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Preparation of high performance nanofiltration membrane by different dihydric alcohol in aqueous phase

Lei Wen[a,*], Wei Wang[a,b]

[a]*State Key Laboratory of Hollow Fiber Membrane Materials and Processes, College of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300160, China*
Email: wenlei35@sina.com
[b]*Tianjin Motian Membrane Engineering and Technology Co. Ltd, Tianjin 300160, China*

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ABSTRACT

Hollow-fiber composite nanofiltration (NF) membranes were prepared by interfacial polymerization method, polysulfone (PSF) hollow-fiber ultrafiltration membrane as base membrane. The effects of different dihydric alcohol in aqueous phase were mainly studied and optimized. Environmental conditions and reaction time on rejection and water flux of prepared composite NF membranes were also investigated. Furthermore, the morphology and chemical structure of composite membranes were examined by Fourier transform infrared spectroscopy (FT-IR), contact angle and scanning electronic microscopy (SEM), respectively.

Keywords: Nanofiltration; Hollow-fiber; Dihydric alcohol; Humidity

1. Introduction

Nanofiltration (NF) is gaining increasing attention in the fields of separation and treatment processes because of obvious advantages such as low operating pressures, high fluxes, high retentions of multivalent salts, low investment, and operation costs [1,2]. These advantages lead to a growing list of applications of the NF membrane, such as water softening, the purification of drinking water, wastewater treatment and reclamation, and the separation of substances [3,4]. NF membranes are generally fabricated using interfacial polymerization [5,6], which is generally employed for composite membrane preparation. Composite membrane technique is one of the most effective methods to prepare NF membranes.

In this technique, a thin film is introduced by forming an ultra-thin dense layer on a porous substrate. The ultra-thin active layer is the key component, which mainly controls the separation properties of the membrane, while the porous substrate gives the necessary mechanical strength. The main advantage of TFC membrane is that the membrane properties can be controlled by optimizing the characteristics of the thin selective layer and support [7]. The separation performance of the resulting NF membrane is dependent on several variables, such as the reactant monomer structures, preparation, and post-treatment condition [8,9]. High flux can be achieved by improving the membrane preparation process or altering the

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*Corresponding author.

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membrane properties [10]. Qiu et al. [11] improved the performance of the membrane by the addition of micromolecule alcohol. A highly hydrophilic NF membrane for desalination and water treatment was developed by Ahmad et al. [12] through the interfacial polymerization of trimesoyl chloride (TMC) with the mixture of piperazine (PIP) and 3,5-diaminobenzoic acid. It was found that the pure water permeability could be improved, as much as 20% by adding 3,5-diaminobenzoic acid into the PIP aqueous phase. The obtained membrane was more negatively charged and exhibited excellent rejection ability towards divalent ions compared to the monovalent ions.

In this study, composite NF membranes were prepared by interfacial polymerization method. polysulfone (PSF) hollow-fiber UF membranes were used as membrane support. TMC, PIP, m-phenylenediamine (MPDA), triethylamine (TEA), and dihydric alcohol were used as interfacial polymerization reaction reagents. The effects of environmental conditions, reaction time, and dihydric alcohol in aqueous phase on the performance of composite membranes were investigated. The salt separation capability and structure of composite NF membranes were characterized.

2. Experimental

2.1. Materials and reagents

The materials used for the study were microporous PSF supporting membranes with a molecular weight cut-off (MWCO) of around 20,000 Da and a water permeability of approximately 115 $\mathrm{L\,m^{-2}\,h^{-1}}$, purchased from Tianjin Motian Membrane Engineering and Technology Co. Ltd. (China). The reagents were PIP, MPDA, TEA, polyethylene glycol 200 (PEG200), ethylene glycol (EG), TMC, and $MgSO_4$, purchased from Tianjin Kemiou Chemical medicine Co. Ltd. (China). All reagents were analytical grade and used without further purification.

2.2. Fabrication of the composite NF membranes

The active skin layer of the composite NF membrane was prepared by interfacial polymerization technology. To begin with, the aqueous solution was prepared by dissolving 2 wt.% PIP, 0.5 wt.% MPDA, 1 wt.% TEA and a certain amount of dihydric alcohol in deionized water, where as the organic phase solution was composed of 2 wt.% TMC and organic solvent. Then, 10 mL aqueous phase and the organic phase solution were poured into the internal surface of the support PSF hollow-fiber UF membranes in proper sequence, respectively. Excess solution was drained from the soaked surface, and air-dried at room temperature until no remaining liquid [13]. After a certain period of residence, the excess solution was poured off. Finally, it was polymerized actually in air for a period of time.

2.3. Performance tests of the composites NF membranes

The performance tests of the composite NF membrane samples were evaluated at 0.7 MPa and room temperature. Test solution was dissolved 2,000 $\mathrm{mg{\cdot}L^{-1}}$ $MgSO_4$ in deionized water. NF membrane samples were placed in the test cell with the active skin layer facing the incoming feed. To ensure that the membrane surface performance is stable, the pressure was kept at 0.7 MPa for 10 min. The rejection (R) and water flux (F) were calculated using the following equations:

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \tag{1}$$

where R (%) is the rejection to $MgSO_4$, C_p (g/L) is the permeate concentration, and C_0 (g/L) is the feed concentration. NF performance was calculated by averaging the results of six membrane tests.

$$F = \frac{V}{S \times t} \tag{2}$$

where F ($\mathrm{L\,m^{-2}\,h^{-1}}$) is the water flux, V (L) is the permeate volume, S ($\mathrm{m^2}$) is the effect square of NF membrane, and t (h) is the permeate time of a certain volume.

All of the filtration processes were repeated three times.

2.4. Characterization of composite NF membranes

The chemical structures of PPENK membranes were verified by Fourier transform infrared spectroscopy (FT-IR, Bruker VECTOR-22, Germany). All membrane samples were used vacuum, prior to remove water.

The scanning electron microscope (SEM, S-4800, Japan) was used to analyze the surface as well as cross-sectional morphology of membranes. The samples of NF membranes were fractured in liquid nitrogen and gold sputtered samples were viewed with the microscope at 5 kV [14].

Contact angle reflects the hydrophobicity/hydrophilicity of the materials. Contact angle measurement for NF with deionized water was performed with contact angle meter (YH-168A, Hake, China). The membrane was cut as a small trip, and then was fixed on the glassed with double faced adhesive tape, to keep the surface of the testing sample level.

3. Results and discussion

3.1. The effects of dihydric alcohol in aqueous phase on composite NF membrane

In this research, the concentration and composites of dihydric alcohol were optimized to obtain the most suitable one for the formation of the better performance of the composite membrane. Firstly, the effects of the kinds of dihydric alcohol in aqueous solution on the performance of composite membrane to 2,000 mg L^{-1} $MgSO_4$ test solution were separately investigated at 0.7 MPa and room temperature. The result is shown in Fig. 1.

It was observed that the water flux of all the NF membrane increased with the addition of different dihydric alcohol, but the extent of increasing was different. The highest water flux was shown at the composite NF membrane of EG in the aqueous solution. When the dihydric alcohol changed from EG to PEG400, the water flux decreased gradually. But the rejection of different NF membrane changed little. Therefore, the addition of EG and PEG200 had a positive and significant impact on water flux of NF membrane.

FT-IR spectra of PSF UF membrane and composite NF membranes with EG and PEG200 in aqueous phase are shown in Fig. 2.

From the FT-IR spectra of composite NF membrane prepared by EG in aqueous phase, the spectrum of membrane showed the significant characteristic absorption bands of the ester bond at 1,735 cm^{-1}, stretching vibration of $-CH_2$ at 2,931 cm^{-1} and stretching vibration of intermolecular hydrogen bond O–H at 3,407 cm^{-1}. It can be illustrated that the hydroxyl group at one end of EG reacted with TMC successfully [11], the other terminal hydroxyl affected the membrane surface hydrophilicity.

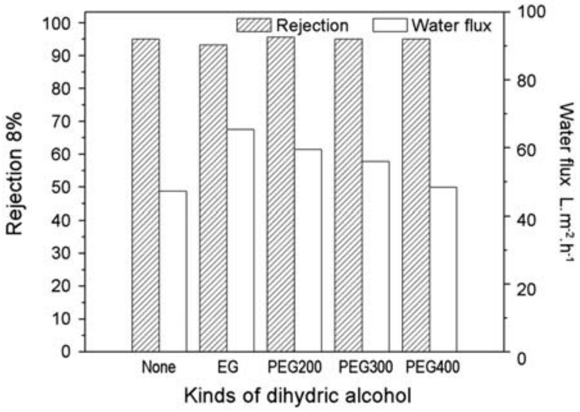

Fig. 1. Effects of different dihydric alcohol on performance of NF membrane.

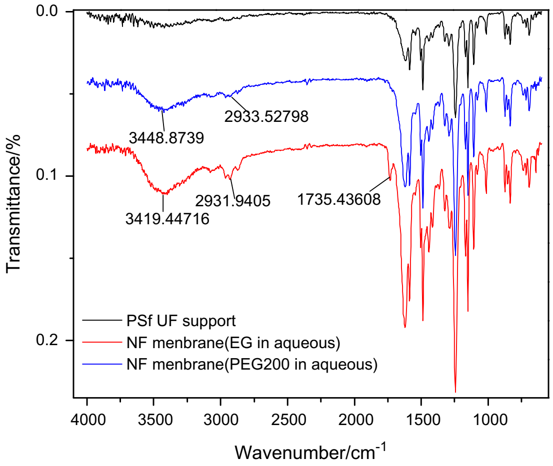

Fig. 2. FT-IR spectra of PSF UF membrane and composite NF membranes.

It was found that there was not any esterification reaction between PEG200 and acid chloride from infrared spectroscopy and several experiments. It was similar to space occupying or inlay. Therefore membrane surface appeared only a small amount stretching vibration region of the $-CH_2$ group at 2,933 cm^{-1} and relatively strong stretching vibration of the hydroxyl group at 3448 cm^{-1}. PEG200 concentration should be controlled in order to avoid excessive concentration affected the membrane structure perfect.

Table 1 shows the contact angle of PSF UF membrane, and composite NF membrane with dihydric alcohol in aqueous phase. The lower contact angle represents the higher hydrophilicity of the membrane and water permeation ability of composite NF membrane [14]. It can be seen that the addition of EG and PEG200 in aqueous phase increased the hydrophilicity of NF membrane.

Table 1
Contact angle of membranes

Kind of membrane	Contact angle (°)
PSF UF membrane	49.97
NF membrane with EG in aqueous phase	12.99
NF membrane with PEG200 in aqueous phase	15.63

The effects of EG concentration on composite NF membrane are shown in Fig. 3. The water flux declined and the rejection increased until the concentration of EG in aqueous phase enhanced to 1.5%. As EG concentration enhanced, the declination of rejection slowed down and the flux increased slowly.

It can be seen from Fig. 3 and Table 1 that one hydroxyl group of EG was reacted with an acid chloride, the other one was connected to the polymer molecules. These hydroxyl groups distributed at the membrane surface uniformly, so that the water flux of the membrane increased significantly with the increasing hydrophilicity of the membrane. The esterification reaction went on with increasing EG concentration. As a result, membrane surface became compact, leading to lower water flux. As the concentration exceeded 1.5%, network structure of NF membrane started to generate defects due to the existence of excess hydroxyl group, resulting in the decline of rejection and the increase of water flux. Therefore, NF membrane showed the best comprehensive separation performance with 1.5% EG in aqueous phase.

The influence of PEG200 concentration on performance of NF membrane is shown in Fig. 4. It was found that the rejection and water flux of NF membrane were relatively stable with increasing PEG200 concentration.

From Fig. 4 and Table 1 it can be seen that PEG200 has only space occupying or inlay in microporosity of the NF membrane. Therefore, 1.5% PEG200 in aqueous phase was able to guarantee the stability of the membrane performance.

To examine the stability of the membrane performance, PEG200, and EG were mixed in different ratios as the total concentration was 1.5%. The experimental results are shown in Fig. 5. It can be seen that the rejection was gradually increased but the flux changed slightly with increasing proportion of PEG200 and EG. When the ratio was over 1.25, the water flux of the membrane decreased. Under comprehensive evaluation, the best rejection of NF membrane was 96.3% and water flux was 67.8 L m^{-2} h^{-1} with the ratio of PEG200 and EG was 1.25 in aqueous solution.

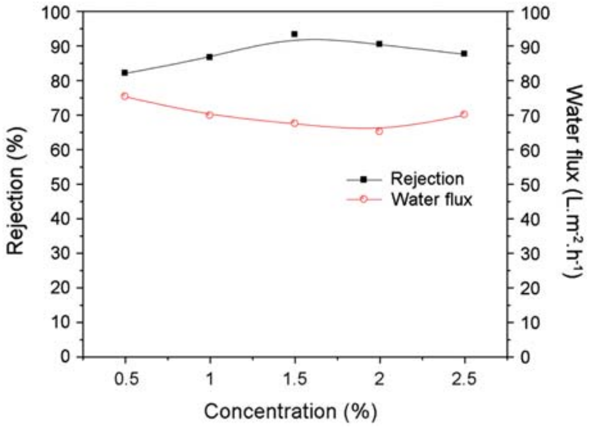

Fig. 3. Effects of EG concentration on performance of NF membrane.

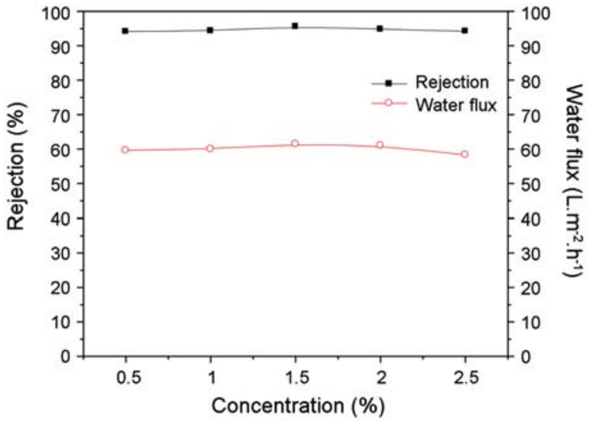

Fig. 4. Effects of PEG200 concentration on performance of the NF membrane.

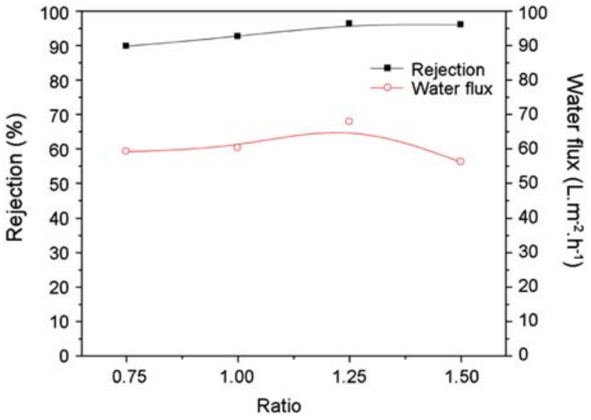

Fig. 5. Effects of ratio between PEG200 and EG on performance of NF membranes.

The morphologies of the membranes are shown in Fig. 6. It can be seen clearly from Fig. 6, that the top surface of composite membranes was rougher than substrate membranes. Therefore, it can be demonstrated that the active layer of composite membranes was successfully prepared on UF membranes. Similarly, the resultant can be confirmed by cross-section morphologies of the membranes.

3.2. The effects of environmental conditions

The effects of environmental temperature and humidity on water flux and rejection of NF membrane

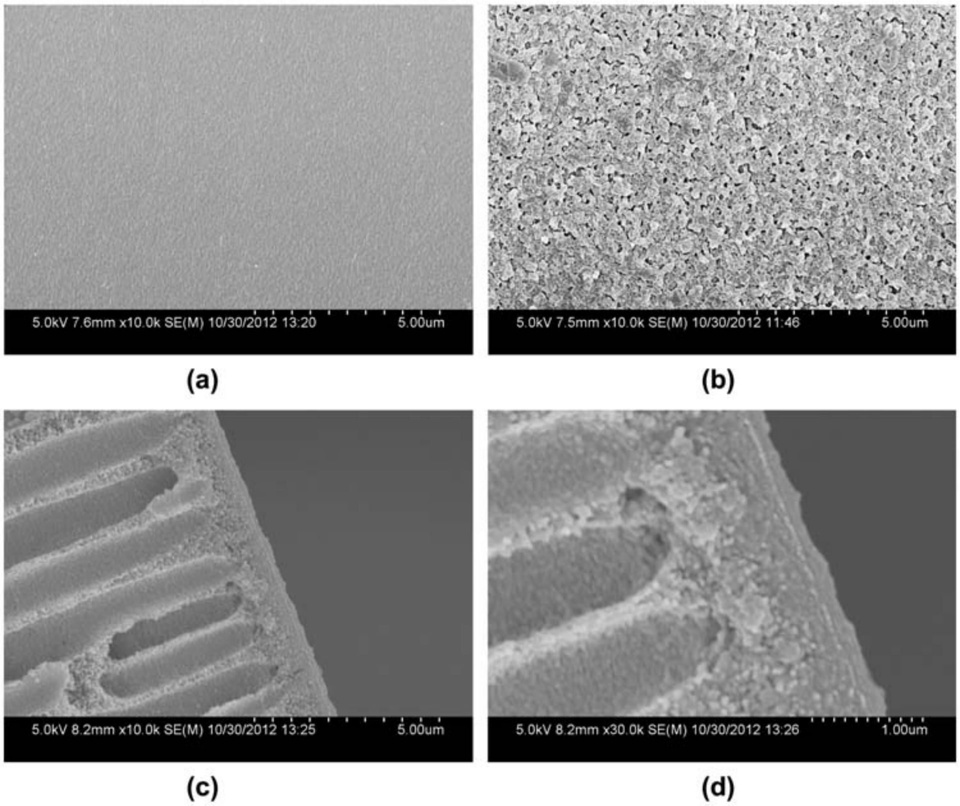

Fig. 6. SEM photographs of the surface of membranes. (a) Surface of PSf UF membrane, (b) surface of composite NF membrane, (c) cross-section of composite NF membrane enlarged 100,000%, and (d) cross-section of composite NF membrane enlarged 300,000%.

were discussed in this study. The results are shown in Figs. 7 and 8, respectively.

It can be seen from Fig. 7 that the rejection of membranes increased from 90 to 95.1% and the water flux of membranes increased from 55.3 to 65 L m^{-2} h^{-1} as temperature increased from 9 to 22°C. Then the rejection declined with the increasing temperature, the obvious enhancement of flux is mainly because of the decrease of rejection. The best temperature for preparation of NF membrane in laboratory was 24°C.

Both rejection and water flux increased rapidly within the whole testing scope (Fig. 8). The rejection

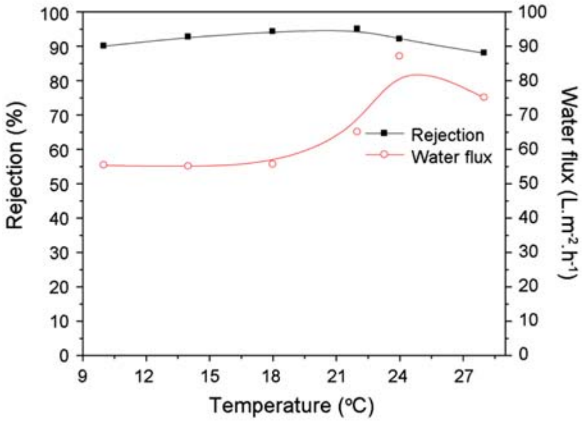

Fig. 7. Effects of preparation temperature on performance of NF membranes.

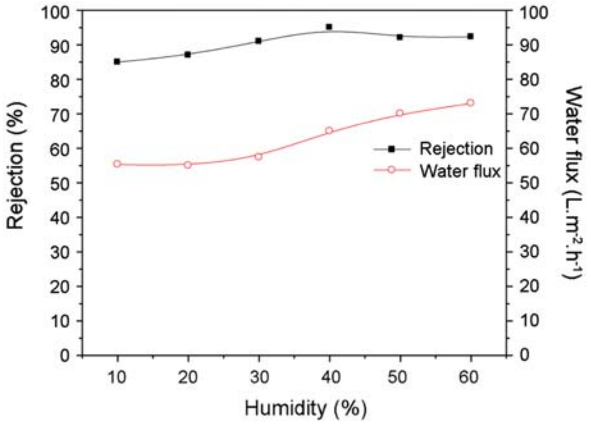

Fig. 8. Effects of preparation humidity on performance of NF membranes.

reached around 95% and the water flux increased to 73 L m^{-2} h^{-1}, which could be interpreted the performance of NF membrane was guaranteed in terms of the increment of humidity. To obtain the better rejection and water flux, the optimal humidity in the laboratory was 60%.

3.3. The effects of reaction time

The effects of reaction time between aqueous and organic phase on the performance of composite membranes were investigated at 24°C and 60% in laboratory. The results are shown in Fig. 9. The variation of membrane performance showed the different trend with polymerization time [15]. When reaction time increased, the water flux of membranes decreased and the rejection firstly increased and then kept stable.

It is well known that interfacial polymerization between diamine and acid chloride occurs on the organic side of the aqueous-organic interface, and the reaction is diffusion-controlled, and exists in a self-limiting phenomenon. Reaction time plays an important role in determining the extent of polymerization. For shorter reaction time, the extent of cross-linking was lower. But longer reaction time induced compact thin layer on top of the PSF support and increased the molecular weight of poly (PIP amide). Therefore, the flux of membranes descended and rejection of membranes enhanced. After a certain period of reaction, the rejection kept constant because both the thickness and compactness of selective skin layer became fixed [15]. Therefore, 55 s was the optimal reaction time under comprehensive evaluation.

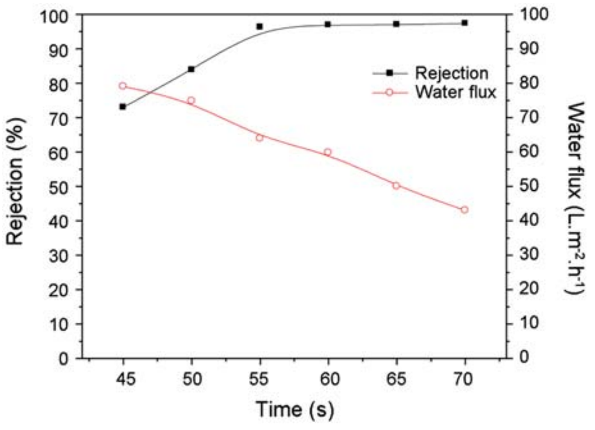

Fig. 9. Effects of reaction time on performance of NF membranes.

4. Conclusions

Hollow-fiber composite NF membranes were prepared by interfacial polymerization method. The morphologies, chemical structure, and hydrophility of composite NF membrane were shown by SEM photographs, FT-IR spectra, and contact angle test, respectively. The results indicated that PEG200 and EG had positive and significant influence on composite NF membranes performance. After optimizing the optimum conditions of preparation and the experimental results, the optimal preparation parameters for the composite NF membranes were as follows: 22°C and 60% humidity in laboratory, 55 s reaction time and the ratio between PEG200 and EG was 1.5 with total concentration of 1.5 wt.% in aqueous phase. At these optimal conditions, the best rejection of NF membrane to 2,000 mg L^{-1} $MgSO_4$ was 96.3% and water flux was 67.8 L m^{-2} h^{-1} at 0.7 MPa and room temperature.

Acknowledgments

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