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Electrolysis-assisted mitigation of reverse solute flux in a three-chamber forward osmosis system

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ABSTRACT

Forward osmosis (FO) has been widely studied for desalination or water recovery from wastewater, and one of its key challenges for practical applications is reverse solute flux (RSF). RSF can cause loss of draw solutes, salinity build-up and undesired contamination at the feed side. In this study, *in-situ* electrolysis was employed to mitigate RSF in a three-chamber FO system ("e-FO") with Na_2SO_4 as a draw solute and deionized (DI) water as a feed. Operation parameters including applied voltage, membrane orientation and initial draw concentrations were systematically investigated to optimize the e-FO performance and reduce RSF. Applying a voltage of 1.5 V achieved a RSF of 6.78 ± 0.55 mmol m^{-2} h^{-1} and a specific RSF of 0.138 ± 0.011 g L^{-1} in the FO mode and with 1 M Na_2SO_4 as the draw, rendering ~57% reduction of solute leakage compared to the control without the applied voltage. The reduced RSF should be attributed to constrained ion migration induced by the coactions of electric dragging force ($\geq$1.5 V) and high solute rejection of the FO membrane. Reducing the intensity of the solution recirculation from 60 to 10 mL min^{-1} significantly reduced specific energy consumption of the e-FO system from 0.693 ± 0.127 to 0.022 ± 0.004 kWh m^{-3} extracted water or from 1.103 ± 0.059 to 0.044 ± 0.002 kWh kg^{-1} reduced reversed solute. These results have demonstrated that the electrolysis-assisted RSF mitigation could be an energy-efficient method for controlling RSF towards sustainable FO applications.

1. Introduction

Osmotically driven membrane processes are being developed to address global freshwater shortage, wastewater reuse and water-energy nexus (Cath et al., 2013; Ng et al., 2006). Among those processes, forward osmosis (FO) uses osmotic pressure gradient across a semi-permeable membrane to reclaim high-quality water for versatile applications, such as irrigation, food processing and life support (Cath et al., 2006). The major advantages of FO-based water treatment systems include reduced operating pressure, high rejection of undesired compounds, low fouling intensity of FO membranes, and less energy demand if energy-intensive draw regeneration can be properly addressed (Liu et al., 2011; Su et al., 2012).

A key challenge and also impediment for FO applications is the reverse solute flux (RSF) (Achilli et al., 2009; Hancock and Cath, 2009). RSF is defined as the cross-membrane diffusion of draw solutes to the diluted feed, and can result in severe loss of draw solutes and gradual salinity build-up at the feed side, leading to reduced osmotic driving force, increased fouling propensity, and elevated operation cost due to periodical replenishment of draw solutes (Achilli et al., 2010; Boo et al., 2012). Accumulation of the reversed draw solutes will require further treatment of the feed solution before it can be discharged to a natural water body (Phillip et al., 2010). Thus, mitigation of solute accumulation at the feed side is important, and several approaches have been proposed and studied, including the use of microorganisms to biologically degrade specific draw solutes in the feed, such as NH_4^+, NO_3^-, VFAs and EDTA, (e.g. anammox and osmotic membrane bioreactor, OMBR) (Holloway et al., 2015; Li et al., 2015), and continuous desalination of the concentrated feed through integrated electrodialysis (ED), filtration (e.g., microfiltration), and/or bioelectrochemical systems (BES) with recoverable draw solutes (Lu and He, 2015; Luo et al., 2015; Qin and He, 2014). Although those methods can effectively reduce salinity accumulation at the feed side, they cannot mitigate or reduce RSF. Alternatively, novel membrane fabrication/modification methods can render reduced RSF, such as chemically cross-linked layer-by-layer polyelectrolytes and biomimetic membrane embedded with Aquaporin Z (Qiu et al.,

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2011; Wang et al., 2012). However, a notable trade-off between RSF and water flux as well as unsatisfied mechanical strength were observed in these modified membranes (Chung et al., 2012a).

The researchers have also attempted to decrease RSF through selection of appropriate draw solutes. Inorganic solutes were extensively investigated in FO systems, and the candidates with a lower ratio of RSF to water flux (J_s/J_w) were of great interest (Table S1, Appendix. A Supplementary Materials) (Achilli et al., 2010). It was reported that multivalent ions with larger hydrated radii, e.g. PO_4^{3-}, Ca^{2+}, and Mg^{2+}, could exhibit a lower cross-membrane diffusion rate and hence decrease solute leakage (Achilli et al., 2010; Nguyen et al., 2015). However, they could serve as the precursor of inorganic scaling, leading to severe membrane fouling (Phillip et al., 2010). The viability of some low J_s/J_w solutes, for instance $MgSO_4$, was hindered by their relatively high specific cost ($7.35 to make 1-L draw solution with an osmotic pressure of 2.8 MPa) (Achilli et al., 2010). Magnetic nanoparticles were also proposed as an emerging solute because they exhibited low RSF and could be separated by magnetic field and/or ultrafiltration (Ling and Chung, 2011a, b). Nonetheless, agglomerated nanoparticles required further ultrasonication for performance recovery, leading to weakened magnetic properties (Chung et al., 2012b; Ling et al., 2010).

Given the importance of RSF to FO applications, there is a critical need for developing effective methods to reduce RSF (Zou and He, 2016). In our previous study, a hybrid OMBR-ED system was developed for efficient draw solute recovery and mitigation of salinity build-up at the feed side (Lu and He, 2015). In an ED module, migration of ions across the ion-exchange membranes is achieved under the applied electric field. Herein, we employed the concept of electrolysis to an FO system for *in-situ* reduction of RSF. This electrolysis-assisted FO (e-FO) system contained two draw chambers (hydraulically connected) and one feed chamber; such a design was to minimize the effect of pH on the electrodes. Na_2SO_4 was chosen as a draw solute due to its relatively low specific cost, desired J_s/J_w ratio (half of the commonly adopted NaCl under same osmotic pressure, Table S1) and stable chemical property (cannot be electrolyzed in a solution). The specific objectives of this study were to (1) demonstrate the effectiveness of applied voltage on reducing RSF; (2) examine the ion migration pattern and other key performance parameters, such as water flux, recirculation rate, and fouling intensity; and (3) analyze energy consumption by electrolysis and system operation. To the best of our knowledge, this is the first study accomplishing *in-situ* RSF reduction in FO systems through operational strategies.

2. Materials and methods

2.1. e-FO system setup and operation

The three-chamber e-FO system consisted of two bilateral draw chambers (hydraulically connected) and one middle feed chamber (Fig. 1). Two pieces of cellulose triacetate (CTA) membranes with a total surface area (S) of 0.0032 m^2 (Hydration Technologies Inc., Albany, OR, USA) were installed with their active layers facing the feed (FO mode), creating an identical volume of 16 mL for each chamber (4 × 4 × 1 cm). Two stainless steel meshes (4 × 4 cm, ~1.4 cm distance), acting as both the electrode and swelling control, were placed close to the FO membrane (~0.2 cm) in the draw chambers and connected to an external power supply (CSI3644A, Circuit Specialists, Inc., Mesa, AZ, USA).

During operation, 200 mL of 1-M Na_2SO_4 (conductivity 87.1–88.4 mS cm^{-1}) was used as a draw solution; the effluents from both draw chambers were mixed and then recirculated back to the draw chambers. Deionized (DI) water was used as the feed solution and recirculated between the feed chamber and an external storage bottle; DI water was supplemented periodically to maintain a constant liquid volume of 500 mL. For each batch test, the e-FO system was operated for 24 h with water sampled every hour for the first 6-h operation and at the end of each test. The experiment was operated without any biological activities and in a temperature-controlled lab (20 ± 2 °C).

2.2. Experimental procedure

The feasibility of the e-FO system was first examined with an external voltage supply of 0 V (control system) and 3 V (experiment system), respectively. No voltage was applied to both systems in the first hour. When some solute ions gradually migrated to the feed side due to RSF, the feed conductivity was expected to increase and then the external power supply was turned on (at the end of the first hour) for the experiment system. The recirculation rate was set at 60 mL min^{-1} (4 cm s^{-1}) for all the draw and feed chambers in the feasibility test (Table S2). A series of system optimizations were then performed for the e-FO in terms of applied voltage (1 V, 1.5 V, 2 V and 3 V), membrane orientation (active layer facing feed and draw, i.e. FO and PRO mode), and initial draw concentration (0.5 M, 1 M, and 1.5 M) (Table S2). Fouling situation of the FO membrane was studied through monitoring water flux performance in three successive batch tests (24 h, FO mode) with 1 M Na_2SO_4 (200 mL) as the draw and DI water as the feed (500 mL constant). Because Na_2SO_4 was the only solute involved, fouling was mainly expected on the porous supportive layer (draw chamber, FO mode). Effective removal of residual foulants was achieved by *in-situ* osmotic backwashing: DI water (1 L) and 1 M Na_2SO_4 (200 mL) were pumped into the draw and the feed chambers, respectively, for 6 h, followed by 30 min rinse with DI water.

2.3. Measurement and analysis

The detailed methods for water quality analysis were provided in the Supplementary Materials. The voltage across the external resistance (1 Ω) in the circuit was recorded every 2 min by a digital multimeter (Keithley Instruments Inc., Cleveland, OH, USA). Water flux was determined by measuring the change of water weight on an electronic balance (Scort Pro, Ohous, Columbia, MD, USA) at a 30-s interval according to a previous study (Yuan et al., 2016). Quantification of water flux was based on Eqs. S1–S3 (Supplementary Materials). Flux recovery rate in fouling test was calculated as the ratio of maximum water flux (in the first hour) between backwash and pristine membranes. The solute build-up (SBU) at the feed side was quantified by Eq. (1) with a unit of mmol m^{-2} h^{-1} (Zou and He, 2016). SBU is typically resulted from the concentrating effect in the feed (due to membrane rejection of the feed solute) and reverse solute flux (RSF, mmol m^{-2} h^{-1}) from the draw solution (Phillip et al., 2010). When DI water is used as the feed, $C_{i,F} = 0$ and hence no concentrating effect is observed. Under such a case:

$$SBU = RSF = \frac{n_{f,F} - n_{i,F}}{S \times t} = \frac{V_F \times \left(C_{f,F} - C_{i,F}\right)}{S \times t} \tag{1}$$

where $n_{i,F}$ and $n_{f,F}$ are initial and final mole of Na_2SO_4 in the feed, respectively. $C_{i,F}$ and $C_{f,F}$ are initial and final Na_2SO_4 concentration in the feed, respectively. V_F is feed volume (500 mL constant). t (h) stands for operating time. S (m^2) is the total surface area of the FO membrane. Specific RSF (g L^{-1}) was also calculated for comparison with previous studies (Phillip et al., 2010), and defined as the ratio of J_s (g $m^{-2}h^{-1}$, GMH) and J_a (LMH):