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Functionalized thermo-responsive microgels for high performance forward osmosis desalination

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ABSTRACT

Stimuli-responsive hydrogels were recently proposed for energy-saving forward osmosis (FO) process. However, their low water flux and dewatering ability for reuse make them less attractive for industrial desalination process. In this work, the co-polymer microgels of N-isopropylacrylamide and acrylic acid with different mixing ratios were synthesized using surfactant-free emulsion polymerization to produce submicron-size hydrogels with high surface area and fast swelling-deswelling response. The microgels were employed as draw agents in a laboratory scale FO desalination system. The microgel-based FO process performed a high water flux up to 23.8 LMH and high water recovery ability of 72.4%. In addition, we explored a new conductivity measurement method to online analyze water flux of the FO system. This on-line conductivity analysis approach appeared to be an accurate and efficient method for evaluating microgel-based FO desalination performance. Our experimental data revealed that the stimuli-responsive microgel was an efficient draw agent for FO desalination.

1. Introduction

Water scarcity is one of the top global challenges that currently affects over one-third of world population in water-stressed countries and this situation is worsen due to increasing population, water pollution, industrialization, and climate change (McCutcheon et al., 2006; Elimelech and Phillip, 2011). Over 96% of water resources worldwide are in the ocean, which have high salinity and cannot be directly used without desalination process (Smalley, 2005). To date, reverse osmosis (RO) process via a polymeric membrane is the most widely used technology for seawater desalination. However, the high energy and capital costs together with the low water permeability and fouling resistance associated with RO membrane have been an on-going challenge for its industrial applications. There is a pressing need for the development of a cost-effective desalination process.

In the recent years, forward osmosis (FO) membrane process has gained a great attention due to its low energy costs for membrane separation process. The FO desalination is a two-stage desalination process where the water is drawn from a saline solution as a result of osmotic gradient and then the water can be recovered from draw solute by means of membrane separation, distillation, external magnetic field, extraction, precipitation and combination of these separation processes (Luo et al., 2014). Inorganic salts, such as $MgCl_2$, $MgSO_4$, NaCl, KCl, $KHCO_3$, $Ca(NO_3)_2$, NH_4HCO_3 have been employed as the draw solutes for FO processes (Achilli et al., 2010). Although these inorganic reagents have excellent capability to create significant osmotic pressure gradient,

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pressure-driven membrane processes such as nanofiltration and reverse osmosis are still required to recover water from these salts (Zhao et al., 2012). That leads to substantial energy costs for the FO process. Furthermore, reverse salt flux and internal concentration polarization are presented when these salts are employed as draw solutes, which subsequently reduce the performance of separation process. Scientists found that the use of ammonium bicarbonate (NH_4HCO_3) as the draw agents could lead to a low energy FO process, as water can be recovered via low temperature distillation process using low grade heat (McCutcheon et al., 2006; McGinnis and Elimelech, 2007). The draw solute can decompose into ammonia and carbon dioxide upon heating and leave water phase. Unfortunately, the purity of water resulted from such process was not able to meet standard drinking water regulation due to very high ammonium bicarbonate leaked to the water (Ge et al., 2013).

Subsequent research proposed that poly(ethyleneglycol) diacid-coated superparamagnetic nanoparticles could be used as draw solutes and the adsorbed water can be recovered using external magnetic field to produce fresh water (Ge et al., 2010). However, water flux was far below the water flux generated by inorganic salts. Furthermore, these magnetic nanoparticles formed aggregates during the recovery stage which decreased their effectiveness to be reused (Ling and Chung, 2011; Ling et al., 2011). Other materials have also been explored for FO processes, including the sodium salt of polyacrylic acid (Ge et al., 2012), 2-methylimidazole-based organic compounds (Swee Kuan et al., 2010), switchable polarity solvent (Stone et al., 2013), hydroacid complexes (Ge and Chung, 2013), Na^+ functionalized carbon quantum dots (Guo et al., 2014) and N,N′,N″-triacylated tris(2-aminoethyl)amine (acyl-TAEA) derivatives (Noh et al., 2012). Although these materials displayed reasonable water flux, their low water recovery ability is a drawback for their applications in industrial desalination processes.

Stimuli-responsive hydrogels are three dimensional polymer networks that swell and deswell in respond to the applied stimuli, such as temperature, pH, external magnetic field, ionic strength, and light. Due to their ability to reversibly swell and deswell, they have been recently introduced as a new class of draw agent for FO desalination. Li et al. (2011) synthesized the hydrogel using N-isopropylacrylamide and hydrophilic monomers of sodium acrylate or acrylamide. The water contained in the hydrogels was recovered by heating the hydrogels and pressure. Unfortunately, the water flux of this hydrogels (0.30–0.96 LMH) with salt rejection of 95.4% was relatively lower than other types of synthetic draw agents. In order to improve the performance of hydrogels-based FO process, composite hydrogels were recently prepared by incorporating inorganic nanoparticles such as carbon particles, magnetic nanoparticles and reduced graphene oxide (rGO) (Razmjou et al., 2013a; Zeng et al., 2013). These composite hydrogels showed an enhanced water flux and the water recovery ability. However, the recovered water from hydrogels was mostly in the form of water vapor. Additional condensation unit is then needed to recover water in the form of liquid and will increase the overall costs of FO process.

Currently, the high energy costs for water recovery is still an issue for FO desalination technologies (Altaee et al., 2014). This leads to a higher operational cost of FO desalination compared to RO process due to inappropriate selection of water recovery process and materials employed as draw solutes (McGovern and Lienhard V, 2014). Other major limitations are incomplete separation of draw agents and lower water flux compared to the RO process (Cai et al., 2013). In this study, we applied N-isopropylacrylamide (NIPAM) and acrylic acid (AA) as co-monomers to synthesize functional co-polymer microgels P(NIPAM-AA) as the draw agents for FO process. Our research will focus on studying how the acrylic acid contents could affect the water flux and dewatering ability of the co-polymer P(NIPAM-AA) microgels. The microgels with different ratios of AA and NIPAM were prepared using surfactant-free emulsion polymerization (SFEP) approach to eliminate the contamination of small surfactants. Moreover, a laboratory FO system was established to evaluate the desalination performance of the P(NIPAM-AA) microgel-based FO process. Our results show that the employed P(NIPAM-AA) microgels can significantly improve water flux and water recovery ability of the FO desalination process. For the first time, we use microgels in FO desalination process. The microgels are also functionalized with acrylic acid rather than sodium acrylate to improve the quality of final water product. Besides, we explored and employed new on-line conductivity monitoring method to analyze water flux of the FO system.

2. Materials and methods

2.1. Materials

N-isopropylacrylamide (NIPAM, >98%), purchased from Tokyo Chemical Industry, was purified by recrystallization in n-hexane and dried at room temperature. N–N′-methylenebisacrylamide (MBA, >98%), acrylic acid (AA, >99.5%) and ammonium persulfate (APS) were purchased from Sigma–Aldrich. Sodium chloride was purchased from VWR. Cellulose triacetate forward osmosis (CTA-FO) membranes were purchased from Hydration Technologies Inc. (HTI, USA).

2.2. Synthesis of co-polymer microgels

The P(NIPAM-AA) microgels were synthesized using surfactant-free semi-batch emulsion polymerization. In a typical experiment, 0.5 g of NIPAM and AA at different mass ratios and 0.005 g of MBA were dissolved in 47 mL of Millipore water. The solution was transferred to a 250 mL three-necked flask fitted with a condenser, a mechanical stirrer and gas inlet/outlet. The semi-batch feeding solution was prepared by dissolving 2.5 g of NIPAM and AA at different mass ratios, 0.025 g of MBA and 0.025 g of APS in 30 mL of Millipore water.

After degassing both batch and semi-batch feeding solutions for one hour, the batch solution was heated to 75 °C under nitrogen atmosphere. 3.0 mL of APS solution (0.005 g) was injected to initiate the polymerization. Semi-batch feeding solution was injected slowly at a rate of 6.25 mL/h using a syringe pump after the batch solution turned into cloudy. The polymerization was carried out overnight under continuous stirring. After cooling, the microgels were purified using membrane dialysis (MWCO 12–14 kDa) against Millipore