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Study on removal of organic matters in water by PVA modified PA-TFC nanofiltration membrane

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ABSTRACT

Polyvinyl alcohol (PVA) modified polyamide thin film composite (PA-TFC) nanofiltration membranes were prepared by the interfacial polymerization of trimesoyl chloride (TMC), piperazine (PIP) and PVA on polysulfone supporting membranes, and were used for separating organic compounds from water. The results show that composite nanofiltration membranes are effective in retaining negatively charged organic compounds with molecular weight higher than 100 Da. For example, rejections to tyrosine, salicylic acid, and terephthalic acid were 63%, 77% and 97%, respectively. The effect of operation pressure, feed temparature, pH value and salt concentration on separation performances was also studied. It is found that both the flux and rejection of PVA modified PA-TFC nanofiltration membranes increase with increasing feed temparature and pH value, and decrease with increasing salt concentration. In detail, the flux and rejection of PVA modified PA-TFC nanofiltration membranes are J_{water} = 33.9 l/m^{2}h, $R_{chromic\ acid}$ = 99.5% and R_{NaCl} = 17.0% in simulated dye wastewater treatment at 25°C and 0.6 Mpa operating pressure, indicating that they are efficient in separating of negatively charged organic compounds and inorganic salts.

Keywords: Polyvinyl alcohol; Polyamide; Interfacial polymerization; Composite membrane; Nanofiltration; Organic matter

1. Introduction

Nanofiltration (NF) membranes are a kind of pressure-driven semi permeable membranes with properties between reverse osmosis and ultrafiltration membranes. The pore sizes of NF membranes are between 0.5 and 2 nm and they are usually operated under a pressure between 0.5 and 4 MPa. NF membranes have been widely applied in water softening, wastewater treatment and substances separation [1,2].

Nowadays, NF is competitive with other organic matter removal technologies such as conventional clarification and granular activated carbon (GAC) adsorption because of the following advantages: simple operation, high flux with low cost, and environmental friendly [3]. NF membranes can effectively remove organic matter, and retain large organic compounds like polysaccharides and humic substances. Meylan et al. [4] have investigated the permeability of low molecular weight organic molecules through nanofiltration membranes. Many researchers have also evaluated the ability of NF membranes to trap various pharmaceuticals. For example, Shi et al. [5] have made the concentration of benzylpenicillin sodium by polyimide NF membrane. The removal of several hormones and antibiotics by NF membranes was studied in mixed solutions [6]. Four commercial nanofiltration

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membranes NF90, NF200, NF270 and DK were applied in the removal of dimethoate and atrazine from aqueous solution [7]. Two commercial nanofiltration membranes (NF70 and NF270) have also been used for the removal of small trihalomethane precursors (THMPs) from aqueous solution [8]. These separations by nanofiltration membrane all have achieved good results.

PVA is a well-known membrane material with good hydrophilicity due to a lot of hydroxyl groups appending on the main chain and has been used to improve NF membrane performances [9–12]. Jegal et al. [13,14] have prepared chemically stable NF composite membranes with blend solutions of PVA and sodium alginate (SA), and the flux was improved by adding PVA. PVA was also used as the final barrier layer thin film composite (TFC) NF membranes and achieved optimum balance of flux and rejection [15]. The antifouling performance of NF membranes has been greatly improved by directly coating PVA on the membrane surface [16]. Based on above excellent performance, the PVA modified NF membranes were used in separating a variety of organic compounds. High rejection of organic matter depends on the type of membrane and the experimental conditions [17].

In this paper, the PVA modified PA-TFC NF membrane was prepared by the interfacial polymerization of trimesoyl chloride (TMC), piperazine (PIP) and PVA on the polysulfone supporting membranes. Separation performances of the membrane to different organic molecules in water solution were investigated. Especially, the effect of operating conditions on PVA modified PA-TFC membrane NF performances was systematically studied, aiming to provide a better guide to regulate the separation performances of PVA modified composite polyamide NF membranes for the separation of organic molecules.

2. Experiments

2.1. Materials

Polysulfone ultrafiltration (PSF-UF) support membranes (MWCO = 35000 Da) were supplied by the Development Center of Water Treatment Technology, Hangzhou, China. 1,3,5-benzenetricarboxylic chloride (TMC, >99%) used as an active monomer of organic phase was obtained from Qing Dao Sanli Chemical Engineering and Technology Co., Ltd. Piperazine (PIP) used as an active monomer of aqueous phase was obtained from Sinopharm Chemical Reagent Co., Ltd. PVA are also obtained from Sinopharm Chemical Reagent Co. Ltd., which has alcoholysis degree of 99 (mol)% and average polymerization degree (n) of 2500. Butanol (M.W = 74.12 Da), glycerol (M.W = 92.09 Da), benzyl alcohol (M.W = 108.14 Da), acetic acid (M.W = 60.05 Da), Terephthalic acid (TPA) (M.W = 166.13 Da), salicylic acid (M.W = 138.12 Da) and tyrosine (M.W = 281.30 Da) are analytical grade and used without further purification. Deionized (DI) water with a resistance of 18M was used in all experiments.

2.2. Membrane preparation

The polyamide active skin layer was synthesized by interfacial polymerization technique. An aqueous solution of 0.35 wt.% PIP containing 16% PVA was poured onto the top of a PSF supporting membrane clamped on the glass board by a Teflon frame. After being soaked for about 20 min, the excess solution was drained off the surface. Then the 0.20 wt.% TMC solution in n-hexane was poured into the frame to carry out the interfacial polymerization. After 2 min of residence time, an excess organic solution was poured off the surface, and the resulting composite NF membrane was subjected to a heat treatment at 50°C for 20 min to stabilize the structure. Finally, the composite NF membrane was washed with DI water and stored in 1 wt.% $NaHSO_3$ solution. Chemical structures and compositions of the membrane have been characterized systematically in our previous paper [18].

2.3. Characterization of permeation and rejection performances

NF tests of membranes were conducted by a cross-flow membrane module (the experimental set-up is shown in Fig. 1) with a membrane area of 22.4 cm^2. All experiments were carried out at an operation pressure of 0.6 MPa using 1 g/l organic feed solutions. Membranes were stabilized for at least 30 min with feed solution before testing. Both the retentate and permeate were recycled back to the feed tank to keep a constant concentration of feed solution. The membrane was rinsed thoroughly with DI water after each experiment. Permeate flux is calculated as $F = V/(A \cdot t)$, where V is the total volume of permeated solution during the experiment,

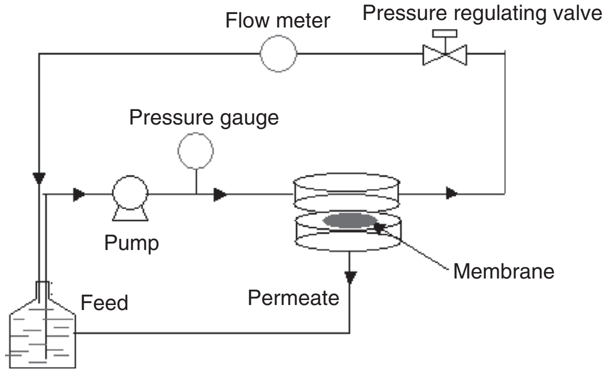

Fig. 1. Schematic representation of membrane property test apparatus.

A is the membrane area, and t is the operation time. The rejection of the membrane is calculated as $R = 1 - \left(\frac{C_p}{C_f}\right)$, where C_p and C_f are the concentration of permeation and feed, respectively. In this work, the concentration of inorganic salt solution was tested with electrical conductivity (DDS-11A, Shanghai Leici InstrumentWorks, China); the concentration of organic molecular solution was tested with total organic carban analyzer (VCSH-TOC, Shimadzu Co., Japan) or UV/VIS Spectrophotometer (UV-120-02, Shimadzu Co., Japan), respectively. The flux and rejection were repeatedly measured by collecting the filtrate at a given period until the permeation flux and rejection were stable.

3. Results and discussion

3.1. Separation performances of PVA modified PA-TFC NF membranes to different organic molecules

Fig. 2 shows separation performances of the modified PA-TFC NF membrane with 16% PVA to different organic molecules. As shown in Fig. 2a, rejections of the membrane to butanol, glycerol, benzyl alcohol and acetic acid are very low, all of which are smaller than 35%. However, its rejections to tyrosine, salicylic acid and terephthalic acid (TPA) are comparatively higher, which are 63%, 77% and 97%, respectively. On the other hand, Fig. 2b shows an inversion variation of the flux to different organic molecular solutions. Charged NF membranes separate a solute not only by the electrostatic repulsive effect, but also by the steric hindrance effect [19]. Thus, there is a higher rejection for the PVA modified PA-TFC NF membrane to those negatively charged organic molecules with molecular weight higher than 100. Moreover, the fluxes of the membrane to tyrosine, salicylic acid and terephthalic acid are a little lower than the others. This may be caused by the stronger resistance for the bond water surrounding with the organic acids.

3.2. Effect of operating conditions on PVA modified PA-TFC membrane NF performances

Fig. 3 and Fig. 4 show the effect of operating pressure and feed temperature on NF performances of the PVA modified PA-TFC membrane with the tyrosine, salicylic acid and TPA feed solution. As shown in Fig. 3, the flux increases almost linearly with increasing the operating pressure, which is accordant with the Spiegler-Kedem model [20]. The flux of membrane is in direct proportion to the trans-membrane pressure, which is the difference between operating pressure and osmotic pressure.

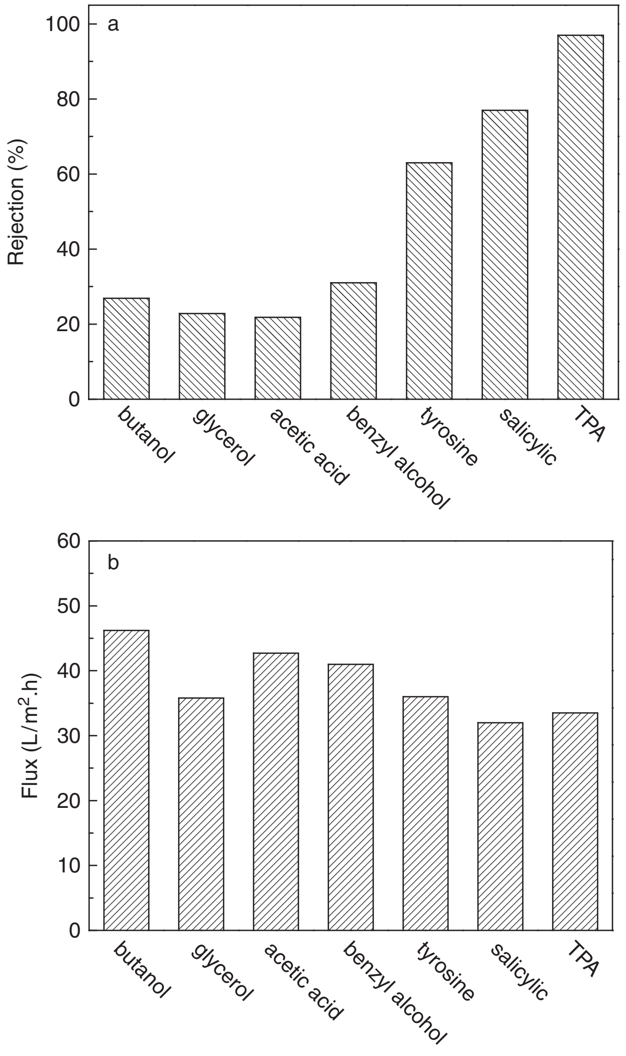

Fig. 2. Separation performances of PVA modified PA-TFC NF membrane to different organic molecules (a) rejection (b) flux ($C_{\text{organic molecule}}$ = 1 wt.%, 25°C, 0.6 Mpa).

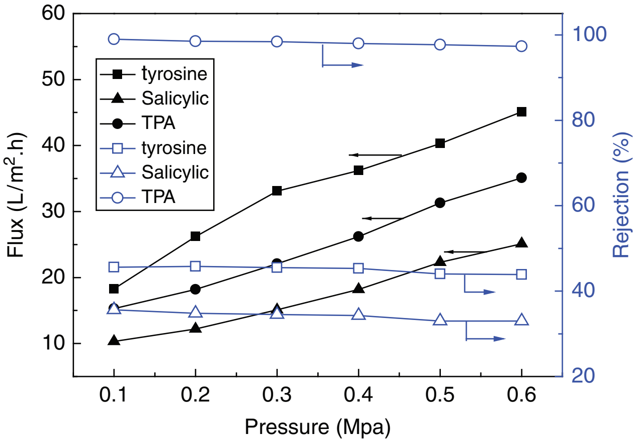

Fig. 3. Effect of pressure on NF performance of PVA modified PA-TFC membrane ($C_{\text{organic molecule}}$ = 1 wt.%, 25°C).

The osmotic pressure can be neglected, because the conductivity of organic acid solution is low here. Thus, the flux of the PVA modified PA-TFC NF membrane increases with increasing the operating pressure. Meanwhile, there is no obvious change for the solute rejection with increasing the operating pressure. From Fig. 4 it is seen that both the flux and rejection increase with increasing the feed temperature. This is different from those reported in previous literatures that the rejection of natural organic molecules decreases with increasing the feed temperature [21,22]. This is probably because the rise of the feed temperature promotes the diffusion and transmission of substances in the membrane. Moreover, increasing the feed temperature is probably more conducive to transfer water molecules through PA-TFC membranes than those negatively charged organic molecules [23]. Therefore, the solute rejection of the membrane increases simultaneously with increasing the water flux.

Fig. 5 shows the effect of feed solution pH on NF performances of the PVA modified PA-TFC membrane. As shown in Fig. 5, the salicylic acid rejection increases from 30.4 to 47% with increasing the feed solution pH form 3.5 to 9.5. Meanwhile the water flux increases from 25.8 to 62.4 l/m^{2}h. A similar variation trend of solute rejection and water flux of the membrane is also found in Fig. 5 when the feeding solution is tyrosine or TPA. Liu, et al. [24], have also found that the water flux of polyamide-urethane reverse membrane increased with increasing the pH value of feed solution. This is probably because the amide groups (-CONH) within PA membrane are turned into carboxyl groups (-COOH) in alkaline solution, resulting in higher negatively charged density and hydrophilicity of PA-TFC membrane. Moreover, those weak acid molecules are more likely to dissociate in high pH feed solutions. Therefore, the solute rejection and water flux increases with increasing the feed solution pH value.

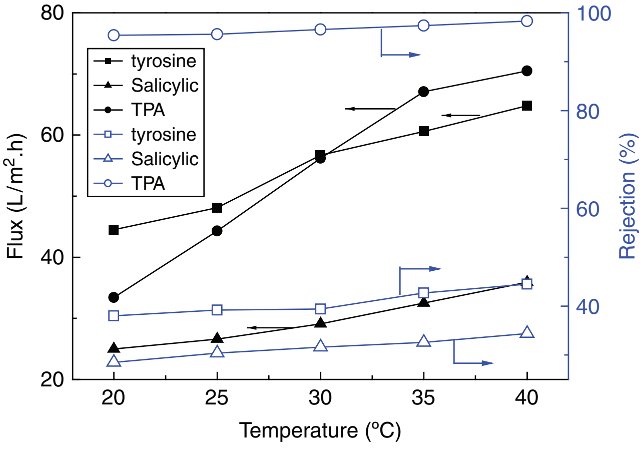

Fig. 4. Effect of temperature on NF performance of PVA modified PA-TFC membrane ($C_{organic\ molecule}$ = 1 wt.%, 0.6 Mpa).

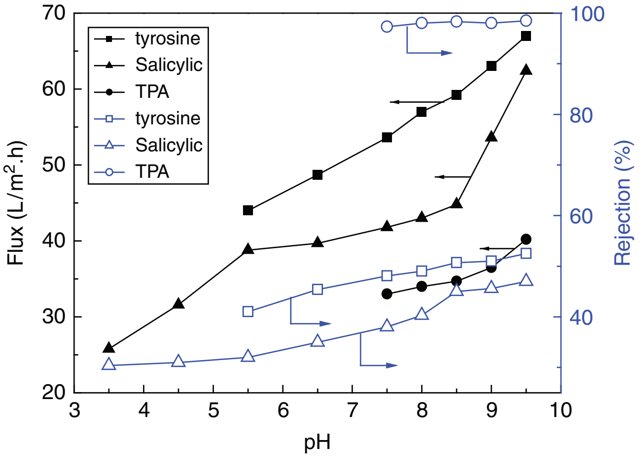

Fig. 5. Effect of pH on NF performance of PVA modified PA-TFC membrane ($C_{organic\ molecule}$ = 1 wt.%, 25°C, 0.6 Mpa).

Fig. 6 shows the effect of salt concentration on NF performances of the PVA modified PA-TFC membrane. As shown in Fig. 6, the flux of the membrane decreases with increasing the NaCl concentration in feed solution. This is probably because the osmotic pressure of the membrane increases with increasing the ionic concentration in feed solution and reduces the actual driven force and the flux. Rejections of the membrane to organic acids increase, meanwhile the NaCl salt rejection of the membrane decreases with increasing the NaCl concentration. The decrease of NaCl rejection is accordant with the normal phenomenon for NF membranes because of the electrostatic shield effect [25]. However, the increase of organic acids rejection is probably because the membrane compaction is enhanced with increasing the ionic strength in feed solution. The hypothesis has ever been

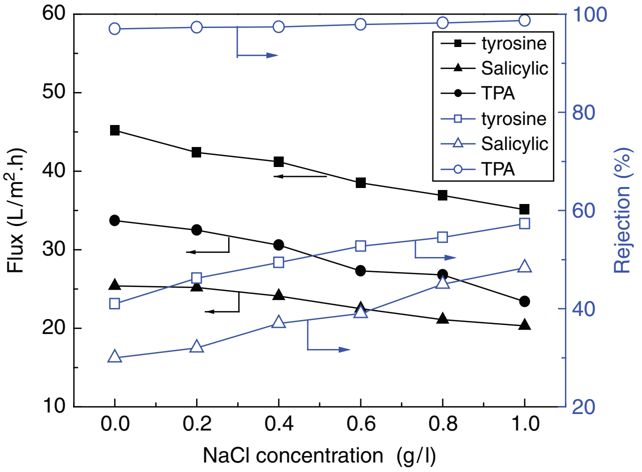

Fig. 6. Effect of NaCl concentration on NF performance of PVA modified PA-TFC membrane ($C_{organic\ molecule}$ = 1 wt.%, 25°C, 0.6 Mpa).

identified by Braghetta, et al. [26], wherein the rejection of organic molecule PEG is increased with increasing the ionic strength of feed solution.

3.3. Separation performances of organic dye and inorganic salt by PVA modified PA-TFC NF membrane

Separation performances of PVA modified PA-TFC NF membrane were tested with a simulated dye solution containing the organic dye (chromic acid) and inorganic salt (NaCl). Fig. 7 shows the changes in flux and rejection of the membrane as a founction of operating pressure. As shown in Fig. 7, the flux increases almost linearly with increasing the operating pressure, which is accordant with the observation in Fig. 3. Both the rejections of chromic acid and NaCl have little variation with increasing the operating pressure. Moreover, the rejection to chromic acid (about 99.5%) is much higher than that to NaCl (about 17%), and the water flux is 33.9 l/m^{2}h at 25°C and 0.6 Mpa operating pressure. This indicates that the PVA modified PA-TFC NF membrane can be used in dye separation or recovery.

3.4. Stability of PVA modified PA-TFC NF membrane

The stability of PVA modified PA-TFC NF membrane was investigated with the chromic acid solution (1g/l) at 25°C for 36 h. From Fig. 8 it is seen that the rejection of chromic acid increases slightly with prolonging the operating time. Meanwhile, the flux firstly decreases and then becomes much more flat. This is probably because the chromic acid molecules that adhere on the surface increase the charge density and thickness of the selective surface [27]. Even though, the rejection and flux of the membrane still maintain at a comparatively high value, which is 99.4% and 29.5 l/m^{2}h, respectively. And the separation performance of the PVA modified PA-TFC NF membrane has acheived the level of some commercial polyamide nanofiltration membranes in organic dye and inorganic salt separation [28]. Therefore, the PVA modified PA-TFC NF membrane has a good stability, and is promising to be applied in dye wastewater treatment.

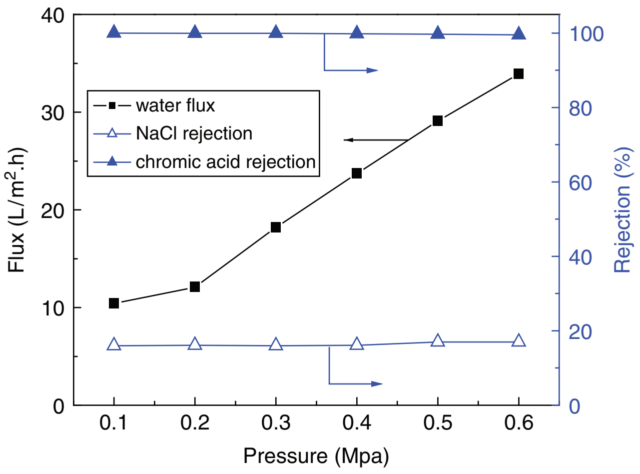

Fig. 7. Separation performances of PVA modified PA-TFC NF membrane as a function of operating pressure ($C_{organic\ molecule}$ = 1 wt.%, C_{NaCl} = 1 g/l, 25°C, 0.6 Mpa).

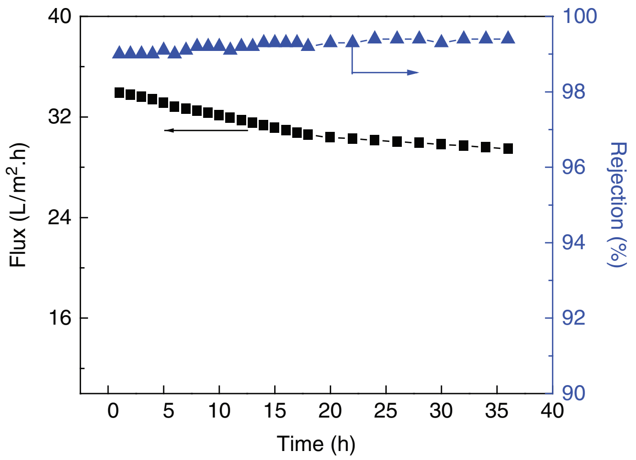

Fig. 8. Separation performances of PVA modified PA-TFC NF membrane as a function of operating time ($C_{organic\ molecule}$ = 1 wt.%, 25°C, 0.6 Mpa).

4. Conclusions

The PVA modified PA-TFC NF membrane has a high solute rejection to negatively charged organic compounds with molecular weight greater than 100. PVA modified PA-TFC NF membrane presents good separation performances in the long-term testing of the simulate dye wastewater. Therefore, PVA modified PA-TFC NF membrane has a good prospect in dye wastewater treatment.

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