Water Research 104 (2016) 389–396

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Zwitterions coated hollow fiber membranes with enhanced antifouling properties for osmotic power generation from municipal wastewater

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ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
10 August 2016
Accepted 21 August 2016
Available online 23 August 2016

Keywords:
Poly(ether sulfone)
Pressure-retarded osmosis
Thin-film composite membranes
Anti-fouling
Zwitterion
Osmotic power

ABSTRACT

Fouling on pressure-retarded osmosis (PRO) membranes leads to severe declines in water flux and power density because their porous substrates are facing the wastewater feed. Thus, inorganics, organics and microorganisms in the wastewater are prone to depositing on the substrate surface and even in its pores. In order to reduce the fouling propensity, coating the substrate surface of PRO membranes with zwitterionic materials proves to be an effective way. In this work, 2-methacryloyloxyethylphosphorylcholine (MPC), is modified and grafted onto the polydopamine (PDA) coated poly (ether sulfone) (PES) hollow fiber substrate. Both the synthesis and surface coating of MPC are easy and facile to be scaled up. Compared with the pristine PES and PES-PDA substrates, the MPC modified substrate (PES-PDA-MPC) exhibits high resistance to protein adsorption as well as bacteria adhesion. By using a state-of-the-art thin-film composite poly (ether sulfone) (TFC-PES) hollow fiber membrane as the control for power generation, the power density of the TFC-PES-PDA-MPC membrane can achieve as high as 7.7 W/m^2 while the unmodified one has only 6.0 W/m^2 after 3 h's PRO tests. In conclusion, the osmotic power generation of PRO membranes can be significantly sustained by modifying the membrane surface with zwitterions.

1. Introduction

The rapid increases in energy consumption and CO_2 emissions have accelerated the exploration of renewable and green energy (Evans et al., 2009). Among them, osmotic energy released from the mixing of water streams with different salinities via pressure retarded osmosis (PRO) has attracted global attention owing to its abundance and renewability (Achilli et al., 2009; Alsvik and Hägg, 2013; Gerstandt et al., 2008; Han et al., 2015; Kim et al., 2015; Ramon et al., 2011). In a typical PRO process, water from the low salinity solution (i.e., feed solution) can spontaneously pass through a semi-permeable membrane to the high salinity solution (i.e., draw solution) due to their chemical potential difference. Consequently, the salty water compartment has an expanded volume with a higher pressure. By releasing the pressurized draw solution through a hydro-turbine, one can harvest electricity as the osmotic energy.

Two factors primarily affect the productivity of a PRO process; namely, the PRO membrane and the feed pair. An ideal PRO membrane requires a high water permeability, high salt rejection, low concentration polarization, high mechanical strength, and minimal fouling tendency. During the last decade, a significant progress has been made on PRO membranes in the configurations of flat-sheet (Bui and McCutcheon, 2014; Cui et al., 2014; Li et al., 2012, 2013; Song et al., 2013; Yip et al., 2011) and hollow fiber (Chou et al., 2013; Han et al., 2013, 2015; Li and Chung, 2014; Sun and Chung, 2013; Zhang and Chung, 2013). In case of feed pairs, in addition to the conventional pair of river water and seawater, the feed pair of concentrated reverse osmosis (RO) brine and wastewater from municipal recycle plants has received great attention because it has a higher salinity gradient and can potentially produce a higher power density (Achilli and Childress, 2010; Altaee and Sharif, 2015; Chung et al., 2015; Han et al., 2015; Kim et al., 2015; Li and Chung, 2014; Sun and Chung, 2013; Thorsen and Holt, 2009; Wan and Chung, 2015, 2016; Zhang and Chung, 2013). In addition, this new feed pair may add extra values such as lowering the overall energy consumption for RO (Chung et al., 2015; Wan and Chung, 2016), diluting the seawater RO brine for

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http://dx.doi.org/10.1016/j.watres.2016.08.045
0043-1354/

ecologically-friendly disposal (Chung et al., 2015; Han et al., 2015) and saving some seawater pretreatment costs (Achilli et al., 2009). However, the new feed pair also creates challenges.

It is known that membrane fouling due to the deposition of inorganic and organic materials and microorganisms onto its surface and pores leads to a rapid decline of power density (Mi and Elimelech, 2010; Xie et al., 2013), but the situation becomes more severe if the wastewater from municipal recycle plants is used as the feed (Chen et al., 2016, 2014, 2015; Gu et al., 2013; She et al., 2013; Wan and Chung, 2015; Zhang et al., 2014). Wan et al. managed to obtain a maximum power density as high as 27 W/m^2 using 1 M NaCl solution and de-ionized water as the feed pair (Wan and Chung, 2015). However, the power density declines fast if de-ionized water was replaced by the municipal wastewater. The fouling not only affects the membrane performance adversely, but also increases the operation cost because of the need for frequent cleaning and maintenance (Chen et al., 2015; She et al., 2013). This necessitates the development of PRO membranes with superior antifouling properties.

Many antifouling methods have been developed for conventional microfiltration, ultrafiltration and RO membranes (Kang and Cao, 2012; Lei and Ulbricht, 2014; Rana and Matsuura, 2010; Escobar and Van der Bruggen, 2011). However, only limited antifouling strategies have been proposed to enhance the anti-fouling properties of PRO membranes. This is due to the fact that fouling occurs differently between PRO and conventional membranes. In RO membranes, fouling mainly takes place on the outer surface of the selective layer, while fouling may occur severely on and in the porous substrate as well as just beneath the selective layer of PRO membranes (Xiong et al., 2016). In addition, challenges may arise from (1) the complexities of internal concentration polarization and reverse salt flux in PRO and (2) the balance among hydrophilicity, mechanical strength, and power density during membrane modifications. One must only modify the porous substrate without sacrificing the mechanical strength and power density. Li et al. developed a dendritic hyperbranched polyglycerol anchored PRO membrane, which is able to reject proteins and bacteria, but not inorganic scaling (Li et al., 2014). Therefore, in the later study, they functionalized the hyperbranched polyglycerol polymer with negatively charged functional groups (Li et al., 2016). Recently, Cai et al. designed a zwitterionic copolymer modified PRO membrane with superior fouling resistance to nonspecific foulants (Cai et al., 2016). Zwitterion is a molecule which contains both positive and negative functional groups while the overall charge neutrality is maintained. It has received increasing attention recently due to its excellent anti-adhesive properties against protein and bacteria (Yu et al., 2014; Zheng et al., 2016). However, the procedures for the synthesis of the zwitterionic copolymers are complicated that may hinder the module scale-up.

Therefore, it is imperative to find simple and effective zwitterions for the surface modification of PRO membranes in order to accelerate the commercialization of PRO for osmotic pressure generation. To meet this objective, this work aims (1) to design and fabricate zwitterionic material coated PES hollow fiber membranes by both simple synthesis and coating approaches, and (2) to investigate their anti-fouling properties for osmotic power generation using wastewater from municipal recycle plants. A state-of-the-art thin-film composite poly (ether sulfone) (TFC-PES) hollow fiber membrane was employed in this study for various surface modifications. As shown in Fig. 1, we incorporated 2- methacryloyloxyethylphosphorylcholine (MPC) on the outer surface (i.e., the substrate surface) of TFC-PES membranes via three steps: (1) The outer surface of TFC-PES membranes was treated by polydopamine (PDA) to obtain PES-PDA; (2) MPC was first converted to thiolated-2-methacryloyloxyethyl phosphorylcholine (MPC-SH) in order to facilitate its grafting onto the PES-PDA surface via Michael addition; (3) MPC with a thiol functionality was grafted onto the PES-PDA substrate via Michael addition. It should be noted that MPC-SH has proven to be not cytotoxic to human lung cells in a previous study since the MPC monomer has the same zwitterionic group as phospholipid (Sangsuwan et al., 2016). The high biocompatibility of MPC-SH avoids any secondary contamination to the water source. To the best of our knowledge, TFC-PES membranes grafted by simple but effective zwitterions have not been investigated in the field of osmotic power generation via PRO processes.

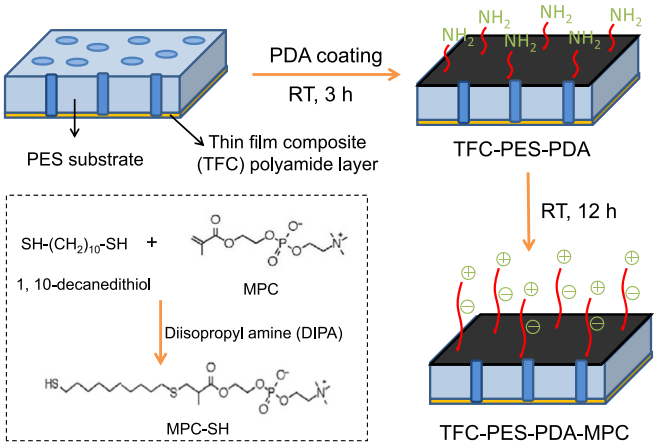

Fig. 1. Illustration of the synthesis of MPC-SH and schematic procedure for the fabrication of TFC-PES-PDA-MPC membranes.

2. Materials and methods

2.1. Materials

Diisopropylamine (≥99.5%), 2-methacryloyloxyethyl phosphorylcholine (MPC, 97%), dopamine hydrochloride (99%), triethylamine (≥99%), tris(hydroxymethyl)aminomethane (tris, ≥99.8%) and fluorescein isothiocynate conjugated bovine serum albumin (BSA-FITC) were all purchased from Sigma-Aldrich and used as received without further purification. 1, 10-decanedithiol (HS-C10-SH) was obtained from TCI (Tokyo, Japan). Gram-negative *Escherichia coli* (*E. coli*, ATCC DH5α) and Gram-positive *Staphylococcus aureus* (*S. aureus*, ATCC 25923) were from American Type Culture Collection, Manassas, VA, USA.

2.2. Synthesis of thiolated-2-methacryloyloxyethyl phosphorylcholine (MPC-SH)

MPC-SH was synthesized by a previously reported method (Goda et al., 2013; Sangsuwan et al., 2016). Briefly, MPC (1.48 g, 5 mmol) and 1, 10-decanedithiol (HS-C10-SH) (2.06 g, 10 mmol) were dissolved in 20 ml degassed chloroform. Diisopropylamine (27.9 μL, 0.2 mmol) was then added to the mixture solution. After stirring for 20 h at room temperature, the solution was precipitated into acetone. The solid product collected was dried and dissolved in water. MPC-SH was obtained as white powder after freeze-drying.

2.3. Preparation of TFC-PES-PDA-MPC hollow fiber membranes

The PES hollow fiber substrate was spun from poly (ether sulfone) as previously described (Wan and Chung, 2015; Zhang and Chung, 2013). Then a thin polyamide selective layer was synthesized on its inner surface by interfacial polymerization (Li et al.,