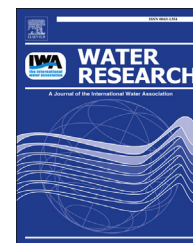


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Evaluation of poly (aspartic acid sodium salt) as a draw solute for forward osmosis



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ABSTRACT

Poly (aspartic acid sodium salt) (PAspNa) was evaluated for its potential as a novel draw solute in forward osmosis (FO). The inherent advantages of PAspNa, such as good water solubility, high osmotic pressure, and nontoxicity, were first examined through a series of physicochemical analyses and atomic-scale molecular dynamics simulations. Then, lab-scale FO tests were performed to evaluate its suitability in practical processes. Compared to other conventional inorganic solutes, PAspNa showed comparable water flux but significantly lower reverse solute flux, demonstrating its suitability as a draw solute. Moreover, fouling experiments using synthetic wastewater as a feed solution demonstrated that PAspNa reversely flowed to the feed side reduced inorganic scaling on the membrane active layer. The recyclability of PAspNa was studied using both nanofiltration (NF) and membrane distillation (MD) processes, and the results exhibited its ease of recovery. This research reported the feasibility and applicability of FO-NF or FO-MD processes using PAspNa for wastewater reclamation and brackish water desalination.

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1. Introduction

Forward osmosis (FO) has gained recognition over the last decade as an emerging technology for water treatment and desalination (Cath et al., 2006; Boo et al., 2013; Shannon et al., 2008; Valladares Linares et al., 2013). In contrast to pressure-driven membrane processes, such as reverse osmosis (RO), this process utilizes an osmotic gradient between two streams separated by a semi-permeable membrane as the driving force for moving water into the higher osmotic potential draw solution. Consequently, the performance of FO mainly

depends on the osmotic pressure exerted by the draw solution among many other factors.

Many researchers have demonstrated the feasibility of FO technology based on its special characteristics, i.e., low energy consumption, high rejection of a wide range of contaminants and easy fouling control (Holloway et al., 2007; Kim et al., 2012). However, FO is still a relatively immature technology and some remaining limitations, such as low membrane performance, hinder its industrial application. One of the key challenges to the further development of FO is identifying a suitable draw solute. The development of an optimized draw

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solute would be a powerful breakthrough for the improvement of FO performance.

The ideal draw solute should be able to provide significantly improved FO performance, and separated easily and completely by means of a low cost recovery method. In this sense, three major criteria can be applied to evaluate the suitability of a draw solute: (1) high water flux; (2) low reverse draw solute flux; and (3) easy and low-cost recovery from the diluted draw solution. Additional points, such as water solubility, nontoxicity, and the potential for commercialization, should be also considered.

Various materials, including conventional inorganic salts, organic solutes, and newly developed materials, have been studied and evaluated in the search for an optimized draw solute. In previous work, traditional draw solutes based on inorganic salts, such as NaCl and MgCl₂, have been extensively studied in various FO fields (Holloway et al., 2007; Achilli et al., 2010). The draw solutions made from inorganic solutes produce reasonably high water flux and can be readily separated by RO. However, both energy requirement of RO recovery and corresponding solute leakage in FO have been found to be high, leading to concerns about operational costs.

To overcome these disadvantages, many novel draw solutes have been proposed and evaluated. Especially, some types of single molecular organic salts and polyelectrolytes, such as EDTA sodium salts, sodium polyacrylate (PAANA), and sodium lignin sulfonate (NaLS) have been investigated as potential draw solutes, taking advantage of their large molecular size (Hau et al., 2014; Duan et al., 2014; Ge et al., 2012; Yen et al., 2010; Stone et al., 2013). These types of solutes not only generated good water flux but also reduced reverse solute flux significantly. The regenerations of these salts, especially EDTA sodium salts and PAANA, were also successfully achieved by low-pressure nanofiltration (NF) (Hau et al., 2014) or ultrafiltration (UF) (Ge et al., 2012), respectively. Despite good performance in the FO process and recovery system, these solutes were ultimately found to be impractical due to drawbacks such as commercial availability.

Water-soluble magnetic nanoparticles (MNPs) have also been investigated as a novel draw solute based on their superparamagnetic properties. Various hydrophilic single molecule- or oligomer-coated MNPs such as 2-pyrrolidone-MNP, triethylene glycol-MNP, poly(acrylic acid)-MNP, and poly(ethylene glycol)diacid-MNP were synthesized to incorporate both large molecular size and magnetic properties and evaluated for their potential as draw solutes (Ling et al., 2010; Ge et al., 2011; Na et al., 2014). The large molecular size of these MNPs is led to better prevention of reverse solute flux but the coating materials on the MNPs adversely affected the magnetic properties. Therefore, this resulted in a low separation rate and the separated MNPs showed irreversible aggregation. The combination of these factors caused difficulty in the recovery and sustainability for these materials. Moreover, the risk assessment for human health and the environmental hazards of synthesized nanomaterials are an ongoing concern in various research fields.

Draw solutes based on thermosensitive materials with temperature dependent phase separation behavior have received increasing attention (Ling et al., 2011; Noh et al., 2012; Zhao et al., 2014; Cai et al., 2013). Solutes such as *N*-acylated

polyethyleneimine (PEI) derivatives and poly (sodium styrene-4-sulfonate-co-*n*-isopropylacrylamide) (PSSS-PNIPAM) are soluble in water under their lower critical solution temperature (LCST), but agglomeration of polymer chains occurs above the LCST (Noh et al., 2012; Zhao et al., 2014). Based on this thermoresponsivity, the diluted draw solutes can be easily concentrated by thermal recovery methods such as membrane distillation (MD). In spite of all these pioneering work, a practical solution to the low performance of FO due to their low osmotic pressure has remained elusive. Despite the enormous research efforts undertaken in terms of these various solutes, each has had serious drawbacks, and therefore, the search for a practical and optimized draw solute must continue if the successful application of FO is to be achieved.

Considering the aforementioned requirements for a draw solute, poly (aspartic acid sodium salt) (PAspNa) is a more suitable candidate than the previously studied solutes. PAspNa, a kind of polyelectrolyte commonly used as an antiscalant, has many properties which suggest it may have potential as an alternative draw solute of FO. It has significantly large molecular size and good water solubility. Furthermore, it is non-toxic and commercially available with reasonable unit price. As these various merits of PAspNa had been verified through our autonomous evaluation procedure for screening draw solutes, in order to show the potential of PAspNa as a new draw solute systematically, this paper is organized with detailed scrutiny for physicochemical analyses and practical performance measurements. The evaluation flow for selecting new draw solute was composed of four stages and all the criteria of each level were categorized in Fig. 1.

To assess the suitability of PAspNa, we first analyzed the physicochemical properties of PAspNa as a draw solute, specifically its molecular characteristics, water solubility, osmotic pressure, viscosity, and toxicity. The basic performance aspects of PAspNa as a draw solute in FO, such as its water flux and reverse solute flux, were examined using deionized (DI) water as the feed solution. The effect of reverse PAspNa flux on inorganic fouling was also assessed through a scaling experiment using inorganic synthetic wastewater as the feed solution. Finally, recyclability studies were explored using nanofiltration (NF) and membrane distillation (MD) processes.

2. Materials and methods

2.1. Preparation of PAspNa

Commercially available PAspNa (CAS-No. 181828-06-8) in powder form was obtained from Lanxess AG (Cologne, Germany). For the characterization analyses, including molecular structure and toxicity, purified PAspNa was used, and the molecular structural data obtained was used to inform the molecular dynamics study of its solvation behavior in water. Unwanted NaOH was removed from the PAspNa through rigorous washing with MeOH/distilled water (1:9 vol%) followed by drying *in vacuo* at 80 °C. For all the FO and recovery tests, unrefined PAspNa was used as supplied, in order to directly evaluate its real-world applicability.

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