



Construction of antibacterial layer on polyvinylchloride three-channel hollow fiber membranes



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ARTICLE INFO

Article history:

Received 10 March 2016

Received in revised form 23 May 2016

Accepted 24 May 2016

Available online 1 June 2016

Keywords:

Remote plasma

PVC hollow fiber membrane

Graft

Antibacterial

ABSTRACT

The inner surfaces of polyvinylchloride (PVC) three-channel hollow fiber membranes were successfully modified with poly(methacryloxyethyl benzyl dimethyl ammonium chloride) (PDMAE-BC) in a module scale via remote plasma-induced surface graft polymerization method. After grafting a PDMAE-BC layer, the PVC surface hydrophilicity was improved greatly due to the introduction of large amounts of oxygen and nitrogen containing polar groups onto polymer backbone. This hydrophilicity improvement directly led to a high pure water flux and a good antifouling property for the obtained PVC-PDMAE-BC membrane module. Meanwhile, the inner surface morphologies of modified PVC membranes changed slightly and the surface structures were maintained well. The tensile strength, though decreased slightly at the remote plasma-treated stage, showed no significant change during overall grafting process. The obtained PVC-PDMAE-BC membrane module exhibited highly effective and stable antibacterial activities against *Escherichia coli*. The antibacterial efficacy of PVC-PDMAE-BC membrane module with only 6 fibers can achieve about 96.3% and could be further enhanced by increasing the packing density. The antibacterial membrane module may have great potential applications in actual wastewater treatment and membrane bioreactor (MBR).

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Introduction

Biofouling and the subsequent formation of biofilm have been generally considered as a bottleneck problem in membrane processes related biotechnology for water treatment [1,2]. During the long-term running in water condition, the adherence of some bacteria to membrane surfaces is a naturally occurring phenomenon. Moreover, once bacteria are attached on the membrane surface, a multistep process eventually leads to the formation of a biofilm [3]. In pilot-scale membrane bioreactors (MBRs) treating municipal wastewater, this biofouling (biofilm) not only significantly shades the overall membrane performance and increases energy consumption, but also shortens the lifespan of membrane modules [4]. Therefore, to decrease the biofouling due to biofilm

formed by bacteria on the membrane surface, creating an antibacterial layer on the membrane surface is desired.

To inhibit biofilm formation on membrane surfaces, there are generally three principal strategies: contact-active, biocide-releasing and microbe-repelling surfaces [5]. As we know, the biocide-releasing acts through a release-based mechanism and biocides are therefore exhausted over time [6]. The microbe-repelling can reduce initial adhesion of bacteria and delay biofilm growth, but bacteria could not be killed. Differently, the contact-active relies on the disruption of the bacterial cell wall or on the removal of structurally critical membrane ions [7]. Till now, numerous antibacterial agents, such as polycations [3,8–13], phosphonium salts (e.g., N-halamine compounds [14]), enzymes (e.g., lysozyme [15]) and antimicrobial peptides (e.g., Peptide Chrysopsin-1 [7]), have been utilized to create antibacterial surfaces via this contact-active strategy. Among these antibacterial agents, polycations have been widely used to fabricate different antibacterial membrane surfaces because of their excellent life safety. In Mei et al.'s work [3], a polycation, polyhexamethylene guanidine hydrochloride (PHGH), was selected and successfully grafted onto polyacrylonitrile (PAN) nanofibrous membrane surfaces. The obtained

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PAN-PHGH membranes not only possessed high bactericidal efficiency against *Staphylococcus aureus* and *E. coli*, but also exhibited easy-cleanability because of the incorporation of hydrophilic spacers. Wang et al. [8] immobilized polyvinyl alcohol/4-vinylpyridine (PVA-g-4VP) on polypropylene non-woven fabric (PPNWF) membrane surfaces and pore walls to improve the hydrophilic and antibacterial properties, and a more antibacterial surface was obtained after quaternizing PVA-g-4VP-PPNWF membranes with benzyl bromide. In Sui et al.'s work [10], the 2-hydroxyethyl methacrylate (HEMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) brushes were covalently immobilized onto the poly(vinylidene fluoride) (PVDF) membrane surfaces and pore walls via atom transfer radical polymerization (ATRP) method. After quaternization, both PVDF-g-PDMAEMA and PVDF-g-PDMAEMA-b-PHEMA membranes showed excellent antibacterial activity against *S. aureus*. Besides, another similar quaternary ammonium salt (methacryloxyethyl benzyl dimethyl ammonium chloride (DMAE-BC)) and its polymers also exhibited excellent bactericidal activities against *S. aureus* and *E. coli* [11]. Recently, the poly DMAE-BC (PDMAE-BC) was successfully covalently grafted onto polypropylene fibrous (PPF) flat membranes and polyethylene (PE) hollow fiber membranes via remote low-temperature plasma in our previous work [16,17]. During the long-term running in the bacteria suspension ($\sim 10^5$ cells/mL), both PPF-PDMAE-BC and PE-PDMAE-BC membranes not only exhibited a high antibacterial activity against Gram-negative *Escherichia coli* (*E. coli*), but also had an antifouling property, an increased water flux and an easy-cleanability. In all, these studies indicated that membrane surfaces functionalized with polycations showed promising antimicrobial activity on contact in actual water treatment, and the non-toxic antibacterial monomer, DMAE-BC, was selected in this work.

In the past decades, different surface modification technologies, such as coating, UV irradiation, chemical reaction, surfactant adsorption, and direct/remote low-temperature plasma treatments, have been employed to prepare antibacterial membranes. And many antibacterial layers were successfully grafted onto either small flat membrane surfaces or outer surfaces of hollow fiber membranes. However, contrary to them, few detailed studies have been reported to construct antibacterial layers onto the inner surfaces for the internal-pressure type hollow membrane modules. As we know, among above technologies, remote low-temperature plasmas, which are high surface selective, environment-friendly and little damage to the bulk (low degradation), have extensively been used to modify different types of membranes [18]. Importantly, this remote plasma is a dynamic plasma flow [19] and can penetrate the thickness of the PE, PES PSF membranes and even five PC and polyethylene terephthalate (PET) track-etched flat membranes [20–22]. Thus, this dynamic plasma flow is especially suitable to activate the inner surface of hollow fiber membranes for the internal-pressure type membrane module (inside-out). Moreover, the active groups (peroxides (ROOH/ROOR)) formed after plasma treatment and contacting air are chemically embedded into the polymer body. These active groups can be easily transformed to peroxyradicals (ROO^{*}) through adjusting operation temperature (≥ 60 °C) for next free radical initiated polymerization. Then, the following graft polymerization layer, which is also covalently bound onto the membrane surface, is very stable. Besides, for the remote plasma-induced graft polymerization process, the plasmas and monomer solutions can be introduced into hollow fiber membrane channels continuously. Then, some commercial hollow fiber membrane units may be modified in their original modules.

In this study, the Ar plasma flow was introduced through the tube-side of membrane module continuously (Fig. 1) to activate inner surfaces of PVC hollow fiber membranes in a module scale,

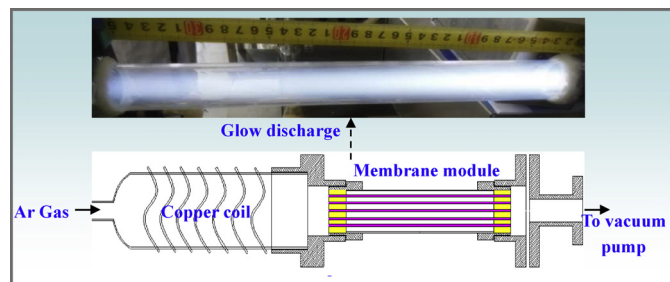


Fig. 1. Remote plasma processing device for membrane modification in a module scale.

followed by contacting air and DMAE-BC monomer solution. Then, PDMAE-BC antibacterial layers were constructed onto the inner surfaces of polyvinylchloride (PVC) three-channel hollow fiber membranes via this remote plasma-induced graft polymerization process. The new PVC-PDMAE-BC hollow fiber membranes were analyzed using water contact angle (CA), scanning electron microscopy (SEM), atomic force microscope (AFM) and Fourier transform infrared spectroscopy (FTIR) spectroscopy. The membrane performances before and after modification, such as mechanical property, pure water flux, antibacterial activity against *E. coli*, protein permeation flux and rejection rate, were also investigated.

Experimental

Materials

PVC hollow fiber membranes with three channels (Internal-pressure type, molecular weight cutoff: 70 kDa, outside diameter: 3 mm, inside diameter: 723 μm) were supplied by Shandong Zhong Shui Yuan membrane technology Co. Ltd. Before packing in a 25 cm length module [19], the PVC hollow fibers were cut into about 30 cm, immersed in ethanol for 24 h and dried at 60 °C for 6 h. The packing numbers were 6, respectively.

Dimethylaminoethyl methacrylate (DMAEMA) was purchased from Li Deshi Chemical Technology Co., Ltd. in Beijing; Benzyl chloride, methylene dichloride (BC), hydroquinone, ethanol and acetone from Guangfu Fine Chemical Co. Ltd.; sodium chloride (AR, NaCl) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, AR) from Beijing chemical works; Ar (>99.99%) and N_2 (>99.99%) gas from Beijing Yongteng Gas Company; Peptone and yeast extract from Oxoid Ltd., Basingstoke, Hampshire, England; and agar from Meng Yimei Biological Technology Co. Ltd. Gram-negative *Escherichia coli* (*E. coli*, ATCC DH5 α) was obtained from Biological Engineering lab of Beijing Institute of Technology. DMAE-BC monomer was synthesized by us according to Lu et al.'s work [11]. Bovine serum albumin (BSA) (67 kDa, Sinopharm Chemical Reagent Co., Ltd.) was selected as a model foulant.

Remote plasma-induced graft polymerization process

The remote plasma processing device for membrane modification in a module scale is shown in Fig. 1. The detailed operation steps of this device were described in our previous work [19]. Differently, the dynamic plasma flowed through the tube-side of membrane module continuously in this work (Fig. 1). By this way, the inner surface of hollow fiber membranes can be easily activated in a module scale. In this experimental system, the standard active plasma flow was generated at 60 W discharge power, 10 Pa pressure and 2.0 mL(STP)/min Ar flowrate. The membrane module was exposed in the plasma flow for 3 min.

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