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Preparation of high-performance nanofiltration membrane with antioxidant properties

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Abstract. In industrial production, the development of traditional polyamide nanofiltration (NF) membrane was limited due to its poor oxidation resistance, complex preparation process and high cost. In this study, a composite NF membrane with high flux, high separation performance, high oxidation resistance and simple process preparation was prepared by the method of dilute solution dip coating. And the sulfonated polysulfone was used for dip coating. The results indicated that the concentration of glycerin, the pore size of the based membrane, the composition of the coating solution, and the post-treatment process had important effects on the structure and performance of the composite NF membrane. The composite NF membrane prepared without glycerol protecting based membrane had a low flux, when the concentration of glycerin increased from 5% to 15%, the pure water flux of the composite NF membrane increased from 46.4 LMH to 108.2 LMH, and the salt rejection rate did not change much. By optimizing the coating system, the rejection rate of Na_2SO_4 and PEG1000 was higher than 90%, the pure water flux was higher than 40 LMH (60psi), and it can withstand 20,000 ppm.h NaClO solution cleaning. When the post treatment processes was adjusted, the salt rejection rate of NaCl solution (250 ppm) reached 45.5%, and the flux reached 62.2 LMH.

Keywords: composite nanofiltration membrane; high flux; oxidation resistance; solution coating method; sulfonated polysulfone

1. Introduction

With the continuous advancement of urbanization, problems such as population growth and environmental damage are increasingly exposed. The demand for fresh water resources has become a major problem to be solved all over the word (Lee *et al*. 2016). In recent, many technologies have been used for seawater desalination, such as distillation (Breschi 1999), ion exchange (Jacob 2007), electrodialysis (Toraj Mohammadi and Kaviani 2003). However, these methods either require complex procedures and consume large amounts of energy, or involve many chemicals which will cause secondary pollution to the product water (Xu *et al*. 2017). Compared with these methods membrane separation doesn't need complex procedures and consume a lot of energy, has the advantages of high efficiency, environmental protection and would not cause secondary pollution to the product water (Guo *et al*. 2021). Among them, nano- filtration (NF) membrane has attracted more and more attention. The molecular weight cut-off of NF membrane was between ultrafiltration and reverse osmosis (Peng *et al*. 2009, Xu *et al*. 2016, 2019), it also had the Donnan effect, so it had a good effect on the separation of low molecular weight organic matter and salt, and had no influence on the separation of biological activity. The NF membranes have been used more and more widely in the food industry, fermentation industry, pharmaceutical industry, dairy industry and other industries (Kaykioglu *et al*. 2017) due to its' energy saving and pollution-free.

The traditional preparation method of NF membrane was interfacial polymerization, in which two monomers that can react with each other to form polymers were respectively dissolved in two insoluble liquids (usually water and organic solvents) to form aqueous phase and oil phase (Guo *et al*. 2020). When the two phase monomers contacted with each other, the polycondensation reaction occurred quickly near the interface to form polyamide layer (Abu Seman *et al*. 2011, Li *et al*. 2014, Seman *et al*. 2010). The thickness of the membrane prepared by this method was smaller and can efficiently intercept the divalent salt. However, the oxidation resistance of polyamide membrane was poor, its low active layer thickness led to relatively low strength, and the process was easy to form defects, unable to achieve high quality production. These characterizations limited the application of this technology in the industrial field (Han *et al*. 2018). Meanwhile, layer-by-layer self-assembly technique, which was prepared by alternating deposition of positive and negative charge polyelectrolyte on the based membrane, has attracted more and more attention due to simple operation, good controllability, environment-friendly, charge controllable, layer controllable. Xu *et al*. (2018) assembled graphene oxide and oxidized carbon nanotubes alternately to form sandwich morphology on a polyacrylonitrile substrate by layer-by-layer self-

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assembly technique, the composite membrane had higher flux compared with reported literatures in which rejection also reached up to 99%, meanwhile, the composite membrane had excellent antifouling performance for Bovine Serum Albumin (Kang *et al*. 2018). However, in order to obtain a defect-free composite membrane, multi-layer assembly was often adopted, which consumed a long time and restricted the further popularization of this technology.

A new preparation method of NF membrane, dip coating, has been proposed and applied in previous study (Chen *et al*. 2013, Elyasi Kojabad *et al*. 2020, Xu *et al*. 2018). Dip coating method was a membrane forming method in which the prepared coating solution was extruded into the substrate membrane and the liquid phase was transferred to the solid phase. And it was a simple method to prepare separation layer. Coronas *et al*. used ZIF-8 and ZIF-67 particles to deposite on top of support layer by dip-coating method (Sarango *et al*. 2018). The results indicated that the membrane exhibited good organic solvent NF performance with a high permeance of 8.7 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and dye rejection of 90%. Chung *et al*. (2018) fabricated a composite NF membrane with a facile coating using polyethyleneimine, the coating conditions and the permeation performance were studied. The results showed that the composite membrane had a higher performance than commercial organic solvent NF membrane. Khan *et al*. (2020) prepared a NF membrane by immobilizing Ag doped TiO_2 nanoparticles on the surface membrane by dip coating method. The results showed that when the concentration of Ag-TiO_2 was 0.5%, the rejection to NaCl increased from 2% for unmodified membrane to 60% for the modified membrane. These studies indicated that dip coating was a simple and effective method to fabricate NF membrane. In addition, the dip-coating method greatly simplified the membrane preparation process, and the process conditions were highly controllable, which can achieve uniform coating and continuous production of mechanical automation.

Sulfonated polysulfone (SPSf) has been widely used in membrane separation progress due to its high oxidation and thermal stabilities (Chen *et al*. 2005, Hu *et al*. 2021). SPSf bulk material was high chargeability and easy to form relatively uniform pores, which was utilized to modify the surface of ultrafiltration based membrane. Xu *et al*. (2016) used the SPSf blending with PSf to modify the PSf based membrane, and the results indicated that the addition of SPSf can improve the hydrophilicity and the surface negative charges. Meanwhile, the flux was improved without any deterioration of the quality during a 8-h long term cycle. Pei *et al*. (2018) fabricated a SPSf/PSf support layer onto a PET mesh, and the content of SPSf was optimized to prepared polyamide layer. The results indicated that the addition of SPSf can affect the hydrophilicity, porosity and pore structure of the substrate, in addition, the thickness, roughness and the crosslinking degree of the polyamide layer was also affected. And the fabricated membrane owned a higher flux and a smaller pore size. These studies demonstrated that the SPSf can not only improve the hydrophilicity and heat resistance of PSf membrane materials, but also effectively improve the selective separation characteristic permeation flux and oxidation resistance of functional membranes.

In this study, the PSf ultrafiltration flat membrane was prepared by phase inversion, then, the dilute solution immersion coating phase inversion technology was used to prepare the composite NF membrane with anti-oxidation and high separation performance. The schematic diagram was shown in Fig. 1. The influence of the status and pore size of the based membrane, the content of SPSf in the coating solution, the degree of sulfonation and the post-treatment process on the structure and performance of the composite membrane was investigated. The membrane was endowed the anti-oxidation and high permeability due to the characteristic of the SPSf.

2. Materials and experimental methods

2.1 Materials

PSf was bought from Solvay, Belgium. SPSf was provided by Shandong Jinlan Special Polymer Co. Ltd. China. Polyethylene glycol and polyvinylpyrrolidone were obtained from Tianjin fukang chemical Co. Ltd. China. N, N-dimethylformamide (DMF, industrial grade) provided by Samsung Co. Ltd. South Korea was used as the solvent. Ethylene glycol monomethyl ether was bought from Dalian Tianhe Chemical Co. Ltd. China. Na_2SO_4 and NaCl were provided by Tianjin Tianli chemical Co. Ltd. China and NaClO was supplied by Shanghai Jingchun Biochemical Technology Co. Ltd. China. All the reagents used in the study were reagent grade.

2.2 Preparation of based membrane

In this study, phase inversion method was used to prepare PSf flat based membrane. The preparation process of the based membrane was as follows: firstly, a solution with PSf, polyvinylpyrrolidone, compound additives and DMF was configured in a preset ratio. Then the polymer solution was stirred at 70℃ for 12 h. After deaeration, the temperature of the coagulation bath and the distance between the scraper and glass plate were adjusted to enter the coagulation bath water solution under a certain tension, and the PSf ultrafiltration flat based membrane was prepared by phase inversion. Finally, the based membrane was treated with a certain concentration of glycerin, and dried at a suitable temperature for later use.

2.3 Preparation of composite NF membrane

The composite NF membrane was prepared by the dip-coating method, and a certain composition of SPSf coating solution was coated on the PSf based membrane. Remove excess coating solution and use proper heat treatment, the SPSf composite NF membrane was fabricated.

2.4 Membrane characterization

The surface and cross-sectional morphology of the composite NF membrane was characterized by field

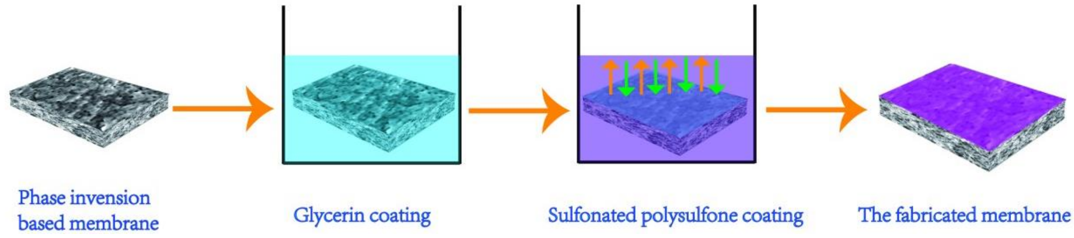

Fig. 1 Schematic diagram for the fabricated NF membrane

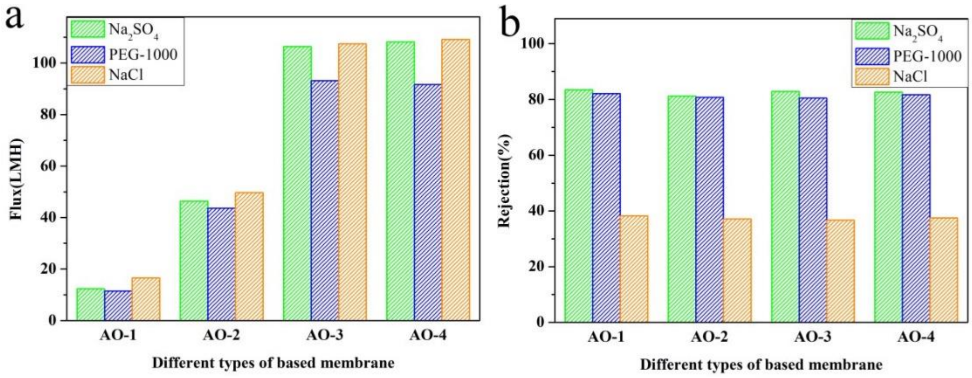

Fig. 2 (a) The flux and (b) Rejection of composite membrane with different types of based membrane

emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). In order to observe the surface morphology of the based membrane clearly, the cleaned and dried sample was tested after vacuum spraying with gold. The surface chemical composition of the NF membrane was analyzed by fourier transform infrared spectroscopy (FTIR, TENSOR37-Bruker, Germany). The samples used for testing were fully immersed and cleaned with deionized water and vacuum dried before testing to avoid adsorption of coating solution. The contact angle was used to analyze the hydrophilicity of the membrane surface. At room temperature, YH-168A contact angle tester (Beijing Harco Experimental Instrument Factory) was used to test the contact angle, four samples were tested for each type to get the average value.

2.5 Separation performance test

The rejection performance and water flux were measured by cross-flow filtration. The pure water flux (*PWP*, $L\cdot m^{-2}\cdot h^{-1}$) of all membrane samples was tested with deionized water before their rejection performance was measured. Firstly, the membrane was pre-pressed at 0.42 MPa for 15 min, then 10 mL permeate solution was received and the corresponding time was recorded. Five sets of permeate solution were received for each sample, and each sample was tested for at least 3 parallel components. The final result was the average of all tests. The conventional rejection (*R*) performance test process was similar to the flux test. The test pressure was 60 psi and the concentration of solution was 250 ppm. The conductivity of the feed solution and permeate solution was used to indicate salt concentration to calculate the desalination rate. The concentration of polyethylene glycol in the feed solution and permeate solution was measured with a TOC analyzer (TOC-VCSH, Shimadzu, Japan). The flux and rejection rate can be calculated by Eqs. (1) and (2):

$$PWP = \frac{V}{A \times t} \tag{2}$$

where V was the volume of permeate (L); A was the effective membrane area of the membrane module (m^2); t was the measure time (h).

$$R = \left(1 - \frac{Cp}{Cf}\right) \times 100\% \tag{2}$$

where Cp and Cf represented the conductivity of the permeate solution and feed solution (μS/cm), respectively.

The oxidation resistance of the membrane was also investigated, at 25℃, the membrane materials were soaked with different concentrations NaClO solution, then, the membrane was rinsed with running water, and dried to test the water flux and rejection performance.

3. Result and discussion

3.1 Effect of based membrane on the properties of composite NF membrane

As a platform for the reaction, the based membrane played an important role in the forming of the membrane. The properties of the based membrane, such as pore size, hydrophilcity and roughness, will influence the formation of separation layer (Yu *et al*. 2020).

Firstly, we studied the different process methods of based membrane. Among them, AO-1 represented that the based membrane was dried naturally, AO-2 represented that the based membrane was dried with 5% glycerol for

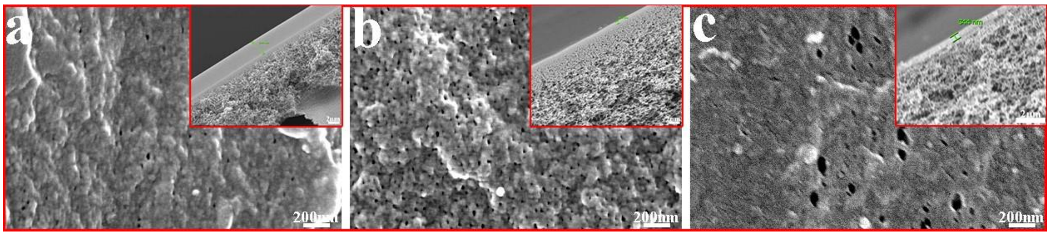

Fig. 3 SEM images of the different pore size of based membrane. (a) 0.04 μm; (b) 0.06 μm; (c) 0.08 μm; The inset images represented the cross-sectional images of the corresponding composite NF membrane, respectively

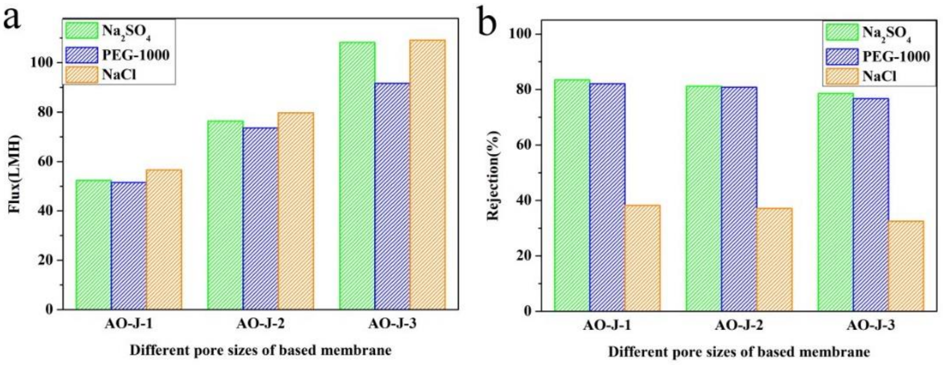

Fig. 4 (a) The flux and (b) Rejection of composite membrane with different pore sizes of based membrane.

protecting, AO-3 represented that the based membrane was dried with 10% glycerol for protecting, AO-4 represented that the based membrane was dried with 15% glycerol for protecting. It can be seen from Fig. 2 that the composite NF membrane prepared by natural air drying of the based membrane had a low flux. This was mainly because the based membrane heated without glycerol for protecting was easy to shrink and collapse. When glycerin was used to protect the based membrane, the flux increased significantly and the salt rejection rate did not change much. As the glycerol concentration increased from 5% to 15%, the water flux of the composite NF membrane increased from 46.4 LMH to 108.2 LMH, and the salt rejection rate did not change much with the increase of glycerol concentration.

The structure of the based membrane has a certain impact on the performance of the composite NF membrane prepared by the dip coating method. If the based membrane has obvious macropores, it is difficult to form a defect-free functional layer through dip coating method on the based membrane, which will affect the performance of the composite NF membrane, especially for the selectivity of the membrane. The properties of the based membrane such as mechanical strength, chemical stability, and thermal stability will also directly affect the performance of the composite NF membrane, so it is necessary to select the appropriate based membrane material and membrane fabrication process. The purpose of the paper was to prepare a composite NF membrane with good separation performance and anti-oxidation performance, therefore, the based membrane was required to have excellent anti-oxidation performance and appropriate pore structure. In this study, polyvinylpyrrolidone and propylene glycol were used as additives to prepare three kinds of ultrafiltration based membranes with different molecular weight cut-offs, and compared the performance of composite NF membranes with these three types of based membrane. Therefore, we studied the effect of pore size of based membrane on the performance of NF membrane. AO-J-1 represented that the pore size of based membrane was 0.04 μm, AO-J-2 represented that the pore size of based membrane was 0.06 μm, AO-J-3 represented that the pore size of based membrane was 0.08 μm. Fig. 3 showed the PSf ultra-filtration flat based membranes prepared with different casting membrane systems. It can be seen from SEM images that the number of open pores and the pore size of the membrane were different. The cross-section structure of composite NF membranes made with different pore sizes based membranes was quite different. It can be seen from the inset images in Fig. 3 that as the pore size of the PSf ultrafiltration based membrane increased, the thickness of the separation layer of the prepared composite NF membrane decreased from 3430 nm to 3440 nm. This may be caused by that with the increase of pore size, lots of SPSf entered to the pore and completed the phase inversion progress.

And the flux and rejection were shown in Fig. 4, with the increase of the pore size of the based membrane, the water flux of the composite NF membrane in different test solutions increased, but the salt rejection rate decreased slightly; among them, when NaCl solution (250 ppm) was used as feed solution, the water flux increased from 56.6 LMH to 109.2 LMH and the salt rejection rate decreased from 38.2% to 32.5%. As the pore size of the ultrafiltration based membrane decreased, under the same dipping coating process conditions, the number of polymer segments of the coating solution entering the based membrane was effectively reduced, and a higher concentration of coating solution was retained on the surface of the membrane. Thus, the thickness of the dense separation layer was increased and it had better uniformity. When the pore size of the based membrane was too large, it was difficult to ensure the

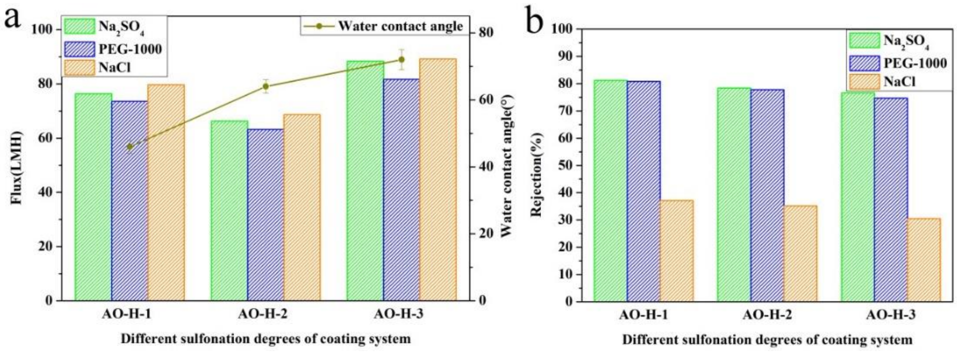

Fig. 5 (a) The flux, water contact angle and (b) Rejection of composite membrane with different sulfonation degrees of coating system

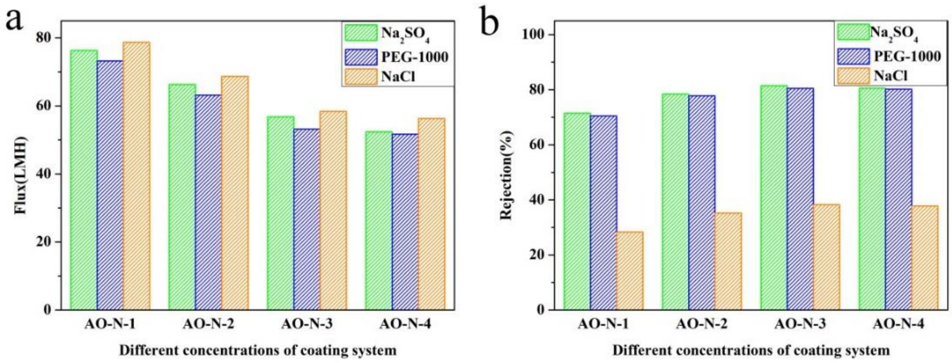

Fig. 6 (a) The flux and (b) Rejection of composite membrane with different concentrations of coating system

uniformity of the separation layer, and lots of defects may be formed on the surface of composite membrane, and the salt rejection rate will be reduced. Considering the rejection and water permeability of the composite membrane, an ultrafiltration flat based membrane with a pore size distribution mainly around 0.06 μm was selected.

3.2 Effect of coating system on the properties of composite NF membrane

The separation layer played decisive role in the performance of the membrane, especially for the rejection performance. Therefore, we studied the effect of the coating system on the performance of composite NF membrane. Among them, AO-H-1, AO-H-2 and AO-H-3 represented that the sulfonation degrees of coating system were 40%, 25% and 15%, respectively. Fig. 5 showed the rejection and water permeability of composite NF membranes with different sulfonation degrees. We can see that the rejection performance of the composite NF membrane was effectively improved as the sulfonation degree of SPSf increased, while the water permeability first decreased and then increased. Among them, the rejection to NaCl solution (250 ppm) increased from 76.6% to 81.2%, meanwhile, the flux decreased from 89.2 LMH to 68.7 LMH and then increased to 79.7 LMH, and the water contact angle decreased from 72° to 46°. With the increase of sulfonation degree of the SPSf, the salt rejection rate of the composite NF membrane also increased. It was mainly due to the following two reasons: on one hand, the surface tension of the coating system decreased, which was beneficial to the wettability of the coating solution and it can effectively reduce the defects of the separation layer; on the other hand, the increase of sulfonic acid groups was conducive to the formation of bridge function and the pore size of separation layer was reduced. As the sulfonation degree increased, the water contact angle of the composite NF membrane decreased, which indicated the increase of the hydrophilcity. This was mainly due to the presence of sulfonic acid groups in the SPSf, and it was hydrophilic groups, thus, the hydrophilicity of the membrane material can be improved. As the sulfonation degree of SPSf increased, the water flux of the composite NF membrane first decreased and then increased, which was mainly caused by the synergistic effect of the thickness, pore size, and hydrophilicity of the separation layer caused by phase inversion. The composite NF membrane with a sulfonation degree of 40% had a higher water flux and salt rejection rate, but the cost was too high to produce, and a risk of material swelling during the application process will reduce the separation performance. Based on the above performance, 25% SPSf was chose to prepare the composite NF membrane.

Because the main separation function of the composite membrane was the coating layer, thus, the concentration of the coating polymer was also studied. AO-N-1, AO-N-2, AO-N-3, AO-N-4 represented that the concentrations of coating system were 0.3 wt%, 0.5 wt%, 0.7 wt% and 1 wt%, respectively. In this paper, SPSf with a 25% sulfonation degree was used as the coating material, ethylene glycol monomethyl ether was used as the solvent, and glycerol was used as the additive, and the heat treatment temperature was

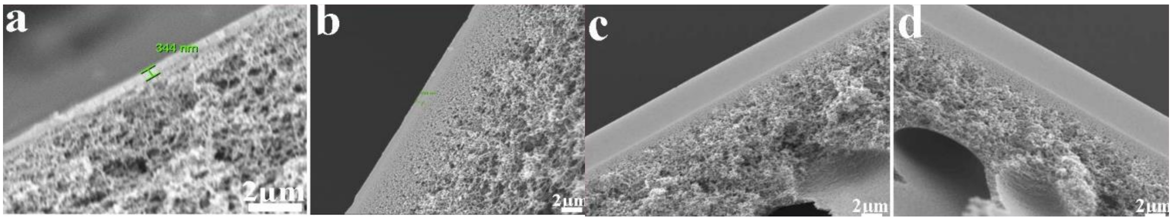

Fig. 7 SEM images of the different concentrations of SPSf; (a) 0.3 wt%; (b) 0.5 wt%; (c) 0.7 wt%; (d) 1 wt%

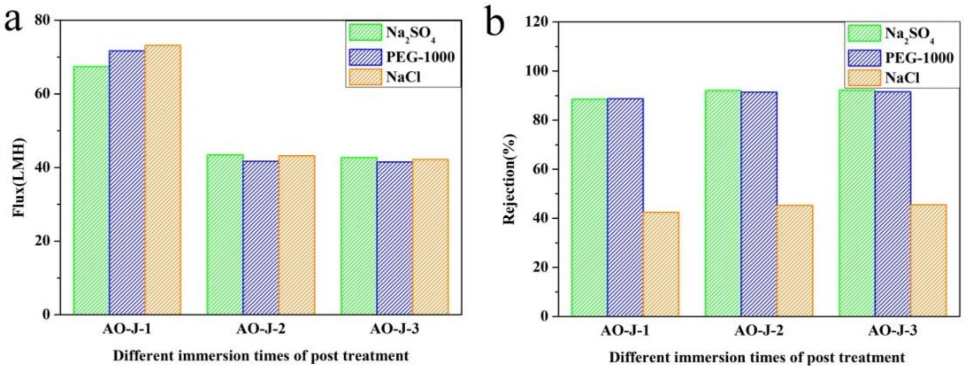

Fig. 8 (a) The flux and (b) Rejection of composite membrane with different immersion times of coating system

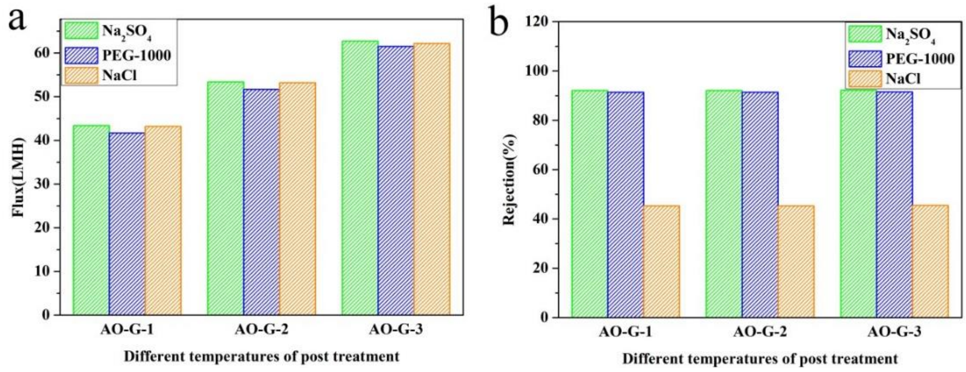

Fig. 9 (a) The flux and (b) Rejection of composite membrane with different temperatures of post treatment

70℃. The relationship between the concentration of coating solution and the performance of NF membrane was investigated by changing the concentration of SPSf. Fig. 6 showed the rejection and permeability of the composite NF membrane with different SPSf concentrations, and Fig. 7 showed the cross-sectional structure of the composite NF membrane. We can see that the overall trend of the desalination rate of the prepared composite NF membrane increased with the increase of the concentration of SPSf in the coating solution, while the flux decreased. When the concentration of SPSf was 0.5 wt%, the rejection to NaCl (250 ppm) reached to 38.3%, which was the maximum. With the increase of the concentration of SPSf, the rejection to NaCl of composite NF membrane increased from 28.3% to 37.8%, and the flux decreased from 78.7 LMH to 56.3 LMH. There are two main reasons for this trend. During the coating process, the equilibrium thickness of the membrane separation layer was proportional to the square root of the viscosity of the coating solution. When the solid content in the dipping dilute solution increased, the thickness of the composite membrane will increase due to the increase of viscosity, resulting in an increase in the rejection rate and a decrease in flux. When the rejection rate rised to a certain level, the influence of the concentration in the dipping dilute solution on it will be weakened, and the increase in the rejection rate will slow down. When the concentration of the dipping dilute solution increased, the effective charge density on the surface of the membrane increased, which resulted in the increase of rejection rate, but when the charge density was too large, the membrane would adsorb counter ions in the solution and neutralize the part charge of the membrane itself, which resulted in the decrease of the rejection rate.

3.3 Effect of post treatment on the properties of composite NF membrane

Different post-treatment processes were also studied. AO-J-1, AO-J-2, AO-J-3 represented that the immersion times of post treatment were 15 s, 30 s and 45 s, respectively. AO-G-1, AO-G-2, AO-G-3 represented that the temperatures of post treatment were nature wind, low temperature air knife and high and low temperature variable frequency air knife, respectively. Figs. 8 and 9 showed the performance

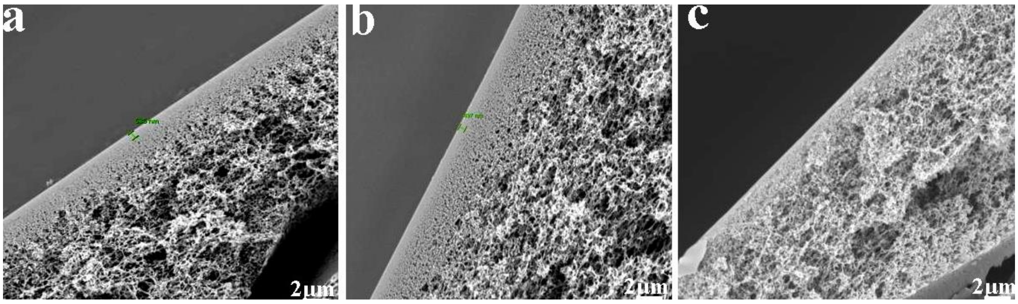

Fig. 10 SEM images of the different temperatures of post treatment progress. (a) nature wind; (b) low temperature air knife; (c) high and low temperature variable frequency air knife

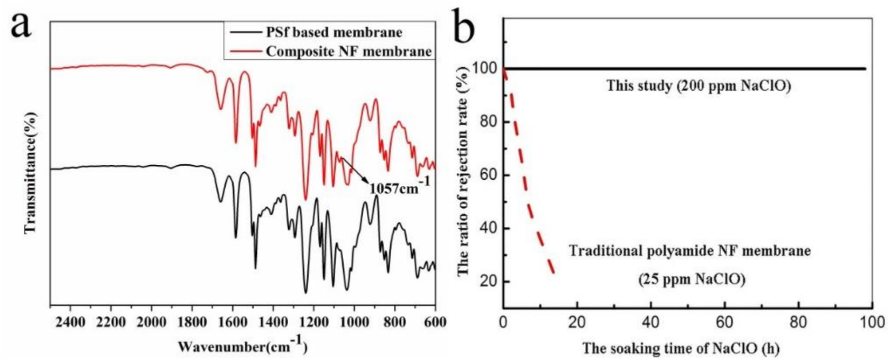

Fig. 11 (a) FTIR and (b) Oxidation resistance of composite NF membranes

of composite NF membranes with different post-treatment processes. It can be seen from Fig. 8 that the rejection performance of the prepared composite NF membrane increased while the permeability decreased as the coating solution immersion time increased. If the immersion time continued to increase, the separation performance of the composite membrane did not change much. Among them, the rejection to NaCl solution (250 ppm) of composite NF membrane increased from 42.5% to 45.3%, and the flux decreased from 73.2 LMH to 42.2 LMH. The separation performance of the composite membrane was mainly enhanced by the immersional wetting, which effectively reduced the defects of the separation layer and increased the thickness of the separation layer. It can be seen from Fig. 9 that the rejection performance of the prepared composite NF membrane was increased and the water permeability was relatively better when the high and low temperature frequency conversion air knife treatment process was adopted. Among them, the composite membrane had a salt rejection rate of 45.5% to NaCl solution (250 ppm) and a flux of 62.2 LMH. On the one hand, high and low temperature frequency conversion air knife drying process can control the phase conversion speed, which was beneficial to the formation of the uniform pore structure, on the other hand, it can also effectively control the thickness of the composite membrane separation layer.

3.4 The functional groups and oxidation resistance of composite membrane

The composite NF membrane was tested by FTIR test, and Fig. 11(a) showed the results. Compared with PSf based membrane, the adsorption peak appeared at 1057cm^{-1} was corresponded to the S=O bond in the sulfonic acid groups (Song *et al*. 2016). It indicated that the SPSf was coated successfully. It can be seen from Fig. 11(b) that the composite NF membrane had good oxidation resistance. Different concentrations of NaClO were used to test the anti-oxidation performance. The tolerance of the fabricated membrane to NaClO can reach 20000 ppm.h, which was much higher than traditional polyamide NF membrane. This was mainly due to the separation layer of the composite membrane, which had good oxidation resistance.

As shown in Fig. 12, the oxidation resistance of the membrane was compared with that of industrial membrane. The result indicated that the fabricated membrane had shorter and more flexible operation process, which can effectively relax the flocculation and precipitation process, without ultra/micro-filtration pretreatment, and can be cleaned quickly. The fabricated membrane can add low concentration of residual chlorine into the water to control biological contamination or use high concentration of NaClO solution to clean the membrane.

4. Conclusions

In this study, the polysulfone ultrafiltration flat membrane was prepared by phase inversion, then, the dilute solution immersion coating phase inversion technology was used to prepare the composite NF membrane with anti-oxidation and high separation performance. The status and structure of the based membrane had an important influence on the performance of the composite NF membrane prepared by dip coating. When a certain concentration of glycerin was used to protect the based membrane, the flux of the composite NF membrane

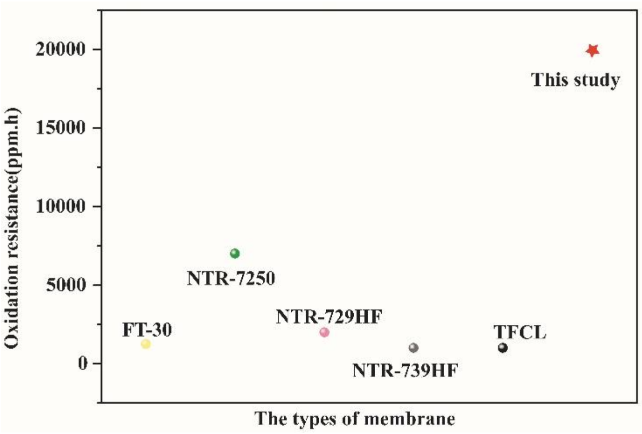

Fig. 12 Performance comparison with other types of membrane

increased significantly, and the salt rejection rate did not change much. As the glycerol concentration increased from 5% to 15%, the water flux of the composite NF membrane increased from 46.4 LMH to 108.2 LMH, and the salt rejection rate did not change much. And considering the rejection and water permeability of the composite membrane, an ultrafiltration flat based membrane with a pore size distribution mainly around 0.06μm was selected.

• The composition of the coating liquid had a great influence on the membrane structure and performance. Considering the performance and cost of the composite membrane, when the concentration of SPSf was 0.5 wt% and the sulfonation degree was 25%, the composite NF membrane prepared by the optimized coating system had a salt rejection rate of 45.2% to NaCl and a rejection rate of 91.3% to PEG1000.

• The post treatment process such as immersion time and oven wind speed had an important influence on the structure and performance of the composite membrane. As the immersion time of the coating solution increased, the rejection performance of the prepared composite NF membrane increased while the water permeability decreased. If the immersion time continued to increase, the separation performance of the composite membrane did not change much. Among them, the rejection rate of composite NF membrane to NaCl solution (250 ppm) increased from 42.5% to 45.3%, and the flux decreased from 73.2 LMH to 42.2 LMH. The rejection performance of the prepared composite NF membrane was increased and the water permeability was relatively better by controlling the temperature using high and low temperature frequency conversion air knife processing technology. Among them, the composite membrane had a salt rejection rate of 45.5% to NaCl solution (250 ppm) and a flux of 62.2 LMH. The tolerance of the membrane to NaClO can reach 20000 ppm.h.

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