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Preparation of polysulfone ultrafiltration membranes modified by silver particles

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ABSTRACT

In this article, polysulfone–silver composite ultrafiltration membranes were successfully prepared with phase inversion technique through two steps. First, silver particles were prepared in *N*,*N*-dimethylformamide (DMF) through reducing silver nitrate via situ reduction method at 120℃. Then, the casting solution was prepared with polysulfone (PSF), *N*-methyl-2-pyrrolidone, polyvinyl pyrrolidone (PVP) (K10, K30, K50 and K70) and the DMF solution containing the formed silver particles. The effects of molecular weight of PVP on the separation performances and break strength of the membranes were investigated. As a result, for both of PSF membranes and silver composite membranes, with the increase in the molecular weight of PVP, the pure water flux and rejection ratio to bovine serum albumin (68 KDa) solution first increased and then decreased. When the same kind of PVP was added, the rejection ratio of all composite membranes was higher than the rejection ratio of PSF membranes. Moreover, when PVP K30 was added, the water flux and the rejection ratio of the silver composite membrane reached the maximum values, $159\,\mathrm{L\,m^{-2}\,h^{-1}}$ and 94%, respectively. It was also found that the break strength of all of the composite membranes was significantly improved by 38–48% compared with the PSF membranes.

Keywords: Polysulfone; Ultrafiltration membranes; Silver particles; Anti-fouling

1. Introduction

Nowadays, ultrafiltration membrane has become one of the most important separation and purification units in industrial applications. In recent decades, with the rapid development of ultrafiltration technique, ultrafiltration is widely used in many areas such as water treatment, food processing, drug concentration and bio-technology [1]. In the field of water treatment, especially for waste water treatment, the membrane is used more frequently. In order to meet the requirement of saving water resources and reducing environmental pollution, the ultrafiltration membrane bioreactor (MBR) is springing up which is a new water treatment technology [2,3]. MBR is a combination of membrane separation and biological treatment, equalling to the secondary settling tank [4–7]. Now,

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ultrafiltration MBR is applied in wastewater treatment and water reuse [8].

But, at present, one of the bottlenecks for further development and application of ultrafiltration is membrane fouling, that is, the biological macromolecules in solution adsorb or deposit on the membrane surface, resulting in pore blockage and decrease of pore size. Serious membrane fouling leads to a sustained decline in separation performances and increases the maintenance cost [9]. To solving these problems, more and more researchers take more attentions on the anti-fouling of membrane, and many studies such as membrane modification, low flux operation, backwash, and chemical cleaning [9] are carried out to prevent and reduce the fouling problems. Nevertheless, membrane fouling is commonly prevented through chemical cleaning during backwash. However, many polymeric membranes cannot withstand the cauterization of chemical cleaners.

In many cases, membrane fouling is caused by microorganisms such as bacterium breeding on membrane surface. Therefore, researchers develop the anti-fouling membrane through inhibiting the growth of bacterium on membrane surface. As we all known, silver has a natural antibacterial property. Sondi and Alt [10,11] showed that silver particles could cause inhibition of the growth of *Escherichia coli*, *Neisseria gonorrhoeae*, *Chlamydia trachomatis* and dozens of pathogenic micro-organisms. Therefore, if adding the silver particles into the membrane, we will get a new kind of composite membrane possessing the separation and antibacterial properties simultaneously, which will improve the resistance to fouling.

In order to get the silver composite membranes, silver particles were usually synthesized by reducing silver ions in solution. The common reduction reagents were pentanediol, hydrazine hydrate solution, formamide and so on [12–14]. Pastoriza and Marzan [15–17] reported that silver ions could be reduced into silver particles by *N,N*-dimethylformamide (DMF) which was commonly used as polymer solvent for membrane preparation. Based on this report, Yu et al. [18,19] successfully prepared silver-loaded cellulose acetate and polyacrylonitrile-silver anti-fouling hollow fiber ultrafiltration membranes through reducing Ag^+ by DMF. Taurozzi et al. [20] also successfully prepared polysulfone (PSF) silver-loading composite membranes in which the silver particles were synthesized via situ reduction of ionic silver by DMF.

In this work, PSF membranes and Ag/PSF composite ultrafiltration membranes were prepared. *N*-methyl-2-pyrrolidone (NMP) and DMF were used as solvents. The separation properties of the membranes were researched. In order to investigate the effects of porogen on membrane performances, four kinds of polyvinyl pyrrolidone (PVP) with different molecular weight were chosen as the porogen. In addition, the change of break strength between PSF and Ag/PSF composite membranes was also researched.

2. Materials and methods

2.1. Materials

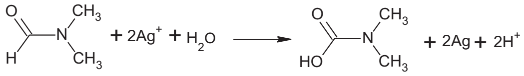
PSF was purchased from Dalian PSF Plastic Co. Ltd., China. NMP (analytical grade) was purchased from Tianjin Bodi Chemical Co. Ltd., China. DMF (analytical grade) and PVP (K10, K30, K50, K70, analytical grade) were all purchased from Tianjin Kermel Chemical Reagent Development Centre, China, Bovine serum albumin (BSA, M_w was 68 KDa) was purchased from Tianjin Rui jinte Chemical Co. Ltd., China. Silver nitrate ($AgNO_3$) was purchased from Beijing Jingxi Chemical Co. Ltd., China. They were all directly used without purification. Distilled water was used throughout the study.

2.2. Preparation of PSF membranes

All membranes were prepared by immersion precipitation phase inversion. The casting solutions contained PSF/DMF/NMP/PVP at a ratio of 20:20:55:5. The membranes were prepared via the following procedure. First, PSF and PVP were dissolved in NMP and DMF at 60°C until they became a homogeneous solution. When the temperature of the solution cooled down to room temperature, a thin film of the casting solution was deposited onto a glass plate using an aluminum casting knife. The nascent membranes were exposed to the air for 20 s, and then, the glass plate and the membranes were quickly transferred to the water bath at 25°C for the remainder of the phase-inversion process. The thickness of each membrane was all about 0.1 mm.

2.3. Preparation and characterization of silver colloid

Silver particles were prepared in DMF through reducing silver nitrate via situ reduction method. First, 0.5% $AgNO_3$ was dissolved in the mixture of water and DMF (volume ratio 1:1) in 0.5 mL. Then the solution was slowly added to boiling DMF to reduce silver under intense stir to allow for particles formation at 120°C. The reaction mechanism was as follows:



The color of reaction solution turned from colorless to yellow after 2 h. The silver colloid was characterized with UV–vis spectrophotometer (T6, Persee, Beijing, China).

2.4. Preparation of Ag/PSF composite membranes

The obtained silver colloid was added to the casting mixture containing PSF/NMP/PVP at a ratio of 20:54.5:5. Once the casting solution became well-distributed, the procedure for preparing Ag/PSF composite membranes was same as the preparation of PSF membranes. The thickness of each membrane was all about 0.1 mm.

2.5. Characterization of membranes

The microscopic cross-section morphologies of the prepared membranes were examined by a scanning electron microscope (SEM) (FEI Quanta 200, USA). For the SEM measurement, the samples were frozen in liquid nitrogen and fractured. After sputtering with gold, the microscopic cross-section morphologies of the membranes were observed with the SEM. The macroscopic morphologies of the membranes were viewed by a digital camera. The break strength of all the membranes was tested by a self-made equipment.

2.6. Permeability and rejection tests

The ultrafiltration performances were carried out on a self-made equipment at room temperature. The concentration of BSA solution was 1.0 mg/mL. The trans-membrane pressure was kept at 0.1 MPa by nitrogen gas. All membranes were pressed with water at 0.15 MPa for half an hour before measurements. Pure water permeation flux and rejection to the BSA solution were measured after circulating for 5 min. Permeation flux, J ($\mathrm{L\,m^{-2}\,h^{-1}}$) was calculated by the following equation:

$$J = \frac{m}{At} \tag{1}$$

where m was the mass of permeation water, A was the membrane area (7.1 $\mathrm{cm^2}$), and t was the permeation time. The rejection (R) was calculated by the following equation:

$$R = \left(1 - \frac{C_{\mathrm{p}}}{C_{\mathrm{f}}}\right) \times 100 \tag{2}$$

where C_{p} and C_{f} (mg/mL) was the concentration of BSA solution in the permeation and feed side, respectively.

3. Results and discussion

3.1. UV–vis absorption spectrum of silver colloid

The absorption of light by noble metal particles with certain size results from surface plasmons resonance. For silver particles, the strong absorption peak was near 410 nm [21]. So, for the prepared silver particles, we could not only judge the proceed of whole reaction from the color-change of the solution but also from the UV–vis spectrum. Fig. 1 verifies that silver ions were successfully reduced to silver particles in the liquids phase.

3.2. Morphologies of membranes

Fig. 2 shows the macroscopic morphology of the membranes when PVP K30 was as progen. The surface color of the Ag/PSF composite membrane was absolutely changed compared with PSF membrane. Some materials would have yellow color when silver particles were added [22]. The experimental result was fully consistent with this phenomenon. It implied that the silver particles were successfully formed and distributed in the surface of outer layer of Ag/PSF membranes.

Fig. 3 shows the cross-section morphologies of the membranes prepared at the condition when PVP K30 was as porogen. It shows that the membranes have typical asymmetric structures, consisting of porous sublayer and thin skin layer. Compared the PSF

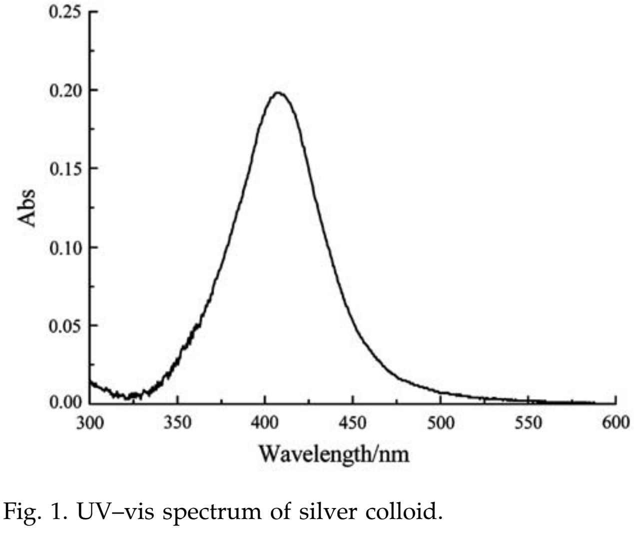


Fig. 1. UV–vis spectrum of silver colloid.

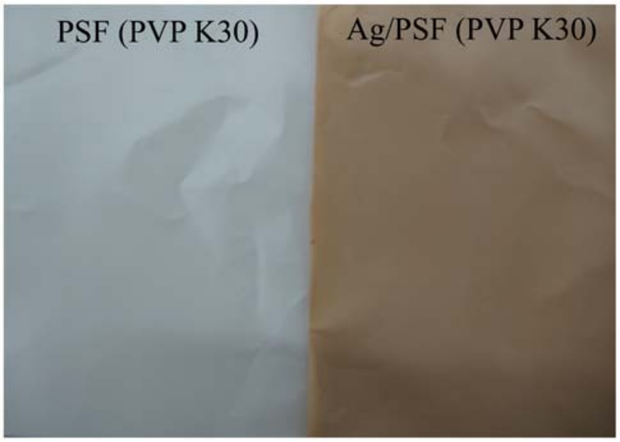


Fig. 2. Macroscopic morphologies of PSF (PVP K30) and Ag/PSF (PVP K30) composite membranes.

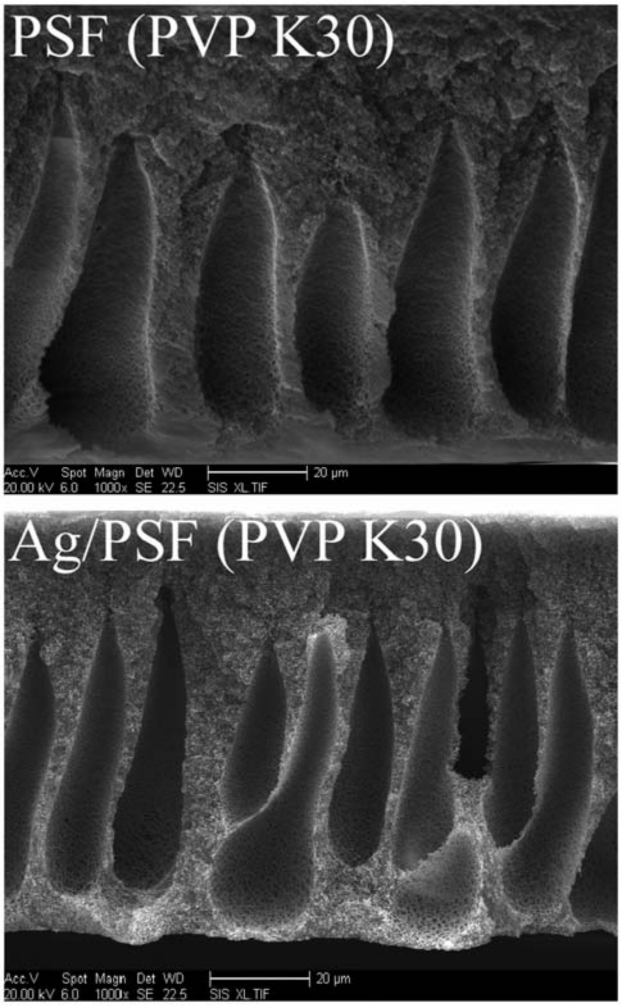


Fig. 3. SEM images of cross-section of PSF (PVP K30) and Ag/PSF (PVP K30) composite membranes.

membrane with the Ag/PSF membrane, it seems that there are no distinct differences in the membrane structure when using the same molecular weight of PVP as the porogen.

3.3. Properties of membranes

Table 1 lists the break strength of the membranes prepared with four kinds of PVP as porogen. It presents that the break strength of the Ag/PSF composite membranes are significantly improved compared with the PSF membranes. The break strength of all of the composite membranes is improved by 38–48%. Therefore, addition of silver particles in the membranes indicated that the strength of the membranes could be improved.

Fig. 4 shows the scatter diagram of the pure water flux and rejection ratio to BSA of the membranes. It shows that when the same kind of PVP was added, the rejection ratio to BSA of all of Ag/PSF membranes is higher than the rejection ratio of the PSF membranes. For the PSF membranes, with the increase in the molecular weight of PVP, both of the pure water flux and rejection ratio to BSA solution first increase and then decrease. It was found that when PVP K30 was added, the water flux and the rejection ratio of the PSF membrane both reached the maximum values, $178\,\mathrm{L\,m^{-2}\,h^{-1}}$ and 91%, respectively. The changing trend of Ag/PSF composite membranes was same to the PSF membranes, which was with the increase of the molecular weight of PVP, the pure water flux and rejection ratio to BSA solution first increased and then decreased. When PVP K30 was added, the pure water flux and rejection ratio of the composite membrane reached the maximum values of $159\,\mathrm{L\,m^{-2}\,h^{-1}}$ and 94%, respectively.

Fig. 5 shows the content effects of PVP K30 on water flux and rejection ratio of Ag/PSF composite membranes. Generally, high concentration of porogen would inhibit the formation of hole structure and improve the connectivity and porosity [23]. The hydrophilic nature of PVP K30 accelerated the gel speed after the membranes were immersed in the water bath, resulting in a rapid phase separation. When more PVP K30 was added in casting solution, more porous would form after the nascent membranes were dissolved in water bath. All these factors leaded to the water flux increased while the rejection ratio decreased with the content increase in PVP K30. In summary, the proper mass content of PVP K30 in this experimental system was 5%.

Table 1
Break strength (MPa) of membranes

Type of membranes	PSF	Ag/PSF
PVP K10	3.9 ± 0.1	5.4 ± 0.3
PVP K30	3.6 ± 0.4	5.1 ± 0.2
PVP K50	3.8 ± 0.4	5.4 ± 0.3
PVP K70	3.5 ± 0.2	5.2 ± 0.6

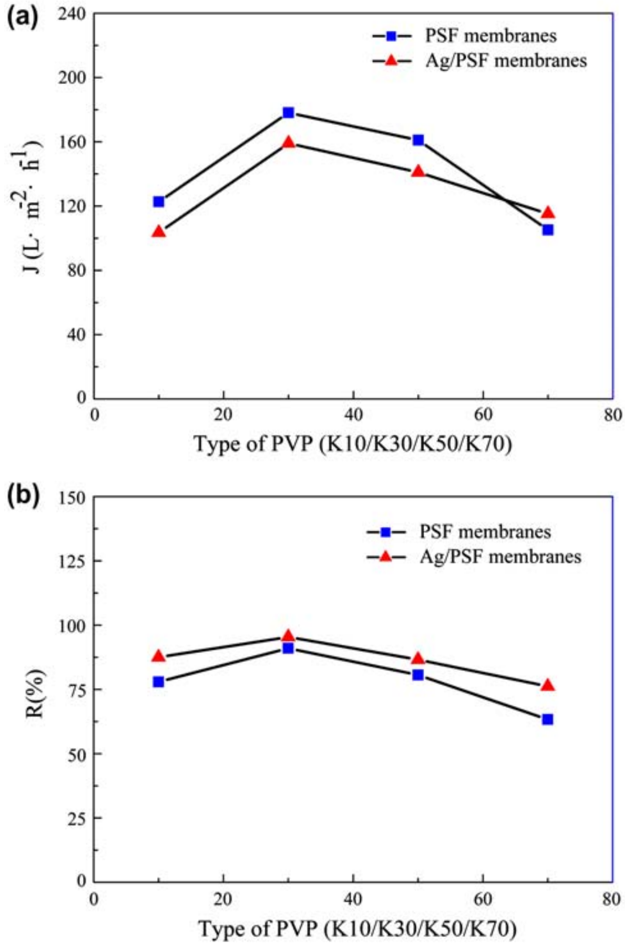


Fig. 4. Pure water flux (a) and rejection ratio to BSA (b) of all membranes.

4. Conclusions

In this article, Ag/PSF composite membranes were successfully prepared through reducing silver nitrate by DMF via situ reduction method. The effects of molecular weight of PVP on membrane properties were investigated. Conclusions were as follows:

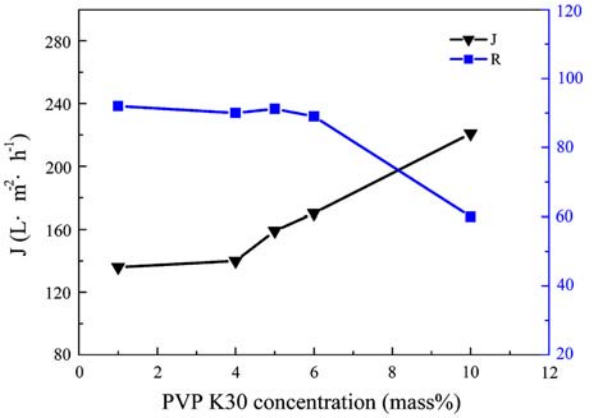


Fig. 5. Ag/PSF composite membranes with different content of PVP K30.

(1) For both of PSF membranes and Ag/PSF composite membranes, with the increase in the molecular weight of PVP, the pure water flux and rejection ratio to BSA solution first increased and then decreased. When the same kind of PVP was added, the rejection ratio of all Ag/PSF composite membranes was higher than the rejection ratio of PSF membranes. Moreover, the break strength of Ag/PSF composite membranes was significantly improved by 38–48% compared with PSF membranes.

(2) For PSF membranes, when PVP K30 was added, the water flux and rejection ratio of PSF membrane reached the maximum values, 178 $\mathrm{L\,m^{-2}\,h^{-1}}$ and 91%, respectively. The Ag/PSF composite membrane prepared from the casting solution having the composition of PSF/NMP/DMF/PVP K30/$AgNO_3$ = 20/54.5/20/5/0.5 showed the best performances. The pure water flux and rejection ratio were 159 $\mathrm{L\,m^{-2}\,h^{-1}}$ and 94%, respectively.

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