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Preparation polyamide nanofiltration membrane by interfacial polymerization

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ABSTRACT

Nanofiltration (NF) composite membrane was prepared by interfacial polymerization of 1,6-hexylenediamime, o-phenylenediamine or piperazine with trimesoyl chloride (TMC) on the surface of polysulfone support, respectively. Meanwhile, two polysulfone support membranes with different molecular weight cut off (MWCO) were introduced into this experiment, hoping to find the influence of porous substrates on the prepared membrane performance. Furthermore, the water flux and salt rejection rate of those three kinds of newly-prepared NF composite membranes were compared by water filtration experiment. In order to make interfacial polymerization much more effective, kinds of reaction ratios between piperazine and TMC were designed. It can be seen from the results that piperazine reacts better with TMC compared to the other two chemical medicines, and the salt rejection rate of poly (piperazine) NF composite membranes can arrive at 55% under the condition of laboratory; however, the effects of polysulfone supports on NF performances were various when different polyamines were put to use and polysulfone support membrane M (the one with higher molecular weight cut-off) was preferred to prepare the poly (piperazine).

Keywords: Trimesoyl chloride; Piperazine; Water flux; Salt rejection rate; Water treatment; Nanofiltration

1. Introduction

In recent years, nanofiltration (NF) process is widely increasing in the application of drinking water treatment due to high removal efficiency in natural organic matter (NOM), the disinfection by-product (DBP) precursors, and in water softening for removing divalent cations from natural waters [1–3]. NF is in between ultrafiltration (UF) and reverse osmosis (RO), with a lower operating pressure than RO and a higher rejection than UF. The filtration process takes place on a selective separation layer formed by an organic semi permeable membrane, which has a relatively high charge and 'pores' in the order of about 1 nm. NF membranes have the advantages of providing a high water flux at low operating pressure and maintaining a high salt and organic matter rejection.

The desirable properties of membrane materials, such as high water permeability, high salt rejection, and chemical resistance, are most appealing. Two different techniques have been adopted for the development of preparing polymeric membranes: the phase-inversion method for asymmetric membranes and interfacial polymerization. Now most of the commercial nanofiltration membranes are thin-film composite (TFC) membranes. TFC membrane preparation technique is based on interfacial polymerization (polycondensation) reaction between two monomers. The polymerization takes place at the interface between two immiscible phases upon contact. In this technique, a thin film is introduced by forming an ultra-thin dense layer on a porous substrate. In interfacial polymerization method, reactive monomers are dissolved in two immiscible phases and the polymerization of the reactive monomers occurs on the surface of the porous support membrane.

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The advantage of interfacial polymerization is that the reaction is self-inhibiting through passage of a limited supply of reactants through the already formed layer resulting in an extremely thin film of thickness within 50 nm range [4]. The benefit of TFC by interfacial polymerization is that the membrane properties can be controlled by optimizing the characteristics of the selective layer and support. The selective layer can be optimized for solute rejection and solvent flux by controlling the coating conditions and characteristics of the reactive monomers. The microporous support can be selectively chosen for porosity, strength and solvent resistance [5]. Considerable interest concerning the fabrication of TFC membranes for the NF process and their performance has been generated in recent years on the synthesis of new polymeric materials after interfacial polymerization was developed by Cadotte at the North Star Research Institute for reverse osmosis applications [4,6–9].

In this study, we prepared polyamide TFC NF membranes for the investigation of the permeation rates and salts rejection. Membrane flux and rejection as well as the chemical properties of the prepared film were evaluated as a function of monomer concentration.

2. Experimental

2.1. Materials

Trimesoyl chlorine (TMC) was purchased from Sigma-Aldrich (Oakville, Canada). N-hexane (AR, 97%), 1,6-hexylenediamime (AR, 99.0%), o-phenylenediamine (CP, 98.5%), piperazine (BR, 99.5%), sodium carbonate (Na_2CO_3) (AR, 98.5%) and magnesium sulfate ($MgSO_4$) (AR, 98.0%) were purchased from Shanghai Guoyao Company. Polysulfone (Psf) ultrafiltration (UF) membrane M (MW~100000) and K (MW~30000) used as support were offered by Beijing Sheng Wan Quan New Star membrane science and technology Co. Ltd., Deionized water (18.2 MΩ cm) used for all experiments was produced by a Millipore Milli-Q system (MA, USA). All the solvents were used as received.

2.2. Membrane preparation

The composite membrane was prepared by coating a layer of chloramine onto a Psf porous substrate. The top chloramine layer of the composite membrane was crosslinked interfacially by depositing acyl chlorides and amine materials under the normal temperature. 1,6-hexylenediamime, o-phenylenediamine and piperazine were dissolved separately into water to form a homogeneous solution, which was used as the water phase. Blank Psf-UF membranes support (the effective area is 57.6 cm^2) were immersed in this water phase containing different amine materials for a specified period (water phase soaking) to which 2.0 wt.% of sodium carbonate (Na_2CO_3) had been added as a surfactant, and then were taken out. After the excessive solution was removed from the surface by gently pressing an absorbing surface to the support membrane, the membranes were then submerged in a solution of TMC in n-hexane (organic phase soaking) for a specified period. This resulted in the formation of a thin chloramine film on the surface of Psf-UF membrane. The obtained composite membranes then underwent heat treatment in an oven (at 100°C) for 10 min and necessary ultrasonication for 3 min to attain the desired stability of formed structure. Finally, the membrane was preserved in deionized water for further use.

2.3. Measurement of the membrane

The membrane samples were checked carefully under a fluorescent lamp to avoid some obvious defects before test. Their performance were evaluated at 0.5 MPa using 2000 ppm $MgSO_4$ solution (pH 7.0) at 25°C in a membrane cell. Elliptic membrane sample, whose effective area is around 57.6 cm^2, was placed in the membrane cell with the active skin layer facing the incoming feed. All the membranes were initially subjected to pure water with pressure of 0.5 MPa for 4 h prior to performing the NF test experiments. The water flux was determined by direct measurement of permeate flow in terms of litre per squaremeter per hour (l/(m^2 h)). The salt rejection of the membrane was defined as below:

$$R_j(\%) = (1 - \frac{C_i}{C_0}) \times 100$$

In which R_j is the salt rejection, C_i (mg/l) is the permeate concentration and C_0 (mg/l) is the feed concentration. The salt concentration was measured by a conductance meter (Shanghai Leici, DDS –307) and samplings were collected every half hour for 4 h. All membrane samples were prepared and tested at least three times, results of which had been averaged.

Schematic experimental unit is shown (Fig. 1) as follows:

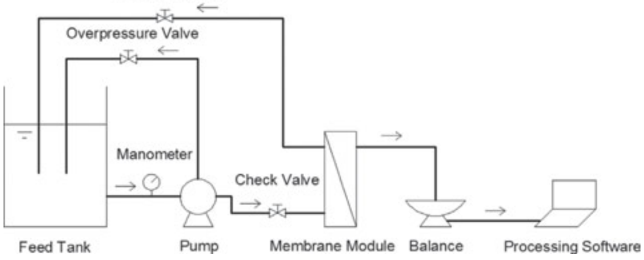

Fig. 1. Schematic experimental unit for NF membrane.

The membrane cell was made accordingly by Toray in Japan and the balance was purchased from Ohaus Instrument (Shanghai) Co. Ltd.

3. Results and discussion

3.1. Effect of water phase and the polysulfone support on NF performance

In order to study the performance of NF composite membranes, 1,6-hexylenediamime, o-phenylenediamine and piperazine were selected as water phase to react with TMC on the surface of polysulfone support by interfacial polymerization, respectively. Meanwhile, two polysulfone support membranes named M and K with different molecular weight cut off (MWCO) which is 100000 in membrane M, while 30000 in membrane K.) were introduced into this experiment, hoping to find the influence of porous substrates on the prepared membrane performance.

Table 1 shows the sample ID of prepared Psf-based membranes, their corresponding monomers in the interfacial polymerization process and the Polysulfone support membrane used. Moreover, the initial flux and the salt rejection after 4 h operation of these composite membranes are presented as well.

It can be seen from the Table 1 that NF composite membranes made of 1,6-hexylenediamime had a negligible salt rejection after 4 h condition, especially when polysulfone support K was used, such as K11 and K14 whose salt rejections were obviously below 5%. With the increase of soak time for water and organic phases from 20s to 120s, the salt rejection of NF composite membrane prepared on the polysulfone support M was raised accordingly from 15% to 24% while the intial flux met a decline. Nevertheless, it seems that the change of soak time had little effect on the salt rejections of those prepared on the polysulfone support K as there was hardly any improvement of salt rejection from K11 to K14. This particular case might not be an accident but shows the different effects of two polysulfone support membranes. As to NF composite membranes made of 1,6-hexylenediamime, the effect of soak time depends largely on the polysulfone support used.

By adjusting the soak time and type of polysulfone support, the performance including the initial flux and the salt rejection after 4 h operation of NF composite membranes made of o-phenylenediamine remained insignificant but almost constant, indicating that the soak time and type of polysulfone support may have less influence on membrane performance when o-phenylenediamine was selected to form the water phase. Therefore, some other methods might be adopted for ameliorate this kind of NF composite membranes.

However, NF composite membranes made of piperazine had a decent salt rejection after 4 h condition, the lowest one of which was 44% among the M13, M16, K13 and K16. Along with the continue of interfacial polymerization, the initial flux of all those NF composite membranes decreased visibly while their corresponding salt rejection experienced a satisfactory rise. To find out its cause, the chair shape of piperazine in its lowest energy state made the cross-linked polyamide molecules more difficult to pack together, providing more free volume and larger pore sizes to the polyamide active layers, which would no doubt benefit the water flux. On the other hand, the cross-linked

Table 1
Sample ID of different Psf-based membranes and their corresponding compositions, initial flux and salt rejection after 4 h condition

Membrane ID	Water phase (soak time)	Organic phase (soak time)	Polysulfone support membrane (MWCO)	Initial flux (L/h/m^2/bar)	Salt rejection after 4 h condition (%)
M11	1,6-hexylenediamime (20s)	TMC (20s)	100000	8	15
M12	o-phenylenediamine (20s)	TMC (20s)	100000	15	16
M13	piperazine (20s)	TMC (20s)	100000	10	53
K11	1,6-hexylenediamime (20s)	TMC (20s)	30000	32	<5
K12	o-phenylenediamine (20s)	TMC (20s)	30000	13	16
K13	piperazine (20s)	TMC (20s)	30000	11	44
M14	1,6-hexylenediamime (120s)	TMC (120s)	100000	1	24
M15	o-phenylenediamine (120s)	TMC (120s)	100000	12	16
M16	piperazine (120s)	TMC (120s)	100000	5	64
K14	1,6-hexylenediamime (120s)	TMC (120s)	30000	11	<5
K15	o-phenylenediamine (120s)	TMC (120s)	30000	14	16
K16	piperazine (120s)	TMC (120s)	30000	4	52

Note: The mass fraction of water phase is 1.0 wt.%; the mass fraction of organic phase is 0.5 wt.%. Sodium carbonate (Na_2CO_3) had been added as a surfactant.

structure in the poly (piperazineamide) contained the carboxylic acid functional groups, the partial hydrolysis of acyl chloride unit of TMC. The content of those groups affected water flux and electrostatic repulsion between ions or charged molecules and membrane surface. Therefore, poly (piperazineamide) had an efficient performance and piperazine was selected for later study. As far as the polysulfone support used, membrane M appeared more suitable for the self-preparation of NF composite membranes because of their higher salt rejections compared to those of the NF prepared on membrane K.

After 4 h condition, the water flux of most NF composite membranes became stable and comparable. From Fig .2, the curve of M11 was quite different from that of K11, so it was the same with M14 and K14, indicating that if 1,6-hexylenediamime is selected as water phase, the effect of polysulfone support might not be ignored. The changing trend of M12, K12, M15 and K15 were shown in Fig. 3, showing clearly that the soak time and the type of polysulfone support are not the main consideration during the interfacial polymerization by o-phenylenediamine. These two conclusions drawn here are fairly in accord with those obtained from Table 1.

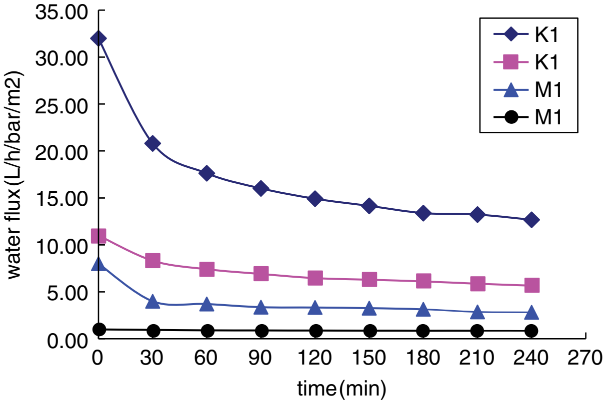

Fig. 2. Water flux against time at 25°C for NF composite membranes made of 1,6-hexylenediamime.

The results in Fig. 4 showed that the differences of curves between M13 and K13 was relatively slight, so was that between M16 and K16. Nevertheless, the salt rejection after 4 h of M13 was higher than that of K13 and meanwhile M16 and K16 had the similar relationship in Table.1. It demonstrated that as to poly (piperazine) NF composite membrane, the type of polysulfone support would mainly influence the salt rejection of ions or charged molecules rather than the water flux. Therefore, polysulfone support M was selected for later use.

3.2. *Effect of monomers concentration on NF membrane performance*

Based on the previous study, piperazine was chosen as the water phase while polysulfone support M was used as the substrate. In order to make interfacial polymerization much more effective, kinds of reaction ratio between piperazine and TMC were designed. Table 2 shows the sample ID of prepared Psf-based membranes and their corresponding compositions in the interfacial polymerization. Moreover, the initial flux and salt rejection after 4 h condition of these composite membranes are presented as well.

Obviously, there was an order about the salt rejection rate for these poly (piperazine) NF composite membranes: M25 > M26 > M24; M28 > M29 > M27. When the mass fraction of piperazine was fixed, the higher the mass fraction of TMC in the crosslinking solution, the lower the water flux. However, the rejection of composite membrane increased accordingly, not only to hydrone but also to charged molecules.

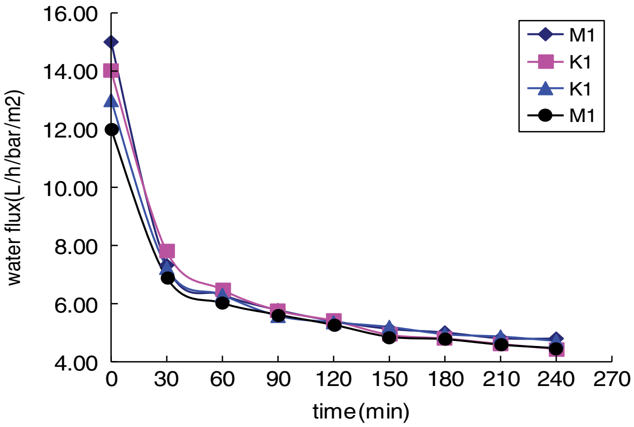

Fig. 3. Water flux against time at 25°C for NF composite membranes made of o-phenylenediamine.

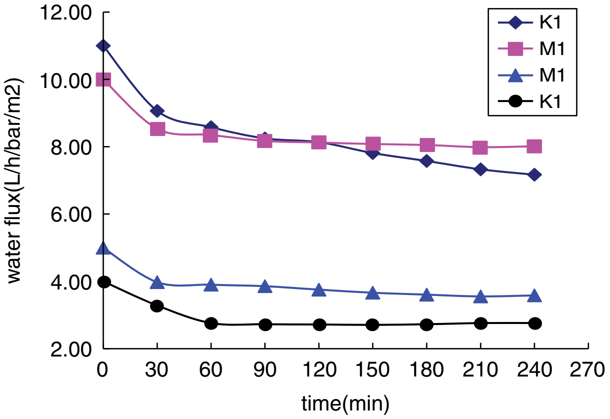

Fig. 4. Water flux against time at 25°C for NF composite membranes made of piperazine.

Table 2
Sample ID of different Psf-based membranes and their corresponding compositions, initial flux and salt rejection after 4 h condition

Membrane ID	Piperazine (mass fraction) (%)	TMC (mass fraction) (%)	Initial flux (L/h/m^2/bar)	Salt rejection after 4 h condition (%)
M21	0.2	0.1	21	<5
M22	0.2	0.5	32	<5
M23	0.2	1.5	31	<5
M24	1	0.1	20	24
M25	1	0.5	12	46
M26	1	1.5	7	31
M27	1.5	0.1	13	29
M28	1.5	0.5	9	55
M29	1.5	1.5	5	48

Note: The soak time in the water phase and organic phase is 20s, respectively. Sodium carbonate (Na_2CO_3) had been added as a surfactant.

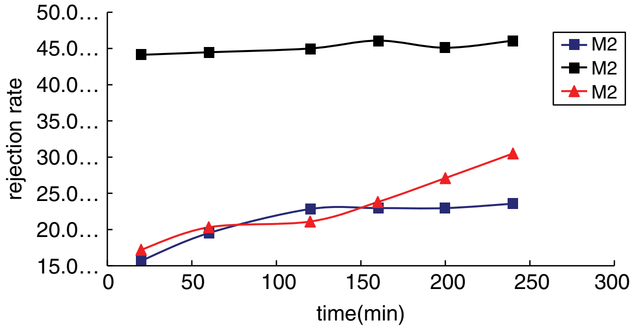

Fig. 5. Rejection rate against time at 25°C for poly(piperazine) NF composite membranes when the mass fraction of piperazine was fixed at 1.0%.

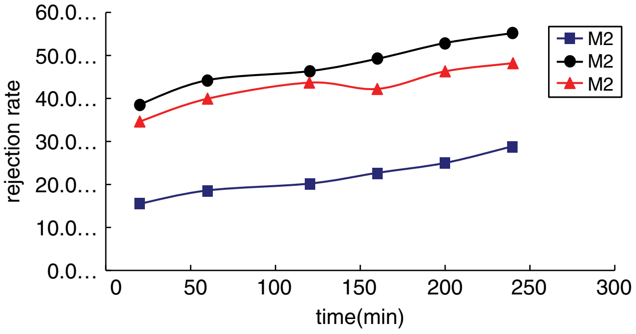

Fig. 6. Rejection rate against time at 25°C for poly (piperazine) NF composite membranes when the mass fraction of piperazine was fixed at 1.5%.

Furthermore, this two kinds of raise were not totally at the same speed. As depicted in Table 2 and Figs. (5 and 6), when the mass fraction of piperazine was fixed at 1.0% (or 1.5%) and that of TMC stayed at 0.5%, composite membranes had a better rejection rate. M25 (M28) was more willing to reject charged molecules than hydrone compared to M24 (M27), and this tendency enhanced gradually as the mass fraction of TMC increased from 0.1% to 0.5%. On the contrary, M26 (M29) preferred to reject hydrone to charged molecules in relation to M25 (M28) with the increase of the mass fraction of TMC from 0.5% to 1.5%. It is inferred that there exists a best-fit ratio for piperazine to react with TMC from 0.1% to 0.5% when the mass fraction of piperazine is controlled.

4. Conclusion

NF composite membranes were successfully prepared from 1,6-hexylenediamime, o-phenylenediamine and piperazine through interfacial polymerization. Among all the self-prepared ones, poly (piperazine) NF composite membranes based on polysulfone support M had a comparably better performance including the water flux and the salt rejection after 4 h operation. After optimizing the preparation condition, it was found that there might be a best-fit ratio for piperazine to react with TMC and this value would be obtained at the apex of an inverted U.

Compared with commercial NF membranes such as HL and NF270, whose salt rejections were able to reach more than 95% and whose water flux could keep stable for long, our self-prepared NF composite membranes had relatively inferior performances. However, by using ATR-FTIR we found that most characteristic absorption peaks of the inner construction of commercial NF membranes were quite similar to those of our self-prepared NF membranes. It was inferred that there might exist certain relationship between our self-prepared NF membranes and commercial ones. The study will be continued.

Acknowledgements

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