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A novel salt-responsive TFC RO membrane having superior antifouling and easy-cleaning properties

Jianqiang Meng*, Zhen Cao, Lei Ni, Yufeng Zhang, Xiaoyan Wang, Xin Zhang, Enhua Liu

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, China

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ABSTRACT

A novel salt-responsive thin-film composite (TFC) reverse osmosis (RO) membrane was prepared by tethering a zwitterionic polymer poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PSVBP) onto a commercial RO membrane. The graft polymerization was conducted by surface-initiated free radical polymerization of SVBP initiated by a $K_2S_2O_8$–$NaHSO_3$ redox system. The membrane surface before and after graft polymerization was investigated in detail using ATR-FTIR, XPS, zeta potential, water contact angle and SEM. The change on surface chemical composition demonstrated successful grafting of PSVBP onto the RO membrane surface. The PSVBP grafting added negative charge onto the membrane surface and significantly improved membrane surface hydrophilicity. The RO test indicates that PSVBP grafting can increase the rejection from 98.0% to 99.7% with the trade-off 20% of the permeation flux. A cross-flow protein fouling test as long as 100 h indicates that the resulted PA-g-PSVBP membrane had superior antifouling property in the short term but lost the advantage for long-term operation. In spite of the long-term fouling, the PA-g-PSVBP membrane can restore 90% of the initial flux by rinsing with brine. The salt-responsive property of the PSVBP brush is believed to provide a driving force for the release of protein foulants.

1. Introduction

With the population growth and industrialization across the world, the problem of water shortage became more and more serious. Today, many countries face chronic water shortages due to intense population growth and increased water pollution. Reverse osmosis (RO) is considered as a reliable and economic technology to solve the water crisis and has been widely used in seawater and brackish water desalination, waste water reclamation, pure water fabrication etc. [1,2]. The mainstream reverse osmosis membranes commercially available are polyamide thin-film composite membranes (PA TFC). The PA TFC membrane was made by interfacial polymerization of an aromatic polyamine (for example m-pheylenediamine (MPD)) with one or more aromatic polyacyl halides (for example trimesoyl chloride (TMC)) over a porous polysulphone support membrane [3]. It has several advantages such as high water permeability and ion rejection, resistance to pressure compaction, wide operation temperature and pH ranges. However, membrane fouling has limited the applications of RO because it leads to deteriorated membrane performance, shortened membrane service life and increased system cost [4].

Significant amount of work has been dedicated to membrane surface modification for improved anti-fouling performance. The most frequently used strategy is to build a fouling-resistant and hydrated layer on the membrane surface. Usually the obtained membrane was fouled less and slower than the unmodified membranes or commercial membranes [5]. However, fouling still occurs, which means that membrane cleaning is inevitable. Currently, the fouled RO membranes are routinely cleaned by specialized chemicals to restore its performance. The chemical cleaning often leads to continuous membrane degradation and chemical waste, resulting in the second pollution.

Alternatively, a more realistic and efficient solution to membrane fouling is to develop membranes having self-cleaning or easy-cleaning properties. Following this clue, Madaeni and coworkers attempted to modify the RO membrane with nano-TiO_2 by a self-assembly method [6]. The modified membranes showed improved water flux and antifouling performance due to the obvious improvement of membrane surface hydrophilicity. But there remains a question whether TiO_2 particles and UV irradiation can degrade the membrane itself. Shi and coworkers immobilized trypsin onto PMAA-g-PES membranes [7]. The results suggested that the enzyme-resided membrane had desirable anti-fouling and

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* Corresponding author. Tel.: +86 22 8395 5078; fax: +86 22 8395 5055.
E-mail address: jianqiang.meng@hotmail.com (J. Meng).

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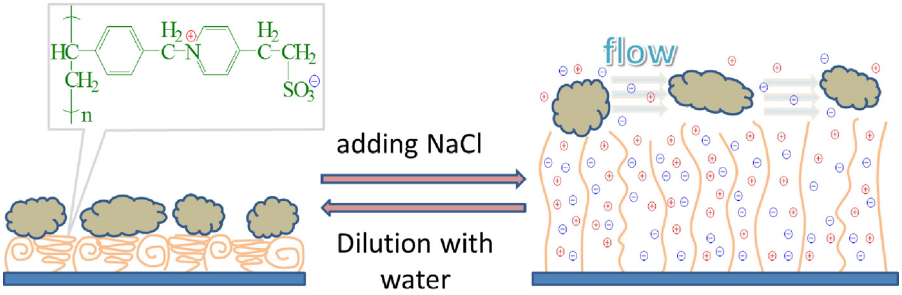

Scheme 1. Synthesis of the salt-responsive TFC RO membrane having antifouling and easy-cleaning properties.

self-cleaning properties, but the long-term stability of the trypsin on the membrane surface may be questionable. Zhao et al. designed membrane surfaces covered with hydrophilic and low surface energy brushes. The obtained membranes were demonstrated to have superior antifouling and self-cleaning abilities [8].

Stimuli-responsive polymers are capable of translating changes in their local environment to changes in their physical/chemical properties. This allows stimuli-responsive polymers to be used for a wide range of applications and to draw intensive attention in recent years [9,10]. Stimuli-responsive membranes have also drawn great attention, with the focus on responsiveness of the membrane permeability and selectivity to environmental stimulus. In fact, the abrupt switch between hydrophobicity and hydrophilicity together with the conformation change of the polymer chains responsive to environmental stimulus endows the stimuli-responsive polymer tunable ability to release the foulants, i.e., self-cleaning properties [11]. Yu and coworkers modified TFC polyamide membranes by depositing P (NIPAM-co-Am) on the membrane surface [12,13]. It was found that the application of PNIPAm layer improved the fouling resistance and cleaning ability of the membrane. However, in spite of the encouraging results, modulating the temperature of the RO feed will be hard to implement in the system, if considering the energy cooling down or heating up tons of the feed solution.

Zwitterionic polymers have been the focus as an excellent material for fouling control of membranes very recently [14–16]. However, their salt-responsive conformation change and adsorption properties have been rarely visited for membrane applications [17]. As one of the typical zwitterionic polymer, poly (4-(2-sulfoethyl)-1-(4-vinylbenzyl) pyridinium betaine) (PSVBP) exhibits salt-responsive properties. It is insoluble in pure water but readily soluble in the presence of halide salt. In this work, PSVBP was grafted onto a commercial TFC RO membrane via redox initiated graft polymerization. It is anticipated that the resulting membrane will have anti-fouling and easy-cleaning properties. The mechanism is shown in Scheme 1. PSVBP itself can form a hydration layer on the membrane surface, alleviating foulants adsorption and accumulation. In addition, PSVBP chains will fold, forming a collapsed hydration layer at pure water or low salinity conditions, and will extend, forming a swelling hydration layer at high salinity conditions. In that case, the foulants can be released by tuning the salt concentration in the feed solution. In order to test this theory, fouling and cleaning experiments were conducted. In addition, the effects of PSVBP grafting on membrane surface composition, hydrophilicity and charge properties were addressed in detail.

2. Experimental

2.1. Materials

Commercial TFC RO membranes used in this study were XLE RO membrane purchased from Dow chemical Co. (Filmtec, USA). 2-(4-pyridine) ethanesulfonic acid, 4-vinylbenzyl chloride, sodium persulfate, sodium bisulfite and bovine serum albumin (BSA) were purchased from Sigma Aldrich Co. Potassium chloride and sodium chloride were purchased from kermel Co (china). All chemicals were analytical purity grade and used as received. SVBP was synthesized according to a method reported in the literature [18]. The deionized water (DI water) with a conductivity of less than 1 μs/cm was obtained from a Millipore Milli-Q Advantage A10 water purification system having a stable effluent pH of 6.8–6.9 (18.2 MΩ cm^{-1} at 25 °C, 1.2 μg/L TOC, Billerica, MA, USA) and was used as the solvent for preparing aqueous solution as well as for soaking and rinsing the membranes. The membrane coupons were soaked in DI water for 24 h with the water changed every 6 h to remove the membrane additives.

2.2. Synthesis of the PA-g-PSVBP membrane

The PA-g-PSVBP membrane was synthesized by free radical graft polymerization of SVBP from the XLE membrane surface initiated by the $K_2S_2O_8$–$NaHSO_3$ redox system. For a typical operation, the XLE membranes were split into 20 cm × 5 cm and immersed in aqueous solution containing SVBP (2 mmol L^{-1}), $K_2S_2O_8$ (1 mmol L^{-1}) and $NaHSO_3$ (1 mmol L^{-1}). After purging with pure nitrogen for 20 min to remove all of the dissolved oxygen, the reaction vessel was sealed and put into a water bath thermo state at 25 °C. After keeping the reaction for a prescribed time, the obtained membranes were thoroughly washed with DI water for 24 h to remove the residual reactant and homopolymer.

2.3. Membrane surface characterization

ATR-FTIR spectra of the membrane surface were determined using a Vector 22 FTIR spectrometer (Bruker, Germany). The membrane samples were entirely rinsed with DI-water and then dried at 25 °C in a vacuum oven overnight before analysis. ATR-FTIR spectra of the membranes were recorded in wave number of 600–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher K-alpha X-ray photoelectron spectrometer (Thermo Scientific, USA) with a monochromatic Al-K α X-ray source ($h\nu = 1486.6$ eV). Survey XPS spectra were obtained by sweeping over 0–1000 eV electron binding energy with a resolution of 1 eV. Each survey spectrum was the average of five survey scans. Scanning electron microscopy (SEM) images were taken on a field emission SEM (Quanta 200, FEI, USA). Imaging was carried out at 3 kV with a working distance of 7.7 mm. The dry membrane samples were mounted on aluminum stubs, using aluminum tape and Au coated before imaging. The water contact angles of pristine and modified membrane surfaces were measured by the circle-fitting method using a Drop Shape Analysis System DSA 100 (Krüss, Switzerland) at 25 °C and 60% relative humidity. Droplets of distilled water (2 μL) were placed at different spots of the membrane surface. The obtained value is an average of 5 measurements. The zeta potentials were calculated based on the streaming potential method reported previously [19,20]. A Teflon gasket was placed as a spacer between the