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A study of poly (sodium 4-styrenesulfonate) as draw solute in forward osmosis

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HIGHLIGHTS

- Novel draw solutes based on PSS have been studied.
- The pH, conductivity and viscosity of PSS have also been investigated.
- 0.24 g·mL^{-1} PSS (70,000) draw solute exhibits the best FO performance.
- The repeatability of FO performance improves with increasing the PSS Mw.
- The PSS was easily recycled by a low pressure-driven UF system under 2 bar.

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ABSTRACT

Draw solution (DS) has a great influence on the forward osmosis (FO) technology. The study of novel draw solute is essential in the development of FO technology. In this paper, poly (sodium 4-styrenesulfonate) (PSS) polyelectrolytes with different molecular weights (Mws) and different concentrations were studied. The physical properties, such as pH, conductivity and viscosity, have also been investigated. The conductivity increases with the increase of PSS concentration, which may lead to higher osmotic pressure. Higher viscosity, lower diffusion coefficient and more severe concentration polarization, which is generated by the polyelectrolyte with higher Mw, result in a lower water flux. Among the PSS polyelectrolytes, 0.24 g·mL^{-1} PSS (70,000) exhibits the best FO flux. Experiment results demonstrate the advantage of using PSS as draw solute to conventional ionic salt of 0.5 mol·L^{-1} NaCl.

The regeneration of PSS from diluted DSs and the repeatability of the FO performance after recovery have been evaluated. The PSS was easily recycled by a low pressure-driven ultrafiltration (UF) system under 2 bar with low energy consumption. In order to realize a satisfactory regeneration of PSS DS in the FO process, it is necessary to select or prepare an appropriate UF membrane with accurate MWCO.

1. Introduction

Forward osmosis (FO) technology, utilizing the natural phenomenon of osmosis, is an emerging and a novel technology for seawater/brackish desalination [1,2], wastewater treatment [3,4], food processing [5,6], power generation [7,8], protein and pharmaceutical enrichment [9,10]. FO has edge over pressure-driven membrane processes, such as reverse osmosis (RO), nanofiltration (NF) in terms of energy consumption and fouling consistence [11,12]. In the FO unit, the energy required to transport water across the membrane is almost negligible. Moreover, FO exhibits high rejections to many contaminants [1]. By virtue of these unique features, FO has gained attentions of the worldwide researchers.

Both the semi-permeable membrane and draw solution (DS) have great effects on the FO process. Lots of efforts reported in the literatures have focused on the development of FO membranes [13–16] and the design or economics of process [17–19]. Less attention has been paid to find potentially appropriate draw solutes and their regeneration methods. The draw solute leakage in FO process and high energy consumption during the recovery of draw solutes from diluted DSs are the main issues, which constrain the development of FO technology. Desirable draw solutes are supposed to possess the following characteristics: (1) high osmotic pressure which may induce a high water flux; (2) minimal reverse draw solute flux; (3) easy recovery from the

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diluted DS. In addition, it should be nontoxic, reasonably low cost and required to be compatible with the FO membrane. In recent years, some researchers have been focused on inorganic salt draw solutes, such as ammonium carbonate [13], fertilizer [20–22], and magnetic nanoparticles [23–25]. Ammonium carbonate has been the most promising system with very high osmotic pressure and relative ease of regeneration. However, its recycle method is energy intensive and even a trace level of residuals may deteriorate the taste of the product water. Fertilizer has been also employed as draw solute. The diluted fertilizer after FO process can be directly used for fertigation without recovering draw solutes. However, it's only applicable to agriculture. Magnetic nanoparticles, which can generate high osmotic pressure and multifunctional nanoparticles [26] have been found to be used as new DS recently. The efficient regeneration of the magnetic nanoparticles via heat-facilitated magnetic separation is a distinct advantage. But the particles are prone to agglomerate during recycling process via magnetic or electric separators. And the methods have not been tested on a large-scale level. In addition, the synthesis of the magnetic nanoparticles is relatively complicated. Lately, stimuli-responsive polymer hydrogel draw solutes have also been widely investigated due to their requiring less energy in the regenerative process [12,27,28]. However, the water flux was low. Furthermore, switchable polarity solvents [29] have also shown a potential to be used as DS. Wilson and his coworkers [29] demonstrated that switchable polarity solvents can be mechanically separated from the purified water after polar to nonpolar phase shift. Nevertheless, it has degradation effects on the cellulose triacetate (CTA) FO membrane. A range of other possible draw solute candidates including organic ionic salt [30,31] and organic compounds [32,33] have also been investigated, which encounter the trade-off between high osmotic pressure and easy regeneration. So far, almost no suitable draw solute can meet all the aforementioned criteria [34].

Strong polyelectrolytes may be an appropriate option, which meet all the aforementioned requirements. Polyelectrolyte of polyacrylic acid sodium salt (PAA-Na) has been explored as draw solute in the FO process [35]. However, it's relatively energy-intensive for the PAA-Na regeneration by ultrafiltration under pressure of 10 bar. Moreover, the mechanism about the molecular weight (Mw) and concentration of the PAA-Na on the water flux has yet to be elaborated on clearly. The following experimental data indicates that the water flux generated by 0.24 $g \cdot mL^{-1}$ PSS (70,000) (18.20 LMH) is higher than that of the 0.24 $g \cdot mL^{-1}$ PAA-Na (1800) (underneath 12 LMH) [35], where both the tests were conducted in the mode of the membrane active layer facing the DS and deionized (DI) water was used as feed solution (FS). Therefore, the aims of this paper are to explore cost-effective draw solutes which can (1) generate a high water flux with a minimal reverse salt diffusion and (2) be easily regenerated by recovery from the diluted DS using ultrafiltration (UF) system with low energy consumption. Poly (sodium-4-styrenesulfonate) (PSS) is chosen as the draw solute for the following reasons: (1) It is highly water-soluble and high degree of dissociation, therefore it can generate high osmotic pressure, which may induce high water flux; (2) its expanded structure with a chain pendant would be expected to minimize the reverse salt diffusion, easily and efficiently separate from diluted DS by low pressure-driven UF process. In this work, three different Mws of PSS salts have been investigated as draw solutes in the FO process. The water flux and reverse salt leakage of the PSS were estimated in FO process. The regeneration of PSS from diluted DSs and the repeatability of the FO performance after recovery have also been evaluated. It is a promising candidate for the use as DS and shows potential in FO applications.

2. Materials and methods

2.1. Materials

Poly (sodium-4-styrenesulfonate) (PSS, Mw = 70,000, 200,000, 1,000,000, Sigma-Aldrich, USA) was used as draw solute. Sodium chloride (NaCl, crystalline, ≥99.5%) was provided by the National Medicine Group Chemical Reagent Co. Ltd. (China). DI water was produced by an ultrapure water system (Molecular$\sum$$H_2O$®, China).

2.2. The preparation of PSS solution and NaCl solution

The 0.48 $g \cdot mL^{-1}$ of PSS (70,000) solution was prepared by dissolving 72 g of PSS (70,000) powder into DI water at room temperature. The resultant solution was stirred at room temperature until all was dissolved and finally the volume of the solution was fixed at 150 mL. 0.24 $g \cdot mL^{-1}$, 0.12 $g \cdot mL^{-1}$, and 0.04 $g \cdot mL^{-1}$ of PSS (70,000) solutions were achieved by dilution method. A similar procedure was followed for the preparation of 0.48 $g \cdot mL^{-1}$, 0.24 $g \cdot mL^{-1}$, 0.12 $g \cdot mL^{-1}$, and 0.04 $g \cdot mL^{-1}$ of PSS (200,000) solutions. In addition, as the viscosity of PSS (1,000,000) is higher than that of PSS (70,000) and PSS (200,000), PSS (1,000,000) is not easily soluble in water when the concentration is greater than 0.24 $g \cdot mL^{-1}$. So only 0.04 $g \cdot mL^{-1}$, 0.12 $g \cdot mL^{-1}$, and 0.24 $g \cdot mL^{-1}$ of PSS (1,000,000) solutions were prepared by the similar method as that of PSS (70,000). As comparison, a 0.5 $mol \cdot L^{-1}$ NaCl solution was used as the DS. All solutions were stored in a fridge refrigerator at 4 °C.

2.3. Characterization of PSS

At these concentrations, the pH values of PSS (70,000), PSS (200,000) and PSS (1,000,000) were tested by an acidometer (PB-10, Sartorius, Beijing, China).

Electrical conductivity of the solutions was measured by Ray Magnetic Conductivity Meter (DDSJ-308A, Rex Electric Chemical, China) to estimate the degree in ionization.

The viscosity of PSS (70,000), PSS (200,000) and PSS (1,000,000) of different concentrations is measured by a viscosity meter (DV-II, Brookfield, America) at 25 °C, 30 °C, 35 °C, and 40 °C, respectively.

2.4. FO process

FO experiments were conducted on a lab-scale system, as shown in Fig. 5(a). Commercial thin film composite (TFC) FO membranes from Hydration Technologies Inc. (HTI, USA) were used, which involve a dense selective active layer onto a phase inversed polysulfone supporting layer. DSs were prepared from PSS (70,000), PSS (200,000) and PSS (1,000,000). DI water was used as the FS during FO experiments. The test was conducted with the membrane active layer facing the DS at room temperature (23 °C ± 1), and both FS and DS circulated at a fixed volumetric flow rate (184 mL/min). A balance (BSA6202S-CW, Sartorius, Beijing, China) connected to a computer logged the mass of water permeating into the DS from the FS over a selected period of time.

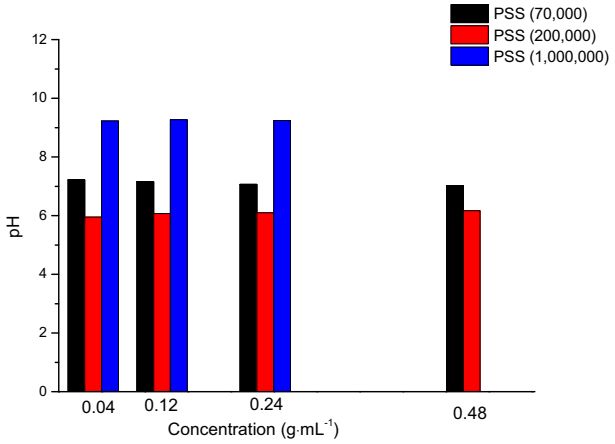

Fig. 1. A comparison of pH of PSS (70,000), PSS (200,000) and PSS (1,000,000).