

# Preparation of Positively Charged Nanofiltration Membrane from 2-Hydroxypropyltrimethyl Ammonium Chloride Chitosan by 1,4-Butanediol Diglycidyl Ether Cross-Linking

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**ABSTRACT:** A novel positively charged composite nanofiltration (NF) membrane was prepared using 2-hydroxypropyltrimethyl ammonium chloride chitosan as active layer, polyacrylonitrile ultrafiltration membrane as substrate layer, and 1,4-butanediol diglycidyl ether as cross-linking reagent. The observation from scanning electron microscope revealed its composite structure. At room temperature and cross-flow rate of 40 L h<sup>-1</sup>, the permeability for pure water was 14.3 L h<sup>-1</sup> m<sup>-2</sup> MPa<sup>-1</sup>. With an increase in operating pressure, the flux increased linearly.

The rejection to different salt solutions was decreasing in the order of CaCl<sub>2</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub>, NaCl, and Na<sub>2</sub>SO<sub>4</sub>, revealing the rejection characteristic of positively charge NF membrane. And it had good ion perm-selectivity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2358–2364, 2010

**Key words:** 2-hydroxypropyltrimethyl ammonium chloride chitosan; 1,4-butanediol diglycidyl ether; positively charge composite NF membrane; cross-linking

## INTRODUCTION

Nanofiltration (NF) membranes, which are a kind of pressure driven membrane between reverse osmosis and ultrafiltration membrane, are gaining worldwide interest because of advantages such as low operating pressure, high permeating flux, and high rejection of multivalent ion salt.<sup>1–3</sup> It has a strong potential for water treatment and for separation of molecular species in the food, pharmaceutical, and bio-industries.<sup>4–6</sup>

At present, internationally developed NF membranes are generally neutral or negatively charged.<sup>7</sup> There are few reports on positively charged NF membranes. In fact, a positively charged membrane is actually needed in some cases such as for the retention of multivalent cations and the recovery of cathode electrophoresis lacquer. Therefore, it is of great significance to investigate the preparation and characteristics of positively charged NF membrane.

Chitosan, as a natural biopolymer, has a good forming-membrane characteristic, and there are active groups such as hydroxyl and amino in chitosan; hence, it can be chemically modified easily. Quaternized chitosan, that is, 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) as one of its derivatives, shows the same forming-membrane characteristic as chitosan.<sup>8,9</sup> The cross-linking reagents applied are epoxy, diisocyanate, and aldehyde. However, to our knowledge, there is no literature available on composite membrane using 1,4-butanediol diglycidyl ether (BDGE) as cross-linking reagent of quaternized chitosan.

Hence, an attempt was made to prepare a novel positive charge NF membrane with HACC layer coating as active layer, PAN UF membrane as substrate layer, and BDGE as cross-linking reagent. Effects of preparation conditions such as HACC concentration, BDGE concentration, and cross-linking time on membrane performance were investigated, and the characteristics of this membrane were also determined including structure of membrane and permeation characteristics.

## EXPERIMENTS

### Materials and apparatus

HACC with a quaternization degree of 89.3% was prepared according to the former literature.<sup>10</sup> PAN

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UF membrane with molecular weight cut-off (MWCO) of  $1 \times 10^5$  Da (supplied by the Development Center of Water Treatment Technology State Oceanic Administration, Hangzhou, China) was used as a substrate membrane for coating of HACC. BDGE,  $\text{MgCl}_2$ , NaCl, and other reagents were of analytical grade.

Scanning electron microscopy (SEM JEOL JMS-840, Japan) was applied to investigate the structure of composite membrane. A Model DDS-11A conductivity meter (Shanghai Leici Instrument, China) was used to measure salt concentration. PMI membrane evaluation apparatus was provided by the Development Center of Water Treatment technology, State Oceanic Administration (Hangzhou, China).

### Membrane preparation

HACC/PAN composite membrane was first prepared by coating 2.0 wt % HACC aqueous solution onto PAN support layer and vaporizing the solvent at  $50^\circ\text{C}$  for 2 h. The mentioned membrane was secondly immersed into 0.31/75 wt/wt BDGE/acetone solution to carry on the cross-linking reaction at pH 2 or so and  $50^\circ\text{C}$  for 22 h. When the time came, the cross-linked membrane was taken out to heat treat at  $50^\circ\text{C}$  for 30 min. The resultant membrane was washed thoroughly with deionized water and immersed in deionized water for 24 h.

The performance of the composite membranes was examined at a testing pressure of 0.4 MPa. If not otherwise specified, the concentration of  $\text{MgCl}_2$  solution was fixed at  $1000 \text{ mg L}^{-1}$ . The effective area of membrane sample was kept at  $19.6 \text{ cm}^2$ . Every experiment described here was performed at a cycling flow of  $40 \text{ L h}^{-1}$ . The average data were determined from two pieces of the membrane tested. The rejection ( $R$ ) was calculated by the changing concentration through the membrane according to eq. (1).

$$R = 1 - C_p/C_f \quad (1)$$

Where  $C_p$  and  $C_f$  denote the permeate concentration and feed concentration, respectively. The flux ( $F$ ) was determined by the volume of the permeate solution through the membrane during a certain period of time and calculated according to eq. (2).

$$F = V/At \quad (2)$$

Where  $F$  is the flux,  $A$  is the effective area of the membrane,  $t$  is the time for permeation, and  $V$  is the volume of permeate solution through the membrane. In this study, the data presented were the averages of two measurements conducted with a standard deviation of 5% or so.

### Structure of membrane

The top surface and cross-sectional images of the resultant membrane were observed with a scanning electron microscope (SEM). The membrane was immersed in liquid nitrogen for a while and frozen. The frozen membrane was broken and kept in a desiccator till SEM was studied.

### Permeation characteristics of composite membrane

The pure water flux was measured at the operating pressure in the range of 0.4–1.4 MPa. A serial of the rejection and flux for  $1000 \text{ mg L}^{-1}$   $\text{MgCl}_2$  solution were determined at the pressure varying from 0.6 to 1.4 MPa. Besides, both the rejection and flux for  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , NaCl, and  $\text{CaCl}_2$  solution at a concentration of  $1000 \text{ mg L}^{-1}$  were investigated at a pressure of 1.0 MPa and a cross-flow rate of  $40 \text{ L h}^{-1}$ .

### MWCO of the HACC/PAN composite NF membrane

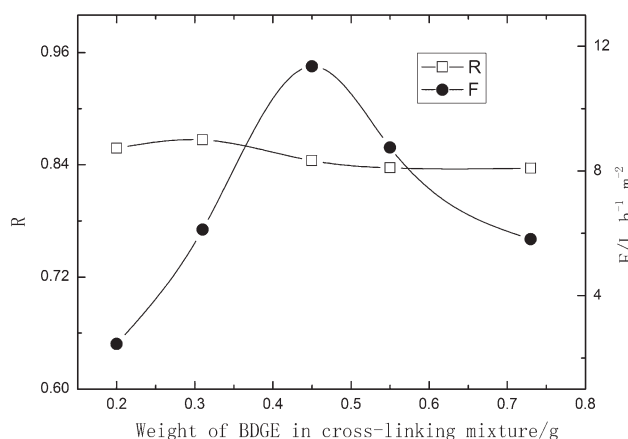
To determine MWCO, a set of reference solutes in the molecular weight range of 198–1000 Da was chose, namely glucose, sucrose, and polyethylene glycols (PEGs 600, 800, 1000) at a concentration of  $1000 \text{ mg/L}$ . The MWCO was the molecular weight of organic substance with a retention of 90%.<sup>11</sup>

## RESULTS AND DISCUSSION

### Effect of preparation conditions on membrane performance

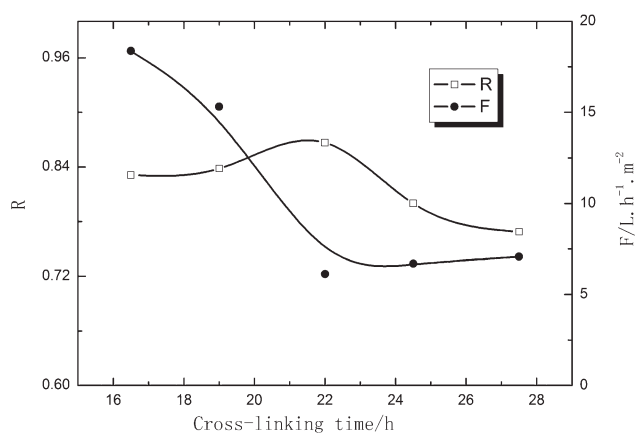
#### Effect of BDGE concentration on membrane performance

There are epoxy groups in BDGE, whereas there are many  $-\text{OH}$  and unsubstituted  $-\text{NH}_2$  groups in HACC. The activity of  $-\text{NH}_2$  group is stronger than  $-\text{OH}$ , so the cross-linking reaction was carried on preferentially between epoxy groups in BDGE and unsubstituted  $-\text{NH}_2$  in HACC, hydrophilic  $-\text{OH}$  group was introduced and the relatively larger cross-linking net work was formed. The  $-\text{OH}$  group introduced after cross-linking was helpful to improve the permeability property of composite membrane, BDGE was adopted as cross-linking reagent and it was speculated that the membrane had a lager flux. Here, acetone was chose to the solvent of BDGE through the earlier experimental study, and there was 75 g acetone in cross-linking mixture. Figure 1 shows changes in rejection and flux as a function of BDGE content in cross-linking mixture. The flux initially increases with increasing BDGE content in the cross-linking mixture passing through a maximum at about 0.45 g BDGE before decreasing



**Figure 1** Effect of BDGE concentration on membrane performance.

beyond this point. The rejection increases slightly with an increment of 1% until the weight of BDGE reaches 0.31 g and then continuously decreases when it is higher than 0.31 g. The cross-linking degree and hydrophilicity may be increased with increasing BDGE content because of  $-OH$  group after cross-linking reaction, while the membrane structure became more compact because of the complete reaction. An enhancement of cross-linking degree resulted in an increase in rejection. Both membrane structure and hydrophilicity are responsible for flux. The compactness of membrane structure led to a reduction in flux, whereas the increasing hydrophilicity resulted in an increasing flux; consequently, flux was determined by the competition of these two factors. However, the further increasing BDGE content may lead to an increase in steric hindrance, which made cross-linking reaction difficult; therefore, the cross-linking degree decreased. A reduction in cross-linking degree was unfavorable for rejection, so a decrease in rejection was observed later.



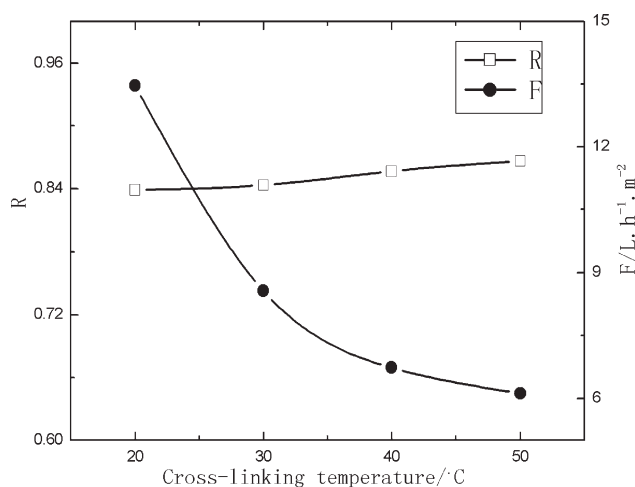
**Figure 2** Effect of cross-linking time on membrane performance.

#### Effect of cross-linking time on membrane performance

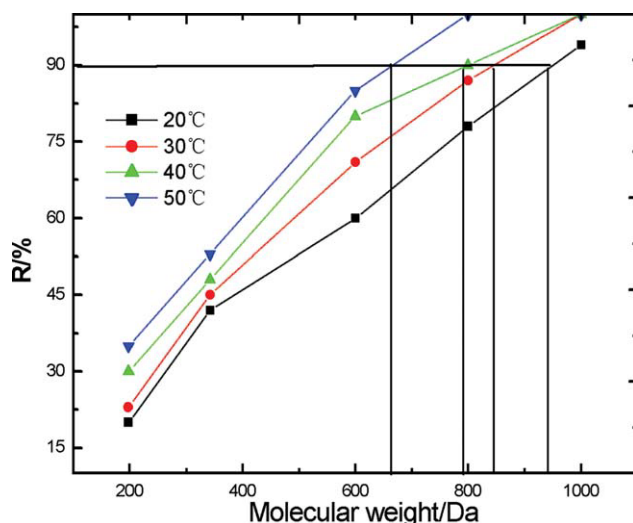
For this effect, the cross-linking time in the range of 16.5–27.5 h was investigated. As illustrated in Figure 2, the rejection increases until it was kept at 22 h and then decreases when prolonging the cross-linking time, while the flux shows the opposite trend. An increase in cross-linking time made the cross-linking reaction complete, resulting in the enhancement of cross-linking degree. And the hydrophilicity of membranes improved during the cross-linking reaction. According to the method mention in Section “MWCO of the HACC/PAN composite NF membrane,” MWCOs of these membranes were 900, 750, 660, 590, and 500, respectively; with the increasing time, it can be seen that the membrane structure became compact. As explained in Section “Effect of BDGE concentration on membrane performance,” an enhancement of cross-linking degree resulted in an increase in rejection, and flux was determined by the competition of hydrophilicity and membrane structure. However, when the cross-linking time is prolonged further, the rejection had the trend to decrease. We can not provide a reasonable explanation about it.

#### Effect of cross-linking temperature on membrane performance

To observe the effect of cross-linking temperature on membrane performance, the cross-linking temperature varying from 20 to 50°C was adopted. The results were shown in Figure 3, the rejection increases slightly along with the remarkably decreasing flux when increasing cross-linking temperature. Cross-linking temperature was beneficial to cross-linking reaction, leading to an increasing cross-linking degree, therefore the rejection improved. An increase in



**Figure 3** Effect of cross-linking temperature on membrane performance.



**Figure 4** Molecular-weight cut-off curves for the composite membranes. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

cross-linking temperature made both active layer and support layer shrink. The shrinkages always resulted in a decreasing flux, whereas the increasing hydrophilicity resulted in an increasing flux. Besides, the MWCOs of these membranes prepared with different temperature were measured according to the method in Section "MWCO of the HACC/PAN composite NF membrane," the results were listed in Figure 4. The MWCO curves of are shown in Figure 4. Clearly, the MWCO values are 940, 845, 790, and 660 Da for the composite membranes prepared with different temperature from 20°C to 50°C, respectively. It can be seen that the MWCO decreased, that is, the membrane pore became shrink with an increase in cross-linking temperature. When the shrinkage markedly dominated hydrophilicity, flux decreased rapidly, as observed in this experiment.

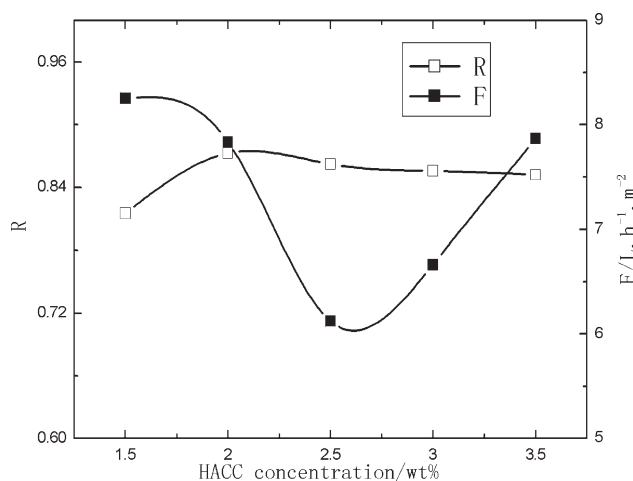
#### Effect of HACC concentration on membrane performance

Here, the method of coating and cross-linking sequentially was applied in membrane preparation, so it would fail when the casting solution was too thick or thin; in other words, HACC concentration was too large or too small. Thus, HACC concentration in the range of 1.5–3.5 wt % was investigated. When a serial of these membranes was prepared, HACC solutions with different concentration were measured by the same volume and coated on the support layer with the same size. The less solvent was vaporized during the gelation process, when the concentration improved; thus, the membrane became thicker with an increasing HACC concentration. The results were shown in Figure 5, rejection passes through a maximum when increasing HACC

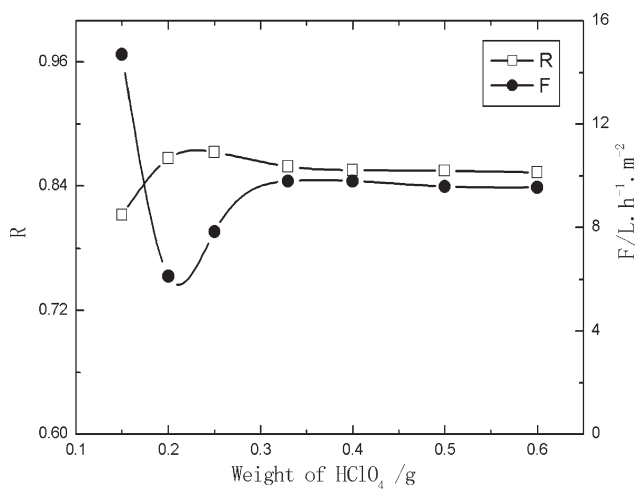
concentration, while flux shows the opposite changing trend. The increasing HACC concentration improved the effective charge density on the membrane surface, leading to an increase in rejection. Meanwhile, the increasing HACC concentration enlarged the membrane thickness, which augmented the resistance through membrane, thus the membrane allowed a decrease in flux. However, when the hydrophilic of the membrane was enough to overcome the resistance from the thickness of the membrane, the composite membrane exhibited a higher flux.

#### Effect of pH in the cross-linking system on membrane performance

The cross-linking reaction was carried out under acid condition. Considering that the nucleophilicity of  $\text{ClO}_4^-$  in  $\text{HClO}_4$  was relatively bad, thus there was almost no assistant reaction between  $\text{HClO}_4$  and BDGE,  $\text{HClO}_4$  was conducted to adjust pH of the cross-linking system. Here, the cross-linking system tested contained 0.31 g BDGE and 75 g acetone, pH was controlled by adding the weight of  $\text{HClO}_4$  varying from 0.15 to 0.60 g. As demonstrated in Figure 6, with the increasing weight of  $\text{HClO}_4$ , that is, the enhancement acid of this system, rejection increases and then decreases slightly, while flux shows the opposite change. When the weight is 0.2 g, rejection reaches a maximum (0.87), together with a minimal flux of  $6.12 \text{ L h}^{-1} \text{ m}^{-2}$ . Finally, the composite membrane has a stable performance, rejection and flux approach to a stable level at a value of 0.85 and  $9.6 \text{ L h}^{-1} \text{ m}^{-2}$ , respectively. The cross-linking degree may be enhanced and hydrophilicity was strengthened by improving the weight of  $\text{HClO}_4$ , while membrane structure became more compact. The enhancement of the cross-linking degree led to



**Figure 5** Effect of HACC concentration on membrane performance.



**Figure 6** Effect of pH of membrane performance.

an increasing rejection; however, as described in Sections “Effect of BDGE Concentration on Membrane Performance” and “Effect of Cross-Linking Time on Membrane Performance,” the flux was determined by the competition of hydrophilicity and membrane structure. BDGE may be apt to auto-aggregation with the acidity of the cross-linking system increasing, which made the cross-linking degree decline, leading to a decrease in rejection later. Considered both rejection and flux integrally, the weight of HClO<sub>4</sub> is controlled at 0.3 g, here pH of the system should be 2 or so.

### Structure characteristic of HACC/PAN NF membrane

Figures 7 and 8 show the SEM surface and cross-sectional images for the PAN UF membrane and the NF membrane prepared in Section “Membrane Preparation,” respectively. It was not difficult to find that the

NF membrane has a thin active layer on finger-like and porous support layer by a comparison between two cross-sectional images, revealing the composite structure of the NF membrane. The active layer thickness of the composite membrane was obtained at 0.5–5 μm by SEM. Besides, compared with the surface cross-sectional image of the PAN UF membrane, the surface of the NF membrane is relatively compact. And many gelled grains are distributed on the NF membrane surface, the surface is relatively coarse, so it was expected that the NF membrane has a higher flux. The NF membrane would be used to perform the following permeation experiments.

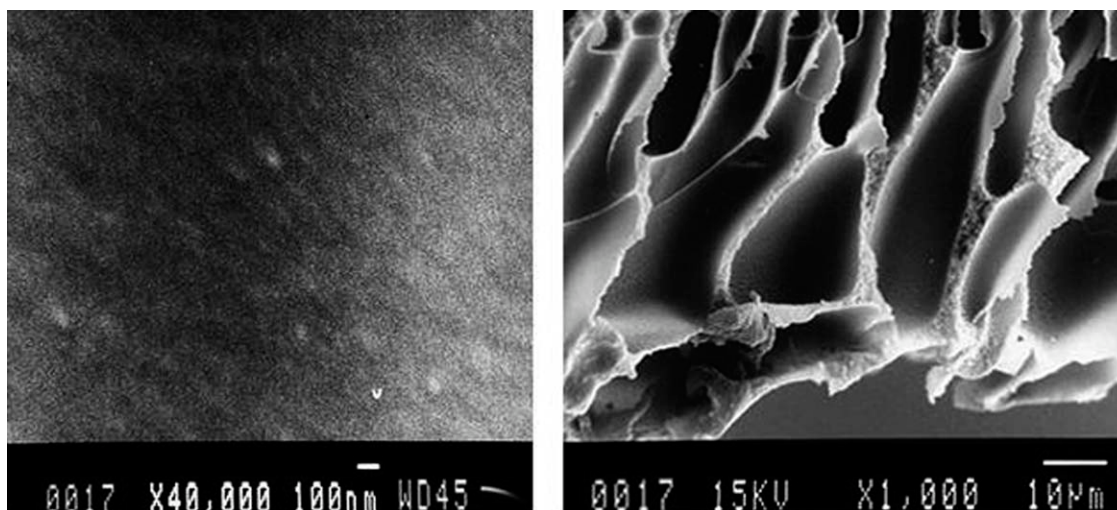
### Permeation characteristic of HACC/PAN NF membrane

#### Pure water permeability

Before the solute rejection experiment, the flux for pure water was measured. A plot of the flux for pure water versus operating pressure from 0.4 to 1.4 MPa is given in Figure 9. As illustrated in Figure 8, the flux almost increases linearly with an increase in operating pressure. According to Spiegler-Kedem Model,<sup>12</sup> the pure water permeability is obtained at 14.3 L h<sup>-1</sup> m<sup>-2</sup> MPa<sup>-1</sup>. It appears that this membrane shows a relatively strong permeability, which is consistent with the structure characteristic of this membrane mentioned in Section “Structure characteristic of HACC/PAN NF membrane.” Meanwhile, it testifies the speculation in Section “Pure Water Permeability.”

#### Effect of operating pressure on HACC/PAN NF membrane performance

The effect of operating pressure, ranging between 0.6 and 1.4 MPa, on the flux and rejection of



**Figure 7** SEM images of PAN UF membrane (Left) surface, (Right) Cross section.

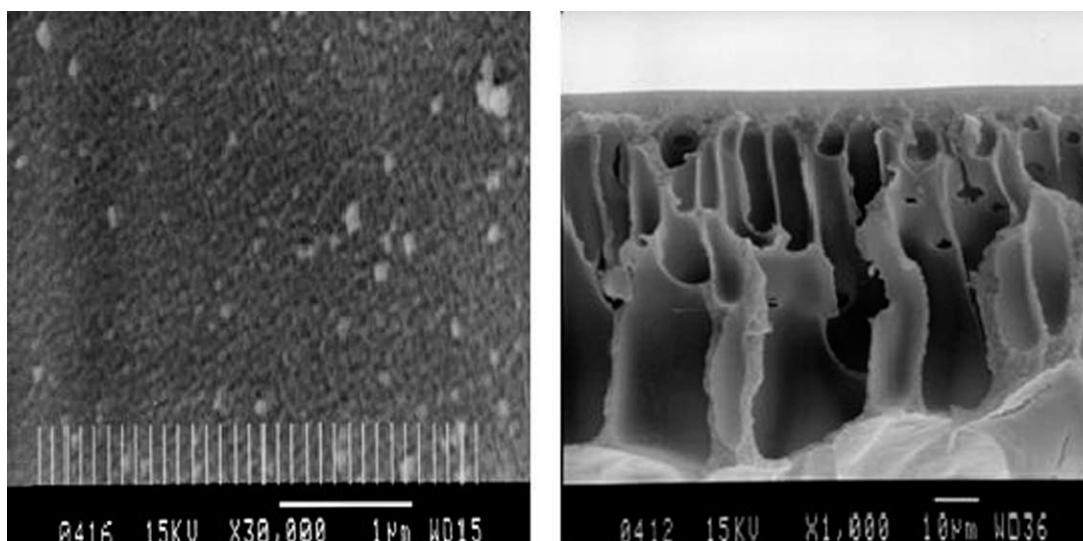


Figure 8 SEM images of HACC/PAN NF membrane (Left) surface, (Right) Cross section.

1000 mg L<sup>-1</sup> MgCl<sub>2</sub> solution is shown in Figure 10. The rejections often increase with the increasing operating pressure, and sometimes reach a threshold.<sup>10,13</sup> Exceptions to the above change, the rejection improves slightly with an improvement of 1% until operating pressure is 0.8 MPa, but when it exceeds 1.0 MPa, the rejection reveals the trend to decline slowly. The phenomenon had been reported Sun et al.<sup>14</sup> When the operating pressure was relatively high, these ions in feed solution were prone to permeate through membrane due to the carry of water transport on impel of operating pressure, resulting in a decreasing rejection in the latter experiment. The flux increases linearly when increasing operating pressure.

Effect of the kind of feed on HACC/PAN NF membrane performance

The separation property to different salt solution by HACC/PAN NF membrane is shown in Table I. As illustrated in Table I, the order of rejection to different salt solutions is CaCl<sub>2</sub> > MgCl<sub>2</sub> > MgSO<sub>4</sub> > NaCl > Na<sub>2</sub>SO<sub>4</sub>, revealing the positively charged characteristic of this membrane. The results obtained strongly suggest that the rejection difference among salts mainly stems from a cationically charged active layer; therefore, the Donnan ion repulsion dominates in rejection. For the salt solutions with the same anion, the repulsion force to high-valent cation was stronger than low valent one, so the membrane exhibited consistently high rejection for high-valent

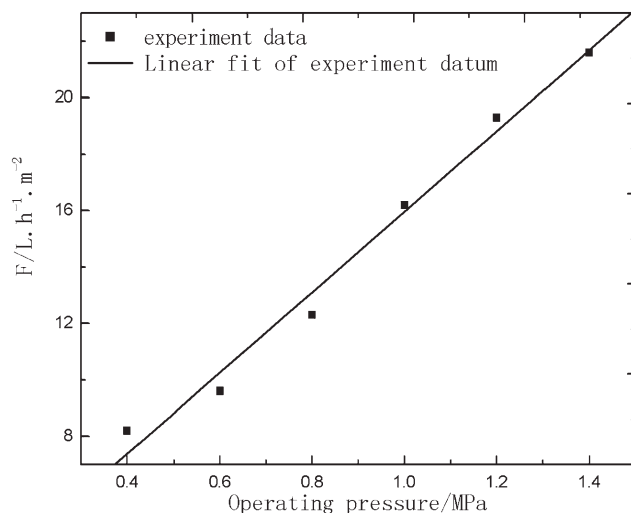


Figure 9 Flux for pure water against operating pressure.

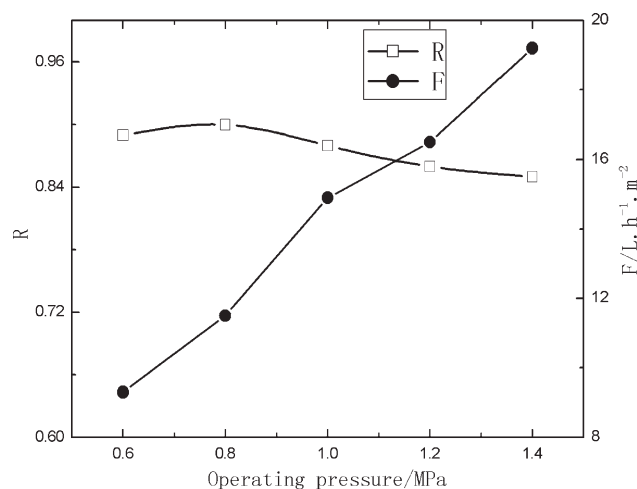


Figure 10 Effect of operating pressure on membrane performance.

**TABLE I**  
**Effect of the Kind of Feed on Membrane Performance**

The kind of feed	R	F (L h <sup>-1</sup> m <sup>-2</sup> )
MgCl <sub>2</sub>	0.88	14.9
CaCl <sub>2</sub>	0.90	14.8
MgSO <sub>4</sub>	0.45	15.2
NaCl	0.37	15.2
Na <sub>2</sub> SO <sub>4</sub>	0.11	15.0
Pure water	–	16.2

Operation conditions: at room temperature, 1.0 MPa and a cross-flow rate of 40 L h<sup>-1</sup>.

cation, that is, MgCl<sub>2</sub> > NaCl and MgSO<sub>4</sub> > Na<sub>2</sub>SO<sub>4</sub>; however, for the salt solutions with the same cation, the attractive force to high-valent anion was stronger than low-valent one, so lower rejections were observed for high-valent anion, that is, MgSO<sub>4</sub> < MgCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> < NaCl. Besides, this membrane has the rejection to CaCl<sub>2</sub> and MgCl<sub>2</sub> solution higher than 0.88, whereas the rejection to other salt solutions is lower than 0.50, suggesting the good ion perm-selectivity of this membrane. And it is not difficult to find the flux to salt solutions is lower than pure water due to solvent effect.

### CONCLUSIONS

A novel positively charged composite NF membrane was prepared using HACC as active layer, PAN UF as support layer, and BDGE as cross-linking reagent. These preparation conditions such as BDGE concentration, cross-linking time, and HACC concentration have influence on membrane performance. The structure of the resultant membrane was observed by SEM, suggesting its composite structure.

Additionally, the permeation characteristics of this membrane were also measured. The permeability for pure water was 14.3 L h<sup>-1</sup> m<sup>-2</sup> MPa<sup>-1</sup> at room temperature and a cross-flow rate of 40 L h<sup>-1</sup>. With an increase in operating pressure, the rejection increased slightly, and then decreased slowly, while the flux increased linearly. The order of rejection to different salt solution was CaCl<sub>2</sub> > MgCl<sub>2</sub> > MgSO<sub>4</sub> > NaCl > Na<sub>2</sub>SO<sub>4</sub>, revealing the positively charged characteristic of the resultant membrane.

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