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A novel method to improve flux of nanofiltration composite membrane prepared by interfacial polymerization

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ABSTRACT

Thin film composite (TFC) nanofiltration (NF) membranes based polyamide were prepared with piperazine (PIP) and trimesoyl chloride (TMC) through interfacial polymerization technique on the polysulphone supporting film. The poly(dimethylsiloxane) (PDMS) was added in oil TMC solution to optimize membrane performance. The results showed that compared with the NF membrane without adding PDMS, the NF membrane with adding PDMS had higher water flux (maximum about 2 times); and rejection for PEG200 and NaCl decreased with increase of Molecular weight of PDMS, but Rejection for Na_2SO_4 keep stable. The average roughness (Rq) of NF membrane increased with the molecular weight of PDMS increasing by the AFM results, higher Rq leads to bigger effective area. The best PDMS with molecular weight63000 was obtained. With PDMS63000 content increasing, the molecular weight cut off (MWCO) of NF membrane with PDMS63000 increased from 200Da to 340Da, the flux increased from 40 $l/m^2{\cdot}h$ to 70 $l/m^2{\cdot}h$ at 1.0 MPa, while the rejection for Na_2S0_4 unchanged with the concentration of PDMS increasing when PDMS63000 content was less than 0.5%.

Keywords: Poly(piperazineamide); Nanofiltration; Poly(dimethylsiloxane); Thin-film composite membrane; Interfacial polymerization; Molecular weight cut off

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1. Introduction

Thin film composite (TFC) membranes, including Reverse osmosis (RO) membranes and Nanofiltration (NF) membranes have been successfully applied in commercial water treatment and water pollution control [1–5]. A numerous new polymeric materials for thin films of active layers [6–8] and some novel membrane preparing methods [9–11] lead to the current worldwide expansion and diverse application of the RO/NF technology.

Rejection and the flux are two essential direct parameters of membrane in the RO/NF process which determined by the solubility and diffusivity of solutes and solvents to the active-layer polymers [12]. Much attention was focused on how to improve TFC membrane flux because high membrane flux means to high filtration efficiency.

Zhang et al. [13] prepared a new material, sulfonated cardo poly(arylene ether sulfone) bearing pendant amino groups, and mixed with m-Phenylenediamine (MPD) in aqueous phase for preparing the high flux composite RO membranes. Mansourpanah et al. [14] studied the effects of addition of cationic cetyltrimethylammonium bromide (CTAB), non-ionic (Triton X-100) and anionic sodium dodecyl sulfate (SDS) surfactants in organic phase for preparing the composite nanofiltration membranes and found that the prepared membranes

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using SDS showed higher flux compared to the other membranes, but SEM surface images demonstrate some defects and cracks on the thin layer surface of the membrane prepared with SDS. Raval et al. [15] treated polyamide RO membrane with chlorine to enhance flux, it was found that low concentration of chlorine up to a certain time may give synergistic effect on membrane and improve its performance, high concentration of chlorine leading to deterioration in performance. The key point was to treat RO membrane by controlled chlorine treatment. Yoon et al. [16] produced high flux thin film nanofibrous composite (TFNC) membranes by interfacial polymerization of polyamides containing different ratios of piperazine and bipiperidine on electrospun polyacrylonitrile (PAN) nanofibrous scaffold. The results showed that TFNC membranes on electrospun polyacrylonitrile (PAN) nanofibrous scaffold exhibited over 2.4 times more permeate flux than TFC membranes with the same chemical compositions on a commercial PAN ultrafiltration (UF) support, while maintaining the same rejection rate (ca. 98%). Further more, hydrophilization of thin film composite reverse osmosis membranes, chemical treatment of thin-film composite (TFC) reverse osmosis (RO) membranes by hydrofluoric and fluosilicic acids [17] were also used to increase flux of membranes.

The purpose of this study is to improve the permeate flux without decline of divalent ion rejection by adding poly(dimethylsiloxane) (PDMS) with methyl terminated in oil phase. The thin-film-composite nanofiltration membrane was prepared with trimesoyl chloride (TMC)/PDMS and piperazine (PIP) through interfacial polymerization technique on porous polysulphone supporting membrane. Fig. 1 was the chemical structure of two monomers and PDMS. NF membranes with high water permeability coefficient could be prepared through optimizing the content and average molecular weight of PDMS adding in the oil phase. The membranes were characterized using permeation experiments with different inorganic/organic solute aqueous, X-ray photoelectronic spectroscopy (XPS) and Atomic force microscopy. The pore size of the NF membrane was evaluated with organic solute aqueous. The relation of NF performance and structure of membranes was elucidated.

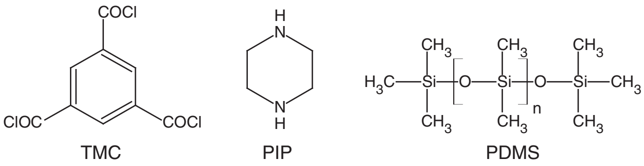


Fig. 1. Chemical structure of monomers and PDMS in this study.

2. Experimental

2.1. Preparation of TFC nanofiltration membrane

To fabricate the TFC membrane, support membrane composed of microporous polysulphone (The Development Center of Water Treatment Technology, SOA, China) was clamped between two Teflon frames that were 0.8 cm high and inner cavity 15 cm × 24 cm in an assembly clean room. An aqueous solution of piperazine (PIP, Shanghai AMINO-CHEM CO.LTD, purity >99.5%) was poured on top of the support membrane and allowed to soak for 2 min. The surface was rolled with a soft rubber roller to eliminate some little bubble during soaking procedure. Excess solution was drained off the surface by standing the holder on the top and bottom edge until no excess liquid exists. The holder was then held at a 30 degree and the organic solution of trimesoyl chloride (TMC, Qin Dao Ocean Chem. Co, purity >99.0%) was poured into the frame from top to bottom; the holder was then lowered quickly. After a 20 second residence time, the excess organic solution was poured off the surface, and the frame with membrane was held at 80°C in a hot air dryer for five min so that a skin layer was formed on the supporting membrane. The composite nanofiltration membranes were washed in pure water (<2 μs/cm) and kept in 0.5% $NaHSO_3$ solution.

The aqueous solutions in this study contained total 0.24% (w/v) of PIP, acid acceptor (sodium phosphate) to absorb the hydrochloric acid (HCl) from the interfacial reaction. The organic solution was IP1016 solution (isoparaphin type hydrocarbon oil made by IDEMITSU Chemical Co. Ltd.) containing 0.2% (w/v) of TMC and PDMS.

2.2. Characterization of TFC membrane

The membranes used for the chemical structure analysis of skin layer were rinsed at 0.5 MPa using pure water (<2 μs/cm) for four hours in order to remove the PIP. Then the samples were dried in a vacuum dryer at 80°C, 200 Pa for 10 h.

Surface chemical characterization was carried out by X-Ray photoelectron spectra (XPS), which was a Perkin Elmer PHI 5000C ESCA System with Mg/Al Dual Anode Hel/Hell ultra violet source (400 W, 15 kV, 1253.6 eV). For each membrane, XPS analysis was carried out three times using different samples. Membranes were irradiated separately and for a maximum of 20 min to minimize X-ray-induced sample damage.

The surface morphology was determined by Atomic force microscope (AFM, Park Instrument Auto Probe CT).

2.3. Membrane performance evaluation

Tests for NF performance were conducted in cross-flow cells (Fig. 2) with pure sodium chloride aqueous,

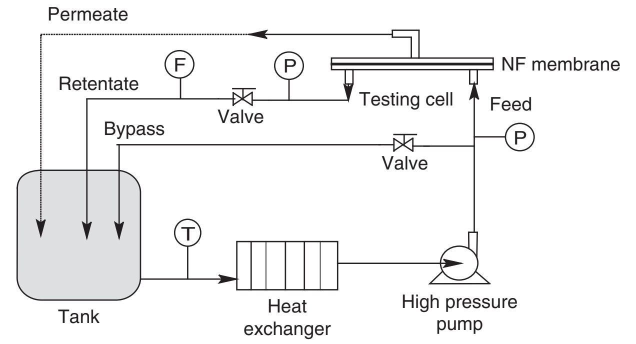


Fig. 2. Schematic description of NF performance testing equipment.

pure magnesium sulfate, pure sodium sulfate aqueous, and the PEG aqueous respectively under certain operating conditions (20°C, 1.0 MPa, solute concentration and pH = 7.1–7.5). Circular membrane samples with a diameter of 80 mm were placed in the test cell with the active skin layer facing the incoming feed. The effective membrane area (for each cell) was around 20 cm^2. The water flux was determined by direct measurement of the permeate flow in terms of liter per square meter per hour ($l/m^2\cdot h$). The permeate returned to feed tank after testing. The solute rejection rate was measured by the solute concentration of permeate and feed solution. The inorganic aqueous obtained through measurements of the chloride and sulfate ion content using titration and the organic aqueous obtained through TOC-620CTOC (total organic carbon) analyzer. All membrane samples were prepared and tested in at least duplicate with a total of 6 membranes tests for NF performance, results of which have been averaged.

3. Results and discussion

3.1. Effect of Molecular weight of PDMS on performance of NF membrane

The molecular sieving and charge effects are two key factors for solute rejections of NF membrane [18]. The rejection of the NF membranes were tested using a series of electrolytes and neutral organic solutions of different molecular sizes, such as sodium chloride (NaCl), sodium sulfate (Na_2SO4), poly ethylene glycol (PEG200). Table 1 and Table 2 showed the observed flux and rejection of the test ions and molecules. The rejection for PEG200 and NaCl decreased with increase of Molecular weight of PDMS, but Rejection for Na_2SO_4 kept stable. Compared with the NF membrane without adding PDMS, the NF membrane with adding PDMS showed high water flux (about 2 times) with little sodium sulfate solute rejection loss, relative big sodium chloride and PEG200 loss. The retention for PEG200 was decided mainly by pore size of NF membranes because PEG200 was non-charged solutes.

For transportation of charged solutes (NaCl and Na_2SO_4) through nanofiltration charged membranes, Donnan exclusion and the mobility of the ions across the membrane are the two important factors affecting the retention rate of the ions. Donnan exclusion of the solute co-ions occurs at the interface of a membrane with fixed charges. As the fixed charges can not freely 'move out' of the membrane matrix the membrane will absorb solute counter ions and repel solute co-ions. Furthermore the mobility of the ions across the membrane will also play an important role on the retention rate of the ions; diffusion coefficient and effective size of ions determine the mobility. The lower diffusion coefficient (Table 3) suggests that the transport rate in the membrane of SO_4^{2-} will be lower than that of Cl^-, leading to higher retention of Na_2SO_4.

These results indicate that the adding PDMS can fabricate NF membrane with larger effective "nano-pore" size. The NF membranes with adding PDMS63000

Table 1
Effect of molecular weight of PDMS on performance of NF membrane (organic solution)

Molecular weight of PDMS	Rejection for PEG200(%)	Flux (l/m^2h)
no PDMS	92 ± 2.1	36.3 ± 1.0
237	89 ± 2.6	51.9 ± 2.2
1250	87 ± 2.5	55.0 ± 2.8
6000	85 ± 4.1	59.1 ± 2.5
63000	83 ± 3.2	69.3 ± 3.3

(PEG200 0.1%w/w; 20°C, 1.0 MPa, and pH = 7.1–7.5)

Table 2
Effect of molecular weight of PDMS on performance of NF membrane (inorganic solution)

Molecular weight of PDMS	Rejection for Na_2SO_4(%)	Rejection for NaCl(%)
no PDMS	99 ± 1.2	50 ± 5.2
237	96 ± 1.1	40 ± 4.3
1250	97 ± 1.2	45 ± 4.5
6000	97 ± 1.7	42 ± 6.1
63000	99 ± 1.1	43 ± 5.5

(Na_2SO_4, NaCl solution 0.01%w/w; 20°C, 1.0MPa, and pH = 7.1–7.5)

Table 3
Mobility and dimension of ions

Ion	Diffusion coefficient at infinite dilution [$10^{-9}\cdot m^2/s$]	Hydrated radius [nm]	Pauling radius [nm]
Na^+ [19,20]	1.33	0.36	0.095
Cl^- [19,20]	2.03	0.33	0.181
SO_4^{2-} [19,20]	1.06	0.38	0.290

exhibits the highest water permeability and considerable salt rejection, and so the effect of PDMS63000 concentration on membrane performance was investigated next.

3.2. The skin layer chemical structure of the NF membrane

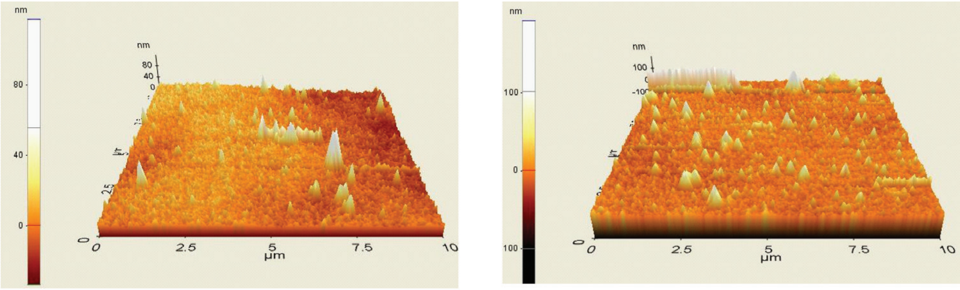
3.2.1. XPS

The composite membranes consisted of a thin layer of polyamide (about 0.2 μm) deposited on a polysulfone porous support. So the chemical information obtained through XPS analysis was derived only from the near surface of the top layer, and the polysulfone layer was not probed; thus, the main chemical elements studied by XPS were C, N, O (the polyamide characteristic elements) that shown in Table 4. There was a distinguished excess of oxygen with respect to the corresponding theoretical ratio for polyamide (O/N=1), which indicated a

Table 4
XPS result of TMC/PIP membrane adding PDMS with different molecular weight

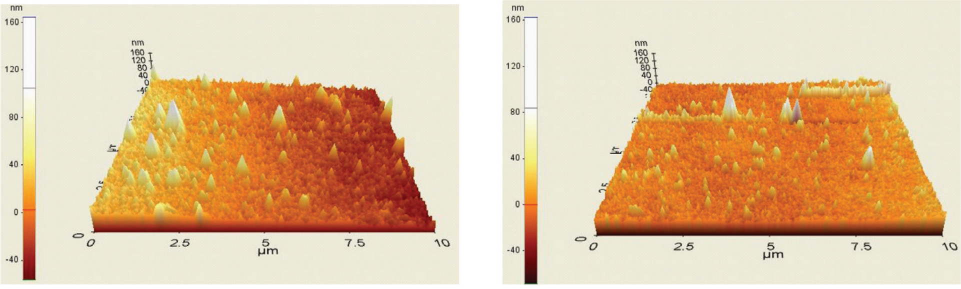
	C	O	N	Si	O/N
Totally crosslinking structure	71.42	14.29	14.29	0	1.00
Linear structure with COOH pendant	68.42	21.05	10.53	0	2.00
no PDMS	73.36	15.46	11.18	0	1.36
0.5% PDMS(MW:237)	72.35	15.35	12.1	0.2	1.25
0.5% PDMS(MW:1250)	72.42	15	11.81	0.57	1.22
0.5% PDMS(MW:6000)	71.61	15.87	11.57	0.95	1.26
0.5% PDMS(MW:63000)	71.06	15.8	11.91	1.23	1.22

Note: The effect of PDMS on O/N of membrane containing PDMS was calibrated.



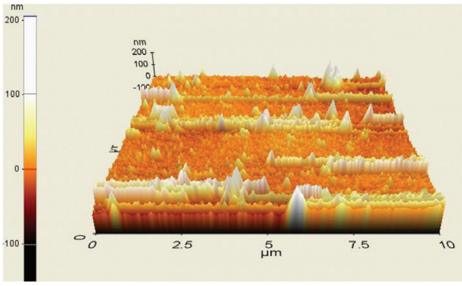
(A) Composite Membranes with PDMS237

(B) Composite without PDMS Membranes



(C) Composite Membrane with PDMS1250

(D) Composite Membrane with PDMS6000



(E) Composite Membrane with PDMS63000

Fig. 3. AFM Image of Composite Membrane with different molecular weight PDMS.

high content of —COOH on the surface of these membranes which come from the hydrolysis of the acyl chloride. The chemical structure of the membrane skin layer was cross-linking poly (piperazineamide) with pendant group of —COOH and the NF membrane prepared was negative charged.

And more, the O/N ratio of membrane without PDMS was higher than that of membrane with PDMS. In the process of interfacial polymerization, the PIP reacted with TMC in oil near to aqueous solution to form a thin film, and then PIP diffused from aqueous solution to oil and permeated through the film to react with TMC. The larger effective "nanopore" size mentioned in 3.1 was good for diffusion of piperazine from aqueous solution to oil. So TMC/PiP ratio in reacting area decreased.

3.2.2. AFM

AFM was chosen for morphological characterization of the surface of composite membranes. The surface of all composite membranes showed a typical nodular (hills and valleys) morphology. This morphology can be viewed as a fingerprint of the TFC polyamide composites prepared by the interfacial polymerization. We could thus expect to distinguish between the morphologies of composite membrane surfaces with different PDMS. AFM images of five membrane samples are shown in Fig. 3. Apart from occasional "white spots line" (see Fig. 3B,D,E), which could be small patches of a polymer(PDMS) ,but they should have no significant effect on the performance. Statistical analysis shows that the average roughness of NF membranes (see Table 5) increases with PDMS molecular weight increasing, which lead to increase of membrane specific surface area.

Table 5
RMS data of composite membrane surface

	Rq (nm)
no PDMS	6.547
0.5% PDMS(MW:237)	8.814
0.5% PDMS(MW:1250)	11.201
0.5% PDMS(MW:6000)	14.338
0.5% PDMS(MW:63000)	23.834

3.3. Effect of PDMS63000 content on performance of NF membrane

The transportation of non-charged solutes through nanofiltration (NF) membranes is usually characterized by the term of molecular weight cut-off (MWCO) that is in the range of about 200–1500 Dalton [21]. The rejection of the NF membranes with adding PDMS63000 were tested using a series of electrolytes and neutral organic solutions of different molecular sizes, such as sodium chloride (NaCl), sodium sulfate (Na_2SO_4), poly ethylene glycol (PEG200, PEG600) and sucrose (Fig. 4 and Fig. 5).

From Fig. 4, it can be seen that the order of rejection for ethylene glycol (PEG200, PEG600) and sucrose was R(PEG200) < R(sucrose) < R(PEG600), and with the increase of PDMS63000 content, the rejection of glycol (PEG200, PEG600) and sucrose decrease gently. Ethylene glycol (PEG200, PEG600) and sucrose were neutral organic solutions so that the retention for them was decided mainly by pore size of NF membranes. These results indicate that effective "nanopore" size of NF membranes with PDMS63000 increase with the increase of PDMS63000 content.

In Fig. 5, the NF membrane with adding PDMS showed high water flux with sodium sulfate solute rejection loss and relative big sodium chloride loss, compared with the NF membrane without adding PDMS. With the increase of PDMS63000 content, the rejection of sodium

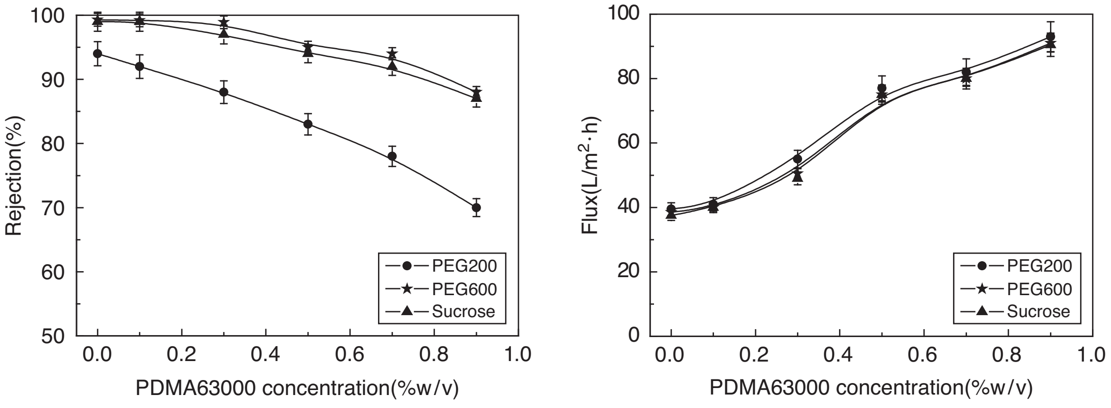


Fig. 4. Effect of PDMS63000 content on performance of NF membrane (PEG200, PEG600, sucrose concentration 0.1%w/w; 20°C, 1.0 MPa, and pH = 7.1–75).

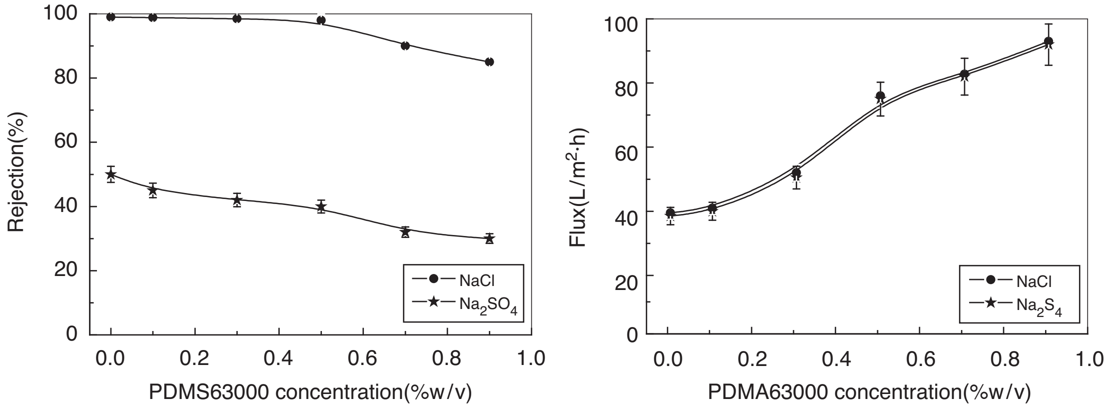


Fig. 5. Effect of PDMS63000 content on performance of NF membrane (Na_2SO_4, NaCl solution 0.01 %w/w; 20°C, 1.0 MPa, and pH = 7.1–7.5).

sulfate keeps stable when PDMS63000 content was less than 0.5%, and then decreases sharply; and the rejection of sodium chloride decreases gently. Because SO_4^{2-} was larger than Cl^-, the rejection of sodium sulfate decided mainly by charge effects when PDMS63000 content was less than 0.5%, and then decided by charge effects and molecular sieving with PDMS63000 content increase.

4. Conclusions

Poly(piperazineamide) NF membrane with high flux was prepared successfully with PIP and TMC through interfacial polymerization technique on the polysulphone supporting film with adding poly(dimethylsiloxane) in oil TMC solution. The flux of NF membrane with adding PDMS increased with increase of Molecular weight of PDMS; and rejection for PEG200 and NaCl decreased with increase of Molecular weight of PDMS, but Rejection for Na_2SO_4 keep stable. The average roughness of NF membrane increased with the molecular weight of PDMS increasing by the AFM results. The best molecular weight of PDMS was 63000. With PDMS63000 content increasing, the molecular weight cut off (MWCO) and the flux of NF membrane with PDMS63000 increased, while the rejection for Na_2S0_4 unchanged with the concentration of PDMS increasing.

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