Preparation and antibacterial property of PES/AgNO₃ three-bore hollow fiber ultrafiltration membranes

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ABSTRACT

In this study, a three-bore polyethersulfone (PES) hollow fiber ultrafiltration (UF) membrane with antibacterial properties was prepared by phase inversion, using PES as the membrane material, N,N-dimethylacetamide (DMAC) as solvent, polyvinylpyrrolidone (PVP) and AgNO₃ as additives. The silver particles were detected by X-ray photoelectron spectroscopy. The effect of AgNO₃ content on the antibacterial properties and separation performance was studied in detail. The membranes showed good antibacterial activity against Escherichia coli after adding AgNO₃ and the antibacterial rate of PES/AgNO₃ UF membrane with AgNO₃ content of 1 wt% could reach 99.9% after running for 48 hours. Moreover, the bovine serum albumin solution filtration results indicated that the PES/AgNO₃ membranes had a certain degree of antifouling performance. Therefore, three-bore PES/AgNO₃ membranes have a potential application to reduce both bacterial and organic fouling in water treatment.

INTRODUCTION

Polyethersulfone (PES) is a favorable material for the preparation of ultrafiltration (UF) membranes due to its excellent chemical resistance, good thermal stability and mechanical properties (Zhao et al. 2011; Sawada et al. 2012). However, the fouling property of the membrane made from PES without modifications is not satisfactory in water treatment, which results in the loss of water throughput, increased energy usage, and system downtime for cleaning (Ciston et al. 2008; Singh et al. 2012). Among all types of fouling, biofouling cannot be reduced by pretreatment, because of its self-replicating nature (Singh et al. 2012). Therefore, it is necessary to endow the membrane with a self-antibacterial property to inhibit the development of biofilm using various techniques, including coating, surface grafting, and blending. Among these methods, blending has the advantage of easy preparation using the phase inversion method (Yan et al. 2006; Yang et al. 2011).

Silver has been widely used as an effective antibacterial metal; it exhibits a powerful antibacterial property and has a broad antibacterial spectrum toward many different bacteria. Currently, silver nanoparticles as an antibacterial agent have been widely used or studied in the UF process. Zodrow et al. (Zodrow et al. 2009) prepared silver nanoparticles (nAg) incorporated into polysulfone ultrafiltration membranes (nAg–PSf) using the wet phase-inversion process by physical blending of PSf casting solution with nAg. It was observed that the membrane exhibited antimicrobial properties towards a variety of bacteria, including Escherichia coli K12 and Pseudomonas mendocina KR1. Chou et al. (2005) prepared silver-loading asymmetric cellulose acetate (CA) hollow fiber membrane via dry jet-wet spinning technique by using N,N-dimethylformamide as a reducing agent for reducing AgNO₃ in the spinning dope into silver nanoparticles. The membrane exhibited antibacterial activity against Escherichia coli and Staphylococcus aureus.

Slistan-Grijalva et al. (2008) reported that silver ions can be reduced into silver nanoparticles by polyvinylpyrrolidone (PVP). In addition, Basri et al. reported that PVP can improve distribution of silver particles in the polymer matrix (Basri et al. 2010, 2011). The results also revealed that membrane contact angle decreased when Ag-loading was increased, mainly due to hydrophilicity improvement. Increasing the hydrophilicity of a membrane surface is widely accepted as a useful way to improve organic antifouling properties (Sawada et al. 2012).
Hollow fiber membrane has been widely used in the field of water treatment owing to its advantages including large ratio of membrane area to unit volume and being self-supporting which means it can be back-flushed for liquid separation (Yu et al. 2003). Nevertheless, the drawbacks of the hollow fiber membrane are its low strength, poor rigidity, and easy deformation, which limit the widespread use of the membrane. In this case, our group (Dang et al. 2012) have designed a novel spinneret with three bores and used it to fabricate three-bore PES hollow fiber UF membranes to improve the strength of the membranes. Moreover, these studies have also found that blending of inorganic material compounds in the membrane casting solution has led to improved hydrophilic and antibacterial performance of the membrane.

Based on our previous study, the objective of this work is to synthesize a three-bore PES hollow fiber ultrafiltration membrane loaded with silver particles, which endows it with antibacterial and antifouling properties. To characterize the membranes, water flux and rejection tests, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and contact angle were employed. Then, the antibacterial duration of these membranes was investigated by the viable cell counting technique. Finally, the antifouling performance of these membranes was examined using bovine serum albumin (BSA) solution as a foulant. To our knowledge, there are few reports about the fabrication of PES/AgNO3 three-bore hollow fiber ultrafiltration membrane with both antibacterial and antifouling properties.

**EXPERIMENTAL SECTION**

**Materials**

Polyethersulfone (PES, MW 15,000 Da) was supplied by BASE Company. Polyvinylpyrrolidone (PVP, MW 40,000 Da) and polyethylene glycol (PEG, MW 10 kDa) were purchased from Kermel®, China. N,N-dimethylacetamide (DMAC) was supplied by Shanghai Xiangyang Chemical Factory, China. Other reagents were all of analytical grade and used without further purification. The used water is deionized water.

**Membrane preparation**

PES (20 wt%), PVP (8 wt%), AgNO3 of various concentrations (0 wt%, 1 wt%, 2 wt%, 3 wt%), and surfactant were dissolved in DMAC to prepare the casting solution. Then, the casting solution was filtered with a cloth filter, deaerated under vacuum conditions. Finally, three-bore PES hollow fiber UF membranes were spun at room temperature employing the dry/wet-spinning method. A detailed description is provided in our previous work (Dang et al. 2012).

**Characterization**

A cross-flow filtration device was used to measure the water flux and rejection (operating pressure: 0.1 MPa). The concentration of PEG 10000 was obtained by UV spectrophotometer. The morphology of the membranes was observed using SEM (JSM-6700F). The elemental composition of the membrane surface was analyzed by XPS (ESCALAB 250) and EDS. The tensile strength of the membrane was measured by a material test machine (SHIMADZU, Japan) under ambient conditions. The hydrophilicity of the membranes was determined using a contact angle system (OCA20, Dataphysics Instruments, and Germany).

**Test of antibacterial properties**

The antibacterial duration of these membranes was investigated by examining the antibacterial rate of the viable cell counting technique (Chen et al. 2012; Zhang et al. 2012). *Escherichia coli* were inoculated in 5 ml of LB liquid nutrient medium, and shaken for 12 h at 37 °C. The actual number of cells used for a given experiment was determined by the standard serial dilution method. Membranes (0.03 g) were cut and sterilized by autoclaving for 20 min. To test the antibacterial activity, the membranes were added into the 5 ml solution inoculated by about 10^7 CFU (colonies-forming units)/ml of *E. coli*, which were then incubated at room-temperature. After 24 h, the membranes were retrieved from cultures and washed by normal saline. The washing bath was collected and diluted by deionized water till the concentration decreased to 10^-3 of the original value. A volume of 0.2 ml of dilution solution was spread onto LB culture medium and all the plates were incubated at 37 °C for 24 h. The numbers of colonies on the plates were determined by the plate count method.

**Antifouling experiments**

For fouling investigations, BSA solution at a concentration of 1 g/L was prepared for the filtration experiment using Tris-HCl buffer solution (pH 7.5) and the crossflow velocity.
was about 0.35–0.40 m/s. The pure water flux was recorded as \( J_0 \). After that, the BSA solution was forced to permeate through the membrane at the same pressure and the flux was recorded as \( J \). After the filtration of the BSA solution was continued for 150 min, and then the fouled membranes were washed with 0.01 mol/L NaOH solution for 30 min followed by deionized water. The water flux of the cleaned membranes \( J_R \) was measured again. Such a cycle of filtration was carried out continuously several times. In order to evaluate the antifouling property of the membranes, the flux recovery ratio (FRR) was calculated as follows:

\[
FRR\% = \left( \frac{J_R}{J_0} \right) \times 100
\]

RESULTS AND DISCUSSION

Microstructure and element analysis

The outside diameter of the three-bore hollow fiber membranes prepared in this study is about 2.50 mm, the inner diameter of the bores is 0.75 mm, and the breaking strength of the membranes is 8.7 MPa. The cross-section morphology and internal surface image of the tested membranes were observed and the SEM images are shown in Figure 1. As we can see, cross-sectional images of the membranes showed similar morphologies. All the membranes were highly porous and asymmetric with finger-like structures. These findings indicate that the addition of AgNO\(_3\) did not affect the microstructure of the membranes. In addition, XPS analysis was used to confirm the existence of silver particles. As shown in Figure 1(h), the PES/AgNO\(_3\) UF membrane with 1 wt% AgNO\(_3\) exhibited Ag 3d peaks at around 373.4 eV (Ag 3d\(_{3/2}\)) and 367.1 eV (3d\(_{5/2}\)) (Basri et al. 2011; Sawada et al. 2012). A high density of crystalline silver particles with uniform distribution on the internal surface of membranes (Figures 1(f) and 1(g)) could be observed clearly.

The content of silver element in the PES/AgNO\(_3\) UF membranes was analyzed by energy dispersion spectroscopy (EDS), and the result is shown in Figure 2. The results showed that the content of silver element in the membranes decreases with the increase of the operation time of the membranes, but it tends to be stable after running for 48 hours. A similar result was reported by Zhu et al. (2010) where the silver content in the chitosan membrane was basically kept in the stable state after running for 18 hours. As shown in Figures 1 and 2, the content of silver element in the membranes and the size of silver particles increased with the increase of the AgNO\(_3\) content in the spinning dope. The results also indicated that the silver content of as-spun hollow fiber was about 80% of the original silver concentration in the dope. About 20% of silver was lost during spinning. This phenomenon was due to the accessibility of silver ions to water and the poor adhesion to the PES matrix. Small ions were able to permeate through the

![Figure 1](image-url)
bigger pore size of membranes, while the reduced silver was more difficult to dissolve or be ion-exchanged into the solution (Zhu et al. 2010). In comparison, the silver content in the PES membrane after running for 4 days (see Figure 2) is much larger than that in the polyacrylonitrile membrane (Yu et al. 2003), which indicates that the employment of PVP has a beneficial effect on silver reduction, and the membrane stability became better after adding PVP. In addition, the content of silver element in the new membranes or membranes after running for 48 hours were higher than the content of copper element in the new membranes or membranes after running for 48 hours (Dang et al. 2013), respectively. The results indicate that the PES/AgNO₃ UF membrane was much more stable than the PES/CuCl₂ UF membrane.

**Antibacterial property**

The antibacterial activity of PES hollow fiber UF membranes was tested by the viable cell counting technique. The antibacterial effect is shown in Figure 3 and the result is shown in Table 1. As shown in Figure 3(b), significant bacterial growth was observed from the pure PES membrane. Compared with PES membrane, for the sample with PES/AgNO₃ UF membrane (Figure 3(c)), there was a considerable reduction in the numbers of bacterial colonies. PES/AgNO₃ UF membrane with AgNO₃ content of 1 wt% had a high antibacterial efficacy for *E. coli* and the antibacterial rate could reach 99.9% after running for 48 hours. In comparison, the antibacterial rate of pure PES membrane was only 26%. Cao et al. (2010) explained that the antibacterial activity of the hybrid membranes was mainly caused by the antibacterial agent. In our previous work, the antimicrobial activity of Ag particles has been studied (Zhang et al. 2013). In a similar way, the antibacterial mechanism of PES/AgNO₃ UF membrane could be interpreted as follows: silver ions would be produced and released when silver particles are exposed to aqueous environments. The silver ions could react with cysteine by replacing the hydrogen atom of the thiol group to form an S–Ag complex, thus hindering the normal enzymatic function of the affected protease. This kind of denaturing of the enzyme is lethal for living bacteria (Zhu et al. 2010).

**Effect of AgNO₃ content on water flux and rejection**

The effect of AgNO₃ content (0, 1 wt%, 2 wt%, 3 wt%) on water flux and rejection were investigated and the results were shown in Figure 4. As AgNO₃ content increased, water flux of PES UF membranes decreased. The reason was that an increase in AgNO₃ concentration...
results in an increase in the number and size of the silver particles, resulting in the reduction of water permeability because the silver particle creates a barrier to water transport (Sawada et al. 2012). The rejection of PEG 10000 increased with the increase of the AgNO₃ content and could be maintained above 92%, partially due to the blocking of the membrane pores induced from the existence of silver particles (the diameter of AgNPs is about 300 nm). This is reasonable because the Flory radius for PEG 10000 was about 10 nm (Jokerst et al. 2014) and larger than the pores of the membranes (<6 nm).

Antifouling performance

Normalized flux (\(J/J_0\)) was used to analyze the antifouling performance of the tested membranes. As shown in Figure 5, membrane fouling caused the permeation flux to decline dramatically. In order to verify the antifouling performance for the membranes, the flux recovery ratio (FRR) after cleaning was analyzed for the tested membranes. After cleaning with 0.01 mol/L NaOH solution, the FRR were 90.6 and 97.3% for the pure PES membrane and the PES/AgNO₃ membrane, respectively. By increasing the operating time, the FRR decreased for all membranes. However, in every cycle, the FRR for the PES/AgNO₃ membrane was higher than that of pure PES membrane. It is suggested that the PES/AgNO₃ membranes had a certain degree of antifouling performance. This can be attributed to the improvement of the membrane surface hydrophilicity by addition of Ag particles.

Water contact angle measurement is one of the methods for characterization of the hydrophilic properties of the membrane surface. From Table 2, it was clearly seen that the contact angles of the PES/AgNO₃ membranes gradually decreased up to the membrane with AgNO₃ content of 3 wt%, as the content of AgNO₃ was increased in the PES/AgNO₃ membranes. This phenomenon could be attributed to the presence of Ag particles, which have lowered the surface tension of pristine PES so that water can easily spread on the membrane surfaces (Basri et al. 2011).

CONCLUSIONS

A novel three-bore PES hollow fiber UF membrane with both organic antifouling and antibacterial properties was spun by a wet and dry/wet phase inversion process in this study. The XPS result showed that silver particles existed on the surface of these three-bore PES/AgNO₃ membranes. The membranes showed good antibacterial activity against *E. coli* and a certain degree of antifouling performance, which have the potential to reduce the fouling in water treatment.

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