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Enhancing antibacterial performances of PVDF hollow fibers by embedding Ag-loaded zeolites on the membrane outer layer via co-extruding technique

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ABSTRACT

Ag-loaded zeolites were synthesized and embedded into the outer layer of poly(vinylidene fluoride) (PVDF) dual-layer hollow fiber membrane (D) using a dry-jet wet-spinning co-extruding technique. The distribution of the Ag-loaded zeolites in the outer layer was confirmed by field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX). It was found that the D contained only 54% of the amount of Ag-loaded zeolites that were distributed throughout the cross section of PVDF single-layer hollow fiber membrane (S), as calculated by thermogravimetric analysis (TGA). However, D showed excellent antibacterial efficiency and resistance to bacterial adhesion because of the higher concentration of Ag^+ in the outer layer of the membrane. The surface morphologies, pure water flux, mean pore size, pore size distribution, and thermal stability of both PVDF membranes were also investigated.

1. Introduction

Membrane techniques have been widely used as effective and energy-saving techniques for water treatment through processes such as microfiltration [1], ultrafiltration [2], nanofiltration [3], reverse osmosis [4]. Poly(vinylidene fluoride) (PVDF)—one of the most outstanding polymeric membrane materials—has been widely researched and applied in membrane bioreactor systems [1,5]. Because of their hydrophobicity, PVDF membranes tend to be fouled by organics [6,7] and microorganism [8,9] in the separation process; this fouling decreases the permeability and increases the operating cost. To reduce the fouling caused by organics [5–7], much effort has been made to improve the hydrophilicity of PVDF membranes; however, only a few studies report the reduction of direct fouling caused by bacteria.

The strategies to fabricate PVDF membranes with antibacterial properties can be divided into three categories: (i) addition of inorganic antibacterial agents [10–12], (ii) hydrophilic surface modification [7,13], and (iii) combination of the above two strategies [14]. Damodar et al. [11] showed that a PVDF composite membrane with 4% TiO_2 possessed the highest antibacterial property due to the presence of reactive oxygen species like $O_2^{\cdot-}$, H_2O_2 and $HO^{\cdot}$. Sui et al. [7] bonded poly(hydroxyethyl methacrylate) (PHEMA) and poly((dimethylamino)ethyl methacrylate) (PDMAEMA) brushes onto PVDF membrane surface via atom transfer radical polymerization (ATRP), and obtained 98% antibacterial efficiency. Rahimpour et al. [14] combined the hydrophilic modification and antibacterial agent together to prepare PVDF/SPES blend membrane with 4 wt% TiO_2 nano-particles, to demonstrate dramatic photo-anti-bactericidal effect on *Escherichia coli*. However, most reports above were focused on PVDF flat sheet membranes. Few were reported on improving the antibacterial properties of PVDF hollow fibers, especially for dual-layer ones.

As an effective antibacterial agent, the antibacterial activity of Ag-loaded zeolite has been explored [10,15–19]. However, the mechanism of antibacterial action is far from being completely understood. In this paper, we report the successful fabrication of antibacterial PVDF single- and dual-layer hollow fibers via phase inversion by a dry-jet wet-spinning technique. Ag-loaded zeolites were introduced into the bulk of the single-layer fiber and the outer layer of the dual-layer fiber. The embedding of Ag-loaded zeolites on the outer layer of the dual-layer hollow fiber promoted the enrichment of Ag^+ and improved antibacterial efficiency. The structures and properties of the resulting single-layer and dual-layer antibacterial PVDF hollow fiber membranes were investigated and compared.

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2. Materials and methods

2.1. Materials

Poly(vinylidene fluoride) (PVDF, 301F, Solvay) was applied by CMDIC Xiamen Import & Export Co., Ltd. China. N,N-dimethyl acetamide (DMAc) and hydrochloric acid (HCl) were analytical reagents, together with polyvinyl pyrrolidone (PVP K-30, M_w = 40,000) were all purchased from Sinopharm Chemical Reagent Co., Ltd. China. NaY zeolites were provided by Anhui Mingmei MinChem Co., Ltd. China. Silver nitrate ($AgNO_3$), sodium chloride, glucose, anhydrous sodium dihydrogen phosphate, anhydrous disodium hydrogen phosphate, absolute ethanol, glutaradehyde, peptone, beef extract, yeast extract were all purchased from Aladdin Chemistry Co., Ltd. China. Nutrient agar and *Escherichia coli* (*E. coli*, ATCC 25922) were purchased from Guangdong huankai microbial sci. &tech Co., Ltd. China. 4′,6-diamidino-2-phenylindole (DAPI) was supplied by Beijing Solarbio science & Technology Co., Ltd. All reagents were used as received. Deionized water was used during the whole experiment.

2.2. Preparation of Ag-loaded zeolites

The incorporation of silver in zeolites was carried out by ion exchange reaction. 10 g NaY zeolite particles were added into 0.1 mol/L $AgNO_3$ solution at the solid–liquid ratio of 1–10, and the mixture was stirred continuously at 60 °C for 4 h. The whole ion exchange reaction process was carried out in the dark. After that, the particles were centrifugated several times until Ag^+ in the supernatant fluid could not be detected by HCl titration. Then the prepared Ag-loaded zeolites were dried in a vacuum oven at 60 °C for 24 h before any characterization tests and further use.

2.3. Preparation of hollow fiber membranes

The PVDF hollow fiber membranes were fabricated through a dry-jet wet-spinning process via co-extruding by a triorifice spinneret. The dimensions of these three channels are ⌀1.70:1.50 mm (o.d.:i.d. of the outer orifice), ⌀1.20:0.70 mm (o.d.:i.d. of the middle orifice) and ⌀0.40 mm (diameter of the inner orifice), respectively. The spinning solutions were prepared as follows: the pre-calculated quantity of PVDF powders and PVP (K-30) were added in DMAc, stirred at 60 °C for 24 h until the polymer powders were totally dissolved, then the Ag-loaded zeolites were added in the solution and stirred at 60 °C and 1000 rpm for another 24 h. At last, the solution was degassed at 60 °C under negative pressure to remove air bubbles produced in the process of stirring. The compositions of the spinning solutions and the spinning conditions were listed in Tables 1 and 2 respectively. The dope solutions were extruded by two high pressure syringe pumps (Model 74903-00 series, Cole-Parmer). There were only a few differences between the fabrication process for the single- and dual-layer membranes: the outer orifice was not used when preparing the single-layer membrane and other conditions were the same as the dual-layer membrane. The fabricated polymeric-matrix composites membranes were stored in deionized water at room temperature for about 72 h, and the water was changed every 24 h, in order to remove the residual solvent and additive. Finally, the composite membranes were dried at room temperature after immersed in absolute ethanol 30 min for further characterization. Wet membranes were directly used for the test of filtration experiment.

Table 1
Composition (wt%) of the spinning solutions.

Membranes		PVDF	PVP	DMAc	Ag-loaded zeolites
S		15	7	77	1
D	Inner layer	15	3	82	0
	Outer layer	15	7	77	1

S: single-layer hollow fiber membrane; D: dual-layer hollow fiber membrane.

Table 2
Spinning parameters of the PVDF hollow fiber membranes.

Parameters	Values
Bore fluid	Deionized water
Bore fluid temperature (°C)	30
Coagulation bath	Tap water
Coagulation bath temperature (°C)	30
Air gap (cm)	10
Bore fluid flow rate (mL/min)	20
Dope flow rate S	17
Dope flow rate D (inner layer)	17
Dope flow rate D (outer layer)	11
Winding-up speed (m/min)	12

2.4. Characterization of Ag-loaded zeolites

The crystalline structures of the zeolites were characterized by Powdery X-ray diffraction (XRD, Bruker AXS D8 Advance, Germany) and the morphologies were examined with FE-SEM (Hitachi S-4800, Japan). The Ag^+ content that loaded in the zeolites was measured by the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin–Elmer Optima 2100, US).

2.5. Characterization of PVDF hollow fiber membranes

The morphologies of hollow fiber membranes were observed by a FE-SEM. The membranes were fractured in the liquid nitrogen to obtain the cross-section. The fractured membranes were coated with platinum under vacuum. EDX (Hitachi S-4800, Japan) was used to detect the zeolites on the membrane surfaces.

The pure water flux was measured by a self-made dead-end filtration cell. Before the tests, the fibers with effective length of 70 cm were pre-compressed at 0.12 MPa for 30 min to compromise the compaction effect, then the pure water flux was tested at 0.1 MPa via outside-in module. The average pure water flux was calculated from three tests. The pore sizes and pore size distribution of the membranes were determined by a liquid–liquid porometer (LLP-1200A, Porous Materials Inc. US) as reported before [12].

TGA (Pyris Diamond TG/DTA, Perkin–Elmer) were performed to evaluate the thermal stability and the quantity of the Ag-loaded zeolites in the composite membranes. The samples were heated from 50 to 800 °C at the heating rate of 10 °C/min under a nitrogen atmosphere.

2.6. Determination of the antibacterial activity

2.6.1. Bacteria killing test

The antibacterial activities were tested using *E. coli*. The *E. coli* were cultivated in 100 mL of a 3.1 wt% yeast–dextrose broth (containing 10 g/L peptone, 8 g/L beef extract, 5 g/L sodium chloride, 5 g/L glucose, and 3 g/L yeast extract at a pH of 6.8) at 37 °C with shaking at 100 rpm for 24 h [7,20]. The bacteria were then harvested through centrifugation at 3000 rpm for 10 min. The *E. coli* cell culture was washed three times with PBS (containing 4.70 g of anhydrous sodium dihydrogen phosphate and 8.66 g of anhydrous disodium hydrogen phosphate in 1 L of deionized water, adjusted to pH 7.0), and re-suspended in PBS at a concentration of about 10^7 cells/mL. The bacterial cell concentration was measured by the optical density (OD) at 600 nm with the assumption that the