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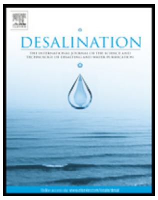

Thermo-sensitive polyelectrolytes as draw solutions in forward osmosis process

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HIGHLIGHTS

- New thermo-sensitive polyelectrolytes were prepared and evaluated as draw solutions for FO.
- Hot ultrafiltration was used as a low-energy method to recover the water from draw agents.
- The ease of water recovery and reuse make the polyelectrolyte a good candidate for FO.

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ABSTRACT

A series of polyelectrolytes were evaluated as draw solutions for the forward osmosis (FO) process. Such polyelectrolytes were synthesized by copolymerization of N-isopropylacrylamide with different amounts of sodium acrylate. These polyelectrolytes were thermo-sensitive and water soluble. Hot ultrafiltration (HUF) operated at 45 °C and 2 bar was used as a low-energy method to recover the water from the polyelectrolyte draw solutions. The results showed that 4%PNIPAM-SA solution worked best among nine polyelectrolytes in the forward osmosis process and HUF process, and its FO water flux was 0.347 LMH while the feed solution was pure water and its water recovery fraction was 65.2%.

1. Introduction

Forward osmosis (FO) is a process in which a semi-permeable membrane is used as a separation medium, and the differential of osmotic pressure of two sides of membrane acts as driving force [1]. On the permeate side of membrane is the draw solution with higher chemical potential, while on the other side is the feed solution with lower chemical potential flow through. The difference of chemical potential between the draw solution and the feed solution drives the pure water from the feed solution to the draw solution; meanwhile ions are rejected by the semi-permeable membrane. Different terms are used in literature to name the higher chemical potential solution, such as draw solution, draw agent, osmotic agent, osmotic media, driving solution, osmotic engine and so on [2]. Due to its high rejection and operating at low pressure or without additional pressure, the forward osmosis process has found a wide range of applications such as in wastewater treatment, water purification, seawater desalination, food processing, and pharmaceutical industry [2–5].

The performance of semi-permeable membrane and draw solution has a great effect on the forward osmosis process. The chemical potential of draw solution is the driving force. Many different draw solutions with high osmotic pressures have been studied, including salts, fertilizer, saccharide, hydrogel, hydrophilic nano-particle, polyelectrolyte etc. Salts can generate high osmotic pressures, but it is difficult to separate the water from salt solutions. McGinnis in 2002 disclosed that combination of ammonia and carbon dioxide gases in a specific ratio could produce a draw solution with high osmotic pressure in excess of 250 atm. Elimelech and co-workers have intensively investigated ammonium bicarbonate as draw solute for seawater desalination. The draw solute could be decomposed to ammonia and carbon dioxide gases at 65 °C by heating, and readily recovered [6]. Since ammonia is highly soluble in water, thus the product water is unsuitable for drinking directly [7]. Further processing is needed to eliminate ammonia in water to reach the 4th edition *Guidelines for Drinking-water Quality* (1.5 mg/l for ammonia, World Health Organization),

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which increase the total cost of desalination. In 2012, Wilson explored switchable polarity solvents as draw solutes for forward osmosis, switchable polarity solvent can be mechanically separated from the purified water after polar to nonpolar phase shift induced by introduction of 1 atm carbon dioxide to 1 atm of air or nitrogen with mild heating. However, the switchable polarity solvent was found to degrade the commercially available FO membrane [8]. In 2011, a fertilizer was evaluated as draw solutions for FO desalination, and 1 kg of fertilizer could extract 11 to 29 l of water from seawater; the diluted fertilizer solution was directly applied for fertigation [9]. Saccharide solution can be used directly without requiring separation in some applications such as in hydration bags, and emergency lifeboats after the forward osmosis step since saccharide solution is directly drinkable [2,10]. The water flux induced by hydrogel draw agents was relatively lower, but it required less energy to recover water from the draw agents [1,11]. In addition, the use of hydrophilic nanoparticles as draw solutes resulted in a moderate water flux and could be separated by a magnetic field, but nanoparticles tend to aggregate after recovery, which has an adverse effect on reuse of nanoparticles [12–14]. In 2011, an integrated FO–UF (forward osmosis–ultrafiltration) system was studied as a potentially sustainable way to recover the hydrophilic nanoparticles. The novel FO–UF process was tested for 5 continuous runs for the purpose of desalination without increasing nanoparticle draw solute size or reducing osmotic functionality [15]. At the same time, thermo-sensitive magnetic nanoparticle was investigated as smart draw solutes in FO without particle size changes upon magnetic separation [16]. Very recently, polyelectrolyte (PSA) was used as draw solute; the molecular weights of PSA used were 1200, 1800 and 5000, and the water flux produced by these PSA solutions was 17 LMH, 15 LMH, 12 LMH, respectively when the PSA concentration was 0.48 g/ml [17]. The polyelectrolyte solution was recovered using with 1 kDa and 3 kDa ultrafiltration membranes at a feed pressure of 10 bar. Even though PSA could be recovered by ultrafiltration, the process consumed a significant amount of energy. Therefore there is still a need for development of new draw solutions for the FO process.

Stimuli-responsive polymer hydrogels are a class of hydrogels whose structure, physical property and chemical property change with external environment. The environmental stimuli include pH, ionic strength, temperature, light, electric field, specific chemicals etc. Crosslinked poly (N-isopropylacrylamide) (PNIPAM) is a classical thermo-sensitive hydrogel with both hydrophilic groups and hydrophobic groups in the network. Simultaneously, when it is heated to over 32 °C, it undergoes a reversible phase transition, transferring from hydrophilic to hydrophobic and gradually releasing the water absorbed. This phase transition temperature is termed as lower critical solution temperature (LCST) [1]. This unique characteristic of PNIPAM makes it effective and convenient to recover water from the hydrogel through heating over LCST. Since PNIPAM hydrogel is a cross-linking polymer, the swelling ratio is restricted by its network. According to the recent study carried out at Wang's group [11], a swelling ratio of PNIPAM of 11.9 was observed in the FO step and a water recovery fraction of 17% was achieved in the dewatering step. By co-polymerization of NIPAM with sodium acrylate (SA), poly (NIPAM–SA) possessed ionic segments of sodium acrylate, and thus showed enhanced swelling ratio. Another study showed that modification of hydrogel by incorporating carbon particles led to improved swelling ratio and water recovery fraction [1].

The objectives of the present work are the preparation of thermo-sensitive draw solutions with NIPAM and sodium acrylate, and the evaluation of the forward osmosis water flux performance of the synthesized draw solution and the regeneration with hot ultrafiltration.

2. Experiments

2.1. Materials

N-isopropyl acrylamide (NIPAM, purity >98%) was supplied by Tokyo Chemical Industry Co., Ltd and recrystallized by n-hexane before use. Acrylic acid (AA, purity ≥98%), ammonium persulfate (APS, purity ≥98%), and sodium hydroxide (NaOH, purity ≥96%) were supplied by Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of polyelectrolytes

Sodium acrylate (SA) was prepared from acrylic acid by neutralizing it to pH 7–8 by 30% sodium hydroxide solution. The resulting solution without further purification was dried in a vacuum oven at 35 °C.

Nine polyelectrolyte samples were synthesized by free-radical polymerization of SA and NIPAM in aqueous solutions, as shown in Fig. 1 [18–21]; the ratios of sodium acrylate (SA) and N-isopropylacrylamide (NIPAM) of polyelectrolytes were 0:100, 2:98, 4:96, 6:94, 10:90, 20:80, 35:65, 50:50, and 100:0. Typically, sodium acrylate (SA) and N-isopropylacrylamide (NIPAM) were dissolved in deionized water to form a 14.28 wt.% solution. Ammonium persulfate (APS) was used as an initiator without further purification, and the molar ratio of monomer and initiator was fixed at 100:1. Then the solution was deaerated by bubbling with nitrogen for 30 min after the initiator was dissolved in the solution. The resulting solution was stirred in a capped bottle at 70 °C for 2 h to complete polymerization. The polyelectrolytes synthesized with 2%, 4%, 6%, 10%, 20%, 35%, and 50% of sodium acrylate (SA), were denoted as 2%PNIPAM–SA (2-P), 4%PNIPAM–SA (4-P), 6%PNIPAM–SA (6-P), 10%PNIPAM–SA (10-P), 20%PNIPAM–SA (20-P), 35%PNIPAM–SA (35-P) and 50%PNIPAM–SA (50-P), respectively.

2.3. Physical properties of polyelectrolytes

2.3.1. LCST of polyelectrolytes

Polyelectrolyte solutions were put in conical flasks, and those conical flasks were placed into an oil bath pan. The temperature of oil rose from 20 °C to 80 °C until the clear solution became milky, and this transition temperature was recorded as the LCST. The temperature interval in this process was 1 °C, and the samples were kept at each temperature for 30 min to reach equilibrium.

2.3.2. pH of polyelectrolytes

The pH value of polyelectrolyte solutions was tested with a pH meter (FE20-FiveEasy pH, Mettler Toledo). 1 g of polyelectrolyte was dissolved in 6 g pure water to form the test solution. Before testing,

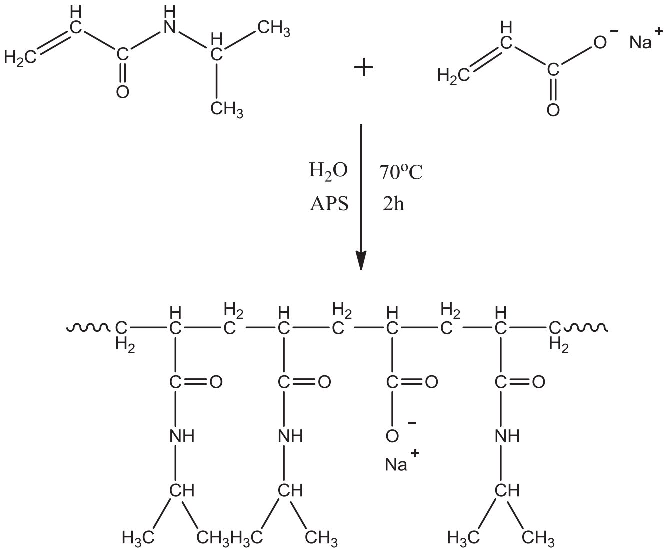

Fig. 1. Routes of synthesis of thermo-sensitive polyelectrolytes.