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Constructing zwitterionic surface of nanofiltration membrane for high flux and antifouling performance

Yi-Fang Mi[a], Feng-Yang Zhao[a], Yao-Shen Guo[a], Xiao-Dan Weng[b], Chun-Chun Ye[a], Quan-Fu An[a,c,*]

[a] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China
[b] College of Chemical Engineering and Bioengineering, Zhejiang University, Hangzhou 310027, China
[c] Beijing Key Laboratory for Green Catalysis and Separation, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

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ABSTRACT

Antifouling performance of nanofiltration membrane is critical in applications like water treatment. In this study, surface zwitterionization was conducted by 1, 3-propanesultone ring-opening directly on the nanofiltration membrane prepared by interfacial polymerization of 3,3′-diamino-N-methyldipropylamine and 1, 3, 5-benzenetricarboxylic chloride. The zwitterionic structures improve the hydrophilicity of nanofiltration membrane, thus increase the water permeability and antifouling performance. The zwitterionic membrane have a 72 L m^{-2} h^{-1} water flux at the optimize condition, which was about 2.4 times that of the pristine membrane without zwitterionization, and with a 89% rejection of $MgCl_2$. Meanwhile, the zwitterionic membrane will have better antifouling performance to protein and polysaccharose. The flux recovery ratio of bovine serum albumin, sodium alginate and lysozyme were all above 95%. The prepared zwitterionic membrane presents prominent high water flux and fouling-resistance performance, indicating it's promising application potential in organic wastewater treatment.

1. Introduction

Increasing world population and contamination of natural water sources are stringent problems in today's world, thus resulting in burgeoning demands on high efficacy water purification technologies [1,2]. Membrane separation technologies, such as ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), are emerging as competitive solutions for clean water due to the advantages of low energy consumption, easy operation and high efficiency [3–5]. Among all these technologies, NF membranes, with typical pore size of 1 nm and charged surfaces, play a vital role in water treatment owing to unique separation mechanism (steric hindrance and electrostatic repulsion) and low operation pressure [6].

Thin-film composite polyamide membranes prepared with interfacial polymerization are widely used for the production of pure water in NF processes [7]. A thin selective layer (about 100–200 nm) without defects will be generated during interfacial polymerization, which results in relatively higher water flux compared with other preparation methods [8–10]. However, problems such as fouling associated with these membranes restrict their application for water purification technology [11–13]. Membrane surface property is one of the most important factors influencing the permeability and antifouling performance, thus, surface modifications, primarily via surface coating and grafting, are an effective approach to tuning the characteristics of membranes and reduce membranes fouling [14–16]. Although grafting or coating long-chain polymers onto dense surfaces could drastically inhibit the adsorption of foulants, the pore size and pore size distribution of membranes were drastically changed after modification [17,18]. Second, the antifouling properties can be satisfactorily manipulated via controlling the grafting density. Though antifouling performance is usually enhanced with increasing grafting density, water permeability may decrease. This phenomenon can happen even in atom transfer radical polymerization grafting modification (ATRP) [19–21]. Thus, it is highly desirable to develop novel method to overcome the above issues.

Zwitterions, which consist of pendant groups of phosphobetaine, sulfobetaine or carboxylbetaine, provide robust fouling resistance chemistry [22]. Compared with other hydrophilic materials, zwitterions possess both negatively and positively charged units and create stronger and more stable hydration layer via electrostatic interactions [23,24]. Uniformity of charge distribution and charge neutrality are two important factors affecting the antifouling properties of zwitterions [25]. Benefiting from above properties and the ease of functionalization, modifying membrane surfaces with zwitterionic materials, has been

* Corresponding author at: MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China.
E-mail address: anqf@zju.edu.cn (Q.-F. An).

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demonstrated as a promising method to address membrane fouling problems and increase membrane water flux [26–28]. A few attempts have been made to modify polyamide membranes with small molecules by creating a zwitterionic thin film on membrane surface via chemical vapor deposition [29,30], concentration-polarization-enhanced radical graft polymerization [31] or click reaction [32,33]. These approaches, however, require specialized setup that is very difficult to scale up or specific azido functionality. Therefore, an efficient but simple method for modifying zwitterionic moieties onto the polyamide membrane is highly desirable. It is well-known that most methods to synthesize the zwitterions are via ring opening of lactone [34,35]. Thus, in our work, 1, 3-PS monomer was used as modifier and simultaneously synthesized zwitterion in situ via ring-opening reactions between tertiary amines and lactone. This process enabled the application of zwitterionic moieties directly onto nanofiltration membrane surface.

To this end, this work aimed at surface modification of nanofiltration membrane in molecule level design, avoiding introducing dense modification layer by introducing zwitterion moieties in situ. Specifically, the positive polyamide NF membrane was firstly fabricated by interfacial polymerization of 3, 3′-diamino-N-methyldipropylamine (DNMA) and trimesoyl chloride (TMC). Then the tertiary amines in the polymer chains subsequently reacted with 1, 3-PS to construct zwitterionic structures directly. The effect of reaction time on membranes compositions and separation properties will be discussed. The modified membrane would also improve the water permeability and show good resistance to different foulants such as polysaccharides sodium alginate, protein bovine serum albumin and lysozyme aqueous solution as model foulants. Notably, this architecture protocol provides better antifouling performance and increases membrane transport properties.

2. Experimental

2.1. Materials and reagents

1,3-propanesultone (1,3-PS) and 3,3′-diamino-N-methyldipropylamine (DNMA) were purchased from TCI (Shanghai) Development Co., Ltd. 1,3,5-benzenetricarboxylic chloride (TMC, > 99%), analytical standard bovine serum albumin (BSA), sodium alginate (NaAlg), lysozyme (LYZ), Congo red (CR) , Victoria blue B(VBB) and methylene blue (MB) were received from Shanghai Aladdin Reagent Company. hexane, sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium sulfate (Na_2SO_4), magnesium chloride ($MgCl_2$), sodium chloride (NaCl), calcium chloride ($CaCl_2$), polyethylene glycol (PEG, Mw = 200, 400, 600, 800 and 1000 Da), methanol (pre-standardized), ethanol and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized (DI) water with a resistance of 18 MΩ was used in all experiments. Polysulfone UF supporting membranes (MWCO = 20,000) were supplied by the Development Center of Water Treatment Technology, Hangzhou, China. All the reagents were all analytical standard and used without any further purification.

2.2. Fabrication of zwitterionic NF membranes

First, DNMA-TMC membrane was prepared via interfacial polymerization of DNMA and TMC monomers (Fig. 1). Polysulfone (PSF) UF supporting membrane was immersed in 0.5 wt% DNMA aqueous solution for 1 min, then excess liquid was removed and the membrane was dipped into TMC/hexane solution (0.2 wt%) for 1 min. Interfacial polymerization generated polyamide selective layer on the UF supporting membrane. The pristine membrane was dried in air for 30 min for the full evaporation of hexane. Then the membrane was immersed into 1, 3-PS/methanol (0.1 g/mL) solution for a specific time at 40 °C [25]. The obtained membrane (referred to as NFM-t, where *t* refers to the modification time) was rinsed with pure ethanol and deionized water alternately to remove unreacted 1, 3-PS molecules, and stored in DI water.

2.3. Membrane characterizations

Prior to any characterizations, all membranes were dried under vacuum (30 °C, 24 h).

Chemical structures were evaluated by Attenuated total reflectance Fourier transform infrared spectroscopy (ATR- FTIR, Germany) and X-ray photoelectron spectroscopy (XPS, a PerkinElmer PHI 5300 ESCA system with Mg/Al Dual Anode Hel/Hell ultraviolet source) was used to quantitative analyses the elemental contents of the membranes. The ratio of zwitterion on the membrane surface was calculated from XPS spectra. The detected sulfur atom and nitrogen atom only originated from 1, 3-PS and DNMA, respectively , since the thickness of the polyamide layer was thicker than the detection depth of the XPS technique (about 10 nm). So the value of $Ratio_{zwitterion}$ was calculated by the following equation [36]:

$$Ratio_{zwitterion} = \frac{1,3-PS(mol)\times 100\%}{1,3-PS(mol)+DNMA(mol)} = \frac{S(mol\%)}{N(mol\%)} \quad (1)$$

The membrane morphologies were visualized by a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). Membranes were sputter-coated with a thin layer of gold before all SEM measurements. Atomic force microscopy (AFM) was operated in air atmosphere at room temperature with silicon tips (NSG10, Nt-MDT, a resonance frequency of ca. 330 kHz) in tapping mode. The root mean-square (RMS), as surface roughness of each membrane, was measured from height profile of three-dimensional AFM images.

Surface hydrophilicity of nanofiltration membranes was evaluated by dynamic water contact angles (OCA 20, Data Physics Instruments GmbH, Germany) using the sessile drop method at ambient temperature. The interfacial free energy ($-\Delta G_{SL}$) can be determined on modified the Young-Dupre equation [37] (2):

$$-\triangle G_{SL} = \gamma_L \times (1+\cos\theta/\Delta) \quad (2)$$

in which γ_L is pure water surface tension (72.8 m J m^{-2}, 25 °C), θ is water contact angle and Δ is relative surface area obtained from AFM image.

The membrane surface charge was evaluated from a streaming potential method using an electrokinetic analyzer (SurPASS Anton Paar, GmbH, Austria). A 0.001 M KCl aqueous background solution was used for the determination of the zeta potential of the membranes at 25 °C and pH ranging from 4.0 to 8.0. The data presented are average values from three samples of each membrane type.

2.4. Membrane performance evaluation

2.4.1. NF tests

NF performance tests of membranes were conducted by cross-flow filtration equipment at 25 °C and 0.6 MPa. The filtration unit contained three parallel test cells, and the averaged measurements were reported. The membranes with effective area of 22.4 cm^2 were equilibrated with DI water at 0.7 MPa to reach a stable state before the NF performance tests. After compacted, the pure water flux was recorded. The salt solution (1 g L^{-1}) including NaCl, $MgCl_2$ $CaCl_2$ and Na_2SO_4 or water-soluble dye solution (VBB, CR, MB, 0.5 g L^{-1}) was forced to permeate through the membrane at 0.6 MPa, respectively. Finally the system was rinsed cleanly with deionized water. Both the water flux (J) and the rejection (R) were used to evaluate membranes' NF performance. J and R were determined according to the following Eqs. (3) and (4) respectively:

$$J = V/(A\times t) \quad (3)$$

where A denotes effective membrane area (m^2), and V (L) represents total water volume which is collected during time t (h).

$$R = ((C_f - C_p)/C_f)\times 100\% \quad (4)$$

where C_f (g L^{-1}) and C_p (g L^{-1}) are solute concentration of feed

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