



Gas-responsive cationic microgels for forward osmosis desalination

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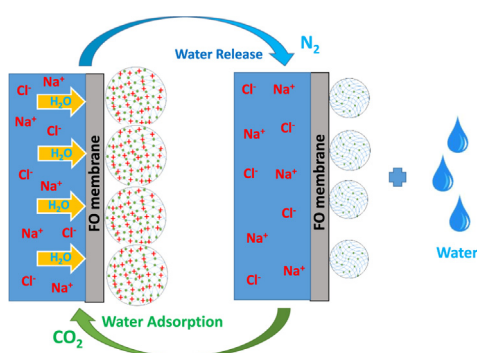
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HIGHLIGHTS

- Gas-responsive microgels as draw solute for FO desalination.
- Effect of crosslinkers on the FO performance of the microgels.
- High water flux is achieved due to presence of charges in the protonated microgels.
- CO₂-responsive microgels show promising recyclability for water flux and recovery.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymers as draw materials for forward osmosis (FO) desalination have attracted increasing attention in recent years, where the water adsorption and dewatering abilities of draw materials are crucial to overall desalination performance. Here, we developed gas-responsive microgels as new draw materials for FO desalination in which water adsorption and dewatering are driven by sweeping CO₂ and N₂. Cationic microgels of 2-(diethylamino) ethyl methacrylate (DEAEMA) and 2-(dimethylamino) ethyl methacrylate microgels (DMAEMA) were synthesized. The gas-responsivity of these microgels on water-flux and water recovery was systematically examined in a laboratory FO desalination system. CO₂ is able to protonate DEAEMA microgels to enhance water adsorption. The DEAEMA microgels with 1 wt% polyethylene glycol diacrylate crosslinker show the highest water flux of 56 LMH. At the isoelectric points, the adsorbed water can be released by purging N₂ gas at room temperature due to the hydrophobic characteristics of deprotonated DEAEMA microgels. Water recovery by 50% can be achieved for these microgels. Comparing with more hydrophilic DMAEMA microgels, the gas-responsive DEAEMA microgels perform higher swelling ratio, water-flux and recovery capability. Our results reveal that these gas-responsive microgels can be used as promising draw materials for future FO process with high water permeability and low-operation cost.

1. Introduction

During the last decades, membrane technologies have received increasing R&D attention for industrial separation processes, such as water treatment, filtration, desalination [1–4] and gas separation [5–7].

Desalination is a sustainable technology to produce fresh water from ocean to meet the increasing global water demand. Currently, reverse osmosis (RO) is the most commonly used technology for seawater desalination [2,8–10]. However, high energy consumption and membrane fouling have been the significant issues in RO process [7]. Forward

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osmosis (FO) appears to be a promising technology for desalination due to its low energy requirement [11]. In a FO process, water passes through a semi-permeable membrane driven by the natural osmotic pressure provided by a draw solute, and subsequently the adsorbed water can be separated from the draw solute by a dewatering process. The main economic and technical challenge to use the FO technology is the development of cost-effective draw solutes for industrial desalination processes [12].

To date, many inorganic and organic draw solutes for FO desalination have been reported. The most favourable draw solutes should be able to provide high osmotic pressure, and are cost effective and environmental-friendly. Apart from high water adsorption ability, draw solutes should also be able to release adsorbed water through a low-cost and highly efficient dewatering process. Inorganic salts such as $MgCl_2$, $MgSO_4$, $NaCl$, KCl , $KHCO_3$ and $Ca(NO_3)_2$ can provide high osmotic pressure and water-flux. However, further nanofiltration or RO process is needed to recover these salts for reuse [13]. Ammonium bicarbonate (NH_4HCO_3) is another draw solute that shows desirable performance for FO desalination as it can release adsorbed water after decomposition into ammonia and carbon dioxide using low-grade heat. However, ammonia might be released to water due to its high solubility.

The physicochemical properties of stimuli-responsive polymers can be tuned by an external stimulus such as temperature, pH, light, electric or magnetic field [14]. These polymers have been reported in recent years as new draw materials for FO desalination as they are able to reversibly swell/deswell to adsorb/release water using a proper stimulus [15–18]. Thermo-responsive ionic liquid polymers were utilized for FO desalination in the form of hydrogels or solutions [19–21]. These poly(ionic liquid) materials can provide high osmotic pressures owing to their innate ionic properties and display high water fluxes [19]. However, a hydrogel showing high water flux may perform low dewatering ability for water recovery. N-isopropylacrylamide (NIPAM) hydrogels were synthesised with co-monomers of sodium acrylate or acrylamide as thermo-responsive hydrogels for FO desalination, in which the adsorbed water can be released upon heating to a temperature beyond the lowest critical solution temperature (LCST) of PNIPAM [18]. Hartanto and the co-workers synthesised thermo-responsive NIPAM microgels with different anionic and cationic co-monomers [22,23], and found water flux of microgels is significantly higher than hydrogels. The charged co-monomers in microgels promotes water flux, but attributes low dewatering ability for water recovery. Introduction of cationic co-monomers leads to a high increment in water flux [23]. Besides, hydrogel composites have also been studied to enhance water recovery. Incorporating carbon particles [24] or magnetic nanoparticles [17,25–28] to thermo-responsive hydrogels facilitates water recovery. The pH-responsive draw materials, such as CO_2 -responsive poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) were also explored [29]. Experimental data indicated that CO_2 purging is not sufficient for dewatering and an extra heating to $60^\circ C$ is required to assist polarity switching. Switchable-polarity solvents (SPS) reversibly switch their hydrophilicity-hydrophobicity upon pH change [30,31], and low pressure filtration is able to remove SPS from water [32]. However, back

diffusion and internal concentration polarization (ICP) negatively affect their long-term performance.

Considering the dewatering processing cost and recovery ability of polymeric draw materials, we here develop novel CO_2 -responsive cationic microgel draw materials for FO desalination, in which the protonation and deprotonation of the synthesized microgels can be simply triggered by CO_2 and N_2 purging. To the best of our knowledge, this is the first time to use gas-responsive microgels as draw materials in a FO desalination process, where high water flux and water recovery can be achieved simultaneously via sweeping gas at room temperature.

2. Experimental

2.1. Materials

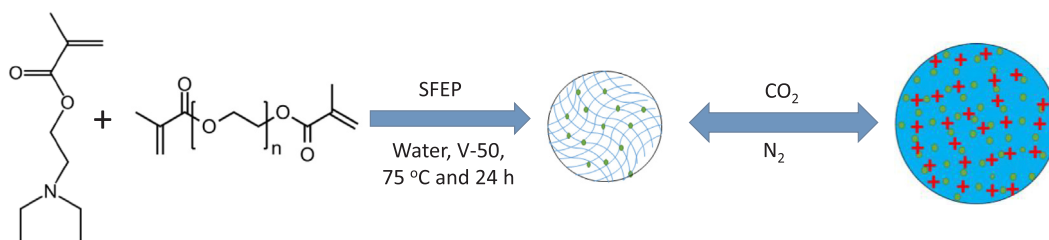
Monomers of 2-N,N'-(diethylamino)ethyl methacrylate (DEAEMA) and 2-N,N'-(dimethylamino) ethyl methacrylate (DMAEMA), and three crosslinkers of N, N'-methylene-bisacrylamide (BIS), poly (ethylene glycol diacrylate) (PEGDA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma-Aldrich. The chemical structures of monomers and cross-linkers are shown in Fig. S1. Nonionic initiator of N,N'-azobisisobutyronitrile (AIBN) (Acros Organics) and cationic initiator of 2,2'-azobis (2-methyl propionamide dihydrochloride) (V-50) were from Novachem. Poly(vinyl pyrrolidone, MW 360,000, PVP360, Sigma) were used as the stabilizer for dispersion polymerization, and absolute ethanol was purchased from Merck. Cellulose triacetate forward osmosis (CTA-FO) membranes were supplied by Hydration Technologies Inc. (HTI, USA).

2.2. Synthesis of DEAEMA microgels

DEAEMA microgels were synthesised via a surfactant-free emulsion polymerization (SFEP) process [33]. Briefly, a DEAEMA solution (4 wt %) with different crosslinkers at a designated concentration was prepared in a three-neck flask, which was fitted with a gas outlet/inlet, a condenser and a mechanical stirrer. The solution was degassed for 1 h at $40^\circ C$ in an oil bath, and then the temperature was increased to $75^\circ C$. The initiator (V-50) was dissolved in 3 ml DI water and degassed for 5 min at room temperature. The solution turned cloudy within 15 min of initiator injection. After overnight polymerization under continuous stirring under nitrogen protection, the obtained microgels were purified against DI water by membrane dialysis (MWCO: 12–14 kDa) for 4 days to ensure all unreacted compounds were removed. The microgels were dried at $70^\circ C$ and grounded into fine powders. Detailed chemical structures and schematic synthesis of DEAEMA cationic microgels are shown in Figs. S1 & S2 (Supporting Information) and Scheme 1. The conversions were found to be 86%, 79% and 82% for the DEAEMA microgels with PEGDA, EGDMA and BIS crosslinker, respectively.

2.3. Synthesis of DMAEMA microgels

Due to the difficulty of synthesizing DMAEMA microgels using a



Scheme 1. Schematic description on the synthesis of DEAEMA cationic microgels via surfactant-free emulsion polymerization, and its swelling/deswelling behaviour in solution.

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