodynamic database) causing reduced free Na^{+} ions significantly, which is the main mechanism for minimizing reverse salt flux from the mixed draw

solution. At 0.55 M Na3PO4 mixed with 0.3 M EDTA–2Na draw solution, this specific reverse salt flux (Js/Jw= 0.053 g/L) was much lower than the measured value of 0.75 M of EDTA complex-based draw solutes such as EDTA–MgNa2, EDTA–CaNa2, EDTA–MnNa2, and EDTA–ZnNa2, as reported by [38], and corresponded to Js/Jw= 0.2 g/L. Reason is due to the fact that the viscosity of these EDTA complex-based draw solutes at 0.75 M was high (>2.5 cp), resulting in reducing permeability water flux and increasing Js/Jw. Thus, this optimum mixed draw solution was selected for the FO experiments with synthetic brackish water and seawater feeds and the subsequent MD process for draw solution regeneration.
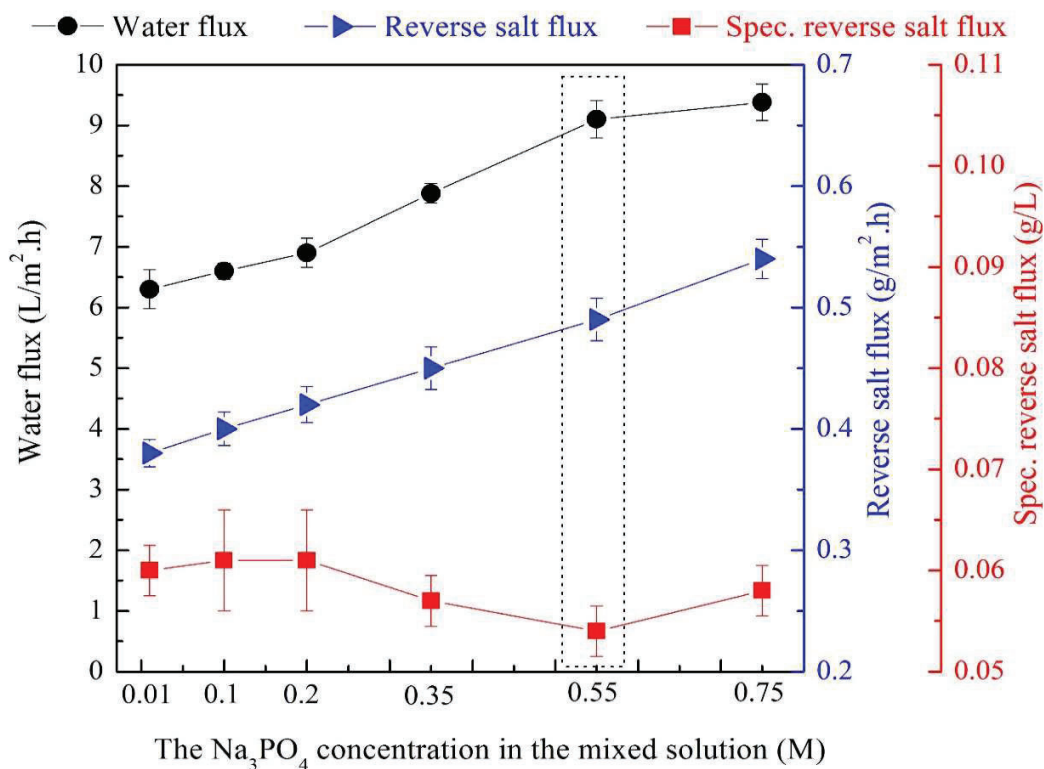
Fig. 5. Water flux, reverse salt flux, and specific reverse salt flux of the FO process using the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution at different Na$_3$PO$_4$ concentrations. The concentration of EDTA-2Na in the mixed draw solution remained at 0.3 M. DI water served as the feed to the FO process. The FO process was operated at feed and draw circulation rates of 0.5 L/min. Error bars represent the standard variations of triple experiments.

3.2. Performance of the FO process with the synthetic brackish water and seawater feeds

The feasibility of the mixed EDTA-2Na/Na$_3$PO$_4$ as a draw solution for the FO process was confirmed in the FO experiments using synthetic brackish water and seawater feeds with salinity ranging from 5,000 to 35,000 mg/L. The experimental results demonstrated the compatibility of the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution at the optimum concentration (i.e. 0.3 M EDTA-2Na/0.55 M Na$_3$PO$_4$) with the FO treatment of brackish water and seawater feeds with respect to water flux. Given its high osmotic pressure, the optimum mixed draw solution achieved relatively high water flux during the FO process with the synthetic brackish water and seawater feeds. For the low-salinity brackish water feed (i.e. 5,000 mg/L), the FO process using the optimum mixed draw solution achieved water flux above 6.12 L/m^2·h, whereas the water flux of this process with the synthetic seawater feed (i.e. salinity of 35,000 g/L) was 3.10 L/m^2·h (Fig. 6). It is noteworthy that the FO process water flux achieved in this study was noticeably higher than those reported in previous studies using feed waters with similar salinities [23], [39], [38].

The results shown in Fig. 6 also indicate the negative impact of the feed water viscosity and the external concentration polarization (ECP) effect on the FO water flux. The experimentally measured water flux decreased by more than 50%, from 6.12 to 3.10 L/m^2·h when the feed salinity was increased from 5,000 to 35,000 mg/L; however, the calculated osmotic pressure difference between the feed and the draw solutions fell by only 38%, from 61.4 to 37.9 atm (Fig. 6). The two main reasons of non-linear correlation between the experimentally measured water flux and the calculated osmotic pressure difference could be attributed to: (1) an increase in the feed water viscosity and (2) an increase in the effect of ECP. Indeed, elevating feed salinity from 5,000 to 35,000 mg/L leads to an increase in feed water viscosity from 0.96 to 1.14 cP (Table 2). Increased feed water viscosity magnifies the ECP effect so as it might reduce the FO process water flux and likewise the increased draw solution viscosity.
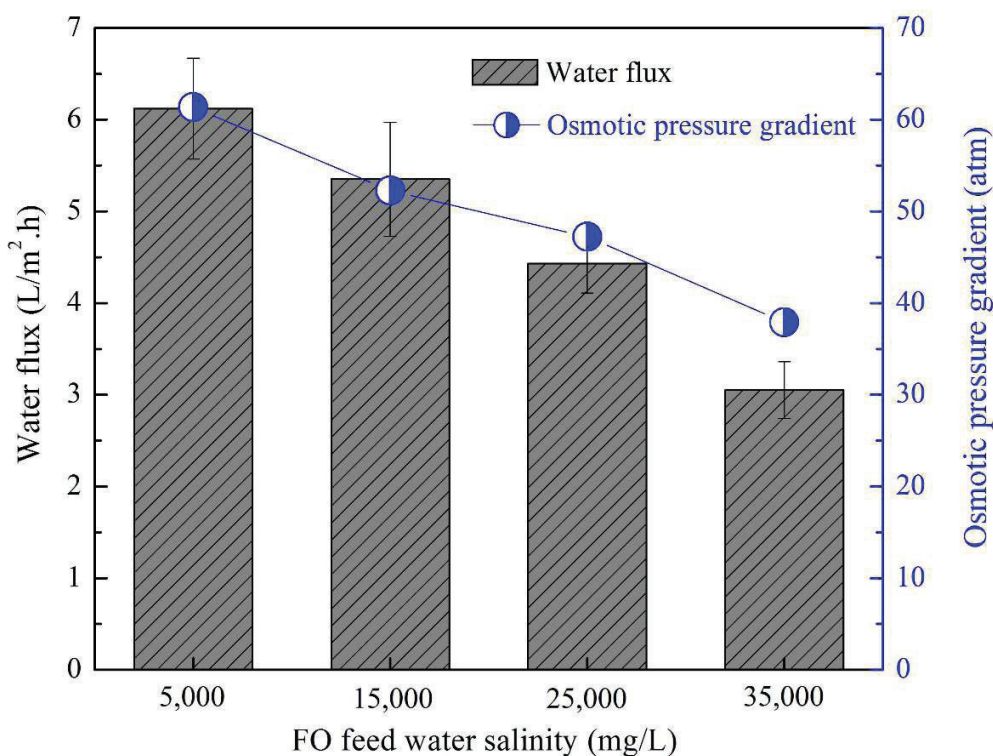
Fig. 6. The experimentally measured water flux and the calculated osmotic pressure gradient during the FO process with the synthetic brackish water and seawater feeds using the optimum mixed 0.3 M EDTA-2Na/0.55 M Na_3PO_4 draw solution. The FO process was operated at feed and draw solution circulation rates of 0.5 L/min, and at a temperature of 25 °C.

3.3. The regeneration capacity of the MD process for the mixed draw solution

The final desalination of the FO process with brackish water and seawater feeds can be achieved when coupling FO with an additional process for draw solution regeneration and in tandem fresh water attainment. In this study, MD was investigated for the regeneration of the diluted mixed draw solution and the simultaneous production of fresh water following the FO process with the synthetic brackish water and seawater feeds. As a thermally-driven desalination method, the MD process was able to regenerate the mixed EDTA-2Na/Na_3PO_4 draw solution despite its hyper salinity at a mild operating feed temperature. The MD process performance indicators (i.e. water flux and salt rejection) were slightly influenced by the increased feed salinity during the regeneration of the mixed EDTA-2Na/Na_3PO_4 draw solution (Fig. 7A). Initially, at the feed salinity of 21,050 mg/L, the MD process achieved water flux of 8.51 L/m^2·h at the feed and distillate temperature of 55 and 25 °C, respectively. When the mixed EDTA-2Na/Na_3PO_4 draw solution was concentrated by 1.8 times (i.e. equivalent to the feed salinity of 38,300 mg/L), the MD process water flux only reduced by 30% to about 6.02 L/m^2·h, hence decrease in recovery time as well as decrease in energy consumption. The salt rejection of the MD process also slightly declined during the regeneration of the mixed draw solution, but it

always remained above 99.99% even at the mixed draw solution concentration factor of 1.8, which demonstrated the benefit of using the mixed draw solution.

The analysis of the distillate obtained during the regeneration of the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution reveals that the combined FO/MD process could achieve high quality fresh water from brackish water and seawater feeds. The total organic content (TOC) and salt ions (e.g. Na$^+$ and PO$_4^{3-}$) in the MD distillate were only detected at trace levels (i.e. ≤2 mg/L) despite their linear increase with the mixed draw solution concentration factor (Fig. 7B). The presence of trace organic matter and salt ions in the MD distillate may be attributable to partial membrane pores wetting or a defect in the membrane. In theory, only water vapour is allowed to permeate through the MD membrane pores, and the MD process can achieve 100% salt rejection and pure distillate. However, all MD processes reported in the literature exhibited salt rejection below 100% due to membrane defect or partial membrane pore wetting resulting from uneven membrane pore size distribution [34, 40, 41].
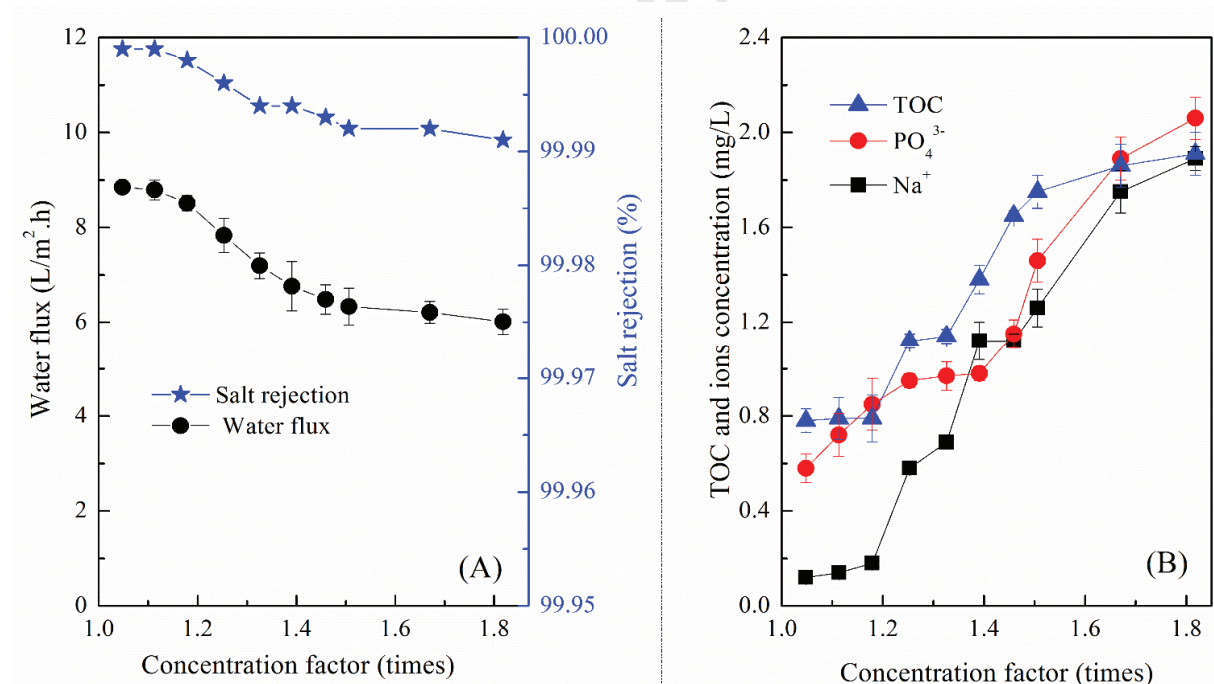

Fig. 7. (A) The MD process water flux and salt rejection and (B) the TOC and ion concentrations of the distillate at different concentration factors during the MD regeneration of the diluted mixed EDTA-2Na/Na$_3$PO$_4$ draw solution. The MD process was operated at feed and distillate temperatures of 55 °C and 25 °C, respectively, and at feed and distillate circulation rates of 1.5 L/min. Error bars represent the standard deviations of triple measurements.

The results reported here demonstrate the viability of the combined FO/MD process with the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution for desalination of brackish water and seawater. The FO process with the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution exhibited noticeably higher water flux and almost comparable reverse salt flux compared to the process with the single EDTA-2Na at the same concentrations. Given its increased osmotic pressure and reduced viscosity, the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution offered high water flux to the FO process with the synthetic brackish water or seawater feeds. The diluted mixed draw solution was then effectively treated by the MD process to reconcentrate the draw solution and simultaneously extract quality fresh water. It is noteworthy that the dominant energy consumption of the combined brackish water or seawater FO/MD desalination process using the mixed EDTA-2Na/Na$_3$PO$_4$ is thermal energy required for the MD regeneration of the draw solution. As the MD process can effectively utilize low-grade heat such as industrial waste heat or solar thermal, the energy cost of the combined FO/MD desalination process can be considerably reduced with the availability of these heat sources.

4. Conclusions

A novel mixed draw solution consisting of EDTA–2Na and Na$_3$PO$_4$ was investigated for the FO process with enhanced water flux and salt rejection. The experimental results demonstrated the considerable advantages of the mixed EDTA–2Na/Na$_3$PO$_4$ over the single EDTA–2Na draw solution. At the same concentrations, the mixed EDTA–2Na/Na$_3$PO$_4$ draw solution exhibited higher osmotic pressure but lower viscosity than the single EDTA-2Na. As a result, the FO process using the mixed draw solution exhibited water flux more than 20% higher than that using the single EDTA-2Na draw solution, while their reverse salt flux was comparable. Water flux of the FO process using the optimum mixed draw solution with the synthetic brackish water and seawater feeds was much higher than those previously reported for other draw solutions. Moreover, the diluted mixed draw solution from the FO treatment of the synthetic saline feeds was effectively regenerated by the MD process. At a mild operating feed temperature of 55 °C, the MD process could almost restore the initial concentration of the mixed draw solution (i.e. 0.3 M EDTA–2Na/0.55 M Na$_3$PO$_4$), and obtain fresh water of excellent quality (i.e. with TOC and ion concentrations <2 mg/L).

Acknowledgements

References

[1] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, Journal of Membrane Science, 281 (2006) 70-87.

[2] J.-J. Qin, W.C.L. Lay, K.A. Kekre, Recent developments and future challenges of forward osmosis for desalination: a review, Desalination and Water Treatment, 39 (2012) 123-136.

[3] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, Journal of Membrane Science, 396 (2012) 1-21.

[4] D.Y. Kim, B. Gu, J. Ha Kim, D. Ryook Yang, Theoretical analysis of a seawater desalination process integrating forward osmosis, crystallization, and reverse osmosis, Journal of Membrane Science, 444 (2013) 440-448.

[5] N. Akther, A. Sodiq, A. Giwa, S. Daer, H.A. Arafat, S.W. Hasan, Recent advancements in forward osmosis desalination: A review, Chemical Engineering Journal, 281 (2015) 502-522.

[6] H. Yuan, I.M. Abu-Reesh, Z. He, Enhancing desalination and wastewater treatment by coupling microbial desalination cells with forward osmosis, Chemical Engineering Journal, 270 (2015) 437-443.

[7] 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, Chemical Engineering Journal, 231 (2013) 484-496.

[8] C.R. Martinetti, A.E. Childress, T.Y. Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, Journal of membrane science, 331 (2009) 31-39.

[9] X.-M. Li, B. Zhao, Z. Wang, M. Xie, J. Song, L.D. Nghiem, T. He, C. Yang, C. Li, G. Chen, Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis–vacuum membrane distillation hybrid system, Water Science and Technology, 69 (2014) 1036-1044.

[10] W.J. Lee, P.S. Goh, W.J. Lau, C.S. Ong, A.F. Ismail, Antifouling zwitterion embedded forward osmosis thin film composite membrane for highly concentrated oily wastewater treatment, Separation and Purification Technology, 214 (2019) 40-50.

[11] F. Volpin, L. Chekli, S. Phuntsho, N. Ghaffour, J.S. Vrouwenvelder, H.K. Shon, Optimisation of a forward osmosis and membrane distillation hybrid system for the treatment of source-separated urine, Separation and Purification Technology, 212 (2019) 368-375.

[12] A. Razmjou, G. Simon, H. Wang, Effect of particle size on the performance of forward osmosis desalination by stimuli-responsive polymer hydrogels as a draw agent, Chemical Engineering Journal, s 215–216 (2013) 913–920.

[13] S.S. Ray, S.-S. Chen, N.C. Nguyen, H.T. Nguyen, C.-W. Li, J. Wang, B. Yan, Forward osmosis desalination by utilizing chlorhexidine gluconate based mouthwash as a reusable draw solute, Chemical Engineering Journal, 304 (2016) 962-969.

[14] Z. Zhou, J.Y. Lee, T.-S. Chung, Thin film composite forward-osmosis membranes with enhanced internal osmotic pressure for internal concentration polarization reduction, Chemical Engineering Journal, 249 (2014) 236-245.

[15] D. Emadzadeh, W.J. Lau, T. Matsuura, M. Rahbari-Sisakht, A.F. Ismail, A novel thin film composite forward osmosis membrane prepared from PSf–TiO2 nanocomposite substrate for water desalination, Chemical Engineering Journal, 237 (2014) 70-80.

[16] S.S. Ray, S.S. Chen, N.C. Nguyen, H.T. Nguyen, N.P. Dan, B.X. Thanh, L.T. Trang, Exploration of polyelectrolyte incorporated with Triton-X 114 surfactant based osmotic agent for forward osmosis desalination, Journal of Environmental Management, 209 (2018) 346-353.

[17] 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.

[18] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, Journal of Membrane Science, 364 (2010) 233-241.

[19] W.A. Phillip, J.S. Yong, M. Elimelech, Reverse Draw Solute Permeation in Forward Osmosis: Modeling and Experiments, Environmental Science & Technology, 44 (2010) 5170-5176.

[20] N.T. Hancock, W.A. Phillip, M. Elimelech, T.Y. Cath, Bidirectional Permeation of Electrolytes in Osmotically Driven Membrane Processes, Environmental Science & Technology, 45 (2011) 10642-10651.

[21] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, Water Research, 41 (2007) 4005-4014.

[22] E.M. Garcia-Castello, J.R. McCutcheon, M. Elimelech, Performance evaluation of sucrose concentration using forward osmosis, Journal of Membrane Science, 338 (2009) 61-66.

[23] R. Alnaizy, A. Aidan, M. Qasim, Copper sulfate as draw solute in forward osmosis desalination, Journal of Environmental Chemical Engineering, 1 (2013 (b)) 424-430.

[24] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, Bioresource Technology, 122 (2012) 207-216.

[25] N.C. Nguyen, S.-S. Chen, Y.-T. Weng, H. Thi Nguyen, S.S. Ray, C.-W. Li, B. Yan, J. Wang, Iodide recovery from thin film transistor liquid crystal display plants by using potassium hydroxide - driven forward osmosis, Journal of Membrane Science, 520 (2016) 214-220.

[26] H. Bai, Z. Liu, D.D. Sun, Highly water soluble and recovered dextran coated Fe3O4 magnetic nanoparticles for brackish water desalination, Separation and Purification Technology, 81 (2011) 392-399.

[27] Q. Ge, J. Su, T.S. Chung, G. Amy, Hydrophilic superparamagnetic nanoparticles: Synthesis, characterization, and performance in forward osmosis processes, Industrial and Engineering Chemistry Research, 50 (2011) 382-388.

[28] H. Han, J.Y. Lee, X. Lu, Thermoresponsive nanoparticles + plasmonic nanoparticles = photoresponsive heterodimers: facile synthesis and sunlight-induced reversible clustering, Chemical Communications, 49 (2013) 6122-6124.

[29] Q. Ge, T.S. Chung, Hydroacid complexes: A new class of draw solutes to promote forward osmosis (FO) processes, Chemical Communications, 49 (2013) 8471-8473.

[30] Q. Ge, F. Fu, T.-S. Chung, Ferric and cobaltous hydroacid complexes for forward osmosis (FO) processes, Water Research, 58 (2014) 230-238.

[31] J. Huang, S. Xiong, Q. Long, L. Shen, Y. Wang, Evaluation of food additive sodium phytate as a novel draw solute for forward osmosis, Desalination, 448 (2018) 87-92.

[32] N.T. Hau, S.-S. Chen, N.C. Nguyen, K.Z. Huang, H.H. Ngo, W. Guo, Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge, Journal of Membrane Science, 455 (2014) 305 - 311.

[33] N.C. Nguyen, S.-S. Chen, H.T. Nguyen, S.S. Ray, H.H. Ngo, W. Guo, P.-H. Lin, Innovative sponge-based moving bed–osmotic membrane bioreactor hybrid system using a new class of draw solution for municipal wastewater treatment, Water Research, 91 (2016) 305-313.

[34] N.C. Nguyen, S.-S. Chen, S.-T. Ho, H.T. Nguyen, S.S. Ray, N.T. Nguyen, H.-T. Hsu, N.C. Le, T.T. Tran, Optimising the recovery of EDTA-2Na draw solution in forward osmosis through direct contact membrane distillation, Separation and Purification Technology, 198 (2018) 108-112.

[35] Y. Zhao, Y. Ren, X. Wang, P. Xiao, E. Tian, X. Wang, J. Li, An initial study of EDTA complex based draw solutes in forward osmosis process, Desalination, 378 (2015) 28-36.

[36] N.T. Hau, S.-S. Chen, N.C. Nguyen, K.Z. Huang, H.H. Ngo, W. Guo, Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge, Journal of Membrane Science, 455 (2014) 305-311.

[37] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, Desalination, 197 (2006) 1-8.

[38] Y. Zhao, Y. Ren, X. Wang, P. Xiao, E. Tian, X. Wang, J. Li, An initial study of EDTA complex based draw solutes in forward osmosis process, Desalination, 378 (2016) 28-36.

[39] R. Alnaizy, A. Aidan, M. Qasim, Draw solute recovery by metathesis precipitation in forward osmosis desalination, Desalination and Water Treatment, 51 (2013) 5516-5525.

[40] H.C. Duong, D. Chuai, Y.C. Woo, H.K. Shon, L.D. Nghiem, V. Sencadas, A novel electrospun, hydrophobic, and elastomeric styrene-butadiene-styrene membrane for membrane distillation applications, Journal of Membrane Science, 549 (2018) 420-427.

[41] N.C. Nguyen, S.-S. Chen, S. Jain, H. Thi Nguyen, S. Sinha Ray, H. Hao Ngo, W. Guo, N. Tuan Lam, H. Duong, Exploration of an innovative draw solution for a forward osmosis-membrane distillation desalination process, 2017.

Figure Captions

Fig. 1. Schematic diagram of the lab-scale FO setup.

Fig. 2. Illustration of the lab-scale MD setup.

Fig. 3. Viscosity and osmotic pressure of the mixed EDTA-2Na/Na$_3$PO$_4$ and the single EDTA-2Na draw solutions at different salt concentrations. The mixed draw solutions were composed of 0.3 M EDTA-2Na and added Na$_3$PO$_4$ at various concentrations. The osmotic pressure was calculated using the Osmometer instrument and Van't Hoff equation, while the viscosity was measured using the viscosity meter. Error bars represent the standard variations of triple measurements.

Fig. 4. Water flux, reverse salt flux and specific reverse salt flux of the FO process using the mixed EDTA-2Na/Na$_3$PO$_4$ and the single EDTA-2Na draw solutions at different salt concentrations. The mixed draw solutions were composed of 0.3 M EDTA-2Na and added Na$_3$PO$_4$ at various concentrations. DI water was used as the feed to the FO process. The FO process was operated at feed and draw circulation rates of 500 mL/min. Error bars represent the standard variations of triple experiments.

Fig. 5. Water flux, reverse salt flux, and specific reverse salt flux of the FO process using the mixed EDTA-2Na/Na$_3$PO$_4$ draw solution at different Na$_3$PO$_4$ concentrations. The concentration of EDTA-2Na in the mixed draw solution remained at 0.3 M. DI water served as the feed to the FO process. The FO process was operated at feed and draw circulation rates of 0.5 L/min. Error bars represent the standard variations of triple experiments.

Fig. 6. The experimentally measured water flux and the calculated osmotic pressure gradient during the FO process with the synthetic brackish water and seawater feeds using the optimum mixed 0.3 M EDTA-2Na/0.55 M Na$_3$PO$_4$ draw solution. The FO process was operated at feed and draw solution circulation rates of 0.5 L/min, and at a temperature of 25 °C.

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Tables

Table 1. Characteristics of the FO and MD membranes.

Characteristics	FO membrane	MD membrane
Material	CTA	PTFE
Pore size	0.37 nm	0.45 μm
Thickness (μm)	50	200
Porosity (%)	–	80
Contact angle (°)	80 ± 7	114 ± 4
pH range	2–9	–

Table 2. Properties of the synthetic brackish waters and seawater

FO feed solutions	TDS (mg/L)	Viscosity (cP)	Osmotic pressure (atm)
Low-salinity brackish water	5,000	0.96	4.02
Medium-salinity brackish water	15,000	1.09	13.25
High-salinity brackish water	25,000	1.11	18.34
Seawater	35,000	1.14	27.78

Figures

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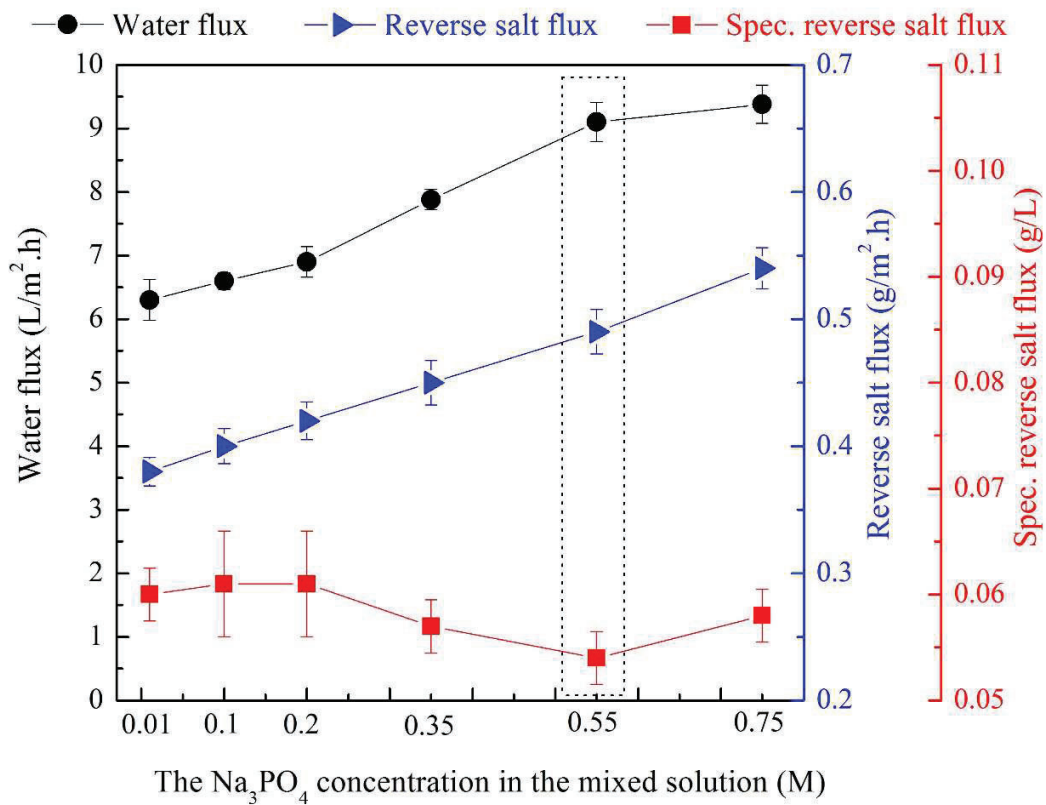
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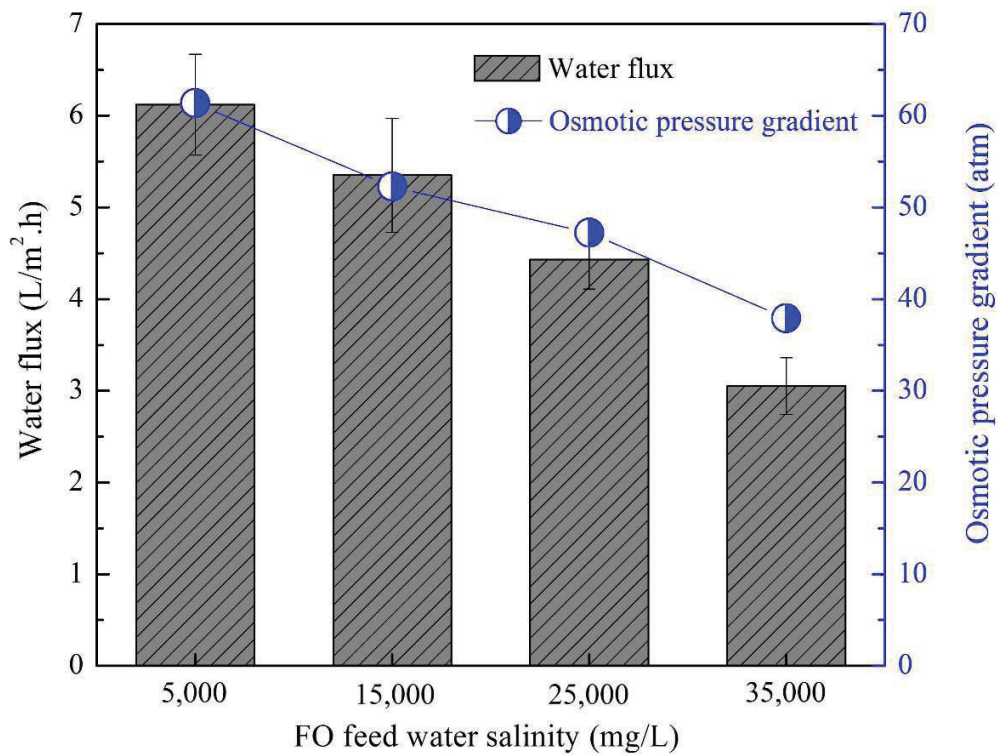
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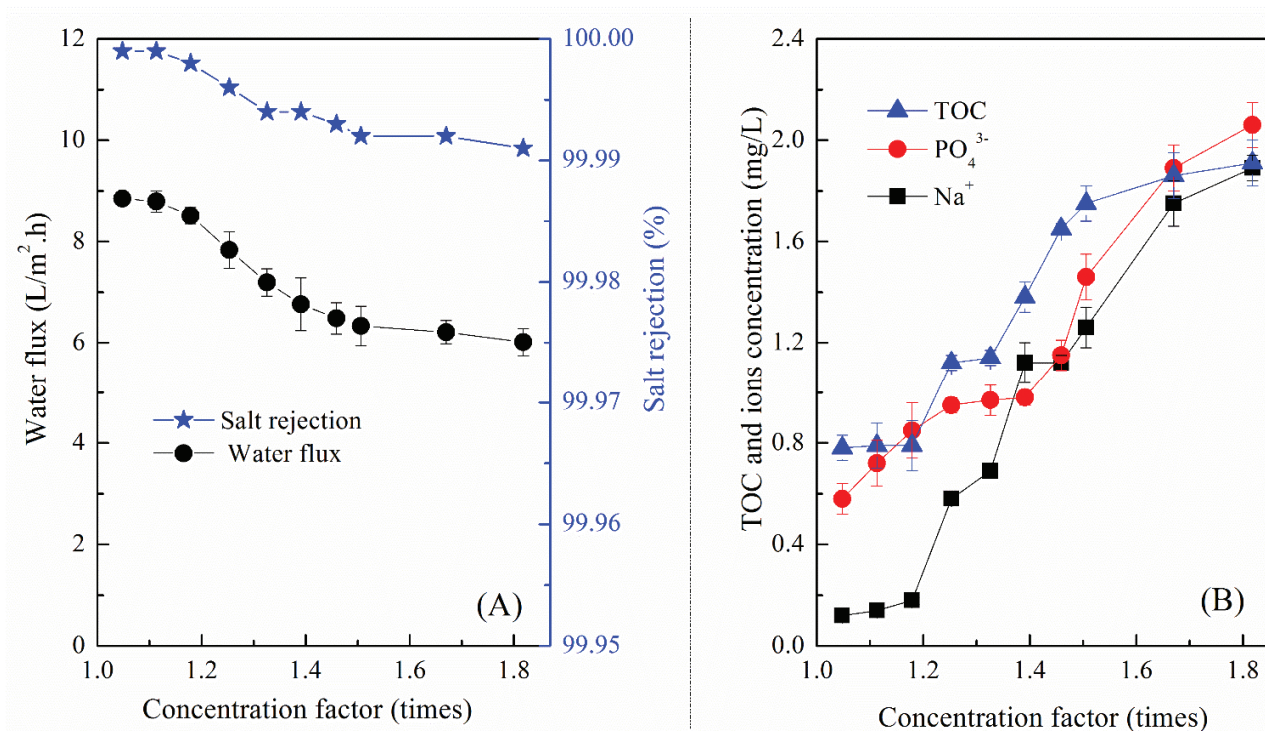
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