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A novel composite nanofiltration (NF) membrane prepared from graft copolymer of trimethylallyl ammonium chloride onto chitosan (GCTACC)/poly(acrylonitrile) (PAN) by epichlorohydrin cross-linking

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Abstract—A novel composite nanofiltration (NF) membrane was prepared by over-coating the PAN ultrafiltration (UF) membrane with a GCTACC thin layer. The effects of membrane preparation techniques and operating conditions on the performance of the composite membrane were studied. The results indicate that a composite NF membrane from 1.0 wt % GCTACC casting solution, vaporized for 2 h at 50 °C, cross-linked for 20 h at 50 °C and pH $\approx$ 12 with ethanol/epichlorohydrin (50/0.45 wt/wt) had optimum performance. The resultant GCTACC/PAN composite membrane was positively charged. Scanning electron microscopy showed its asymmetric and composite features. At 25 °C and 30 L/h of cycling flow, the permeability of pure water through this membrane is 6.3 L/h m^2 MPa. At 25 °C, 1.2 MPa and 30 L/h of cycling flow, the rejection of 1000 mg/L $MgCl_2$, $CaCl_2$, $MgSO_4$, Na_2SO_4, and NaCl solutions is 0.976, 0.972, 0.897, 0.65, and 0.407, respectively, with fluxes of 6.8, 6.12, 6.12, 5.57, and 5.51 L/h m^2, respectively. The order of rejection of different salts follows the decreasing order of $MgCl_2$, $CaCl_2$, $MgSO_4$, NaCl, KCl, Na_2SO_4, and K_2SO_4, which reveals the characteristics of the positively charged NF membrane. In addition, the curve for the streaming potential also illustrates the positively charged characteristics of this membrane, with a pressure osmotic coefficient of 11.7 mV MPa^{-1}.

Keywords: Graft copolymer of trimethylallyl ammonium chloride onto chitosan; Epichlorohydrin; Positively charged nanofiltration membrane; Membrane preparation

1. Introduction

Nanofiltration (NF) membranes have been recognized for having properties in between those of ultrafiltration (UF) and reverse osmosis (RO) and thus have found applications in many areas including water softening and removal of natural matter, treatment of waste water, etc.[1–6]

At present, internationally developed NF membranes are generally neutral or negatively charged.[7,8] There are a few studies on positively charged NF membranes. In fact, a positively charged membrane is actually needed[9] in some cases such as for the retention of multivalent cations and the recovery of cathode electrophoresis lacquer.

Chitosan is readily obtained by deacetylation of chitin, which is abundant in nature, and it shows good membrane forming characteristics. Tan et al.[10] reported the preparation of NF membranes by ultraviolet irradiation using poly(acrylonitrile) (PAN) membranes as support and chitosan as a modifier. The resultant membrane was used in the treatment of E. globulus in wastewater from BCHMP (blue-gum chemical hotgrinding machine plasm) and it was found that the retention to soda increased from 2.5% to 40.1% and the rejections to chroma, COD (chemical oxygen demand) and BOD (biologic oxygen demand) also increased greatly in comparison with a PAN matrix membrane. Musale and Kumar[11] studied the effect of surface cross-linking on sieving characterization of a chitosan/PAN composite NF membrane, and found that the cross-linked

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membranes were stable over a 10-h operating period for pure water permeation and the stability increased with increasing glutaraldehyde concentration. But chitosan only dissolves in dilute acid, not in water, so that the application of chitosan was limited to some extent.

Quaternization is applied to modify chitosan to increase the hydrophilicity and ionic character, and the chitosan derivative, quaternized chitosan, is obtained by grafting trimethylallyl ammonium chloride onto chitosan. It is used as a novel film-forming material for the NF membrane. In this study, a composite NF membrane was prepared using quaternized chitosan as the film-forming material and epichlorohydrin as the cross-linking reagent. The effects of preparation techniques and operation factors on membrane properties have been investigated.

2. Experimental

2.1. Materials and apparatus

Chitosan [$\mathrm{MW} = 5.4 \times 10^5$ Da, degree of deacetylation ($\mathrm{DD} = 90\%$)] was purchased from Haihui Bioengineering (Qingdao, China); trimethylamine alcohol solution, allyl chloride, ammonium ceric nitrate, acetic acid, NaCl, KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4 were of analytical grade; quaternized chitosan was prepared by a modified method according to the literature;[12] PAN UF membrane with MWCO of 1.0×10^5 Da was provided by the Development Center of Water Treatment Technology, State Oceanic Administration (Hangzhou, China).

Apparatus: A model DDS-11A conductivity meter (Shanghai Leici Instrument, China) was used; membrane evaluation apparatus was provided by the Development Center of Water Treatment Technology, State Oceanic Administration (Hangzhou, China); a JEOL JMS-840 scanning electron microscope was applied to investigate the structure characteristic of the membrane prepared.

2.2. Preparation of graft copolymer of trimethylallyl ammonium chloride onto chitosan (GCTACC)

2.2.1. Synthesis of trimethylallyl ammonium chloride (monomer). Twenty milliliter trimethylamine alcohol solution was placed in a 250-mL flask with three mouths, then 10 mL allyl chloride was dripped into the above solution with stirring at rt. After the addition, the temperature rose to 40 °C and the reaction proceeded with stirring for 12 h at this temperature under circumfluence. Finally, the residue was poured into acetone, and the precipitate (trimethylallyl ammonium chloride) was filtered, washed with acetone, and dried at 40 °C.

2.2.2. Preparation of graft copolymer of trimethylallyl ammonium chloride onto chitosan (GCTACC). Two grams of chitosan was dispersed in 85 g of 5% HAC solution at rt. After chitosan had dissolved completely, oxygen was removed for 30 min in order to avoid side reaction, then the temperature rose to 60 °C. Subsequently, 1.0 g ammonium ceric nitrate and 23 g 15 wt % aq trimethylallyl ammonium chloride were added to the chitosan solution with stirring. The reaction was carried out with stirring for 9.5 h at 60 °C. The residue was poured into ethanol, and the precipitate (graft copolymer) was filtered, washed with ethanol, and dried at 60 °C.

2.3. Preparation of GCTACC/PAN composite NF membranes

The casting solution was prepared by dissolving a certain amount of GCTACC in deionized water. After the solution was filtered with a G3 sand filter, it was over-coated on a surface-dried PAN UF membrane. Then the composite membrane was vaporized at a certain temperature, and cross-linked with epichlorohydrin in ethanol at a certain pH in an airtight container. The cross-linked membrane was heat-treated for 5 min at 50 °C again, then washed thoroughly with deionized water and immersed in deionized water for 24 h.

2.4. Permeation experiments

The flux of the membrane was determined by the weight of the permeated fluid through the membrane during a certain period of time and calculated with the following equation:

$$F = W/A \cdot t \tag{1}$$

where F is the flux, A is the effective area of the membrane; t is the time for permeation and W is the weight of the permeating fluid passing through the membrane. Rejection was calculated with the following equation:

$$R = 1 - C_{\mathrm{p}}/C_{\mathrm{m}} \tag{2}$$

where C_{p} and C_{m} are the concentrations of the permeated fluid and the feed concentration, respectively. In this study, salt concentrations are replaced by the conductivity of salt solutions. Two membrane disks were cut from the same sheet, and the data presented are the averages of these measurements with a standard deviation of 5%.

3. Results and discussions

3.1. Effect of preparation conditions on the rejection and flux of GCTACC/PAN composite membranes

The performance tests for the prepared membrane were carried out at 25 °C and 0.40 MPa and the concentration of feed was 1000 mg/L $MgCl_2$ without specification. The recirculation rate of feed was kept at 30 L/h. Due to operating at rather low pressure, the concentration polarization through the membrane test cell may be minimized and ignored. The effective membrane area was 19.6 cm^2, and the membrane was pre-pressurized at 0.4 MPa for 0.5 h before testing. Both the retentate and the permeate were re-circulated to the feed tank to maintain a constant feed concentration during the permeation experiments.

3.1.1. Effect of epichlorohydrin concentration on the rejection and flux of GCTACC/PAN composite NF membranes. Epichlorohydrin was chosen as the cross-linking reagent because it could react with not only –OH, but also $–NH_2$. After the reaction had taken place, the hydrophile –OH was introduced, which strengthened the hydrophilicity of the membrane. In addition, the chains of 2-OH-1,3 propylene introduced were comparatively short, which was beneficial for the formation of the membrane with pore sizes suitable for NF. To investigate the effect of epichlorohydrin concentration, the same preparation technique discussed in Section 2.3 was used and a series of GCTACC/PAN composite membranes with 1.0 wt % casting solution were prepared by changing the weight ratio of ethanol to epichlorohydrin from 50:0.17 to 50:0.75.

As shown in Figure 1, rejection increases with the increase in epichlorohydrin concentration until the mass ratio of ethanol to epichlorohydrin is 50:0.45, above which ratio rejection virtually remains constant. However, the flux decreases all of the time. This phenomenon may be explained as follows: when the epichlorohydrin concentration increases, the cross-linking reaction tends to be complete, which makes the membrane surface less permeable. Thus, the rejection increases and the flux decreases. Considering the flux and rejection of $MgCl_2$ together, a mass ratio of ethanol to epichlorohydrin of 50:0.45 is the optimum ratio.

3.1.2. Effect of evaporation time on the rejection and flux of GCTACC/PAN composite membranes. As noted earlier in the membrane preparation, the membranes are allowed to vaporize solvent to form a dense skin layer. To ensure that the GCTACC casting solution is vaporized completely at 50 °C, it needs at least 2 h. As shown in Figure 2, obviously both rejection and flux decrease with prolongation of evaporation time. In fact, the evaporation process of GCTACC solution is also a conversion process from sol to gel, and the molecules of polymers rearrange continually with the evaporation of solvent. When the arrangement of molecules is in an optimal state, the membrane prepared will show a high rejection and allow moderate flux. According to the results obtained, a curing time of 2 h at 50 °C was adopted for further experiments.

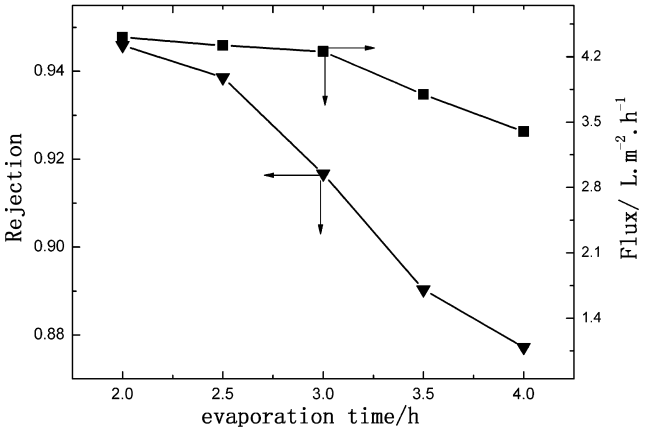

Figure 2. Effect of evaporation time on the rejection and flux of GCTACC/PAN composite membranes.

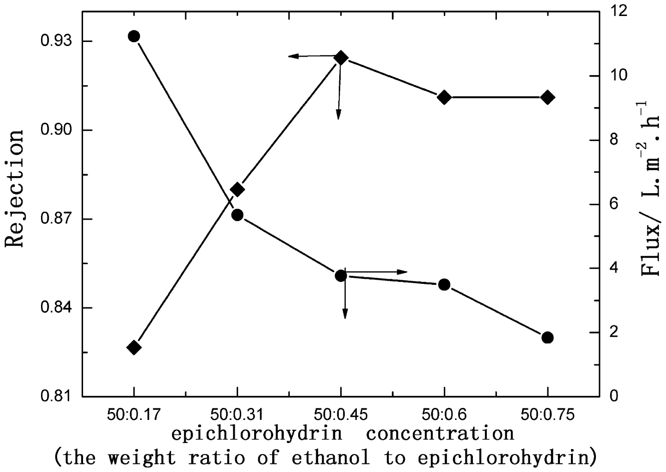

Figure 1. Effect of epichlorohydrin concentration on the rejection and flux of GCTACC/PAN composite membranes.

3.1.3. Effect of different vaporizing methods on the rejection and flux of GCTACC/PAN composite membranes. To investigate the effect of the different vaporizing methods on GCTACC/PAN composite membrane properties, a series of GCTACC/PAN composite membranes was prepared by vaporizing at 50 °C for 2 h, at 60 °C for 1 h and at 18 °C for 18 h, respectively. The results are shown in Table 1. Obviously, vaporizing for a long time at a low temperature (18 °C) or for a short time at a high temperature (60 °C) is unfavorable for the preparation of composite membranes with good performance. Compared with them, vaporizing at 50 °C for 2 h is a satisfactory method, and this membrane has a rejection of 0.946 and flux of 4.4 L/h m^2 at 0.4 MPa.

3.1.4. Effect of GCTACC concentration on the rejection and flux of GCTACC/PAN composite NF membranes. Because the method of over-coating was adopted to form the membrane, the concentration of GCTACC casting solution was a key factor in membrane preparation. It would fail when the concentration of GCTACC solution was too low or too high. Therefore, the concentration of casting solution was chosen to be in the range of 0.25–1.25 wt %. As shown in Figure 3, the rejection increases from 0.844 to 0.946 when the concentration changes from 0.25 to 1.0 wt %, and above this concentration the rejection begins to decrease. However, the flux decreases all of the time from 9.8 to 1.3 L/h m^2. Considering the flux and rejection of $MgCl_2$ together, the optimal GCTACC concentration is 1.0 wt %.

3.1.5. Effect of cross-linking temperature on the rejection and flux of GCTACC/PAN composite membranes. For this test, a series of GCTACC/PAN composite membranes from cross-linking temperatures of 20–60 °C was prepared and measured. The results are shown in Figure 4. The rejection increases from 0.857 to 0.946, whereas the flux decreases from 6.73 to 3.98 L/h m^2, then it remains constant at 4.0 L/h m^2 or so when the cross-linking temperature changes from 20 to 50 °C. They show the same decreasing trend above 50 °C. Considering the flux and rejection of $MgCl_2$ together, 50 °C is the optimum cross-linking temperature.

3.1.6. Effect of cross-linking time on the rejection and flux of GCTACC/PAN composite membranes. To investigate this effect, a series of GCTACC/PAN composite membranes were prepared with different cross-linking times in the range of 18–26 h. As shown in Figure 5, the rejection increases with the increase in cross-linking time until 20 h, which results from the increase in cross-linking degree, pore contraction and tortuosity.[13,14] When the cross-linking time was longer than 20 h, the rejection begins to decrease due to the decrease in degree of cross-linking. However, the flux decreases all of the time. The optimal cross-linking time is therefore 20 h.

Table 1. Effect of vaporizing methods on the rejection and flux of GCTACC/PAN composite membranes

Different vaporizing methods	Rejection	Flux/L m^{-2} h^{-1}
Vaporizing for 2 h at 50 °C	0.946	4.41
Vaporizing for 1 h at 60 °C	0.9	3.06
Vaporizing for 18 h at 18 °C	0.907	2.85

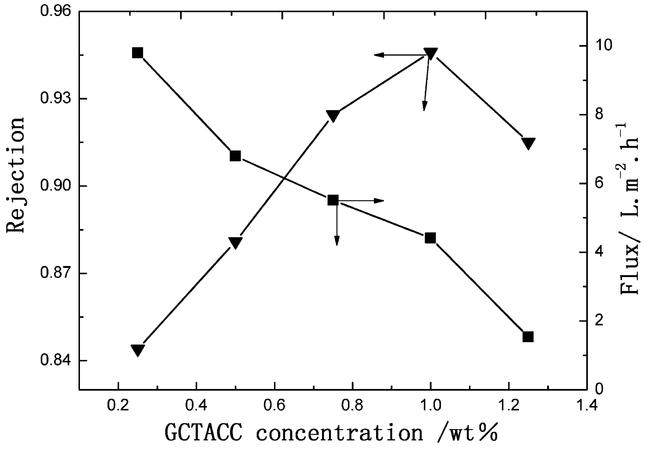

Figure 3. Effect of GCTACC concentration on the rejection and flux of GCTACC/PAN composite membranes.

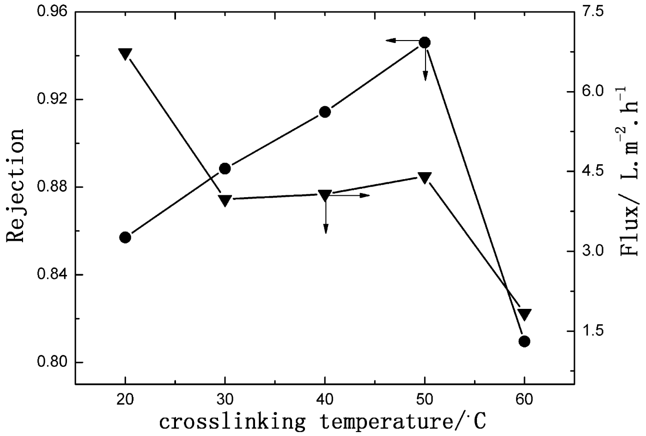

Figure 4. Effect of cross-linking temperature on the rejection and flux of GCTACC/PAN composite membranes.

3.1.7. Effect of pH of the cross-linking system on the rejection and flux of GCTACC/PAN composite membranes. The cross-linking reaction is carried out under alkaline conditions. pH in the cross-linking system is controlled by adding different weights of 50% KOH to the solution containing 50 g of ethanol and 0.45 g of epichlorohydrin. The results are shown in Figure 6. Rejection increases with the increase in alkalinity until 0.32 g of 50% KOH has been added to adjust the solution to pH 12. But when the addition is more than 0.32 g, that is to say, pH is higher than 12, the rejection begins to

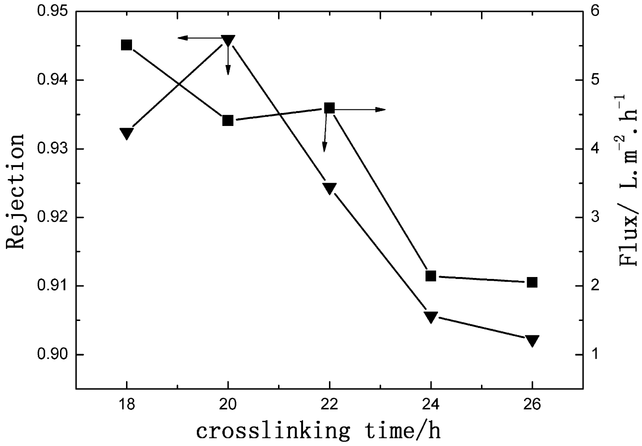

Figure 5. Effect of cross-linking time on the rejection and flux of GCTACC/PAN composite membranes.

decrease, as a result of the decrease in degree of cross-linking due to the auto-agglutination of epichlorohydrin under strongly alkaline conditions.[15] However, the flux increased gradually during the whole process. Therefore, pH in the cross-linking system should be maintained at pH 12.

3.2. Effect of operating conditions on the GCTACC/PAN composite membrane properties

Salt concentrations were determined with a Model DDS-11 A conductivity meter. The membrane performance tests were carried out at 25 °C, and the cycling flow of the feed was kept at 30 L/h. The membrane was pre-pressurized for 30 min prior to the test. The flux and rejection of the membrane were determined according to the equations given in Section 2.3. The membrane for further experiments was prepared from 1.0 wt % casting solution, vaporized at 50 °C for 2 h, and cross-linked for 20 h at 50 °C and pH ≈ 12 with ethanol/epichlorohydrin (50:0.45 wt/wt).

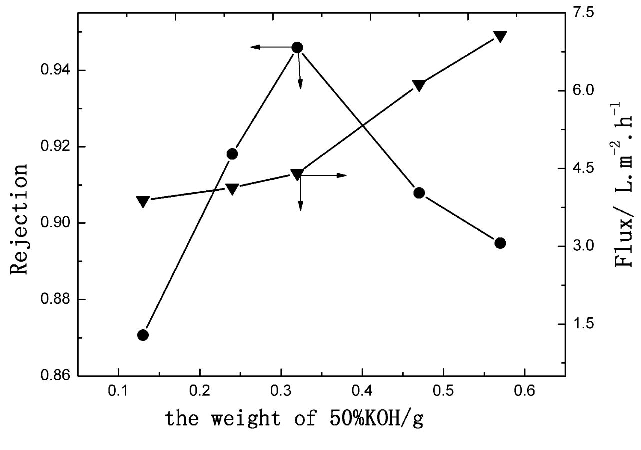

Figure 6. Effect of pH on the rejection and flux of GCTACC/PAN composite membranes.

3.2.1. Permeability of pure water through the GCTACC/PAN composite membrane. The permeability of pure water was measured at different pressures. As shown in Figure 7, the flux of the membrane increased linearly with operating pressure. This linear behavior is described by a slope close to the permeability of pure water according to the Spiegler–Kedem Model:[16,17]

$$J_v = L_\mathrm{p}(\Delta P - \sigma\Delta\Pi) \tag{3}$$

where J_v is the water flux, L_p is the permeability of pure water, ΔP is the operating pressure difference, σ is the reflection factor of the membrane, and $\Delta\Pi$ is the osmosis pressure. Because pure water is the permeating fluid, $\sigma\Delta\Pi$ may be ignored. The permeability of pure water is calculated at 6.3 L/h m^2 MPa for this composite NF membrane by the linear fit of experimental data.

3.2.2. Effect of feed concentration on the GCTACC/PAN composite membrane properties. Figures 8 and 9 show the rejection and flux of $MgCl_2$ with different concentrations at operating pressures in the range 0.5–1.4 MPa, respectively. The rejection shows the same trend of increasing markedly with the increase in operating pressures lower than 1.2 MPa, then an approximately constant value is attained around 0.975; the flux increases almost linearly with the increase in operating pressure regardless of $MgCl_2$ concentration.

3.2.3. Effect of different inorganic electrolytes on the GCTACC/PAN composite membrane properties. In the salt transport process, the electric properties of the NF membrane have a great effect on ion permeation and rejection. Here the concentration of the single salt solutions tested is about 1000 mg/L. The rejection and flux of different inorganic electrolytes by the GCTACC/PAN composite membrane are shown in Figures 10 and 11, respectively. Obviously the rejections to inorganic

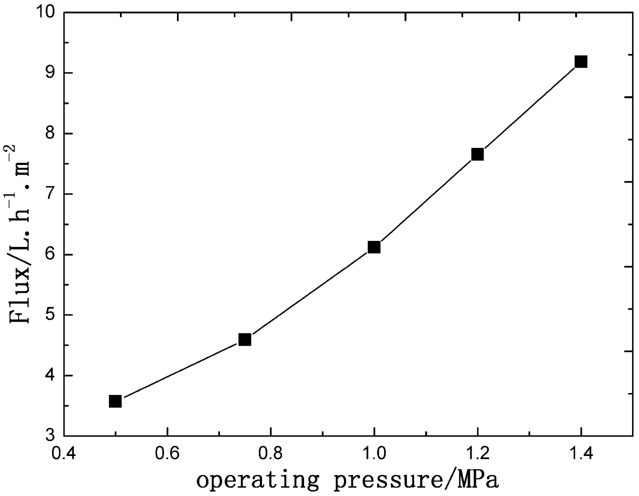

Figure 7. Effect of operating pressure on the flux of pure water.

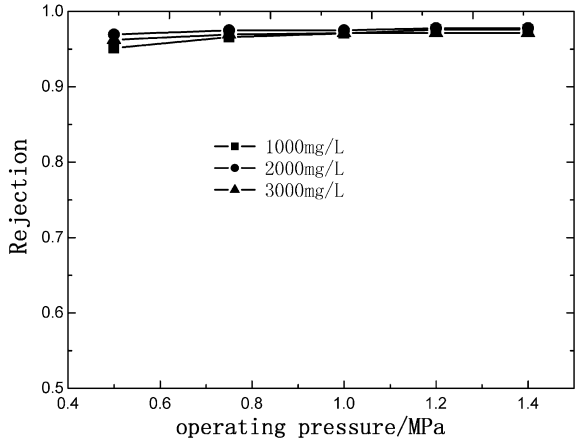

Figure 8. The curves about the rejections on feed solution with a different concentration against operating pressure.

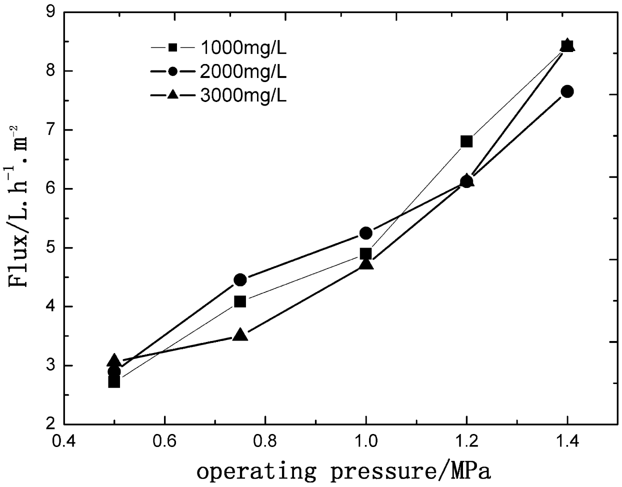

Figure 9. The curves about the fluxes on feed solution with a different concentration against operating pressure.

electrolytes follow the order of $MgCl_2 \approx CaCl_2 > MgSO_4 > NaCl \approx KCl > Na_2SO_4 > K_2SO_4$, which is typical of a positively charged NF membrane and is explained by the electrostatic effect.[18,19] The orders of the rejections: $MgCl_2 \approx CaCl_2 > NaCl \approx KCl$ and $MgSO_4 > Na_2SO_4 > K_2SO_4$, corresponding to the increasing order of the cation charge densities, because the active layer consisting of GCTACC has quaternary ammonium group distribution and allows a stronger repulsion of Mg^{2+}, Ca^{2+} than Na^+, K^+. The order of rejection: $MgCl_2 > MgSO_4$, $NaCl > Na_2SO_4$ and $KCl > K_2SO_4$, goes opposite with the increasing order of anion charge densities, because the active layer of the composite membranes contains quaternary ammonium groups as mentioned above and has stronger attraction forces for SO_4^{2-} than Cl^-. The order of the rejection $MgSO_4 > NaCl$ may be because the repulsion forces on the cation are stronger than the dominant attraction. In addition, the fluxes increase almost linearly with the increase in

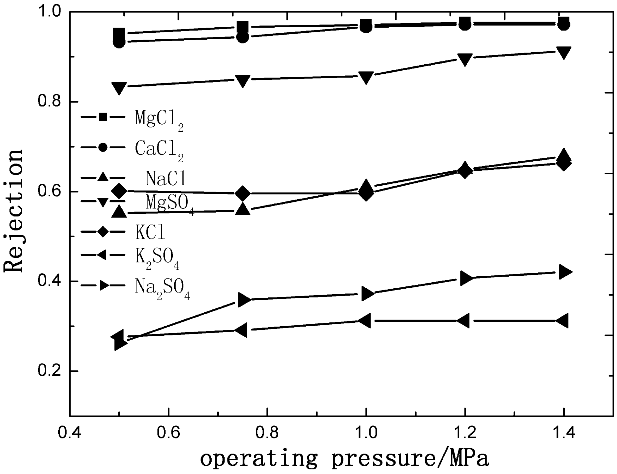

Figure 10. The rejection on different inorganic electrolyte solution against operating pressure.

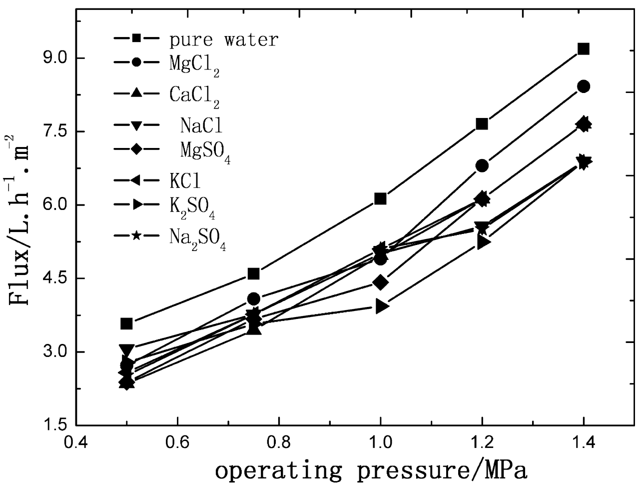

Figure 11. The flux on different inorganic electrolyte solutions against operating pressure.

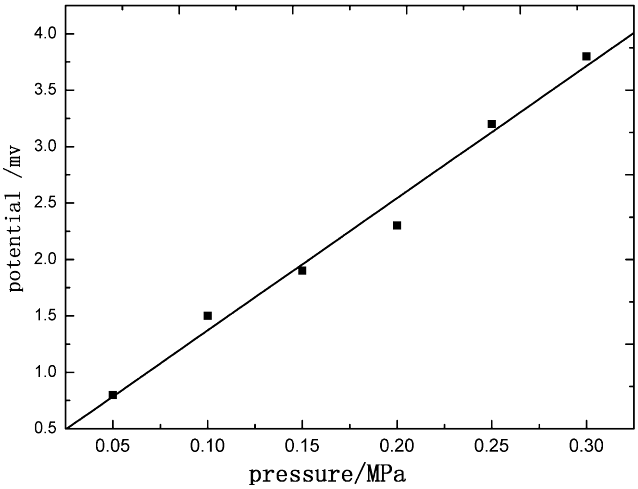

Figure 12. The curves about streaming potential of the GCTACC/PAN composite NF membrance.

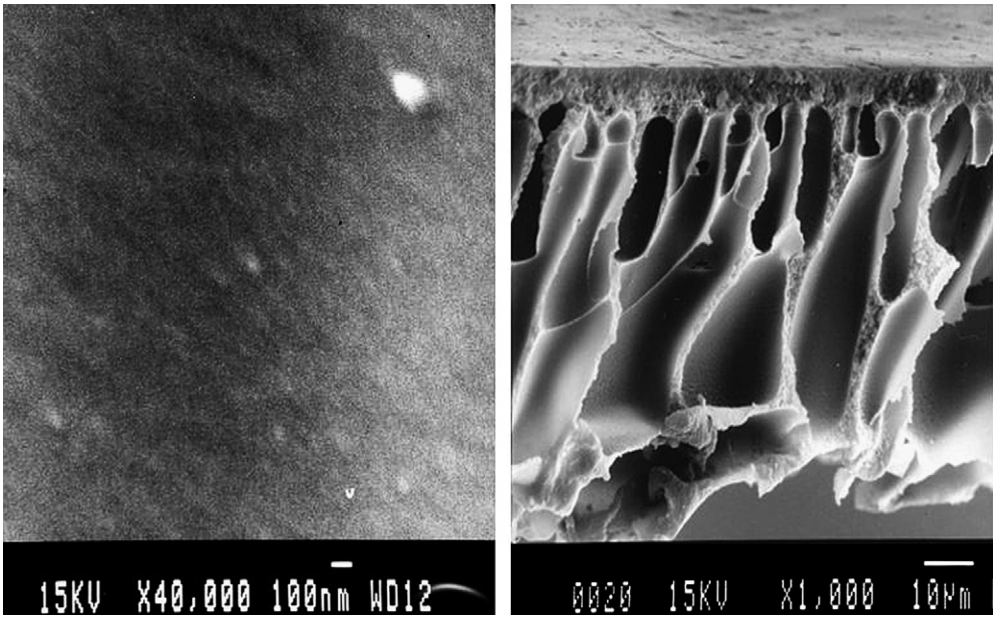

Figure 13. The surface (left) and cross-section (right) images of the composite nanofiltration membrane.

operating pressure, but they are lower than the flux of pure water, which results from the solvent effect.

3.3. Streaming potential of the GCTACC/PAN composite NF membrane[20,21]

The streaming potential of the GCTACC/PAN composite NF membrane was measured at different pressures in 0.1 M KCl solution, which was filled between the sides of the membrane. The curve for the streaming potential against pressure is shown in Figure 12. It can be seen that the streaming potential increases linearly with the increase in pressure and all potentials are above zero, suggesting the characteristics of a positively charged membrane. The pressure osmotic coefficient is attained at 11.7 mV MPa^{-1} for this NF membrane by the linear fit of experimental data.

3.4. Structure characteristic of the GCTACC/PAN composite NF membrane

The cross-section and surface of this membrane were characterized with a JDEL JMS-840 scanning electron microscope and the results are shown in Figure 13. There is a thin active functional layer with a compact surface on a finger-like supporting layer of PAN UF base membrane, revealing the asymmetric and composite structure of this membrane.

4. Conclusions

Positively charged composite NF membranes have been successfully prepared by using chitosan derivative, a graft copolymer of trimethylallyl ammonium chloride onto chitosan (GCTACC) as membrane-forming material, PAN UF as the support layer and epichlorohydrin as the cross-linking reagent. The effect of preparation conditions including GCTACC concentration, epichlorohydrin concentration, cross-linking temperature, etc. on the performance of the composite membrane has been evaluated. The membrane with optimal performance has been determined by adjusting these factors and its structure has been characterized by scanning electron microscopy.

In addition, some performance tests have been conducted for the composite NF membrane. The performances are affected by the feed concentration and the type of feed, etc. The rejections of electrolytes with divalent cations (Mg^{2+}, Ca^{2+}) reach >0.9, whereas rejections of electrolytes with divalent anions and low-valency cations are lower than 0.7, so this membrane has the potential for selective separation of different electrolytes. The rejections follow the decreasing order of $MgCl_2$, $CaCl_2$, $MgSO_4$, NaCl, KCl, Na_2SO_4, and K_2SO_4, which is typical of a positively charged NF membrane. In addition, the curve for the streaming potential also illustrates the positively charged characteristics of the composite membrane.

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