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In situ manipulation of properties and performance of polyethyleneimine nanofiltration membranes by polyethylenimine-dextran conjugate

Anupam Bera [a,b], Jaladhi S. Trivedi [a], Suresh K. Jewrajka [a,b,*], Pushpito K. Ghosh [b,c,**]

[a] Reverse Osmosis Membrane Division, CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar 364002, Gujarat, India
[b] AcSIR-Central Salt & Marine Chemicals Research Institute, G. B. Marg, Bhavnagar 364002, Gujarat, India
[c] Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400019, Maharashtra, India

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ABSTRACT

Polyethyleneimine (PEI) is an inexpensive low-toxic polymer and is used for the preparation of thin film composite (TFC) nanofiltration (NF) membranes. One serious problem with most of the reported high salt rejecting (ca. 90% divalent cation) PEI-based TFC membranes is the low permeate flux and low average monovalent to divalent anion selectivity. There is also no comparative study of antifouling property of the PEI TFC membranes with conventional poly(piperazineamide) TFC membrane. Herein, we report an approach for the in situ manipulation of permeation behavior and antifouling property of PEI-based TFC NF membrane. The approach was based on the use of dextran (Dex) conjugate of PEI (PEI-Dex) as a new monomer or co-monomer for the interfacial polymerization (IP) with trimesoyl chloride (TMC). Particularly, membranes prepared with mixture of PEI-Dex (2.5%, w/v)+PEI (0.25%, w/v) showed ca. 86 $Lm^{-2} h^{-1} MPa^{-1}$ pure water permeate flux and 84%, 85% and 37% rejections of Na_2SO_4, $MgCl_2$ and NaCl, respectively. On the other hand, membrane prepared with PEI (0.25%, w/v) alone gave much lower permeate flux (37 $Lm^{-2} h^{-1} MPa^{-1}$). The membrane prepared with PEI-Dex (3%, w/v) gave permeate flux as high as 163 $Lm^{-2} h^{-1} MPa^{-1}$ with ca. 71%, 72% and 10% rejections of Na_2SO_4, $MgCl_2$ and NaCl respectively under similar experimental conditions. All the PEI-based membranes prepared under suitable experimental conditions showed high average monovalent to divalent ions (cation and anion) selectivity. The active layer thickness decreased with increasing proportion of added PEI-Dex into the aqueous bath. This is the reason for the enhancement of permeate flux of the PEI-Dex membranes. On the other hand, low membrane surface charge at neutral feed pH is responsible for the higher average monovalent to divalent ions selectivity. The PEI-based membranes exhibited much improved antifouling/antiscaling properties compared to that of conventional poly(piperazineamide) TFC NF membranes. These types of membranes are suitable for long-term water softening without frequent cleaning step.

1. Introduction

Nanofiltration (NF) membranes have attracted wide attention due to their utility in various industrial fields for selective separation processes at low applied pressures. NF is also of importance for the pre-treatment of seawater prior to reverse osmosis (RO) desalination. Such pretreatment helps to eliminate scale forming constituents and also reduces the total dissolved solids in seawater making desalination easier [1–4]. A dual-stage seawater NF was recommended for reducing scaling problem and energy consumption for further desalination by RO process [5]. Simulation study had shown that the dual-stage seawater NF-RO process lowers the energy consumption as compared to RO process [6]. Selective elimination of constituents other than NaCl from seawater too is an important goal. For example, substitution of fresh water with seawater for the preparation of brine is required by soda ash manufacturer for commercial applications. Polypiperazineamide [poly(PIP)] thin film composite (TFC) membranes have attracted wide attention for use as NF membranes [7–14]. These membranes are prepared by interfacial polymerization (IP)

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[*] Corresponding author at: Reverse Osmosis Membrane Division, CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar 364002, Gujarat, India.

[**] Corresponding author at: Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400019, Maharashtra, India.

E-mail addresses: skjewrajka@csmcri.org (S.K. Jewrajka), pushpitokghosh@gmail.com (P.K. Ghosh).

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between PIP and trimesoyl chloride (TMC) on ultrafiltration support membrane. The use of PIP has been the most prevalent, employed either singly [7–9] or in conjunction with other additives [10]. However, common problems with the conventional poly(PIP) membranes are the poor fouling resistant efficacy and tradeoff rejection between multivalent cation and anion (with monovalent counter ion). The negative charge on poly(PIP) membrane surfaces is responsible for such rejection behavior of the poly(PIP) membranes.

Polyamines such as polyvinylamine (PVAm) and polyethyleneimine (PEI) have also attracted wide attention for making TFC NF membranes [15–20]. However, these membranes also showed trade-off rejections between multivalent cation and anion. For examples, Liu et al. reported the preparation of TFC NF membrane by the IP between PVAm and TMC on a porous polysulfone (PSf) support membrane [15]. The rejections of $MgCl_2$, Na_2SO_4 and NaCl by this membrane were 32%, 95% and 60%, respectively. This membrane showed 49 $Lm^{-2}\,h^{-1}$ permeate flux at applied pressure 0.6 MPa at neutral feed pH. Chiang et al. prepared TFC NF membranes by reacting PEI with TMC or terephthaloyl chloride [16]. The polyamide (PA) layer was coated on a support membrane cast from a solution containing a mixture of polyacrylonitrile and polyvinyl pyrrolidone (PVP), followed by hydrolysis of the –CN groups. The rejections of $MgCl_2$, Na_2SO_4 and NaCl were 80%, 50% and 44% respectively with permeate flux of 9.5 $Lm^{-2}\,h^{-1}\,bar^{-1}$. This membrane showed high monovalent ion to divalent cation selectivity and very low monovalent ion to divalent anions electivity. Wu et al. prepared series of PEI/TMC membranes through repeated cycles of sequential deposition of monomers on polyether sulfone support membrane [17]. It was noted that the membrane prepared by single cycle of PEI and TMC reaction gave high rejections (95%, 81% and 85%) of $MgCl_2$, Na_2SO_4 and NaCl respectively. This indicated low selectivity between monovalent to divalent ions. In another work, the PEI/TMC membrane formed by IP between PEI and TMC also gave low selectivity between monovalent to divalent ion (rejections of $MgCl_2$, Na_2SO_4 and NaCl are 95%, 68% and 75% respectively) [18]. Park et. al. have prepared NF membrane by using PEI on polyvinylidene fluoride nanofibrous scaffolds [19]. Although the rejection of bivalent ionic salts (Na_2SO_4 and $MgCl_2$) crossed ca. 80% mark, the membrane gave low monovalent to divalent ions selectivity. In another study, polyamidoamine dendrimer-based TFC NF membranes showed higher rejection of $MgCl_2$ and comparatively lower rejection of Na_2SO_4 [20]. Comparative antifouling behavior of these membranes with conventional poly(PIP) membrane was not studied.

In our previous publication, we demonstrated the enhancement of both fouling resistant behavior and monovalent ion to divalent cation selectivity of poly(PIP) membrane by post treatment with PEI and its conjugates. The post treatment process did not much alter the selectivity between monovalent ion to divalent anion [21]. Our main aim of this work is the enhancement of permeate flux, antifouling property and average monovalent to divalent ions (cation and anion) selectivity of PEI-based NF membrane. We proposed to use PEI-dextran (PEI-Dex) conjugate as macromonomer for IP with TMC. It was hypothesized that the use of bulky Dex chain might be helpful to control the diffusion of amine monomers towards the interfacial zone for controlling the active layer thickness. Dex is also known as antifouling polymer. It is important to mention that while this work was completed, a publication of Ma et al. appeared where they reported the use of zwitterionic PEI-sulfobetaine methacrylate for the preparation of electro neutral membrane. The membrane showed enhanced flux and antifouling behavior compared to the control PEI/TMC membrane [22]. The reported membrane exhibited 47%, 50% and 7% rejections of $MgCl_2$, Na_2SO_4 and NaCl respectively. The membrane was used for dye removal application.

Herein, we propose in situ manipulation of membrane properties and performance through IP by the use of PEI-Dex as monomer or commoner with PEI. PEI-Dex conjugate was proposed to use since, Dex is an alternative to PEG in terms of antifouling characteristic, while also having the benefits of thermal stability, low cytotoxicity and natural availability [23,24]. Our specific aim is the enhancement of permeate flux, average monovalent to divalent ions selectivity and antifouling behavior by means of in situ IP. We demonstrate that PEI-Dex as a co-monomer helped to form thinner selective PA layer. Membrane prepared with mixture of PEI-Dex+PEI showed similar pore size and enhanced permeate flux compared to membranes prepared with PEI as a sole monomer. The membranes prepared with appropriate proportion of PEI-Dex conjugate exhibited good antiscaling/antifouling property and enhanced average monovalent to divalent ions selectivity.

2. Experimental

2.1. Materials

PSf (Udel P-35000), from Solvay Polymers, was dried at 80 °C for 2 h prior to the preparation of the casting solution. PEI (M_w=2000 Da), Dex (M_w=11,300 Da), sodium cyanoborohydride ($NaBH_3CN$) and TMC (98%) from Aldrich were used as received. Analytical grade dimethyl sulfoxide (DMSO), methanol, tetrahydrofuran (THF), DMF and hexane were procured from Spectrochem, India and used as received. Non-woven polyester fabric (Nordlys-TS100) was used as received. NaCl, KCl, Na_2SO_4, $MgCl_2$ and $CaCl_2$ were procured from Spectrochem, India and used as received. Seawater was constituted from sea salt, a proprietary salt obtained through complete evaporation of seawater [25].

2.2. Preparation of PEI-Dex macromonomer

PEI-Dex macromonomer was prepared by slightly modified procedure as reported earlier [23,26]. A typical procedure is as follows. PEI (3.75 g) was added into a solution of Dex (10 g) in 100 mL DMSO-water (9:1, v/v) under vigorous stirring. Next, $NaBH_3CN$ (0.2 g) was added into the reaction mixture in 0.05 g lots per 12 h of intervals. The reaction mixture was further stirred for an additional 12 h. The reaction mixture was then precipitated into methanol (300 mL). The solid was filtered, re-solubilized in DMSO and re-precipitated from methanol. This step was done four times to remove unreacted PEI from the PEI-Dex macromonomer. ^{1}H NMR (Fig. S1A, Supplementary material): δ 5.0–4.9 (C1–H, dextrose), δ 4.1–3.4 (C2–C6–H, dextrose) and δ 2.8–2.5 (PEI–H); elemental analysis data: %N, 3.61; %C, 34.88; %H, 9.037. The calculated CHN values are 4.89%, 42.75% and 7.022%, respectively, assuming 1:1 Dex to PEI molar ratio. The lower observed values of N and C, and higher observed value of H, are likely on account of moisture absorption. The molecular weight (M_n) of PEI-Dex was determined to be 15,000 g/mol by ^{1}H NMR considering the known molecular weight of PEI (2000 g/mol) by the following equation:

$$M_n(\mathrm{g/mol}) = \frac{160 \times \mathrm{Int}_{4.99}}{\mathrm{Int}_{2.74}} \times 178 + 2000 \tag{1}$$

where $\mathrm{Int}_{2.74}$ is the integral of back bone proton of PEI (PEI–H), 160 is the number of protons attached to carbon atom in PEI, $\mathrm{Int}_{4.99}$ is the integral of C1–H of Dex, and 178 is the molecular weight of Dex repeat unit. Gel permeation chromatography (GPC) was performed using ultra-hydrogel columns. Water containing Na_2SO_4 (0.3 M) and NaN_3 (0.1%) was used as eluent at flow rate 0.8 mL/min. PEG standards were used for calibration. The GPC traces of Dex and PEI-Dex are given in Supplementary material (Fig. S1B). The GPC