Desalination and Water Treatment
www.deswater.com

18 (2010) 198–205
June

1944-3994 / 1944-3986
doi: 10.5004/dwt.2010.1771

Study of sodium alginate/polysulfone composite nanofiltration membrane

Xiaolin Chen*, Xueli Gao, Weiwei Wang, Duo Wang, Congjie Gao

Chemistry and Chemical Engineering College, Ocean University of China, Qingdao, 266100
Tel.: +86 532 66786513; Fax: +86 532 66782017; email: lindachen0209@hotmail.com, gaoxl@ouc.edu.cn, taiyanghetadezimin@126.com, wangduo@ouc.edu.cn, gaocjie@mail.hz.zj.cn

Received 31 May 2009; Accepted 5 January 2010

ABSTRACT

A novel composite nanofiltration (NF) membrane was prepared by over-coating the polysulfone ultrafiltration membrane with an alginate thin layer. The effects of the membrane preparation techniques and operating conditions on the rejection performance of the composite membranes were studied. The structure of the composite NF membrane was characterized by scanning electron microscopy and infrared spectroscopy. The results suggested that composite membrane with excellent performances was prepared while the concentration of sodium alginate was 2%, the concentration of glutaraldehyde was 0.9%, and the cross-linking time was 4 h at 30°C. Characterization suggested: The salt rejections to Na_2SO_4, $MgSO_4$, NaCl and $MgCl_2$(1000 mg·L^{-1}) were 87.2%, 21.5%, 32.0%, 12.2%, respectively. And the permeation fluxes were 30.6 L·h^{-1}·m^{-2}, 35.2 L·h^{-1}·m^{-2}, 33.5 L·h^{-1}·m^{-2}, 22.4 L·h^{-1}·m^{-2}, respectively. In addition, the curve about the streaming potential illustrated the negatively charged characteristics of this membrane, with a pressure osmobic coefficient of –32.971 mV·MPa^{-1}.

Keywords: Composite nanofiltration membrane; Sodium alginate; Polysulfone ultrafiltration membrane; salt rejection

1. Introduction

Nanofiltration (NF) with separation characteristics is between ultrafiltration (UF) and reverse osmosis (RO). Compared to UF, NF membranes have smaller pore size, so that smaller organic molecules can be retained (MW>200). Compared to RO, a lower retention is found for monovalent ions. The pressure of NF membranes ranges from 0.5 to 1.5 MPa which is much lower than RO membranes [1,2]. Due to the above characteristics, NF membranes have been applied widely in many industry fields such as purification for drinking water (water softening, removal of micropollutants) [3] and wastewater [4]. In recent years, research on composite membrane and its application are highly attention-getting. Especially composite technique for making NF membranes was mostly commercial and has the most yields [5].

Among the hydrophilic polysaccharide type polymers, alginate membrane has gained special interest because it showed the highest flux and separation factor among the hydrophilic materials tested for the pervaporation dehydration. Alginic acid is a heteropolymer containing mannuronic and guluronic acid groups and is commonly found in seaweeds. Its Chemical formula is showed in Fig. 1 [6–8].

However, a very high hydrophilicity of sodium alginate resulting from both of its carboxyl and hydroxyl groups, leads to a significant swelling of membrane in aqueous solution, followed by a remarkable decline of selectivity and mechanical strength [9]. To overcome these drawbacks, several researchers have modified the alginate membranes for the effective dehydration performance. Yeom and Lee [10], crosslinked the sodium

*Corresponding author.

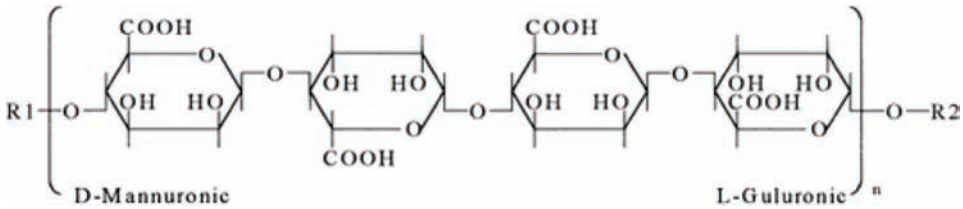

Fig. 1. The chemical structure of alginic acid.

alginate membrane with glutaraldehyde for the separation of water–isopropanol mixture. Haung and coworkers [11] prepared a novel two-ply dense composite membranes using successive casting of sodium alginate and chitosan for the dehydration of isopropanol and ethanol. However, to our knowledge there is few reported literatures on using sodium alginate to prepare composite NF membrane.

In this study, a composite NF membrane was prepared using sodium alginate as filming-forming material and glutaraldehyde as cross-linking reagent.

2. Experiments

2.1. Materials and apparatus

2.1.1. Materials

Sodium alginate was purchased from Chinese Medicine Shanghai Chemical Reagent Limited Company. Polysulfone UF Membrane with molecular weight cut-off (MWCO) of 1×10^5 Da was supplied by the Development Center of Water Treatment technology, State Oceanic Administration (Hangzhou, China). All other reagents and chemicals were of analytical grade and used without further purification. De-ionized water with a conductivity of 2×10^{-4} S/m was used for membrane preparation and permeation experiments.

2.1.2. Apparatus

Scanning electron microscopy (SEM) apparatus was JEOL JMS-840 (Japan). Salt concentrations were determined with a model DDS-11A conductivity meter (Shanghai Leida Instrument, China). Infrared (IR) spectra were measured with an Aratar 360 IR spectrometer purchased from Nicolet. Membrane potential apparatus and PMI membrane evaluation apparatus were provided by the Development Center of Water Treatment technology, State Oceanic Administration (Hangzhou, China).

2.2. Preparation of sodium alginate/polysulfone composite nanofiltration membranes

The casting solution was prepared by dissolving a certain amount (1.0–2.5 wt%) of sodium alginate in de-ionized water. The sodium alginate solution was over-coated on the surface-dried polysulfone UF membrane with a roller. Then the composite membrane was vaporized at 50°C for 2 h, and crosslinked with glutaraldehyde in ethanol solution in an airtight container. The cross-linked membrane was heat-treated for 10 min at 50°C again, then washed thoroughly with de-ionized water and immersed in de-ionized water for 24 h.

2.3. Permeation experiments

The permeation flux of the membrane was determined by the weight of the permeated fluid through the membrane during a certain period of time and calculated as the following Eq. (1):

$$F = \frac{W}{A} \times t \tag{1}$$

where F is the permeate flux, A the effective area of the membrane, t the time for permeation and W is the weight of the permeated fluid passing through the membrane. Rejection was calculated with the following Eq. (2):

$$R = 1 - \frac{C_P}{C_M} \tag{2}$$

where C_P is the permeate concentration and C_M is the feed concentration. Three membrane disks were cut from sheets, and the data presented are the averages of these measurements [1].

3. Results and discussion

3.1. Effect of preparation parameters upon rejection and flux of sodium alginate/polysulfone composite nanofiltration membranes

The sodium alginate/polysulfone NF membrane prepared under optimum conditions was characterized by determining the rejection and flux of individual solutes (Na_2SO_4, $MgSO_4$, NaCl, $MgCl_2$) from their aqueous solution. The performance tests for the prepared membrane were carried out under 1.2 MPa at 25°C in 1.0 g/L Na_2SO_4 solution without specification. The recirculation rate of feed was kept 40 L/h. Both the retentate and permeate were re-circulated to the feed tank to maintain

a constant feed concentration during the permeation experiments. Salt concentration were determined with a model DDS-11A conductivity meter. Before testing the membrane was pre-pressurized for 1 h at 1.2 MPa, and the effective membrane area was 19.6 cm^2.

3.1.1. Effect of the casting solution (sodium alginate solution) concentration on rejection and flux of sodium alginate/polysulfone composite nanofiltration membranes

There is necessary to choose a proper sodium alginate concentration because viscosity of sodium alginate solution is relevant to concentration, and it is not good for preparation of NF membrane if the solution is too dilute or too concentrated. To determine the casting solution concentration, a series of membranes were prepared by changing sodium alginate concentration from 1.0 to 2.5 wt%. As shown in Fig. 2, when sodium alginate concentration changed from 1.0 to 2.5 wt%, rejection increased linearly from 42.6% to 84.0%, whereas permeation flux decreased linearly from 110.2 to 27.2 $L/m^2 h^{-1}$. This was due to the thickness of the selective layer increased with the increase of sodium alginate concentration, which resulted in higher rejection and lower permeation flux. But the rejections began to decrease when the sodium alginate concentration exceeded 2.0 wt%, which might result from the decrease of cross-linking degree of the membrane surface [12]. Considering rejection and flux of Na_2SO_4 together, the optimal concentration of sodium alginate is 2.0 wt%.

3.1.2. Effect of cross-linking reagent (glutaraldehyde) concentration on rejection and flux of sodium alginate/polysulfone composite nanofiltration membranes

Glutaraldehyde is a type of familiar reagent; it can enhance compact degree of the membrane surface. To investigate this preparation parameter, a series of sodium alginate/polysulfone composite NF membranes were prepared by changing glutaraldehyde concentration from 0.5 to 1.5 wt%. The results were shown in Fig. 3. As glutaraldehyde concentration changed from 0.5 to 0.9 wt%, rejection increased from 66.5% to 87.2%, and permeation flux decreased from 50.6 to 30.6 $L/m^2.h^{-1}$, because the reaction was intensified between glutaraldehyde solution and surface of membrane with the increase of glutaraldehyde concentration. However, when it exceeded 0.9 wt%, rejection decreased and flux increased. It may be explained that reversible reaction or side reaction occurred. Considering rejection and flux of Na_2SO_4 together, 0.9 wt% is proper.

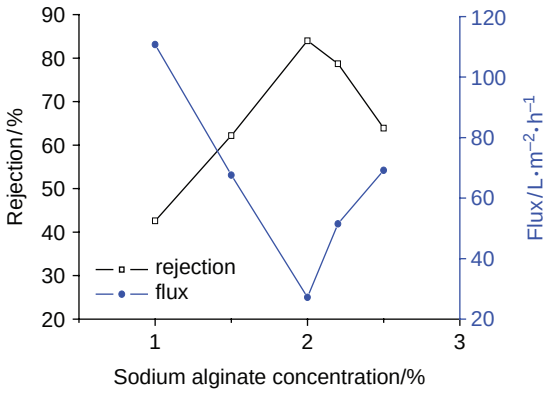

Fig. 2. Effect of sodium alginate casting solution concentration on rejection and flux of sodium alginate/polysulfone membrane.

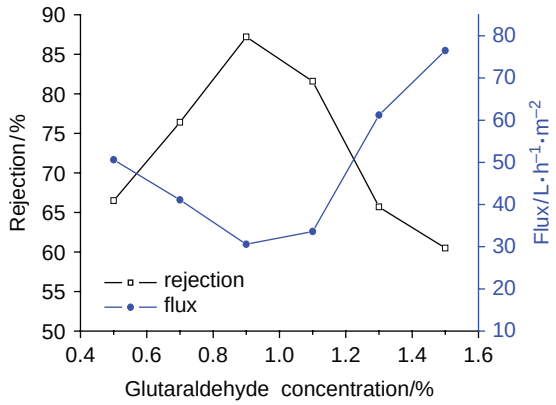

Fig. 3. Effect of cross-linking reagent (glutaraldehyde) on rejection and flux of sodium alginate/polysulfone membrane.

3.1.3. Effect of cross-linking temperature on rejection and flux of sodium alginate/polysulfone composite nanofiltration membranes

For this test, cross-linking temperature varying from 20 to 60°C was investigated. As is shown in Fig. 4,

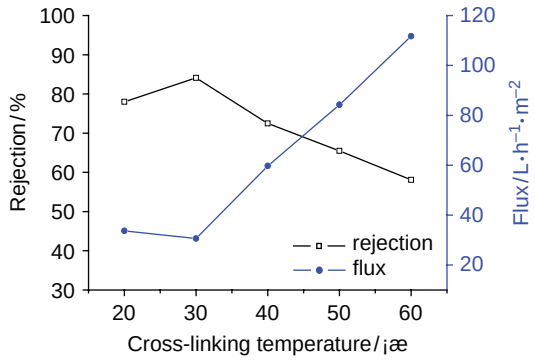

Fig. 4. Effect of cross-linking temperature on rejection and flux of sodium alginate/polysulfone membrane.

rejection increased from 78% to 84% and permeation flux decreased from 33.7 to 30.6 L/m^2.h^{-1} when the cross-linking temperature changes from 20 to 50°C. It could be explained that carbonyls take part into the cross-linking reaction [13] and this reaction will be sufficiency when the temperature is above 30°C. Besides, the membrane surface formed compact reticular structure as a result of cross-linking, leading to decrease of pore size [14], so rejection increased and permeation flux decreased. However, when it is above 30°C, the rejection decreased and flux increased as a result of the decrease in the degree of cross-linking due to the decomposition of cross-linking bonds. Considering rejection and flux of Na2SO4 together, the optimal temperature for cross-linking is 30°C.

3.1.4. Effect of cross-linking time on rejection and flux of sodium alginate/polysulfone composite nanofiltration membranes

To investigate this effect, a series of sodium alginate/polysulfone composite NF membranes were prepared when cross-linking time changed from 1 h to 5 h. As shown in Fig. 5, rejection increased and permeation flux decreased with the increase of cross-linking time until it was 4 h, which may result from the increase in cross-linking degree. However, when cross-linking time exceeds 4 h, rejection decreased and permeation flux increased, because the decomposition of cross-linking bonds occurs, leading to a decreasing rejection and increasing flux. Thus, a cross-linking time of 4 h is proper.

It draws a conclusion from the experiments above that the sodium alginate/polysulfone composite NF membrane prepared from 2.0 wt% sodium alginate solution, cross-linked at 30°C for 4 h with 0.9 wt% glutaraldehyde in ethanol and heat-treated at 50°C for 20 min show excellent properties. The resultant membrane was used to carry out experiments hereinafter.

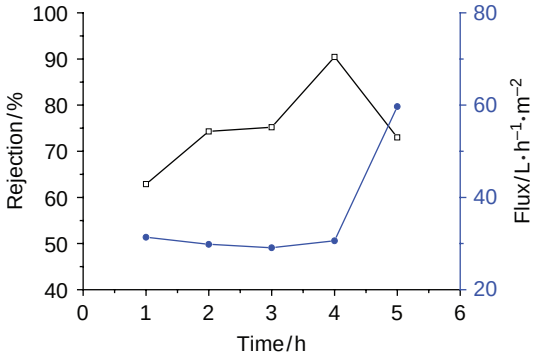

Fig. 5. Effect of cross-linking time on rejection and flux of sodium alginate/polysulfone membrane.

3.2. Characteristics of the sodium alginate/polysulfone composite nanofiltration membrane

3.2.1. Infrared spectra of sodium alginate/polysulfone membranes

The IR spectra of polysulfone UF membrane (a), sodium alginate/polysulfone membrane (b) cross-linked with glutaraldehyde were measured in the range of 1000–3500 cm^{-1}. The absorption band of 1454.35 cm^{-1} in (b) was characteristic of –CH_2 scissors vibration [15], which is very small in (a). It can be explained that more –CH_2 bonds were brought in because of cross-linking. There was a new absorption band at 1166.23 cm^{-1} in (b) correspond to–C–O–C– bond, suggesting ether linkage was formed as the result of cross-linking with glutaraldehyde.

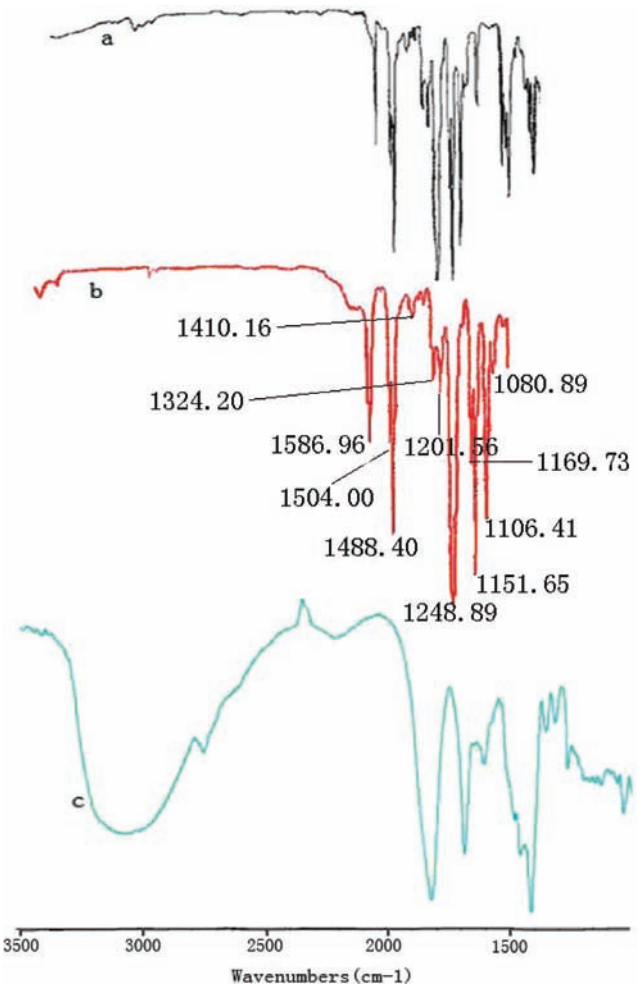

Fig. 6. IR spectra of polysulfone UF membrane (a), sodium alginate/polysulfone composite NF membrane (b), and IR spectra of sodium alginate (c).

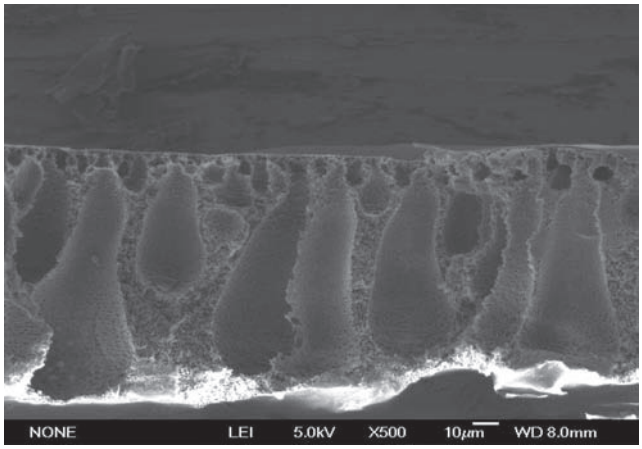

Fig. 7. SEM photograph of cross-section of the composite NF membrane.

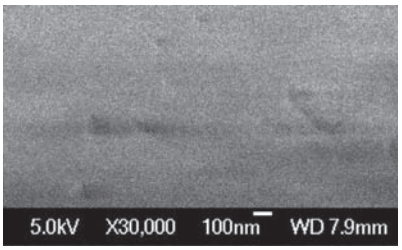

Fig. 8. SEM photograph of surface texture of the composite NF membrane.

3.2.2. Structure characteristic of the sodium alginate/polysulfone composite nanofiltration membrane

The cross-section and surface of the composite NF membrane were characterized with a SEM and the results are shown in Fig. 7 and 8. The two pictures showed that there was a thin active functional layer with a compact surface on a finger-like supporting layer of polysulfone UF base membrane, which suggested that the thin functional layer probably determined rejection performance and permeation flux of sodium alginate/polysulfone composite NF membrane.

3.2.3. Roughness measurement with AFM

Roughness is one of the most important surface properties because it has a strong influence on adhesion and local mass transfer. Fig. 9 show typical surface structure of the membrane. The colorific intensity shows the vertical profile of the membrane surface. The light regions were for the highest points and the dark regions were for the depressions. The total scanning area was 0.25 μm^2. The average roughness of the composite membrane surface was about 0.0112 μm [16].

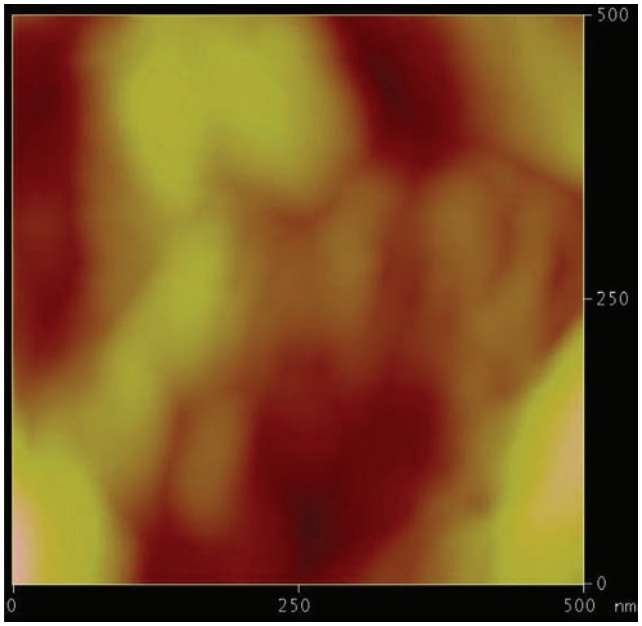

Fig. 9. Two-dimensional AFM image of composite NF membrane.

3.2.4. The streaming potential of the sodium alginate/polysulfone composite nanofiltration membrane

The membrane streaming potential was measured in 0.1 mol KCl aqueous solution filled between the sides of the membrane under the pressure range of 0.1–0.3 MPa. The curve for streaming potential against pressure is shown in Fig. 10, streaming potential decreased linearly with the increase of operating pressure and the pressure osmobic coefficient (β) was about –32.971 mV·MPa^{-1}, suggesting that sodium alginate/polysulfone composite NF membranes active layer was negatively charged [17]. It could be explained that the membrane surface layer absorbed anions from the electrolyte solution.

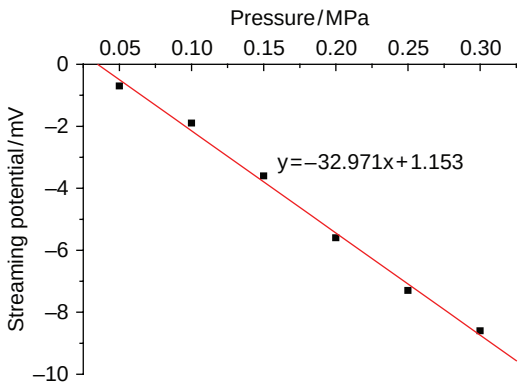

Fig. 10. The effect of pressure on streaming potential of the composite membrane.

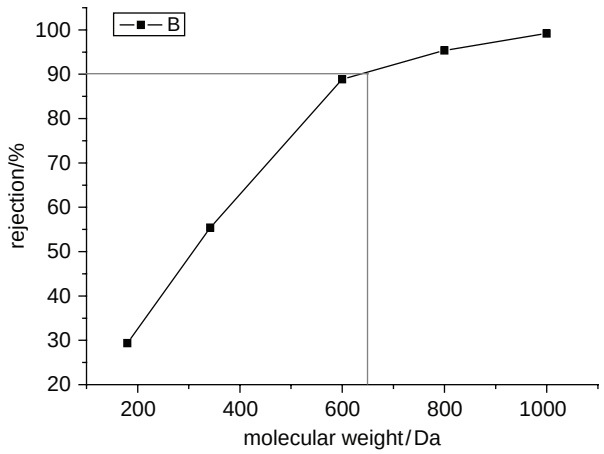

Fig. 11. Rejection of the composite NF membrane to neutral organic matter of different molecular weight.

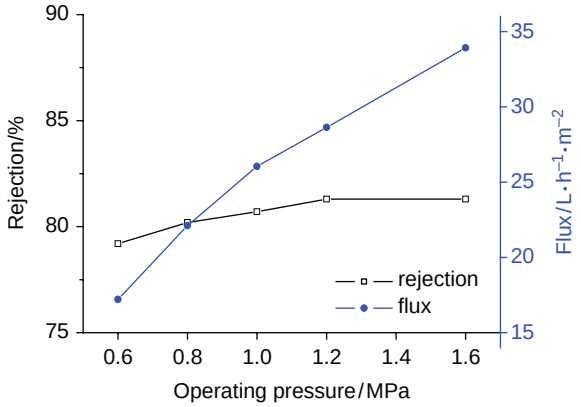

Fig. 12. Effect of operating pressure on rejection and flux of the composite membrane.

3.2.5. Molecular weight cut-off of glycolchitin/poly (acrylonitrile) composite nanofiltration membrane

MWCO of composite membrane was measured with 1.0 g/L aqueous solutions of glucose, sucrose and polyethylene glycols (MW 600–1000) at 25°C under 1.0 MPa. The concentrations of these neutral organic matters in feed and permeated samples were determined by absorptionmetry, from which rejection can be obtained. The MWCO of membrane was the molecular weight of organic substances with retention of 90% [18]. The curve about rejection against molecular-weight is shown in Fig. 11. Obviously the MWCO of this membrane is approximately 625 Da.

3.3. Effects of operating conditions on rejection and flux of the sodium alginate/polysulfone composite nanofiltration membrane

For these tests, the resultant membrane was used. Before testing the membrane was pre-pressurized for 1 h, and the recirculation rate of feed was kept 40 L/h.

3.3.1. Effect of operating pressure on rejection and flux of the sodium alginate/polysulfone composite nanofiltration membrane

The effect of operating pressure on the permeation flux and rejection of the membrane of 1.0 g/L Na_2SO_4 is shown in Fig. 12. Permeation flux increased all of the time with the increase of operating pressure. Rejection increased with the increase of operating pressure until it was 1.2 MPa, after that rejection decreased. It can be explained by dissolution–diffusion model [19]:

$$F_W = A(\Delta P - \Delta\pi) \tag{3}$$

where Fw is water flux, A the water permeation coefficient, ΔP the operating pressure difference, β the polarization factor of the concentration difference, Δπ is the osmosis pressure.

$$F_S = B(\beta C_1 - C_2) \tag{4}$$

where Fs is salt flux, B the salt permeation coefficient, C_1 and C_2 are the salt concentrations on the upstream and downstream sides of the membrane, respectively.

$$\beta = \frac{C_b}{C_m} \tag{5}$$

where C_b is the salt concentration on the membrane surface and C_m is the salt concentration of the feed.

It can be seen from formula (3) that Fw increases linearly with the increase of ΔP. And formula (4) shows that Fs is a function of salt concentration on both sides of the membrane, it has no direct relation to ΔP. Therefore, as ΔP increases, so does the water flux, but salt flux remains constant thereby resulting in an increase in salt rejection. On the other hand, C_2 is reduced by virtue of the increase of Fw and the concentration difference on the two sides of the membrane increases, that is $\beta(C_1 - C_2)$ increased, leading to an increase of Fs, and the rejection decreased, so these two sides cooperated to make the rejection increased in the first instance and decreased afterward [20].

3.3.2. Effect of feed solution concentration on rejection and flux of the sodium alginate/polysulfone composite nanofiltration membrane

The effect of feed concentration on flux and rejection of the membrane of Na_2SO_4 is shown in Fig. 13. It can be seen that both rejections decreased and permeation

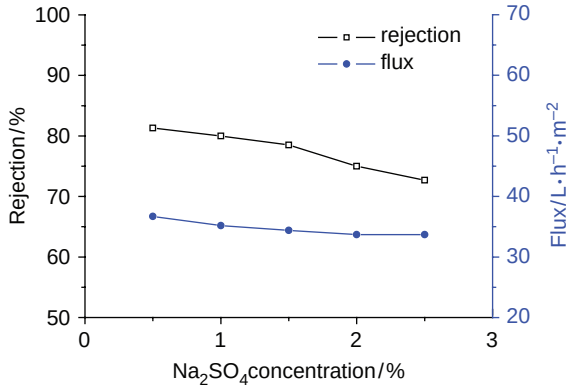

Fig. 13. Effect of Na_2SO_4 concentration on rejection and permeation flux of the membrane.

fluxes decreased with the increase of Na_2SO_4 concentration, which can be explained by Donnan effect. The concentration of Na^+ on the membrane surface increased with the increase of feed concentration, which results in increasing of permeation rate of Na^+, so the electroneutrality between the two sides of the membrane was broken, and in order to maintain the electroneutrality, more SO_4^{2-} permeated from upstream side to downstream side, thereby those rejections decreased.

3.3.3. Effect of different type of feeds on rejection and flux of the sodium alginate/polysulfone composite nanofiltration membrane

To test the rejection performance of sodium alginate/polysulfone composite membrane, NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$ solutions were used as feed solutions. The test was carried out at 25°C under 1.0 MPa and the concentration of feed solution is 1 g/L. The result was shown in Table 1; the rejections to different inorganic electrolytes follow the order of $Na_2SO_4 > MgSO_4 > NaCl > MgCl_2$, which shows the static electrification characteristic of negatively charged NF membrane [21]. The active functional layer of the composite membrane has stronger repulsion to SO_4^{2-} than Cl^-. Therefore, SO_4^{2-} was rejected, so the rejection order is NaCl < MgSO4. On the other hand, Mg^{2+} is easy to get combination with anions on the membrane surface which maybe decreases the effective surface charge of the membrane, and so $MgSO_4 < Na_2SO_4$ and $MgCl_2$ <NaCl. Based on its excellent selective rejections, it can be used to separate mono/divalent salts.

Table 1
Rejections and permeation fluxes of the composite membrane to different types of feed solutions.

Inorganic salts	Rejection/%	Permeation flux/ $L.h^{-1}.m^{-2}$
Na_2SO_4	87.2	30.6
$MgSO_4$	21.5	35.2
NaCl	32.0	33.5
$MgCL_2$	12.2	22.4

4. Conclusions

A novel composite NF membrane with excellent performance have been prepared from 2.0 wt% casting solution cross-linking with 0.9% glutaraldehyde at 30°C for 4 h. The structure of the resultant membrane was characterized by SEM.

In addition, some performance tests have been performed for the composite NF membrane. It was found its properties were influenced to a great extent by feed concentration and the type of model solutions. The order of their rejections is Na_2SO_4 > MgSO4 > NaCl > $MgCl_2$, which is typical characteristic of a negatively charged membrane. Additionally, the curve about the streaming potential illustrates the negatively charged characteristics of this membrane, with a pressure smobic coefficient of –32.971 $mV{\cdot}MPa^{-1}$. The membrane has a high rejection to divalent salts and can be used to wastewater treatment in the future.

Acknowledgements

Financial support from the National Basic Research Program of China (No. 2009CB623402) and Postdoctoral Innovation Fund of Shandong Province (No.82214134).

References

[1] H.W. Sun, G.H. Chen, R.H. Huang and C.J. Gao, A novel composite nanofiltration (NF) membrane prepared from glycolchitin/poly (acrylonitrile) (PAN) by epichlorohydrin cross-linking, J. Memb. Sci., 297(2007) 51–58.
[2] A.G. Boricha and Z.V.P. Murthy, Preparation, characterization and performance of nanofiltration membranes for the treatment of electroplating industry effluent, Sep. Purif. Tech., 65 (2009) 282–289.
[3] W.R. Bowen and J.S. Welfoot, Modelling the performance of membrane nanofiltration-critical assessment and model development, Chem. Eng. Sci., 57 (2002) 1121–1137.
[4] W.R. Bowen and A.W. Mohammad, A theoretical basis for specifying nanofiltration membranes—dye/salt/water streams, Desalination, 117 (1998) 257–264.
[5] G.L. Huan, Y.F. Zhang, Q.Y. Du and Y. Wu, Optimization of composite conditions for composite nanofiltration membrane by orthogonal design, Membr. Sci. Technol., 24 (5) (2004) 77–79 (in Chinese).
[6] Y. Shi, X. Wang and G. Chen, Pervaporation characteristics and solution–diffusion behaviours through sodium alginate dense membrane, J. Appl. Polym. Sci., 61 (1996) 1387–1394.
[7] T. Uragami and M. Saito, Studies on synthesis and permeabilities of special polymer membranes. 68. Analysis of permeation and separation characteristics and new technique for separation of aqueous alcoholic solutions through alginic acid membranes, Sep. Sci. Technol., 24 (1989) 541–554.

[8] R.Y.M. Huang, R. Pal and G.Y. Moon, Chracteristics of sodium alginate membranes for pervaporation dehydration dehydration of ethanol–water and isopropanol–water mixtures, J. Memb. Sci., 160 (1999) 101–113.
[9] S. Kalyania, B. Smithab, S. Sridharb and A. Krishnaiaha, Pervaporation separation of ethanol–water mixtures through sodium alginate membranes, Desalination, 229 (2008) 68–81.
[10] C.K. Yeom and K.H. Lee, Characterization of sodium alginate membrane crosslinked with glutaraldehyde in pervaporation separation, J. Appl. Polym. Sci., 67 (1998) 209–219.
[11] G.Y. Moon, R. Pal and R.Y.M. Huang, Novel twoply composite membranes of chitosan and sodium alginate for the pervaporation dehydration of isopropanol and ethanol, J. Memb. Sci., 156 (1999) 17–27.
[12] J. Miao, G.-H. Chen and C.-J. Gao, A novel kind of amphoteric composite nanofiltration membrane prepared from sulfated chitosan (SCS), Desalination, 181 (2005) 173–183.
[13] H.-Y. Zhu, L. Xiao and Z.-X. Liu, Influence of solvent treatment on the properties and structure of chitosan films, Polym. Mater. Sci. Eng., 20 (2) (2004) 110–113 (in Chinese).
[14] B.O. Krajewska and A. Olech, Pore structure of gel chitosan membranes. I. Solute diffusion measurements, Poly. Gels Networks, 4 (1996) 33–43.
[15] D.A. Musal, A. Kumar and G. Pleizier, Formation and characterization of poly (acrynitrile)/chitosan composite ultrafiltration membranes, J. Memb. Sci., 154 (1999) 163–173.
[16] S.A.L.-J. Shi and A. Neville, An investigation into the relationship between flux and roughness on RO membranes using scanning probe microscopy, Desalination, 189 (2006) 221–228.
[17] J.-X. Mo and S.-M. Liu, Theory experimental method and result of the streaming potential, Technol. Water Treat., 17 (3) (1991) 153–161 (in Chinese).
[18] S.-H. Wu, H. He and S.-Q. Yuan, Barium chloride method and its application in determination of polysulphone membrane performance, Technol.Water Treat., 21 (4) (1995) 193–197 (in Chinese).
[19] Y.-J. Song and B.-H. Sun, Study of factors affecting separation performance of nanofiltration membrane, Technol.Water Treat., 23 (2) (1997) 78–82 (in Chinese).
[20] X.-M. Liang, X.-F. Lu, L.-Q. Shi and Z.-Y. Liu, The preparation of polyarylate composite nanofiltration membrane by interfacial polymerization, J. East China Univ. Sci. Technol., 25 (5) (1999) 489–493 (in Chinese).
[21] R.J. Peterson, Composite reverse osmosis and nanofiltration membranes, J. Memb. Sci., 83 (1993) 81–150.