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Preparation and application of positively charged quaternized chitosan/PEI composite nanofiltration membranes

Runlin Han[a,b,*], Jinghui Zeng[a], Yongqing Wang[b], Qibing Chang[b], Xiaozhen Zhang[b], Jianer Zhou[b]

[a]*College of Materials Science and Engineering, Shaanxi Normal University, Xian 710100, China*
Tel. +86 798 8461173; Fax: +86 798 8461173; email: hanrunlin@163.com
[b]*School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333403, China*

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ABSTRACT

Membrane processes are gaining importance in water applications as a result of the advances in membrane technology and the increasing requirements on water quality. In this work, 2-hydroxypropyltrimethyl ammonium chloride chitosan with positively charged character and good membrane-forming ability was utilized to fabricate the functional layer of the composite nanofiltration (NF) membrane. Reinforced polyetherimide ultrafiltration membrane was used as the support layer for its excellent thermal and solvent resistance. Effects of polymer concentration, reaction time, cross-linking agent concentration, and cross-linking temperature on membrane performance were studied in detail. When the composite membrane was prepared under optimized conditions and tested at 0.3 MPa and 20˚C, the flux of the composite NF membrane was about 10.9 L/m^2h and the $MgCl_2$ rejection of it was about 83.1%. The surface morphologies of the composite membrane and substrate membrane were observed by scanning electron microscopy. The composite membrane showed a classical positively charged membrane character which had higher rejection to multivalent cations.

Keywords: Nanofiltration membrane; Dip-coating; Positively charged membrane; Quaternized chitosan

1. Introduction

The quality of drinking water from the conventional treatment process is not satisfactory, due to the serious pollution of China's surface water. The improvement of the existing water treatment plants is the key to ensure the quality of drinking water in China. Membrane processes are gaining importance in water applications as a result of the advances in membrane technology and the increasing requirements on water quality [1]. Nanofiltration (NF) has recently gained increasing worldwide research interest because of its advantages such as low operation pressure, low investment, low energy consumptions, high permeation flux, and high rejections of multivalent salts [2]. The unique characteristics of NF which lies between ultrafiltration (UF) and reverse osmosis have made it very attractive to many industrial applications, e.g. industrial effluent treatment, and molecular separation involving organic solvent, micropollutants removal, water softening, whey demineralization, etc [3]. Negatively charged thin-film

*Corresponding author.

composite membranes made from aromatic polyamides by interfacial polymerization method currently dominate the market for desalination applications because these membranes provide high fluxes and high rejections [4]. Quaternization is an effective modification method to induct positive charges into polymers. Xu and Yang [5] prepared positively charged composite membrane with quaternized poly (2,6-dimethyl-1,4-phenylene oxide). Su et al. [6] studied the preparation of positively charged NF membrane with quaternized PPESK. Although the positively charged NF membrane showed excellent hydrophilicity and chlorine resistance, the research on the preparation and performance of positively charged NF membrane is still little and positively charged NF membrane has not been commercialized until now. One of the main reasons is that the performance of NF membrane prepared with positively charged polymer is apt to decline because quaternary ammonium group will come off at elevated temperature or strong oxydic conditions [7]. Another reason is that the positively charged polymer is often prepared by the modification of polymer with virulent chloromethylation reagent [8].

NF membrane with quaternary ammonium group endowed an membrane with excellent antibacterial performance and chlorine resistance which expands the utilization area of membrane especially in food industry and traditional Chinese medicine industry. The separation of NF membrane is dominated by both size exclusion and the Donnan effect. Rejection by NF membranes to various salts will change with their surface chemical composition and charge character. Positively charged NF membrane has high-rejection to high-valent cations which are expected to be useful to remove heavy metal ions from industrial wastewater [9,10] as well as in the purification or concentration of cationic dyes [3,11,12].

Chitosan is a kind of cheap and readily available biopolymer because its source chitin is the second most abundant polysaccharide in nature [13]. Quaternized chitosan (2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC)) is prepared by the reaction of chitosan and 2-Hydroxypropyltrimethylammonium chloride which does not involve in the virulent chloromethylation reagent [14]. HACC is a suitable membrane material for preparing the functional layer of positively charged NF membrane for its good membrane formability and positively charged character. Huang has studied the preparation of quaternized chitosan/PAN and quaternized chitosan/PSf NF [15,16] membranes which showed classical positively charged membrane character with good membrane performance. Polyetherimide (PEI) with excellent thermal stability combined with good chemical and mechanical stability is a suitable material to prepare the UF membrane which can be used at harsh conditions such as high temperature wastewater treatment, recycling of hot water, and soybean oil separation [17,18]. So, HACC with positively charged character was utilized to fabricate the functional layer of the composite NF membrane and reinforced PEI, and UF membrane was used as the support layer.

2. Experimental

2.1. Materials and instruments

The PEI UF substrate membranes (tested with polyethylene glycol) are prepared in our laboratory with phase inversion method. The preparation method of the substrate membrane is similar to the reference [19]. The MWCO of PEI UF membrane is 10,000 Da and the flux of the membrane is about 120 L/m^{2}hbar. HACC purchased from Lushen Bioengineering is purified by filter paper under reduced pressure. The substitution of HACC is above 90% which endows the material with good solubility in water and membrane surface with high positively charged density. Glutaraldehyde, epichlorohydrin, NaCl, $MgCl_2$, Na_2SO_4, and other chemicals used in the experiments are all of analytical purity grade and used without further purification. A stainless flat sheet dead-end filtration setup is used to evaluate the composite membrane performance. Magnetic stirring heater (Jiangsu Jiangyin Science Research Instrument Plant, China) was installed in the membrane feed side to reduce concentration polarization. Electrical conductivity meter (DDS-11A, Shanghai Youke Instrument Works, China) is used to measure the concentration of salt in the feed and permeated solutions. Scanning electron microscopy (SEM, JSM-5600LV, JEOL Co., Japan) is used for the analysis of the surface morphologies of the composite membrane and the substrate membrane.

2.2. Membrane preparation

The composite membranes are prepared by dip-coating method on the surface of PEI UF substrate membranes. The PEI UF membranes are soaked in aqueous solutions of HACC. Then, the membrane is taken out from the solution and dried in an oven. These membranes are then immersed in cross-linking agent solutions for the formation of the active layer on the PEI UF support. Afterward, the membranes are dried in an oven for heat treatment. The composite membranes prepared are kept in deionized water before evaluation.

2.3. Membrane characterization

To prepare samples for SEM, the membranes are dried in vacuum at room temperature and plated with gold, before they are transferred into the microscope. The performances of NF membranes and UF membranes are mainly described by product water flux, J, and rejection, R, which was described before [6]. Each membrane is first pre-pressurized by the de-ionized water at 0.4 MPa for 0.5 h to ascertain that the steady state is obtained. All the membranes are tested at 20˚C and 0.3 MPa and the concentrations of feed solutions are all fixed on 1 g/L. Then, it is evaluated at a certain temperature and pressure. All of the filtration processes are repeated three times and the average data are reported.

3. Results and discussion

3.1. Effect of HACC concentration on the performance of composite NF membrane

HACC concentration of functional layer is an important influencing factor on NF membrane performance because the viscosity of the casting solution and compactness of the separating layer determine the membrane performance. HACC is a water-soluble polymer which is dissolved in deionized water to prepare the casting solution. To determine the casting-solution concentration, a series of membranes were prepared by changing HACC concentrations from 1 to 5 wt.%. As shown in Fig. 1, when HACC concentrations were changed from 1 to 5 wt.%, rejections to $MgCl_2$ increased first then declined slightly, whereas permeation fluxes decreased obviously from 88.3 to 7.2 L/m^{2}h when the membranes were tested at 20˚C and 0.3 MPa. This is because the thickness of the selective layer increased with the increase of HACC concentration. When the concentration thickness was further elevated, the cross-linking density might decline a little.

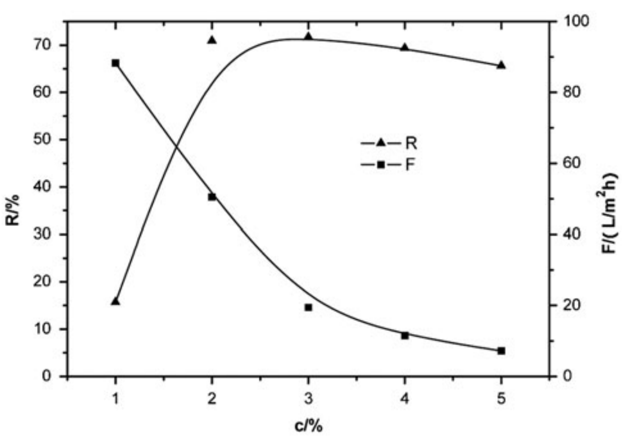

Fig. 1. Effect of HACC concentration on the NF membrane performance.

3.2. Effect of cross-linking reagent (glutaraldehyde) concentration on the performance of composite NF membrane

The permeation and separation performance of composite NF membrane prepared with dip-coating method is mainly affected by variables such as cross-linking agent, cross-linking agent concentration, and reaction time. The performance of the HACC/PEI composite membrane can be effectively controlled by adjusting these parameters [15,16]. From Fig. 2, it was found that the HACC has a lot of reactive groups such as $–NH_2$ and –OH, which can be cross-linked by some cross-linking agent. Glutaraldehyde (GA), which is often utilized as a disinfectant, is a type of familiar reagent with low toxicity. It can enhance the degree of cross-linking of the functional layer and improve the stability of the NF membrane. To investigate this preparation parameter, a series of HACC/PEI composite NF membranes were prepared by changing GA (in water solution) concentrations from 0.7 to 1.1 wt.% when the HACC concentration was fixed at 3 wt.%. The results are shown in Fig. 3. The rejections to $MgCl_2$ were increased with GA concentration and reached to 71.7% when GA concentration was 1%. The flux of the membrane decreased as the GA concentration increased. Suitable cross-linking reagent concentration can improve the rejection of membrane.

3.3. Effect of cross-linking reagent (epichlorohydrin) concentration on the performance of composite NF membrane

Epichlorohydrin is often used for the cross-linking of polymer with $–NH_2$ and –OH for its high reactivity. To investigate the effect of epichlorohydrin concentration on the membrane performance, a series of HACC/PEI composite NF membranes were prepared by changing epichlorohydrin (in ethanol solution) concentrations from 0.7 to 1.1 wt.% when the HACC concentration was fixed at 3 wt.%. The results are

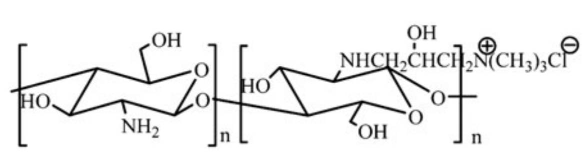

Fig. 2. The chemical structure of HACC.

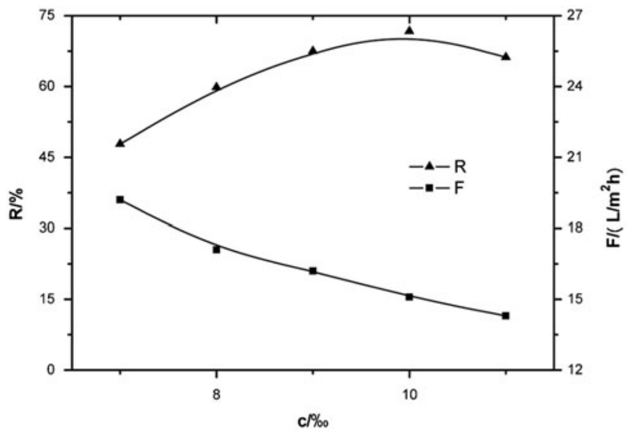

Fig. 3. Effect of cross-linking reagent (GA) concentration on the membrane performance.

shown in Fig. 4. The rejections to $MgCl_2$ were increased with cross-linking concentration. The rejection of the membrane reached 82.9% when epichlorohydrin concentration was 1%, although the membrane flux was 10.1 L/m^{2}h. Suitable cross-linking reagent concentration can improve the rejection of membrane. Compared with Figs. 3 and 4, it was found that the membrane prepared with glutaraldehyde had high flux and relatively low rejection and the membrane prepared with epichlorohydrin had low flux and relatively high rejection. So, in the following section, membrane is cross-linked with 1% epichlorohydrin and the HACC concentration is fixed at 3 wt.%.

3.4. Effect of curing temperature on the performance of composite NF membrane

The rejection to $MgCl_2$ of the NF membrane is very low and the membrane flux is rather high at ambient temperature. Heat curing is often required in preparing composite membrane to facilitate the removal of residual organic solvent from nascent polyamide thin films and to promote additional cross-linking by the dehydration of unreacted amine and carboxyl group. In this work, different curing temperatures from 40 to 80℃ were studied to improve the membrane performance with the curing time fixed at 5 min. From Fig. 5, it is clear that when the curing temperature is 50℃, the rejection of the membrane is relatively high (83.1%) and the flux of the membrane is 10.9 L/m^{2}h. It is because the excessive curing temperature may decrease the contact time of HACC and cross-linking reagent which affect the membrane performance obviously.

3.5. Membrane morphologies

The SEM images of the top surface morphologies and cross-section morphologies of the composite membrane and substrate membrane are showed in Fig. 6. It is apparent that the top surface of substrate PEI UF membrane is rather smooth and the top surface of composite membrane is very dense. The differences between the two pictures demonstrate that the NF membrane with dense skin layer is successfully prepared on the substrate.

3.6. The rejections to different salts and dyes of the HACC/PEI composite NF membrane

The NF membrane has different rejections to different salts according to the Donnan effect. The rejection and flux of different inorganic electrolytes by the HACC/PEI composite membrane are shown in Table 1. Obviously, the rejections to inorganic electrolytes follow the order of $MgCl_2 > NaCl > Na_2SO_4$,

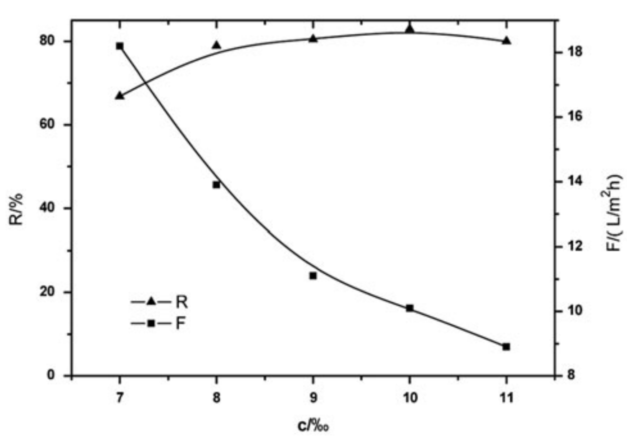

Fig. 4. Effect of cross-linking reagent (epichlorohydrin) concentration on the membrane performance.

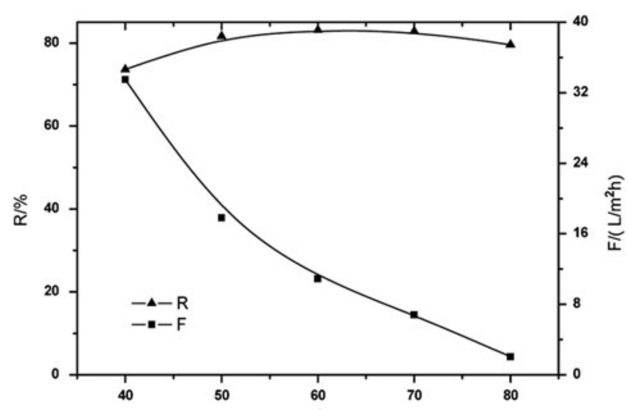

Fig. 5. Effect of curing temperature on the performance of the composite NF membrane.

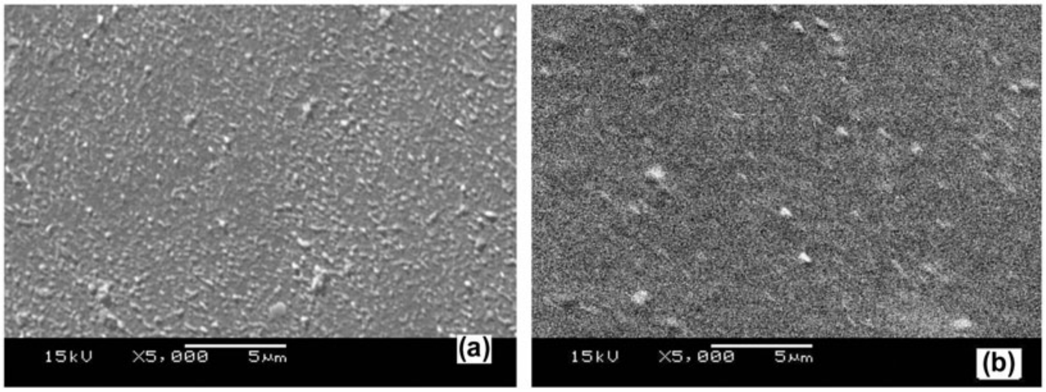

Fig. 6. The morphology difference of the membrane top surface (a, NF; and b, UF).

Table 1
The rejections to different salts of the NF membrane

	$MgCl_2$	NaCl	Na_2SO_4
R (%)	83.1	13.7	12.5
F (L/m^2 h)	10.9	16.2	17.4

which is typical of a positively charged NF membrane and is explained by the electrostatic effect. Thiscorresponds to the increasing order of the cation charge densities, because the active layer consisting of HACC has quaternary ammonium group distribution and allows a stronger repulsion of Mg^{2+} than Na^+ and a strong attraction of SO_4^{2-} than Cl^-. In this work, the membrane prepared has high $MgCl_2$ rejection but low NaCl and Na_2SO_4 rejections, which is very useful in different inorganic salts separation. At the same time, it has higher flux compared with references [15,16] which may be due to the fact that different cross-linking agents may affect the dense layer of the composite membrane.

The rejections to different dyes can be explained by both the sieve effect and the Donnan effect. The rejections to different dyes with different structure character are shown in Table 2. The rejection to Acid chrome blue K is very high because of its high molecular weight although the molecule is negatively charged according to its molecular structure. The rejection to Neutral red with low molecular weight is also high which is affected by the positively charged character of the membrane surface and dye molecule.

The permeability of salt solution was measured at different pressures. As shown in Fig. 7, the flux of the membrane increased with operating pressure. This flux of the membrane increased with the operation pressure can be interpreted by the Spiegler–Kedem model: $J_v = L_p(\Delta P - \sigma\Delta\pi)$. J_v is the water flux, L_p is the permeability of pure water, ΔP is operating pressure difference, σ is the reflection factor of the membrane, and ΔP is the osmosis pressure. Because the concentration of the salts is relatively low, $\sigma\Delta\pi$ can be ignored.

Table 2
The rejections to different dyes of the NF membrane

	Acid chrome blue K	Neutral red	Malachite green oxalate
Molecular formula	$C_{16}H_9N_2Na_3O_{12}S_3$	$C_{15}H_{16}N_4{\cdot}HCl$	$C_{23}H_{25}ClN_2$
Molecular weight	586.40	288.78	364.92
R (%)	97.88	96.73	74.36
F (L/m^2 h)	6.46	6.48	8.01

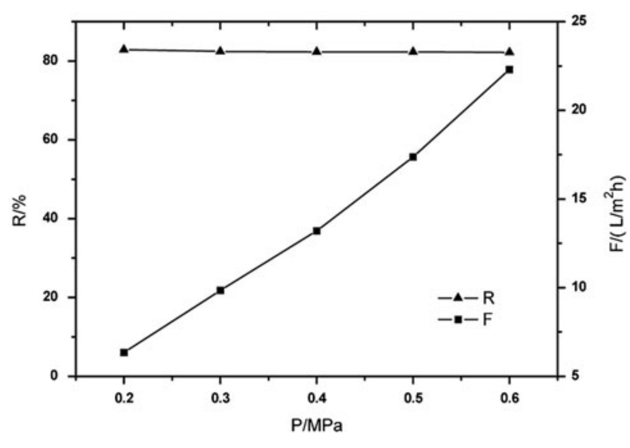

Fig. 7. Effect of operation pressure on the membrane performance.

4. Conclusion

Positively charged HACC/PEI composite NF membranes were prepared on reinforced PEI UF membrane by dip-coating method with cross-linked HACC used as the functional layer. Different fabrication parameters are studied to improve the membrane performance. When the composite membrane is prepared under optimized conditions and tested at 0.3 MPa and 20℃, the flux of the composite NF membrane is about 10.9 L/m^{2}h and the $MgCl_2$ rejection of it is about 83.1% when it is prepared with HACC 3%, epichlorohydrin 1%, and the curing temperature 50℃. The composite membrane prepared showed typical positively charged character with the rejection order as follows: $MgCl_2 > NaCl > Na_2SO_4$. At the same time, the positively charged NF membrane has high rejection to dyes and high flux which is suitable be used in the desalination of dyes.

Acknowledgments

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References

[1] X. Zheng, M. Yu, H. Liang, L. Qi, H. Zheng, H. Exler, W. Schier, F.-B. Frechen, Membrane technology for municipal drinking water plants in China: Progress and prospect, Desalin. Water Treat. 49 (2012) 281–295.

[2] R.L. Han, S.H. Zhang, W.Y. Zhao, X.D. Li, X.G. Jian, Treating sulfur black dye wastewater with quaternized poly(phthalazinone ether sulfone ketone) nanofiltration membranes, Sep. Purif. Technol. 67 (2009) 26–30.

[3] C.S. Ong, W.J. Lau, A.F. Ismail, Treatment of dyeing solution by NF membrane for decolorization and salt reduction, Desalin. Water Treat. 50(1–3) (2012) 245–253.

[4] M. Pontie, H. Dacha, A. Lhassani, C.K. Diawara, Water defluoridation using nanofiltration vs. reverse osmosis: The first world unit, Thiadiaye (Senegal), Desalin. Water Treat. 51(1–3) (2013) 164–168.

[5] T.W. Xu, W.H. Yang, A novel positively charged composite membranes for nanofiltration prepared from poly(2,6-dimethyl-1,4-phenylene oxide) by *in situ* amines crosslinking, J. Membr. Sci. 215 (2003) 25–32.

[6] Y. Su, X. Jian, S. Zhang, G. Wang, Preparation and characterization of quaternized poly(phthalazinone ether sulfone ketone) NF membranes, J. Membr. Sci. 241 (2004) 225–233.

[7] C. Yan, S. Zhang, C. Liu, D. Yang, F. Yang, X. Jian, Preparation, morphologies, and properties of positively charged quaternized poly (phthalazinone ether sulfone ketone) nanofiltration membranes, J. Appl. Polym. Sci. 113(3) (2009) 1389–1397.

[8] D. Xing, S. Zhang, C. Yin, C. Yan, X. Jian, Preparation and characterization of chloromethylated/quanternized poly (phthalazinone ether sulfone) anion exchange membrane, Mater. Sci. Eng. B 157 (2009) 1–5.

[9] R. Du, J. Zhao, Properties of poly(N, N-dimethlaminoethyl methacrylate)/polysulfone positively charged composite nanofiltration membrane, J. Membr. Sci. 239(2) (2004) 183–188.

[10] Y. Ji, Q. An, Q. Zhao, H. Chen, C. Gao, Preparation of novel positively charged copolymer membranes for nanofiltration, J. Membr. Sci. 376(1–2) (2011) 254–265.

[11] Q. Zhang, H. Wang, S. Zhang, L. Dai, Positively charged nanofiltration membrane based on cardo poly(arylene ether sulfone) with pendant tertiary amine groups, J. Membr. Sci. 375(1–2) (2011) 191–197.

[12] S. Cheng, D.L. Oatley, P.M. Williams, C.J. Wright, Positively charged nanofiltration membranes: Review of current fabrication methods and introduction of a novel approach, Adv. Colloid Interface Sci. 164(1–2) (2011) 12–20.

[13] M. Dash, F. Chiellini, R.M. Ottenbrite, E. Chiellini, Chitosan-A versatile semi-synthetic polymer in biomedical applications, Prog. Polym. Sci. 36 (2011) 981–1014.

[14] A.G. Boricha, Z.V.P. Murthy, Preparation and performance of N, O-carboxymethyl chitosan-polyether sulfone composite nanofiltration membrane in the separation of nickel ions from aqueous solutions, J. Appl. Polym. Sci. 110(6) (2008) 3596–3605.

[15] R. Huang, G. Chen, B. Yang, Positively charged composite nanofiltration membrane from quaternized chitosan by toluene diisocyanate cross-linking, Sep. Purif. Technol. 61(3) (2008) 424–429.

[16] R. Huang, G. Chen, M. Sun, Preparation and characterization of quaternized chitosan/poly(acrylontrile) composite nanofiltration membrane from anhydride mixture cross-linking, Sep. Purif. Technol. 58(3) (2008) 393–399.

[17] Y. Wang, L. Jiang, T. Matsuura, T.S. Chung, S.H. Goh, Investigation of the fundamental differences between polyamide-imide (PAI) and polyetherimide (PEI) membranes for isopropanol dehydration via pervaporation, J. Membr. Sci. 318(1–2) (2008) 217–226.

[18] L. Jiang, Y. Wang, T.-S. Chung, X. Qiao, J.-Y. Lai, Polyimides membranes for pervaporation and biofuels separation, Prog. Polym. Sci. 34(11) (2009) 1135–1160.

[19] R. Han, S. Zhang, D. Yang, Y. Wang, X. Jian, Preparation and characterization of thermally stable poly(piperazine amide)/PPBES composite nanofiltration membrane, J. Membr. Sci. 370 (2011) 91–96.