

Reverse osmosis membranes with guanidine and amine enriched surface for biofouling and organic fouling control



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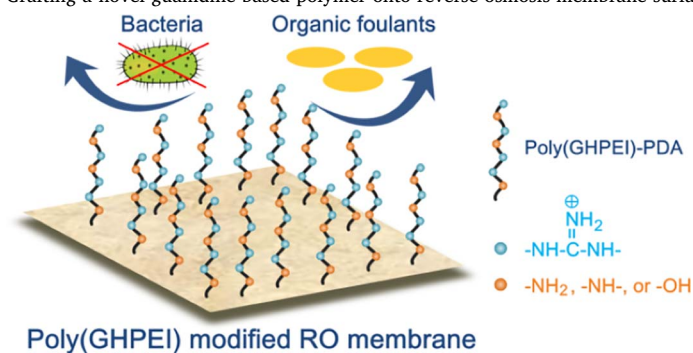
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GRAPHICAL ABSTRACT

Grafting a novel guanidine-based polymer onto reverse osmosis membrane surface to achieve excellent antifouling and antibacterial properties.



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ABSTRACT

Biofouling and organic fouling are intractable problems that degrade the separation performance of reverse osmosis (RO) membranes. In the present work, we report a novel guanidine-based polymer modified RO membrane with excellent antifouling and antibacterial properties. The guanidine-based polymer, namely poly (guanidine-hexamethylenediamine-PEI) (poly(GHPEI)), was first synthesized by a polycondensation method. It contained plenty of guanidine and amine groups and its minimum bactericidal concentration was measured as 12.5 mg/L. Then the poly(GHPEI) modified membrane was fabricated via polydopamine (PDA) immobilization. A series of characterizations including surface morphology, hydrophilicity and charge were performed to analyze the structure changes resulting from poly(GHPEI) modification. Permeate flux and antifouling properties were also measured to investigate the separation properties of the modified membranes. Besides, membrane antibacterial activity and antibiofouling property were evaluated through the sterilization tests against *Escherichia coli* and *Bacillus subtilis*, and the flux decline ratio after immersing the membrane into bacterial suspension, respectively. The results indicated that the grafting modification of poly(GHPEI) endowed the RO membrane with excellent antifouling and antibacterial properties.

1. Introduction

With a great demand for fresh water due to population growth and

industrialization, desalination plays an increasingly significant role in relieving water quality and scarcity problems. Reverse osmosis (RO), as a membrane-based water separation process, has been considered as a

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promising and reliable desalination technology due to its efficiency, low cost and environmental friendliness [1–3]. However, the RO membranes are inevitably suffering severe organic fouling or biofouling once being in contact with feed streams that carry dissolved molecules and microorganisms. The foulants, in particular biofilm attaching on the membrane surface, lead to a dramatic decrease in permeate flux and an increased overall energy requirement of the separation process as a consequence. Thus, organic fouling and biofouling resistance has been one of the primary challenges facing membrane separation processes [4–6]. In the recent decades, considerable efforts have been taken to overcome this challenge by developing membranes with antifouling and antibacterial properties [6,7]. Thin-film composite (TFC) polyamide (PA) membrane has been a mainstream separation membrane used in RO process due to its unrivaled productivity and selectivity performance [8]. In order to further reduce the desalination cost, both industrial and academic researchers are pursuing to prevent the fouling from the rough PA active layer. Surface grafting, as an effective modification approach, has been extensively applied in developing novel membranes due to its simple, efficient and flexible procedure [9–11]. To achieve antifouling and antibacterial properties, the functional materials grafted onto RO membrane surface should be well designed to avoid the attachment of foulants or inhibit the growth of microorganisms [12]. Recently, there are many reports addressing both the biofouling and organic fouling control [13–17].

In order to mitigate the organic fouling, hydrophilic polymers or nanofillers were grafted into the membrane surface to obtain a hydrophilicity improvement and a smooth surface structure. The study of Ni et al. [18] improved the antifouling performance of RO membrane by coating a novel random terpolymer onto the membrane surface. The synthesized terpolymer contained many hydrophilic moieties including quaternary ammonium, hydroxyl and ammonium groups. The study of Ma et al. [19] incorporated zwitterionic colloid nanoparticles into RO membrane surface via interfacial polymerization, resulting in notable elevation of fouling-resistant properties against three model foulants (TA, NaAlg and SDS). In addition, Zhao et al. [20] synthesized a novel diacyl chloride monomer with a phosphonate group and blended this monomer with organic phase monomers to prepare RO membranes. The antifouling property improved owing to the hydrophilic $-PO(OCH_3)_2$ groups.

Numerous antimicrobial agents have been applied to prevent the biofouling of RO membrane, such as silver nanoparticles, copper nanoparticles, graphene oxides, and polymers with quaternary ammonium (N^+) group [21–25]. Recently, polymers containing guanidine or biguanidine groups have received an increasing attention and proved to be effective cationic antimicrobial agents [26,27]. Guanidine and biguanidine polymers have shown outperforming property over other antimicrobial agents, such as the broad-spectrum of antibacterial activity and low mammalian toxicity, and thereby have growing industrial, therapeutic and clinical applications [28–30]. Their antibacterial property against Gram-positive and Gram-negative bacteria is ascribed to the electrostatic attractions between the cationic guanidine and the negative charged surface of bacterial cell containing anionic phospholipids, proteins and lipopolysaccharides, and the consequential leakage of intracellular contents resulting in bacterial death [31,32]. As a member of the polymeric guanidine family, polyhexamethylene guanidine hydrochloride (PHGH) was a limited commercially available product in the form of powder or water-soluble hydrochloride as a mixture of oligomers of different chain lengths [32,33]. The study of Cao et al. [34] reported the fabrication of composite nanofiltration membranes by using interfacial polymerization of PHGH and trimesoyl chloride (TMC). The as-prepared membranes demonstrated an effective bacterial inhibition against *Escherichia coli* (*E. coli*) and an enhanced antibiofouling performance. Nikkola et al. [35] coated RO membrane with PHGH modified polyvinyl alcohol (PVA) to improve antifouling and antimicrobial performance but rendered a sharply decreased water flux. In addition, Zhao et al. [36] coated poly(vinylidene fluoride)

ultrafiltration membrane with PHGH crosslinked PDA to obtain excellent antifouling performance, while the cost of PHGH was high and the antibacterial property of PHGH was strangled. Although PHGH has been proved to be a promising antibacterial polymer, there are still some issues that limit its application in water treatment. On one hand, the reactive groups are scarce in PHGH, limiting the further grafting modification onto the membrane surface. On the other hand, the insufficient quantity of hydrophilic groups in PHGH is unfavorable for building antifouling or antibacterial surface to reduce the deposition of organic molecules or bacteria cells.

In this work, we propose not only a novel guanidine-based polymer with high antibacterial efficiency, but also a polydopamine (PDA) immobilization method to impart guanidine groups onto the active layer of polyamide TFC membrane. In particular, the guanidine-based polymer, poly(guanidine-hexamethylenediamine-PEI) (poly(GHPEI)), was first synthesized via the direct melt polycondensation of guanidine hydrochloride (GH), 1,6-hexamethylenediamine (HMDA) and polyethyleneimine (PEI). The synthesized poly(GHPEI) was assumed to contain majority of amine groups from PEI molecules, which could maintain to be hydrophilic and reactive in the following grafting modification. As a bioinspired adhesive polymer, polydopamine (PDA) has been widely employed as an interfacial glue during the surface modification [37]. Here, PDA was assisted to graft poly(GHPEI) onto the surface of commercial polyamide TFC membrane. The catechol and quinone groups of PDA could react with amine groups of poly(GHPEI) through the Michael-type addition or Schiff base reaction [38,39], ensuring the successful and stable introduction of guanidine groups onto membrane surface. The chemical composition and antibacterial performance of poly(GHPEI) were characterized and evaluated. The modified polyamide TFC membranes were characterized in terms of chemical composition, hydrophilicity, morphology, surface roughness and surface charge. Meanwhile, the effects of poly(GHPEI) modification on membrane permeate flux, salt rejection and antifouling performance were evaluated by using a bench-scale cross-flow RO unit. *E. coli* and *Bacillus subtilis* (*B. subtilis*) were used to examine the antibacterial property of the modified membranes.

2. Experimental

2.1. Materials

The commercial TFC RO membranes (BW30FR) were obtained from Dow Filmtec (USA). Guanidine hydrochloride (GH) (99.5%), 1,6-hexamethylenediamine (HMDA, 99.5%), tris (hydroxymethyl) aminomethane (Tris, 99%), 3-hydroxytyramine hydrochloride (98%, dopamine), polyethyleneimine (PEI, 99%, branched, M_w of ~ 600 g/mol), bovine serum albumin (BSA, 96%) and sodium alginate (SA, 99%) were all purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Methanol of gas chromatography grade, sodium hydrogen sulfite, sodium chloride and calcium chloride were purchased from Jiangtian Chemical Reagent Co. Ltd. (Tianjin, China). All the reagents mentioned above were used without further treatment. Deionized (DI) water was obtained from an ultrapure laboratory water purification system (Hitech Instruments Co. Ltd.) with a conductivity of no greater than 15 $\mu S/cm$.

2.2. Poly(GHPEI) synthesis and characterization

The synthesis of poly(GHPEI) was conducted on the basis of the synthesis procedure of PHGH reported in literature [33,34]. Fig. 1(a) shows the chemical structure of reagents and the synthesis route of poly(GHPEI). Typically, GH (10 g, 105 mmol), HMDA (10 g, 86 mmol) and PEI (5 g, 8.3 mmol) were added into a 250 mL three-necked flask and mixed together. The reaction process consisting of two stages was carried out under the nitrogen protection with mechanical stirring. The mixture first reacted at 90 °C for 1 h and then at 160 °C for 5 h. The

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