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Efficient recovery of polyelectrolyte draw solutes in forward osmosis towards sustainable water treatment
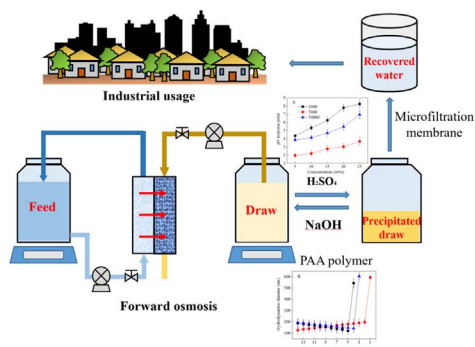
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GRAPHICAL ABSTRACT

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ABSTRACT

Forward osmosis (FO) technology has long been constrained by the slow development of appropriate draw solutes (DS) and the relatively high cost associated with DS recovery. In this study, a series of polyelectrolytes, polyacrylic acid sodium salts (PAA-Na) with different molecular weights, were explored as DS for FO applications with a focus on the recovery using combined pH and microfiltration (MF). The FO system achieved a high water flux of 18.02 ± 0.51 LMH, low reverse salt flux (RSF) of 0.110 ± 0.004 gMH, and the J_S/J_W of 6.1 ± 0.3 mg L^{-1} with 25 wt% PAA-Na (2000 Da) as the DS and DI water as the feed. The DS recovery efficiency by the combined pH + MF approach was 99.68% at pH of 4.35, and the operation cost was estimated at $0.037 \$ m^{-3}. Dynamic light scattering revealed that the hydrodynamic diameter of PAA increased with decreasing pH, resulting in PAA polymers precipitated as aggregates at the pH response point. The 25 wt% 2000 PAA-Na achieved the water flux of 11.56 ± 0.32 LMH from synthetic seawater and 17.19 ± 0.52 LMH from the treated wastewater. These results have demonstrated efficient and cost-effective recovery of PAA DS for FO-based applications.

1. Introduction

Forward osmosis (FO) is an emerging technology for water reuse and desalination, and has potential benefits of lower fouling propensity and lower energy consumption due to the absence of external hydraulic pressure [1,2]. In FO, water migrates across a semipermeable membrane from a feed solution into a draw solution, driven by the osmotic pressure difference [3,4]. In the past decade, FO has been intensively

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studied and developed with respect to draw solutes (DS) selection, membranes, membrane fouling, reactor configuration, and operation optimization [5,6]. One of the key factors that hinders the FO application is the selection of a suitable DS, which has critical influence on the efficiency and sustainability of FO operations [7,8]. An ideal DS should have the desired properties such as a high osmotic pressure, large water solubility, minimal reverse solute flux, economic regeneration, low cost, nontoxicity, chemically stable, as well as compatibility with FO membranes [8–10]. A variety of non-responsive DS including conventional inorganic salts, organic solutes (e.g., fertilizers, edible saccharide, and EDTA sodium salts), and newly developed materials (e.g., hydroacid complexes, micellar, and copolymer), have been studied and evaluated in membrane separation and precipitation for recovery [11–17]. Although membrane separation, e.g. reverse osmosis, can achieve a high water recovery rate, its high energy consumption will significantly increase the operation cost. Chemical recovery by adding calcium/barium hydroxide is also a costly approach with by-products that may require further disposal.

To address the issue of DS regeneration, the responsive DS has been studied to enhance the osmotic pressure of diluted draw solutions upon exposure to an external stimulus such as electric/magnetic field, temperature, or light, thereby producing a significantly high water flux while reducing the cost for regeneration [18–21]. Challenges still exist with those responsive DS. For example, nanoparticles with uniform dimension ($<$ 11 nm) are not easy to be separated even under a strong magnetic field [22]. The water flux generated by thermally responsive hydrogels is not sustainable or reversible because of state change after external stimuli [8]. Although ammonia-carbon dioxide (CO_2/NH_3) can produce a reasonably high water flux and require low energy demand or alternative energy sources for regeneration, the monovalent ions may cause high solute leakage [23].

In addition to those responsive DS, switchable polarity solvents (SPS) that change their affinity with water by using acid/base have also been investigated as DS in FO. Hydrophobic amines are the most commonly deemed as CO_2-responsive draw solutes, because of the presence of tertiary amines in their structure, which can become hydrophilic and ionize upon reaction with CO_2 to yield a draw solution with a very high osmotic pressure. In the regeneration process, CO_2 is removed and the amine restores to its hydrophobic non-ionic neutral state, facilitating phase separation from water [24–27]. However, their compatibility with FO membranes could be an issue because the membrane rejection layer tends to swell and get damaged by their small molecular amines. The CO_2-switchable dual responsive polymers of poly [2-(dimethylamino) ethyl methacrylate] (PDMAEMA) can also serve as DS because of its macromolecular size and thermal response with the Lower Critical Solution Temperature (LCST) behavior, which can achieve high water recovery via an energy-efficient approach [28]. But the synthesis of PDMAEMA is expensive, and extravagant molecular weight will cause high concentration polarization (CP), thereby impairing its application in FO [8]. A commercial and nontoxic pH-responsive polymers of poly (acrylic acid, PAA), which has high solubility in water and flexibility in structural configuration, has a potential for FO application in terms of DS and membrane [29–32]. The carboxylic segments in the structure of PAA can produce a very high osmotic pressure in a form of alkali metal or ammonium salts. Such polyelectrolytes exhibit a decrease in hydrophilicity at low pH and facilitate polymer aggregation, benefiting DS recovery. PAA-Na salts also have good stability and show repeatable performance after many recycles [30]. These unique properties ensure high efficiency in water reclamation and high quality in water product.

Previous studies have investigated PAA-Na as new DS, and employed a pressure- or temperature-driven membrane separation process to recycle these polyelectrolytes [30,31]. However, using ultrafiltration process (UF, under a pressure of 10 bar) for regeneration of PAA-Na DS could be energy intensive, and scaling is another major problem when heat is continuously added for DS recovery. In this study, a new approach for efficient recovery of PAA DS in FO was systematically investigated. This approach was based on the combination of pH adjustment and microfiltration (MF), and could accomplish the regeneration by a low pressure-driven process ($<$ 1 bar). The specific objectives of this study were to: (1) examine the effects of molecular weight (MW) and the concentrations of PAA-Na on the water flux and reverse salt flux (RSF); (2) investigate the recovery efficiency of PAA-Na DS and possible mechanism in different recovery processes (pH only, MF only, and pH + MF); (3) estimate the cost of PAA-Na DS recovery; and (4) provide a preliminary evaluation of potential applications of PAA-Na DS in desalination or wastewater reuse.

2. Materials and methods

2.1. Preparation of PAA-Na

Three polyacrylic acids $[-CH_2CH(COOH)-]_n$ with different MWs were obtained from Polysciences, Inc. (Warrington PA, USA): 2000 Da (sodium salt, powder), 5000 Da (50 w/w% solution), and 50,000 Da (25 w/w% solution). PAA-Na (2000) was dissolved in DI water to achieve 20 g alkaline solution with five concentrations (5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt%). Because PAA-Na (5000) was acidic with pH of 2.4 at the concentration of 50 wt%, NaOH (0.5 M) was added to make the precipitate to dissolve (pH ~7.0). This alkaline solution was dried under vacuum, and the concentration was adjusted to a target value (5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt%). The preparation of PAA-Na (50000) was similar to that of PAA-Na (5000).

2.2. FO system

The flat sheet FO membrane was used in the FO experiments with an effective area of 16 cm^2. The thin film composite membrane (TFC) was obtained from Hydration Technologies Inc., OR, USA. Its active layer was placed facing the feed solution, and support layer was facing the draw solution. For comparison, cellulose triacetate membrane (CTA) was used in some experiments. DI water was used as the feed solution in most FO experiments to evaluate basic FO performance such as water flux and reverse solute flux. In addition, a synthetic seawater containing 35 g L^{-1} sodium chloride and a wastewater effluent (Peppers Ferry Wastewater Treatment Authority, Radford, VA, USA) were used to evaluate PAA DS for desalination and wastewater reuse. Both the feed and draw solutions were recirculated at a flow rate of 10 mL min^{-1} or a cross flow velocity of 0.03 cm s^{-1}. The volume of the draw solution was fixed at 100 mL. All the tests were conducted at room temperature (21 $\pm$ 1 °C).

2.3. Regeneration of PAA-Na

As shown on Fig. 1, the PAA-Na was adjusted to the targeted concentration and served as draw solution in the FO process. After the FO test, the diluted PAA-Na was reversibly switched to the acid form (the compound of PAA) by pH adjustment (98% H_2SO_4). Once protonated, the aggregated PAA polymers became solid precipitation, and then was trapped by microfiltration (0.45 um). The reconcentrated PAA polymer was deprotonated by NaOH (0.5 M) to become polyelectrolyte (PAA-Na) and diluted to a target concentration for the subsequent FO test. The electric energy from membrane recovery process was estimated as:

$$E = Q_p P \tag{1}$$

where Q_p is permeate flow rate ($m^3 s^{-1}$), and P is pressure at module inlet (Pa). The cost for membrane recovery process, pH recovery process, and PAA lost was calculated based on unit cost and the quantity of usage.