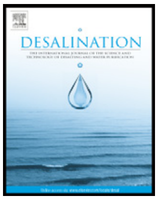
Desalination 378 (2016) 28–36

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



An initial study of EDTA complex based draw solutes in forward osmosis process

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HIGHLIGHTS

- Zinc, manganese, calcium, and magnesium complexes with EDTA are employed as draw solutions for FO.
- EDTA complexes are characterized for pH, conductivity, solution viscosity and osmotic pressure.
- EDTA complexes show superiority in water flux and reverse draw solute flux compared with NaCl.
- The diluted draw solution can be regenerated using a pressure-driven nano-filtration process.

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form 28 July 2015
Accepted 6 September 2015
Available online 30 September 2015

Keywords:
Forward osmosis
Draw solute
EDTA complex

ABSTRACT

The selection of appropriate draw solutes is a critical component for the development of FO technologies. Two significant concerns related to draw solution are the draw solute leakage in FO process and the intensive energy consumption in regenerating draw solute. In this study, a series of EDTA complexes (EDTA-$MgNa_2$, EDTA-$CaNa_2$, EDTA-$MnNa_2$, and EDTA-$ZnNa_2$) were systemically investigated as draw solutes for FO. Their characteristics of high solubility in water, moderate molecular size, expanded molecular structure, nontoxicity, low viscosity, and relatively high osmotic pressure can provide favorable FO performance and easy approaches in regeneration, which ensure the suitability of EDTA complexes as a new class of competent draw solutes. All EDTA complexes demonstrated higher water fluxes in PRO mode and much lower salt leakage in both FO and PRO modes when compared with conventional draw solute of NaCl, while EDTA-$ZnNa_2$ possessed the best performance. The NF regeneration of EDTA complexes at relatively high initial concentration of 0.25 M indicated that all NF membranes performed well with the special water flux and rejection rate ranging between 0.96 and 2.0 LMH/bar, and 96 and 98%. The overall performance proves that the new concept of using EDTA complex based draw solutes in FO process is applicable.

1. Introduction

As an emerging membrane separation technology, forward osmosis (FO) has recently received growing attention in the context of clean water scarcity and energy crisis [1–3]. In FO process, clean water permeates from the feed solution (FS) to the draw solution (DS) driven by the osmotic pressure difference across a semi-permeable membrane which serves as a separation medium; meanwhile, other ions or molecules in the FS are rejected by the semi-permeable membrane. Unlike typical pressure-driven membrane processes, FO holds the advantages of low energy consumption, reduced membrane fouling propensity and easy fouling removal due to no or low hydraulic pressure required [4–6]. Consequently, FO process has found wide applications in seawater/brackish water desalination [7–9], treatment of complex and impaired liquid streams [10], power generation [11–13], food processing [14,15], and pharmaceutical concentration [16,17].

To date, most studies on FO have been focused on membrane development [18–20], mass transfer analysis [21,22], process design and optimization [6,8,23], fouling phenomena and control [24,25], potential applications [26–28], and exploration of novel draw solutes [29–31]. Excellent FO membrane and efficient draw solute are two key factors for the further advancement of FO process [32]. However, in contrast to continuous development and even commercialization of FO membrane [33], to find or synthesize suitable draw solutes becomes particularly crucial. The ideal draw solute should possess the following principal traits: high solubility, minimal reverse draw solute leakage, easy regeneration, nontoxicity, low cost, and compatibility with membrane [3,31]. Many different draw solutes have been studied over the past decades. Achilli et al. [34] developed a protocol for the selection of optimal inorganic-based draw solutions for specific FO applications.

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http://dx.doi.org/10.1016/j.desal.2015.09.006
0011-9164/

Among 14 candidates, $CaCl_2$, $KHCO_3$, $MgCl_2$, $MgSO_4$, $NaHCO_3$, NaCl, and $NaSO_4$ were proved to be promising from the analysis of FO performance and replenishment cost; when taking the potential of scaling into account simultaneously, $MgCl_2$ may be the best draw solute for most water and wastewater applications. NaCl appears to be the most employed draw solute due to its high solubility, low cost and relatively high osmotic potential [35]. However, it is difficult to separate the water from those diluted inorganic salt solutions. McCutcheon et al. [7] have studied ammonium bicarbonate as draw solute for seawater desalination. The draw solute could be recovered easily by distillation at around 60 °C where it decomposed to ammonia and carbon dioxide. This draw solution has been tested and demonstrated in pilot scale desalination processes [36,37]. But it suffered serious reverse diffusion when compared to other draw solutions such as NaCl and $MgCl_2$ solutions [34]. Moreover, a variety of inorganic salts functioned as fertilizers were explored as draw solutes [38]. Despite the fact that the diluted draw solutions can be directly utilized for agricultural irrigation and thus be free from reconcentration, their applications are limited. Meanwhile, the content of final diluted fertilizer draw solution is generally higher than acceptable limits for fertigation, which requires additional process to reduce the fertilizer concentration [39]. Most recently, there has been a significant progress in the development of synthetic materials as draw solutes, such as magnetic nanoparticles, polyelectrolytes, polymer hydrogels, and stimuli-responsive polymer [29,40–42]. Although there is a considerable advancement in regeneration and reverse leakage for those innovative synthetic draw solutes, they suffer problems of poor repeatability, insufficient water flux, inability to generate high osmotic pressures at low viscosity, serious concentration polarization (CP) exacerbated by their low diffusivity, and complexity in the synthesis [3].

When choosing draw solutes, a tradeoff exists between small molecular size to be highly mobile, reduce solution viscosity, and mitigate CP and large molecular size to be easily separated and decrease reverse draw solute flux [32]. The variety of organic compounds and their chemical reactions enables us to screen or freely design organic-based draw solutes to obtain the suitable size. Hau et al. [43] studied EDTA sodium salt as draw solute in hybrid FO–NF process for dewatering high nutrient containing sludge. The results show that EDTA sodium salt had better FO performance relative to common inorganic salt (NaCl) and could be recovered through NF with the highest rejection of 93%. Nevertheless, EDTA sodium salt exhibits good solubility merely at high pH which may be detrimental for membrane. Ge and Chung [44,45] proposed a new class of draw solutes from hydroacid complexes. Superior performance was achieved in terms of high water fluxes and negligible reverse solute fluxes using hydroacid complexes as draw solutes in FO, but its synthesis is relatively complicated. In this work, EDTA complexes with different central metal ions are employed as draw solutes in FO for the first time. The related characteristics, FO performance, regenerability by NF, and FO applications of these EDTA complexes are systematically investigated. EDTA complexes are selected as draw solutes for the following reasons: (i) these compounds give good solubility without adjustment of pH, which is different from EDTA sodium salt; (ii) they are commercially available avoiding the complex synthesis; (iii) their molecular sizes are identified as being moderate (between 358 and 399); (iv) a series of EDTA complexes with different central metal ions help to comprehensively study the relation between properties of complexes and system performance of FO; (v) it is essential to further broaden the exploration of potential draw solutes.

2. Materials and methods

2.1. Materials

Zinc disodium EDTA ($C_{10}H_{12}N_2Na_2O_8Zn$, 98%), manganese disodium EDTA ($C_{10}H_{12}MnN_2Na_2O_8$, 98%), EDTA calcium disodium ($C_{10}H_{12}CaN_2Na_2O_8$, 98%), and EDTA magnesium disodium ($C_{10}H_{12}MgN_2Na_2O_8$, 98%) were supplied by Nanchang Changmao Chemical Industry Co., Ltd. (China) and used following the measurement of crystal water content by thermogravimetric analysis. Sodium chloride (NaCl, 99.5%) was obtained from Chengdu KeLong Chemical Co., Ltd. (China) and used as received. Deionized (DI) water with a resistivity of 18.25 MΩ·cm was produced from an ultrapure water system (MolecularΣH_2O®, China) All solutions of different concentrations were prepared in deionized water.

2.2. Characterizations of EDTA complexes

The pH values of draw solutions at different concentrations were determined using a pH meter (PB-10, Sartorius, China). All electric conductivities were measured with a conductivity meter (DDSJ-308A, Rex Electric Chemical, China) at 25 ± 1 °C. The viscosities of metal–EDTA complex solutions were obtained by a rotary viscometer (LVDV-II + Pro, Brookfield, USA) equipped with the enhanced UL Adapter at 25 ± 0.5 °C. The osmotic pressure differences between NaCl and EDTA complex solutions under the same concentrations were reflected by the direction of water flux in FO [8,13,39]. During the comparison, NaCl solution was placed against the active layer of FO membrane and EDTA complex solution with the same concentration flowed on the other side of the membrane. The osmolality of the EDTA complex solutions was measured with a freezing point osmometer (STY-1A, Tianda Tianfa, China), which can be converted to osmotic pressure using van't Hoff equation.

2.3. FO process

FO experiments were carried out through a lab-scale system as depicted in Fig. 1. Commercially available thin film composite (TFC) FO membrane from HTI (Hydration Technologies Inc., OR, USA) was employed. The physical and chemical properties of this FO membrane have been presented in various literatures [46,47]. Before testing, the FO membrane was immersed into DI water overnight to ensure that the membrane's porous support layer is fully water saturated [48]. In the experiments, FO membrane was held in a customized cross-flow permeation cell which was designed in a plate-and-frame configuration with a rectangular channel (10 cm in length, 4.5 cm in width and 0.2 cm in height) on each side of the membrane. DI water and simulated seawater (0.5 M NaCl solution) were used as feed solutions. Draw solutions were prepared from EDTA-$MgNa_2$, EDTA-$CaNa_2$, EDTA-$MnNa_2$, EDTA-$ZnNa_2$, and NaCl. The initial volumes of feed solutions and draw solutions were 1000 mL and 500 mL, respectively. Both feed and draw solutions flowed concurrently through respective cell channels at the same flow rates of 6.4 cm/s, which can reduce strain on the suspended membrane [7]. The temperatures of the feed and draw solutions were maintained at 25 ± 1 °C. Two membrane orientations of FO and pressure retarded osmosis (PRO) mode were applied in this work. PRO mode indicates that the draw solution is against the selective layer of FO membrane, while FO mode means the draw solution is on the support layer. The integrity of the FO membrane was assessed at the beginning of each experiment using the draw solution of 0.5 M NaCl to confirm that the water flux and reverse solute flux were in a reasonable range. Each test was measured for 30 min after removing air bubbles in the pipeline. The dilution of draw solution was ignored due to a small ratio of permeate water flow to the overall volume.

The water flux, J_w ($Lm^{-2}\,h^{-1}$, abbreviated as LMH) was calculated from the mass change of the draw solution using Eq. (1):

$$J_w = \frac{\Delta m}{A \times \Delta t \times 1000} \tag{1}$$

where Δm (g) is the mass change of the draw solution determined by a digital balance over a given period of time Δt (h), assuming the density of water is 1000 g/L; A is the effective area of FO membrane.