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A facile method for polyamide membrane modification by poly(sulfobetaine methacrylate) to improve fouling resistance

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ABSTRACT

Membrane fouling is a long-standing problem in many industrial and fundamental applications. In this work, a zwitterionic poly(sulfobetaine methacrylate) (pSBMA) is grafted on the surface of an aromatic polyamide membrane to improve membrane fouling using surface-initiated atom transfer radical polymerization (SI-ATRP). The resulting pSBMA-coated polyamide membrane exhibits excellent surface resistance to protein adsorption and high water permeability. As compared to untreated membrane, the adsorption amount of irreversible proteins on the pSBMA-coated membrane is significantly reduced by ~97% and water flux is also greatly improved by ~65%, while rejection rate remains unchanged as large fouling molecules (humic acid, bovine serum albumin) in the solution are filtrated. More importantly, the pSBMA-coated polyamide membrane consistently retains a much higher water flux and improves the rejection rate of NaCl at high operating pressure. These results demonstrate that new pSBMA-coated membrane with easy synthesis can serve as potential promising membranes for membrane industry.

1. Introduction

Membrane separation technology has been widely used for removal of pollution [1], alcohol [2], and salts from various feed waters in many applications of desalination of seawater and brackish water, waste water treatment, environmental engineering, food industry, etc. However, the performance of polyamide membranes is severely hampered by the long-standing problem of colloidal, organic, and other contaminant fouling [3]. Since the chemical and physical properties of the outer layer of membranes play the most important role in membrane performance (e.g. membrane fouling, water flux, and membrane rejection level) [4], many efforts have been made to modify and optimize membrane surface to improve membrane performance. For example, zwitterionic polymers, including poly(*N*,*N*-dimethyl–*N*-(*p*-vinylbenzyl)–*N*-(3-sulfopropyl) ammonium), poly(2-(methacryloyloxyethyl) ethyl-dimethyl-(3-sulfopropyl) ammonium) and poly(2-methacryloyloxyethyl phosphorylcholine), were grafted from cellulose membranes (CMs) via surface-initiated atom transfer radical polymerization (ATRP). Results show that the zwitterionic surface modification can reduce nonspecific protein adsorption by about 60% [5]. Polyethylene glycol (PEG) and poly(vinyl-2-pyrrolidone) are also used to improve the resistance to surface fouling and surface hydrophilicity [6–8]. However, some problems still remain unsolved. PEG is highly sensitive to be oxidized in the presence of both oxygen and transition-metal ions although fresh PEG coated membrane shows good resistance to nonspecific protein adsorption. Those low quality polyzwitterion-modified layers only showed partial fouling resistance. Thus, it is still a challenging task to overcome the fouling of polyamide membranes caused by the nonspecific adsorption of small protein debris and organic molecules.

Moreover, interfacial polymerization is one of the most efficient methods to prepare and produce membranes in membrane industry today. It is valuable to develop an efficient method compatible with interfacial polymerization to improve membrane performance in fouling resistance and water permeability, which will make a contribution for the manufacture of all interfacial polymerized membranes. Thus, the modification of a typical polyamide membrane (reverse osmosis or RO membrane) is chosen to investigate the method for fouling resistance coating. It has been commonly reported that most of the modified RO membranes show an increase of flux with a loss in rejection [9–14]. Thus, it is necessary to develop efficient fouling-mitigation strategies and highly fouling resistant RO membranes.

Our previous studies have demonstrated that the zwitterionic pSBMA-based materials (i.e. polymer brushes, hydrogels, nanoparticles) highly resist long-term nonspecific protein adsorption of < 0.3 ng/cm^2 and bacterial adhesion for up to 10 days when the surface packing is well controlled [15–20]. Motivated by superlow fouling ability of pSBMA, here we first applied the atom transfer

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radical polymerization (ATRP) method [21,22] to graft pSBMA on the polyamide membrane surface, then we systematically examined the fouling resistance and filtration performance of the pSBMA-coated membranes using enzyme-labeled protein assay, attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, atomic force microscopy (AFM), water flux and solute rejection measurement. Results clearly showed that the introduction of pSBMA on the membrane significantly improves the membrane performance including much less amount of adsorbed proteins, increased water flux, highly preserved rejection rate of high molecule solutes. Moreover, the undesired decrease in rejection rate of ions and small organic molecules can be overcome by filtrating at a high working pressure, such as 5.5 MPa, the pressure for commercial seawater desalination. This work demonstrates that the pSBMA-coated RO membranes could be very promising for commercial seawater desalination and waste water treatment.

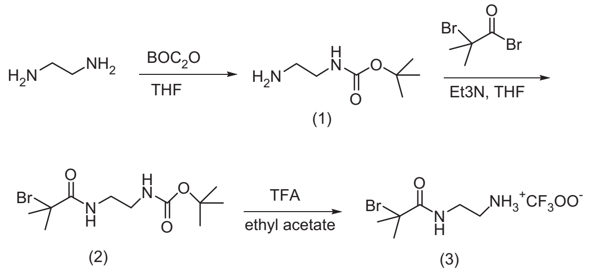
2. Materials and methods

2.1. Materials

The polysulfone (PS) support membrane was supplied by the Development Center for Water Treatment Technology, Hangzhou, China. M-phenylenediamine (MPD), trimesoylchloride (TMC), humic acid (HA), o-phenylenediamine (OPD), CuBr, 2,2-bipyridine (Bpy), ethanediamine (EDA) and bromo-2-methylpropionyl bromide (BIBB) were purchased from Aladdin Reagent Company. Analytical-grade n-hexane, cetyltrimethylammonium bromide, tetrahydrofuran (THF), NaCl, $MgSO_4$ and citric acid were purchased from Sinopharm Chemical Reagent, Shanghai, China. BSA was purchased from Sangon Biotech (Shanghai) Co., Ltd. Deionized water was purchased from Wahaha (Hangzhou) Company. Horseradish peroxidase (HRP)-conjugated goat anti-human lgG (H+L) was purchased from Beijing Biosynthesis Biotechnology Co. Butoxycarbonyl (BOC) was purchased from Shanghai Covalent chemical Co.

2.2. Preparation of EDA–BIBB initiator

The synthetic route is shown in Scheme 1. BOC–ethylenediamine (BOC–EDA) was prepared first. di-tert-butyl pyrocarbonate (di-BOC) (35 ml, 0.152 mol) was added dropwise into the EDA THF solution (100 ml, 1.494 mol) for 2 h in an ice-bath. The solution was stirred for additional 24 h at room temperature before being concentrated. 500 ml brine was added to the concentrated residue and the precipitate was filtered off. The filtrate was extracted by the DCM for three times and the combined organic phase was dried with anhydrous sodium sulfate. The product was obtained by distilling off the DCM in vacuo at 30 °C. ^{1}H NMR($CDCl_3$): 1.39 ($(C\underline{\boldsymbol{H}}_3)_3C$–), 2.74(–$C\underline{\boldsymbol{H}}_2NH_2$), 3.11(–$C\underline{\boldsymbol{H}}_2NH$–).



Scheme 1. The route of initiator synthesis.

Bromoisobutyryl bromide (BIBB) (10 ml, 80.9 mmol) THF solution was added dropwise to the ice cooled flask charged with BOC–EDA (10.057 g, 62.8 mmol), triethylamine (20 ml, 143.4 mmol) and 150 ml THF under nitrogen protection. The solution was stirred overnight before the precipitate was filtered off. The concentrated filtrate was redissolved in ethyl acetate and washed by the saturation Na_2CO_3 solution for three times. Then the organic phase was dried with anhydrous sodium sulfate. The ethyl acetate was removed under vacuum to obtain product **2** (BOC–EDA–BIBB, 8.32 g) as white powder (6.17 g, yield: 34.9%). ^{1}H NMR($CDCl_3$): 1.45($(C\underline{\boldsymbol{H}}_3)_3C$–), 1.96($(C\underline{\boldsymbol{H}}_3)_2C$–), 3.34(–$C\underline{\boldsymbol{H}}_2$–NH–COO–), 3.38(–$C\underline{\boldsymbol{H}}_2$–NH–CO–).

BOC–EDA–BIBB was then treated with 50% (V/V) TFA ethyl acetate solution for 1 h. And the precipitate was filtered off, washed with ethyl acetate and dried to obtain product **3** (EDA–BIBB). ^{1}H NMR (D_2O): 1.93($(C\underline{\boldsymbol{H}}_3)_2C$–), 3.16(–$C\underline{\boldsymbol{H}}_2$–$NH_2$), 3.54(–$C\underline{\boldsymbol{H}}_2$–NH–CO–).

2.3. Preparation of the RO membranes

The RO membranes were prepared by the interfacial polymerization of MPD with TMC on the polysulfone support surface. Briefly, the support PS membrane was immersed in MPD aqueous solution for 5 min before the n-hexane solution of TMC was added and left over for 20 s polymerization. The final membrane was obtained after being dried at 80 °C in oven for 15 min.

2.4. Preparation of the RO membrane with pSBMA

The RO membrane with pSBMA was prepared using the method shown in Scheme 2 [23]. Briefly, after the interfacial polymerization, the membrane was immersed in an aqueous solution of EDA–BIBB for 1 min to obtain the membrane modified with ATRP initiators. After being dried in oven at 80 °C for 15 min, the membrane was immersed in 10 ml N_2-purged methanol/water solution dissolved with SBMA (1.000 g), BPY (156 mg), CuBr (71.5 mg) for predetermined time duration. Then the modified RO membrane was obtained and rinsed with ethanol, phosphate buffered saline (PBS, pH 7.4) and DI water. And the pSBMA-coated membranes were kept in PBS for further characterizations.

2.5. Membrane surface characterization

2.5.1. Surface chemical property analysis

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy by Nicolet Nexus 670 FTIR spectrometer was used to investigate the chemical changes on the membrane surfaces. The samples, untreated RO membrane, initiator immobilized membrane and modified membrane were investigated in air.

2.5.2. Surface roughness analysis

The surface morphology of untreated membranes and modified membranes was imaged by AFM (using Multimode SPM from American VEECO Company) by tapping mode [24]. The AFM images of 5 μm scans were acquired by scanning the sample in air under ambient laboratory conditions. The surface roughness was assessed.

2.6. Fouling resistance assessment

2.6.1. Protein adsorption measurement

The adsorption of HRP-conjugated goat anti-human lgG on the membrane surface was evaluated using sorbent assay. The standard protocol was described as follows. The membranes were fixed into circular shape fixture and soaked for 60 min at 37 °C in