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Preparation and characteristics of quaternized chitosan/poly(acrylonitrile) composite nanofiltration membrane from epichlorohydrin cross-linking

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Abstract

Quaternized chitosan was prepared by modifying chitosan with 2,3-epoxypropy trimethylammonium chloride. A novel positively charged composite NF membrane was prepared by coating aq. quaternized chitosan onto a PAN UF membrane, subsequently cross-linked with epichlorohydrin. The effects of membrane preparation conditions on membrane properties and membrane characteristics were studied. The molecular weight cut-off of the representative membrane was obtained at about 560 Da (in NF range), and the structure was characterized by Scanning Electron Microscope, suggesting the composite structure of this membrane. At 25 °C, the pure water permeability is 9.25 L/h m^2 MPa, and the order of rejection to different model solutes was $MgCl_2 \approx CaCl_2 > NaCl \approx KCl > MgSO_4 > Na_2SO_4$, revealing the characteristic of positively charged NF membranes. The rejections to 1000 g/L $MgCl_2$ and $CaCl_2$ solutes were more than 0.96, so this membrane developed can be expected to use in the hardness removal of waste-water.

Keywords: Quaternized chitosan; Epichlorohydrin; Positively charged NF membrane; Membrane preparation

1. Introduction

In recent years, a number of composite nanofiltration (NF) membranes have been developed. The term NF is drawn from the observation that size selectivity of the membrane towards non-charged solute approximates 10 Å, i.e. a nanometer cut-off. The performance characteristics of the NF membrane stand at between those of reverse osmosis and ultrafiltration (UF) membrane. The NF process has been used in many applications such as wastewater reclamation, water softening, and separation of organic compounds having different molecular weights. Most of commercially available NF membranes are neutral or negatively charged membranes (Matsuyama, Kitamura, & Naramura, 1999; Raman, Cheryan, & Rajagaopalan, 1994). There are few reports about the preparation of positively charged membrane.

Quaternized chitosan, as one of chitosan's derivatives, is a good forming-film material. Zhou (Zhou, 2004) prepared a film from quaternized chitosan, which was used in keeping fruits and vegetables fresh. Xiao et al.(Lin, Jie, & Yi, 2006) prepared quaternized chitosan/filter paper composite membranes by coating quaternized chitosan on filter paper and cross-linking with glutaraldehyde, and investigated the their application in adsorbing bilirubin. However, to the best of our knowledge there is no report about NF membrane prepared from quaternized chitosan except our study. Therefore, it is of interest to report the preparation of a positively charged composite NF membranes from quaternized chitosan.

In this study, quaternized chitosan was prepared by modifying chitosan with 2,3-epoxypropy trimethylammonium chloride (Loubaki, 1991). A positively charged NF membrane, called quaternized chitosan/PAN composite

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NF membrane was prepared using quaternized chitosan as active layer, PAN UF membrane as support layer and epichlorohydrin as cross-linking reagent, respectively. The preparation conditions and characteristics of the composite NF membranes were investigated.

2. Experiment

2.1. Materials and apparatus

Chitosan [MW = 5.4×10^5 Da, degree of deacetylation (dd) = 90%] was purchased from Haihui Bioengineering (Qingdao, China); The quaternizating procedures of chitosan were similar to those reported previously (Huang, Chen, Sun, & Gao, 2006; Huang, Chen, & Wang, 2006), Fig. 1 shown the preparation of quaternized chitosan; sulfuric acid, NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, Na_2SO_4, glucose, sucrose and polyethylene glycol (MW = 600–1000 Da) were of analytical grade; 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: Model DDS-11A conductivity meter (Shanghai Leici Instrument, China); Membrane evaluation apparatus was provided by the Development Center of Water Treatment technology, State Oceanic Administration (Hangzhou, China); IR spectra were measured with an Avatar-360 IR spectrometer from Nicolet; a JEOL JMS-840 scanning electron microscope was applied to measure the structure characteristics.

2.2. Membrane preparation

The casting solution was prepared by dissolving a certain amount of quaternized chitosan in de-ionized water. After the above solution was filtered with a G3 sand filter, it was coated on a surface-dried PAN UF membrane. Then the composite membrane was allowed to stay at 50 °C for 2 h to evaporate the solvent, then cross-linked with epichlorohydrin in a sealed container. The membrane cross-linked was heat-treated at 50 °C for 5 min again, then washed thoroughly with de-ionized water and stored in de-ionized water until ready to use.

2.3. Permeation experiments

All permeation experiments were carried at 25 °C and the cycling flow of 30 L/h. The resultant membrane was characterized in the module after pretreatment with pure water at 0.5 MPa pressure for 30 min. The pure water flux was investigated at the operating pressure varying from 0.25 to 1.2 MPa, and the rejections to 1000 mg/L $MgCl_2$, $CaCl_2$, NaCl, KCl, $MgSO_4$ and Na_2SO_4 solutions were measured at the operating pressure of 1.0 MPa. Besides, the MWCO was measured by the rejections to organic substances at a concentration of 1000 mg/L at the operating pressure of 1.0 MPa.

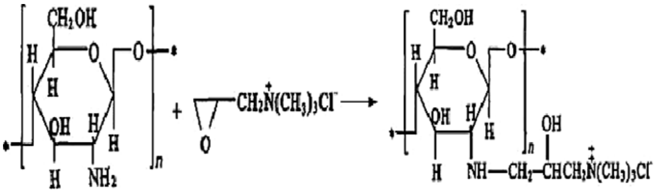

Fig. 1. The reaction between chitosan and 2,3-epoxypropyltrimethyl ammonium chloride.

The permeation flux, F, is calculated according to $F = V/At$, where V is the total volume of the water or solution permeated during the experiment; A represents the membrane area; and t denotes the operation time. Rejection, R, is calculated according to $R = 1 - C_p/C_f$, where C_p and C_f are permeate concentration and feed concentration, respectively.

2.4. Structure characteristics

This membrane for structure analysis was pre-treated by solvent exchange with 50% aq. isopropanol, isopropanol and hexane in that sequence for 0.5 h in each solvent, followed by vacuum drying at 40 °C for 3 days (Musale & Kumar, 2000). Then, the membrane was cryogenically fractured in liquid nitrogen and then coated with gold. The cross-sectional morphologies of the composite membrane was characterized by Scanning Electron Microscopy (*SEM*).

3. Results and discussion

3.1. Effect of preparation conditions on membrane properties

The performance tests of the membranes prepared under different conditions were carried out at 25 °C and operating pressure of 0.40 MPa. The feed was 1000 mg/L $MgCl_2$ solution without specification. The feed cycling flow was kept at 30 L/h. Two membrane disks were cut from sheets, and the datum presented are the averages of both measurements.

3.1.1. Effect of epichlorohydrin concentration

Based on these reasons: firstly, epichlorohydrin can react with –OH in quaternized chitosan; secondly, hydrophile –OH introduced can strengthen the hydrophilicity of membrane due to cross-linking; thirdly, the chains of 2-OH-1, 3 propylene introduced was comparatively short, which was beneficial to the formation of the membrane with small pores, epichlorohydrin was selected as the cross-linking reagent. H_2O is a good solvent of quaternized chitosan, so a little water in the cross-linking system should make for the interaction between epichlorohydrin and quaternized chitosan, thereby ethanol/H_2O (45/5 wt/wt) was applied. Under ethanol/H_2O (wt/wt) of 45/5 in 50 g solution, the weight of epichlorohydrin varied from 0.15 to 0.6 g.

As shown in Fig. 2, the flux decreases from 4.59 to 1.84 L/m^2 h and the rejection increases from 0.703 to

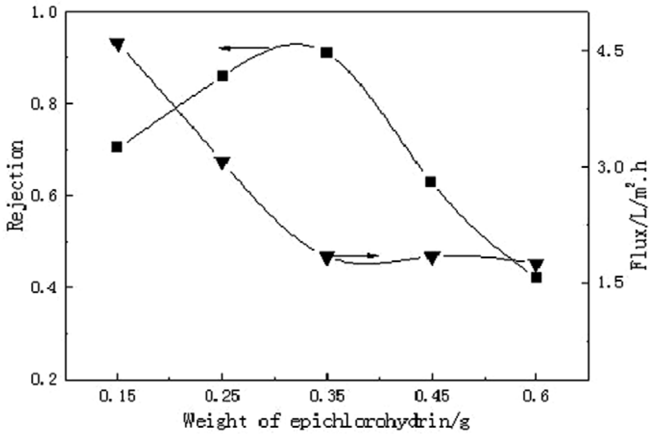

Fig. 2. Effect of epichlorohydrin concentration on membrane properties Preparation: 2.0 wt casting solution, vaporized at 50 °C for 2 h, cross-linked at 50 °C and pH ≈ 13 for 22 h with epichlorohydrin, ethanol and H_2O (0.15–0.6/45/5 wt/wt/wt) with epichlorohydrin.

0.909 as the weight of epichlorohydrin changes from 0.15 to 0.35 g. But it exceeds 0.35 g, the rejection begins to decrease and the flux has a negligible change. The above phenomena may be explained as follows, the increase in epichlorohydrin concentration makes the surface of the membrane more close-grained due to cross-linking. As a result, the rejection increases and the flux decreases. However, the increase in hydrophilicity is enough to compensate for the resistance through the compact membranes due to cross-linking with an increasing in epichlorohydrin concentration, thereby the rejection declines. Thus, epichlorohydrin, ethanol and H_2O (0.35/45/5 wt/wt/wt) were adopted here.

3.1.2. *Effect of quaternized chitosan concentration*

Because casting acted as the method to form membrane, the casting solution (aq. quaternized chitosan) concentration was a key factor in membrane preparation. It would fail when the concentration was too low or too high. Therefore, the membranes prepared from the casting solution concentration in the range of 1.5–3.5 wt% were measured. As shown in Table 1, the flux decreases and the rejection increases with an increasing casting solution concentration until it was 2.0 wt%. This trend indicates the increasing thickness of the active layer and the effective charge on the membrane result in lower flux and higher rejection due to an increase in the casting solution concentration. However, the rejection decreases and the flux increases as the concentration is higher than 2.0 wt%, which is explained as mentioned in Section 3.1.1. The increase in hydrophilicity compensates an increasing resistance through the thick membrane due to cross-linking, leading to a decrease in rejection and an increase in flux.

Table 1
Effect of quaternized chitosan concentration on membrane properties

Quaternized chitosan concentration/wt%	Rejection	Flux/L/m^2 h
1.5	0.891	4.16
2	0.909	1.84
2.5	0.898	2.27
3	0.841	2.79

Preparation: 1.5–3.0 wt% casting solution, vaporized at 50 °C for 2 h, cross-linked at 50 °C and pH 13 for 22 h with epichlorohydrin, ethanol and H_2O (0.35/45/5 wt/wt/wt) with epichlorohydrin.

3.1.3. *Effect of cross-linking temperature*

The cross-linking reaction between epichlorohydrin and –OH in chitosan was carried out above 40 °C (Zheng, Du, Yu, & Xiao, 2000). Besides, the boiling point of ethanol is comparatively low. Thus, the membranes were prepared from different cross-linking temperature in the range of 40–60 °C.The results are listed in Table 2, the rejection increases by 0.1 and the flux decreases by a factor of 80% from 8.67 to 1.84 L/m^2 h when the cross-linking temperature changes from 40 to 50 °C. It is considered that an increasing temperature promotes the cross-linking of polymers and shrinkage of the membrane, which results in higher rejection and lower flux. However, the rejection decreases steeply and the flux changes a little when the temperature was above 50 °C. Considering both the flux and rejection integrally, the cross-linking temperature of 50 °C is proper here.

Table 2
Effect of cross-linking temperature on membrane properties

Cross-linking temperature/°C	Rejection	Flux/L/m^2 h
40	0.796	8.67
50	0.909	1.84
60	0.726	1.96

Preparation: 2.0 wt% casting solution, vaporized at 40–60 °C for 2 h, cross-linked at 50 °C and pH 13 for 22 h with epichlorohydrin, ethanol and H_2O (0.35/45/5 wt/wt/wt) with epichlorohydrin.

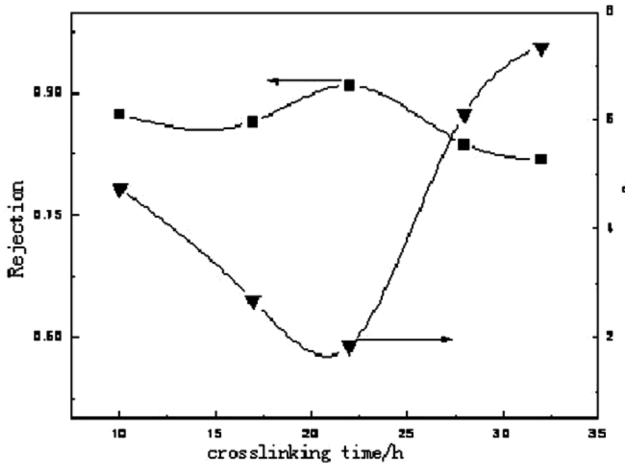

Fig. 3. Effect of cross-linking time on membrane properties Preparation: 2.0 wt% casting solution, vaporized at 50 °C for 2 h, cross-linked at 50 °C and pH ≈ 13 for 10–32 h with epichlorohydrin, ethanol and H_2O (0.35/45/5 wt/wt/wt) with epichlorohydrin.

3.1.4. Effect of cross-linking time

To investigate this effect, a series of the composite membranes were prepared from the cross-linking time varying from 10–32 h. As shown in Fig. 3, the flux decreases and the rejection increases with an increase in the cross-linking time (except for 15 h) until it is 22 h. This trend could be explained by the increasing in cross-linking degree, pore contraction and the increasing in tortuosity due to the prolonging cross-linking time. However, the rejection decreases and the flux increases when it exceeds 22 h. This is because when cross-linking time is prolonged, the excessive contraction of active layer makes membrane come into being stress crack, resulting in an increasing flux and a decreasing rejection. Considering both the flux and rejection integrally, the cross-linking time should be controlled at 22 h.

3.1.5. Effect of pH in the cross-linking system

The changing pH was controlled by adding different weight 50% KOH in the cross-linking system. The cross-linking system adopted contains 45 g ethanol, 5 g H_2O and 0.35 g epichlorohydrin. To investigate this effect, a series of the membranes were prepared by adding 0.18, 0.32, 0.45, 0.55 and 0.66 g 50% KOH into this system, respectively. As shown in Fig. 4, the flux decreases and the rejection increases with an increasing in the weight of KOH until its weight reaches 0.45 g, here pH is about 13. This is because an increase in alkalinity leads to an increasing in cross-linking degree, the above phenomenon happens. However, when it exceeds 0.45 g, the rejection decreases and the flux increases. This trend may be explained as follows. When the alkalinity was too strong, the auto-agglutination of epichlorohydrin would take place (Zheng et al., 2000), which would reduce the reaction chance between epichlorohydrin and quaternized chitosan, leading to a decreasing rejection and an increasing flux. Therefore, pH should be controlled at 13 or so.

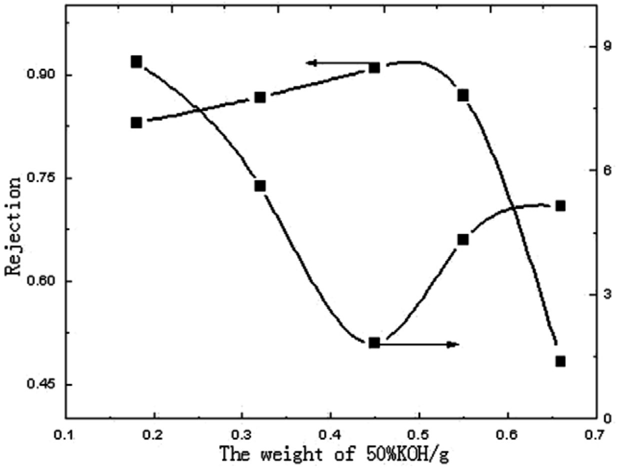

Fig. 4. Effect of pH on membrane properties Preparation: 2.0 wt casting solution, vaporized at 50 °C for 2 h, cross-linked at 50 °C and different pH for 22 h with epichlorohydrin, ethanol and H_2O (0.35/45/5 wt/wt/wt) with epichlorohydrin.

In the end, what's worth mentioning is the composite NF membrane from 2.0 wt% casting solution, vaporized at 50 °C for 2 h, then cross-linked at 50 °C and pH 13 or so for 22 h with epichlorohydrin, ethanol and H_2O (0.35/45/5 wt/wt/wt) will be use to carry out further experiments.

3.2. Permeation characteristics

3.2.1. Pure water permeability of quaternized chitosan /PAN composite NF membrane

The pure water permeability was measured at different pressures varying from 0.25 to 1.2 MPa. As shown in Fig. 5, the pure water flux through this membrane increases linearly with the operating pressure. This linear behaviour was described by a slope close to that of pure water permeability according to the Spiegler-Kedem Model (Xu & Lebrun, 1999):

$$J_v = L_p(\Delta P - \sigma \triangle \Pi) \tag{1}$$

Because pure water is the permeating object here, $\sigma\triangle\Pi$ may be ignored. The pure water permeability L_p is obtained at 9.25 L/h m^2 MPa by the linear of experimental datum.

3.2.2. Permeation of model solutes

It appears that this membrane show different separation performance for different model solutes. As shown in Table 3, the rejection follows the order of $MgCl_2 \approx CaCl_2 > NaCl \approx KCl > MgSO_4 > Na_2SO_4$, which is typical characteristic of positively charged NF membrane and explained by electrostatic effect (Zhang, Jian, & Dai, 2005; Labbez et al., 2003). For $MgCl_2 \approx CaCl_2 > NaCl \approx KCl$ and $MgSO_4 > Na_2SO_4$, corresponding to the increasing order of the cation charge densities, because the active layer has quaternary ammonium groups contribution and has stronger repulsion to Mg^{2+} and Ca^{2+} than Na^+ and K^+, Mg^{2+} and Ca^{2+} are rejected easily. For $KCl > MgSO_4$, it may be related with the attraction forces. When the attraction forces becomes progressively stronger, this membrane

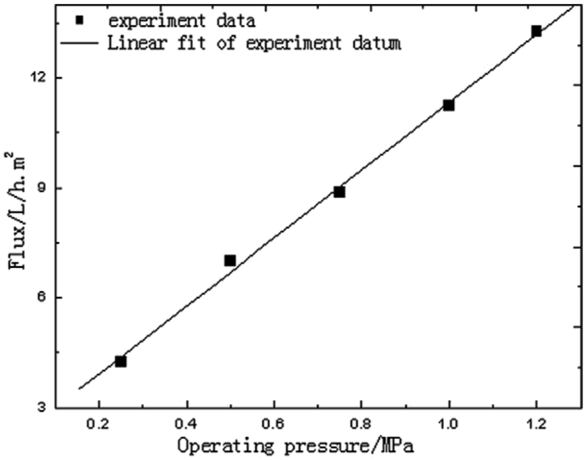

Fig. 5. Flux for pure water against operating pressure Operation: at 25 °C and cycling flow of 30 L/h.

Table 3
The rejection and flux for different model solutes through this membrane

Type of model solutes	Flux/L/m^2 h	Rejection
KCl	16.3	0.561
NaCl	15.9	0.575
Pure water	11.2	–
Na_2SO_4	9.86	0.266
$CaCl_2$	7.35	0.967
$MgCl_2$	7.04	0.967
$MgSO_4$	6.80	0.437

Operation: different model solutes at a concentration of 1000 mg/L; at the operating pressure of 1.0 MPa and cycling flow of 30 L/h.

has stronger attraction forces on SO_4^{2-} than Cl^-, leading to higher rejection for KCl. Besides, it is not difficult to find that this membrane shows the similar rejection to the model solutes with the same valent type such as $MgCl_2$, $CaCl_2$ and NaCl, KCl. Therefore, it comes to a conclusion that due to the inherent charged characteristic, the separation performance is mainly influenced by the electrostatic effect.

3.3. Molecular weight cut-off

A series of polyethylene glycol concentrations were determined with $BaCl_2$ colorimetric method; glucose and sucrose concentrations were determined with anthrone colorimetric method. The MWCO was the molecular weight of organic substance with a retention of 90% (Afonso, Hagmeyer, & Gimbel, 2001).The curve showing rejection verse molecular weight is shown in Fig. 6. Obviously the MWCO of this membrane is approximately 560 Da, which is in NF range.

3.4. Structure characteristics

The scanning electron micrograph of the cross-section of this membrane is shown in Fig. 7. It appears that the presence of $5 \cdot 10^{-3}$ um thick, uniform coating of chitosan on the dense skin of PAN UF base membrane, revealing the composite structure of the NF membrane prepared.

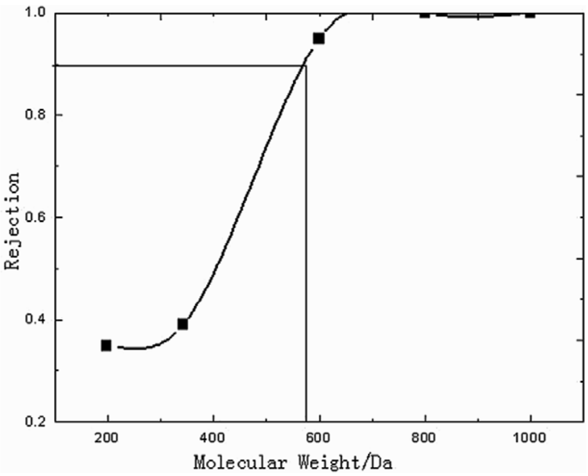

Fig. 6. Molecular weight cut-off curves for the representative membrane operation: at 25 °C and cycling flow of 30 L/h.

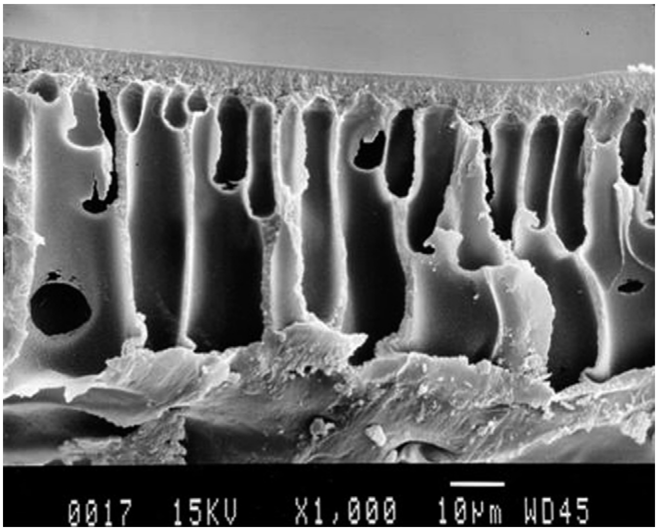

Fig. 7. The cross-section image of the representative membrane (magnified 1000 times).

4. Conclusion

The quaternized chitosan/PAN positively charged composite NF membrane may be prepared by coating aq.quaternized chitosan soluiton on the PAN UF membrane and using epichlorohydrin as cross-linking reagent. Effect of preparation conditions such as casting solution concentration, epichlorohydrin concentration, cross-linking temperature, etc on membrane properties was investigated. Besides, the composite NF membrane from 2.0 wt% casting solution, vaporized at 50 °C for 2 h, then cross-linked at 50 °C for 22 h and pH 13 with epichlorohydrin, ethanol and H_2O (0.35/45 /5 wt/wt/wt) will be applied to be representative for quaternized chitosan/PAN composite NF membranes. And its characteristics were investigated.

The molecular weight cut-off of the representative membrane was about 560 Da (in NF range), and its structure was observed by SEM, revealing the composite structure of this membrane. And the order of rejection to different model solutes was $MgCl_2 \approx CaCl_2 > NaCl \approx KCl > MgSO_4 > Na_2SO_4$, revealing the characteristic of positively charged NF membranes. The rejections to 1000 g/L $MgCl_2$ and $CaCl_2$ solutes were more than 0.96, so this membrane prepared was expected to have application in the hardness of waste-water.

Acknowledgement

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