The Preparation of Composite NF Membrane by Interfacial Polymerization Between Sulfanilic Acid and Trimesoyl Chloride

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Abstract. The nanofiltration (NF) membrane has many characteristics, such as low operating pressure, good selective separation, etc. These advantages make it have a good application prospect in the field of water treatment. The hollow fiber NF membrane was prepared by interfacial polymerization (IP), in which Sulfanilic Acid (SA) was used as water phase monomer and trimesoyl chloride (TMC) was used as organic phase monomer. Its performance was systematically analyzed. IR shows that the IP polymer contains amide group which indicates the occasion of IP between SA and TMC. The flux of NF membrane reduces and rejection increases with the increase of the SA concentration, TMC concentration and IP time. Its flux is lower and rejection is higher as the concentration of sodium carbonate (Na$_2$CO$_3$) and sodium dodecyl sulfonate (SDS) is 1.5% and 0.15%, respectively.

Introduction

The nanofiltration (NF) has lower operating costs than RO because its operating pressure is lower than RO’s. The NF membrane also has better separation performance. One reason is that it has narrower range of cutoff molecular weight (200-1000 Dalton). The other reason is that the most NF membrane takes charge. Charged NF membrane has different rejection for different ions because of Donnan effect. So NF membrane has a good application prospect in many fields, such as drinking water treatment $^{[1,2]}$, wastewater treatment and reuse $^{[3,4]}$, dye purification $^{[5,6]}$, food product $^{[7,8]}$, etc.

The NF membrane prepared by interfacial polymerization (IP) has thinner dense layer and higher flux. IP is currently one of the main techniques to prepare NF membrane $^{[9-10]}$. In this paper the hollow fiber NF membrane has been prepared by IP which SA was used as water phase monomer, and TMC was used as organic phase monomer. Its performance was systematically analyzed. The aim is to provide a reference for the preparation of NF membrane.

Experimental Section

Materials

Trimesoyl chloride (TMC) was obtained from Hai Bang Chemical Co., Ltd. Sulfanilic Acid was purchased from Tianjin sailboat Chemical Reagent Co., Ltd. Sodium dodecyl sulfate (SDS) was purchased from Tianjin Kermel chemical Reagent Co.; Sodium carbonate (Na$_2$CO$_3$) was obtained from Yantai Shuangshuang Chemical Co., Ltd; hexane was purchased from Tianjin Fu Yu fine chemical Co., Ltd. Polyethylene glycol (PEG1000) was obtained from Tianjin Kermel chemical Reagent Co..

Preparation of Polyether Sulfone Support Membrane

Polyether sulfone support membrane was prepared by dry/jet wet spinning technology, in which PFS (22%) was used as a membrane material, PVP (8%) and acetone (0.5%) were used as additives, DAMc was used as solvent. The UF membrane flux was 38.20 L·m$^{-2}$·h$^{-1}$ and rejection for PVA20000-26000 was 94.0% under the operating pressure of 0.35 MPa.
Preparation of Composite NF Membrane

Firstly, the aqueous solution was prepared which contains SA and Na$_2$CO$_3$ and SDS. Secondly, the aqueous solution was pumped into the lumen side of the support membrane and removed from the lumen side of the support membrane after it was kept for 30 min. Then, TMC solution was pumped into the lumen side of the support membrane and kept for a certain time. The IP reaction was carried out in the two-phase interface. IP route was shown in figure 1. The equipment of the IP was manufactured by myself in the laboratory.$^{[10]}$

![Figure 1. Interfacial polymerization route.](image)

Membrane Performance Test

The NF membrane was characterized by measuring the flux and the rejection. The solute in feed liquid was PEG1000, and its concentration was 500mg/L. The operating pressure was kept 0.35 MPa. The PEG1000 concentration was measured with spectrophotometer (Hangzhou Kexin Import & Export Co., Ltd).

Morphology of Membrane

Sample of the support membrane and NF membrane was frozen in liquid nitrogen and then fractured. Their inner surfaces were sputtered with gold, and their morphologies were inspected by scanning electron microscope (S4800, Hitachi, Ltd, Japan).

Polymer FITR-ATR Study

The polymer prepared by IP was dried under vacuum. Then its absorption spectrum was measured with infrared spectropotometer (IR200, Nicolet Instrument Corporation, America) after it was pressed into tablet KBr.

Results and Discussion

Morphology of Membrane

The inner surface SEM of ultrafiltration support membrane and NF membrane was shown in Fig. 3 and Fig4, respectively. It can be seen that the surface forms a dense layer after interfacial polymerization by contrast of Figures 2 and 3.
Effect of IP Conditions on the Performance of NF Membrane

Effect of SA Concentration

The water solution was prepared in which the concentration of SDS and Na\(_2\)CO\(_3\) was 0.3% and 0.15%, respectively. The SA concentration changed from 0.5% to 2.0%. The aqueous solution reacted with the organic phase which contains 0.5% MTC for 3 min under room temperature. The effect of SA concentration on performance of NF membrane was shown in Fig. 4.

Fig. 4 shows that the rejection of NF membrane increases and the water flux decreases with the SA concentration increasing. The changing trend of flux and rejection of NF membrane changes slowly when the SA concentration exceeds 1.5%. The IP speed drastically accelerates which causes the sharp increasing of composite dense layer thickness, and the diameter of network hole in the dense layer becomes quickly smaller with the SA concentration increasing when the concentration of the SA is lower than 1.5%. The change trend is slow because of self-inhibition of IP.

Effect of Na\(_2\)CO\(_3\) Concentration

The water solution was prepared in which the concentration of SA and SDS was 1.5% and 0.15%, respectively. The Na\(_2\)CO\(_3\) concentration increased from 0.05% to 0.4%. The aqueous solution reacted with the organic phase containing 0.5% MTC for 3 min under room temperature. The effect of Na\(_2\)CO\(_3\) concentration on performance of NF membrane was shown in Fig. 5.

![Figure 4. Effect of SA concentration on NF membrane.](image)
It can be seen from Fig. 5 that the rejection of NF membrane gradually increases and the water flux gradually decreases when Na₂CO₃ concentration increases. The rejection reaches maximum and the water flux reaches minimum when Na₂CO₃ concentration reaches 0.2%. The rejection of NF membrane decreases and the flux increases when the Na₂CO₃ concentration further increases. The reason is maybe that HCl produced in IP reaction can be quickly neutralized by Na₂CO₃ and it can increase speed of IP reaction when Na₂CO₃ concentration is lower. But excessive Na₂CO₃ can make more chloride hydrolyze which worse IP reason conditions.

Effect of SDS Concentration

The water solution was prepared in which the concentration of SA and Na₂CO₃ was 1.5% and 0.2%, respectively. The SDS concentration increases from 0.05% to 0.25%. The aqueous solution reacted with the organic phase containing 0.5% MTC for 3 min under room temperature. The effect of SDS concentration on performance of NF membrane was shown in Fig. 6.

Figure 6 shows that the rejection of NF membrane gradually increases and the water flux gradually decreases when SDS concentration increases. But the rejection of NF membrane decreases and the flux increases with the SDS concentration further increasing after the concentration of SDS exceed 0.15%. This result is similar with Zhang Haoqin’s research [11].

Effect of TMC Concentration

The effect of TMC concentration on performance of NF membrane was shown in Fig. 7.

It can be seen from Fig. 8 that the rejection of NF membrane increases and the water flux decreases when the TMC concentration increases. The changing trend of flux and rejection of NF membrane changes slowly when the SA concentration exceeds 1.5%. The reason is similar with the effect of SA concentration change on NF membrane.

Effect of IP Time

The water solution was prepared in which the concentration of SA and Na₂CO₃ and SDS was 1.5%, 0.2% and 0.5%, respectively. The MTC concentration in Organic phase was 0.5%. The effect of IP time on performance of NF membrane was shown in Fig. 8.
Fig. 8 shows that the rejection of NF membrane increases and the water flux decreases with IP time prolonging. The trend doesn’t become significant when IP time exceeds 4 min. It is maybe that the IP reaction has nearly completed. The IP speed becomes lower.

**Separation Performance of NF Membrane**

The NF membrane was prepared by IP under the optimal conditions which sulfanilic acid concentration was 1.5%, Na$_2$CO$_3$ concentration was 0.2%, SDS concentration was 0.15%, TMC concentration was 0.5%, and the polymerization time interface was 4 min. The performance of NF membrane was shown in Table 1.

Table 1 shows that the rejection of NF membrane for neutral red, methyl green, xylenol orange and PEG1000 is 75.58%, 73.21%, 83.89% and 90.93%, respectively. The rejection of NF membrane for NaCl, MgCl$_2$, Na$_2$SO$_4$ is 16.62, 15.95, and 19.91, respectively.

**Conclusion**

The composite NF membrane can be prepared by IP between SA with TMC. The thickness of the composite layer increases and a network hole diameter in dense layer reduces with increasing the concentration of SA in aqueous phase and TMC in organic phase and IP time, so that its flux reduces and rejection increases. The concentration of Na$_2$CO$_3$ and SDS in aqueous phase has influences on the performance of NF membrane. The flux of NF membrane is higher and it is lower when Na$_2$CO$_3$ and SDS concentration is 0.2% and 0.15%, respectively.

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