Effect of the Mass Ratio of Fe_3O_4/PAA on Separation Properties and the Extractive Amount of Fe_3O_4 During the Formation of Fe_3O_4-PES Ultrafiltration Membranes

Zheng-Qing Huang, Ya-Shu Chen, Zhi-Wei Chen, Long-Hui Nie, Zhi Zhang, Hong-Tao Xu, Kai-Mei Zhou

Key Laboratory of Fermentation Engineering (Ministry of Education), Department of Basic Chemistry, School of Chemical and Environmental Engineering, Hubei University of Technology, Wuhan 430068, People's Republic of China
Correspondence to: Z.-Q. Huang (E-mail: huangzq18@126.com)

ABSTRACT: A series of Fe_3O_4-PES ultrafiltration membranes with different mass ratios of Fe_3O_4 and PAA were prepared from suspensions, using the phase inversion process. The suspensions consisted of polyether sulfone (PES), dimethyl formamide, polyacrylic acid (PAA), and ferrosoferric oxide (Fe_3O_4). The separation properties of ultrafiltration membranes with different Fe_3O_4/PAA mass ratio were investigated by a cross-flow experimental system. The Fe_3O_4/PAA mass ratio had little effect on the rejection of membranes to BSA. However, the pure water flux had a slight decline and then rised rapidly with the increase of Fe_3O_4/PAA mass ratio. An interesting phenomenon observed was that the Fe_3O_4 particles could diffuse into the nonsolvent bath during the formation of membrane, and the amount of Fe_3O_4 extracted into the nonsolvent bath nearly kept a constant mass ratio to PAA, even if the Fe_3O_4/PAA proportion was changed. The reasons of this interesting phenomenon were investigated. This result indicates that modified inorganic fillers may be used as the pore-forming agent to prepare the porous membranes like the template leaching method. At the same time, this method does not use any strong acid or base. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3558–3565, 2013

INTRODUCTION

Organic–inorganic hybrid (mixed matrix) ultrafiltration membranes prepared by the addition of mineral filler to polymer membranes exhibit characteristics of both ceramic and organic polymers. The mineral fillers mainly used are Al_2O_3,[1–3] TiO_2,[4–7] SiO_2,[8–11] ZrO_2,[12,13] and Fe_3O_4.[14–16] Organic–inorganic hybrid membranes can be prepared by three ways: directly mixing with the polymer,[1–16] forming inorganic filler during the preparation of membrane,[17,18] and introducing inorganic filler onto the surface or into matrix of a polymer membrane.[19,20] Although the inorganic fillers can improve the antifouling performance of ultrafiltration, the effect is not remarkable due to the weak hydrophilicity of the inorganic fillers.

The earliest inorganic compounds were some salts used as a pore-forming agents in the membrane such as LiCl and Mg $(ClO_4)_2$. Inorganic mineral fillers can also act as a pore-forming agent in the membranes prepared by the template leaching method. The glass membrane is a typical sample.[21] Of course, the template leaching method[22,23] also can manufacture porous polymer membranes. However, some strong acids (or bases)

usually are used to leach the mineral filler out in the template leaching method.[23] On the one hand, the strong acids (or bases) are difficult to be reclaimed and bring about environmental pollution. On the other hand, the strong acids (or bases) may damage the membrane materials and result in a reduction of mechanical strength.

Many types of filler like Fe_3O_4 can form chelate compounds with some organic compounds. Polyacrylic acid (PAA) is highly hydrophilic and dissolves easily in water. In a point of theory, PAA may be fixed in the matrix of polymer by the Fe_3O_4 particles in a form of chelate compound and is expected to improve the antifouling performance of ultrafiltration. In fact, some Fe_3O_4 grains modified by PAA will diffuse into the water coagulation and act as a pore-forming agent during the formation of membrane. This result gives a novel method to prepare porous membranes, which can overcome defects of the template leaching method due to no use of any strong acid or base. This paper gave primary results about the effect of the mass ratio of Fe_3O_4/PAA on separation properties and the extractive amount of Fe_3O_4 during the formation of Fe_3O_4-PES ultrafiltration membranes.

Table I. The Composition of the Casting Solution and the Content of Fe_3O_4 Particles in the Membranes

No.	DMF (mL)	PAA (g)	PES (g)	Fe_3O_4 (g)	$m(Fe_3O_4)/m(PAA)$	$Fe_3O_4/(PES+Fe_3O_4)$ (wt %)
0	80.0	3.0	17.0	0	0	0
1	80.0	3.0	17.0	3.0	1.0	15.0
2	80.0	3.0	17.0	9.0	3.0	34.6
3	80.0	3.0	17.0	15.0	5.0	46.9
4	80.0	3.0	17.0	21.0	7.0	55.3
5	80.0	3.0	17.0	27.0	9.0	61.4
6	80.0	3.0	17.0	33.0	11.0	66.0
7	80.0	3.0	17.0	39.0	13.0	69.6

EXPERIMENTAL

Materials

Polyethersulfone (PES, A201) was purchased from the Solvay Advanced Polymers Limited.Corporation. Polyacrylic acid (PAA, M.W.3000) was purchased from the Jinchun Reagent Limited of Shanghai. N, N-dimethylformamide (DMF) and Fe_3O_4 were of analytical grade. Ferrosoferric oxide was used after being sieved with a 0.08-mm sieve. Albumin bovine V (BSA from Roche, Mr 68000) from bovine serum was used in these experiments. The de-mineralized water (pH 6.50–6.60) with an electric conductivity of 5 μs cm^{-1} was produced using a reverse osmosis system.

Membrane Preparation

Polyacrylic acid (3.0 g) and 80 mL DMF were mixed to form a solution. Following complete dissolution of polyacrylic acid, a different amount of Fe_3O_4 and PES (17.0 g) was added to the solution. The composition of the casting solution and the content of Fe_3O_4 particles in the membranes are listed in Table I. The solution was then shaken at 55°C for 24 h to promote the solution of PES and prevent Fe_3O_4 particles from aggregating. Homogeneous suspension was cooled to room temperature, and the membranes were cast in air (25 ± 1°C, humidity 20–30%) on a glass plate with a glass knife. After a 30 s delay, the glass plate was put into water coagulation. The coatings were taken out after 30 min and then immersed in demineralized water for 48 h. Fe_3O_4 particles in the coagulation was collected with a magnetic iron and flushed with some de-mineralized water, then dried at 60°C until there is no loss of weight.

Characterization of Membranes

The cross-sectional structures of membranes were observed by a scanning electron microscopy (SEM) (JSM-5610LV, Japan). The membranes frozen in liquid nitrogen were broken and sputtered with gold before SEM analysis. The infrared ray (IR) absorption spectra of membranes were taken using an ATR-FTIR spectrometer (NICOLET NEXUS 470, Thermo Electron Corporation, USA) over the range of 700–1800 cm^{-1}. The water contact angles were measured with a contact angle measuring instrument (K100, Kruss, Germany).

Membrane Separation Procedure

The initial pure water flux (J_1) was examined by a cross-flow filtration equipment (SF-SA, Saifei Membrane Separation Limited Corporation of Hangzhou, China, average effective circle membrane areas of 21.23 cm^2, average feed flow rate of 0.25 m s^{-1}) at 25 ± 1°C, with a trans-membrane pressure of 0.10 MPa.

BSA aqueous solution at a concentration of 150 mg L^{-1} was added to the above-mentioned filtration equipment. After 5 min of circulation without any pressure, the pressure was adjusted to 0.10 MPa. Both permeate and retentate were collected to determine the retention rate (R) in the first 5 min. The permeate volume was measured at 5-min intervals to calculate the flux of BSA aqueous solution (J_B). Both permeate and retentate were circulated to the feed tank. The testing temperature was maintained at 25 ± 1°C and the test ended in 60 min. The amount of albumin bovine V in the retentate and permeate was determined using an ultraviolet/visible (UV) spectrophotometer (Carry 50, Varian Australia Pty) at 280 nm.

After that, the fouled membrane was flushed for 10 min by circulation of demineralized water without any pressure. This procedure was repeated three times with fresh demineralized water. The pure water flux (J_2) of the fouled membrane was measured again under the same conditions as the initial pure water flux.

All fluxes of a membrane were calculated using the following equation:

$$J = \frac{V}{A \times t} \quad (1)$$

where J is flux (L m^{-2} h^{-1}); V is the permeate volume collected (L); A is the membrane area (m^2), and t is the sampling time (h).

The membrane rejection (R) was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f are the concentrations of the solute in permeate and feed solutions.

A relative pure water flux (J_r) was calculated using the following equation:

$$J_r(\%) = \frac{J_2}{J_1} \times 100 \quad (3)$$

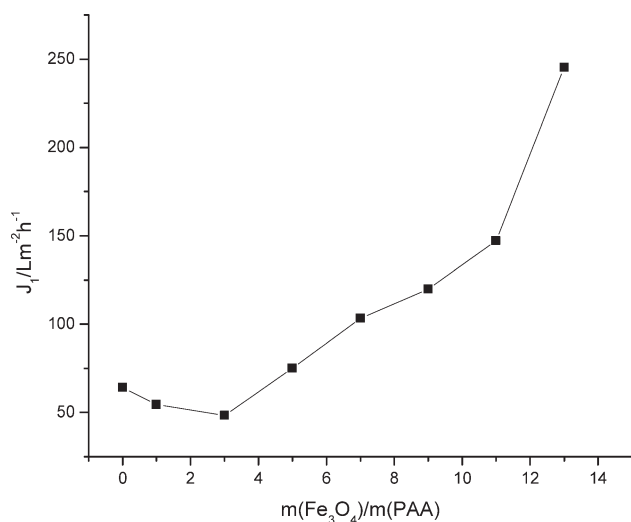where J_2 and J_1 are the pure water flux of a fouled membrane and the initial pure water flux of a membrane.

Figure 1. The initial pure water fluxes.

Measurement of the Residual Fe$_3$O$_4$ Content in a Membrane

The membrane sample was first dried at 105°C to an invariable mass (w) and then calcined at 800°C in an air stream for 4 h. The product calcined was grinded into powder and was dissolved by an appropriate amount of strong hydrochloric acid to form a FeCl$_3$ solution. The FeCl$_3$ solution was cooled and poured into a volumetric flask to make a 1000 mL FeCl$_3$ dilute solution by adding some demineralized water. A FeCl$_3$ dilute solution of 20 mL was added into a conical flask and was adjusted to pH value of 1.8–2.0 with a 10 wt % NaOH aqueous solution. After adding several drops of 100 mg L^{-1} sulfosalicylic acid aqueous solution, the solution was titrated with a 0.01 mol L^{-1} EDTA aqueous solution to the end point (yellow). The residual Fe$_3$O$_4$ content in a membrane was calculated using the following equation:

$$\frac{Fe_3O_4}{PES + Fe_3O_4}(wt\ \%) = \frac{0.01 \times V_{(EDTA)} \times 50 \times 231.53}{w} \times 100 \quad (4)$$

where $V_{(EDTA)}$ is the volume of titrated EDTA aqueous solution, L; and w is the mass of the dried membrane sample, g.

RESULTS AND DISCUSSION

Effect of the Mass Ratio of Fe$_3$O$_4$ /PAA on the Separation Properties

Figure 1 illustrates the initial pure water fluxes of membranes. When the mass ratio of Fe$_3$O$_4$/PAA changed from 0 to 3:1, the pure water flux of membrane had a slight reduction. When the mass ratio of Fe$_3$O$_4$/PAA changed from 3:1 to 11:1, the pure water flux of membrane rised obviously, and further addition of filler would results in an abrupt increase of water flux. This result is similar to the results of literature.[13,16] The observed flux behavior may be attributed to disturbance of the normal phase inversion process because of the presence of the inorganic grains.[13,24] Addition of filler particles in casting solution had little effect on membrane formation in the phase inversion, when the mass ratio of Fe$_3$O$_4$/PAA was below 3:1. Further addition of filler particles to the polymer solution would disturb the normal

phase inverse phase inversion process, which might reduce the sublayer resistance of membrane. The PES-Fe$_3$O$_4$ membrane with 0 wt % Fe$_3$O$_4$ had the tear-like macrovoids in the sublayer (Figure 2, Picture 0). With the increase of the mass ratio of Fe$_3$O$_4$/PAA from 0 to 13:1, the macrovoids in the sublayer became longer and larger (Figure 2, Picture 0 to Picture 7), which would reduce the sublayer resistance of membrane. In addition, the reduction of top-layer thickness also is responsible for the change of flux. When the mass ratio of Fe$_3$O$_4$/PAA changed from 0 to 5:1, the top-layer thickness had no obvious change (Figure 3, Picture 0 to Picture 3). When the mass ratio of Fe$_3$O$_4$/PAA reached 7:1, the top-layer thickness had an obvious reduction (Figure 3, Picture 4 to Picture 7).

Figure 4 shows that the mass ratio of Fe$_3$O$_4$/PAA had little effect on the rejection of membrane. All membranes had over 98% rejection. Zhang[13] also found that the filler of micrometer grains had no influence on the rejection of membrane, when the filler content in a membrane was below 80 wt %. Addition of filler may have no obvious effect on the pore size in the membrane surface.[16,24] Genné[24] evaluated permeability, porosity and skin morphology of polysulfone/z$_r$o$_2$ ultrafiltration membranes by dextran retention and high resolution scanning electron microscopy. Their result revealed that addition of filler had no obvious effect on the pore size in the membrane surface. Their further result[25] indicated that the mean pore size measured by field emission scanning electron images did not change noticeably, although large differences in permeability were measured. Moreover, the cutoff values of membranes confirmed no significant changes in skin pore size, too.

Figure 5 shows the flux changes of membranes with different mass ratios of Fe$_3$O$_4$/PAA in the filtration test of BSA aqueous solution. Fluxes of membranes had a fast decline in the initial 10 min and then dropped slowly, because the adsorption of proteins onto ultrafiltration membranes occurred very quickly.[26] Jaffrin et al.[27] found that the permeate flux quickly declined then reached an equilibrium flux in the ultrafiltration of bovine blood when a stabilization of the protein concentration polarization layer was formed. Therefore, in our tests adsorption may first occur then formation of a concentration polarization layer.

The absolute antifouling performance of a membrane can be compared by either the permeate flux of BSA aqueous solution or the pure water flux of a fouled membrane. Higher fluxes indicate better absolute antifouling ability. Figure 5 also indicates that the membrane with a Fe$_3$O$_4$/PAA mass ratio of over 7:1(over 55.3wt% Fe$_3$O$_4$) had a high flux. Our previous results also indicated that polysulfone- Fe$_3$O$_4$ membranes with 58.3-84.4wt% Fe$_3$O$_4$ had a higher flux in the filtration test of BSA aqueous solution than that of the polysulfone- Fe$_3$O$_4$ membranes with 47.4wt% Fe$_3$O$_4$.[16] Figure 6 indicates that the fouled membrane with a Fe$_3$O$_4$/PAA mass ratio of over 5:1 had a high water flux. The fouled membrane with a Fe$_3$O$_4$/PAA mass ratio of 7:1 had a high water flux, which may be due to BSA molecules on the membrane surface easily flushed away by water. Both the permeate flux of BSA aqueous solution and the pure water flux of a fouled membrane showed that the membrane with a Fe$_3$O$_4$/PAA mass ratio of over 7:1(over 55.3 wt % Fe$_3$O$_4$)
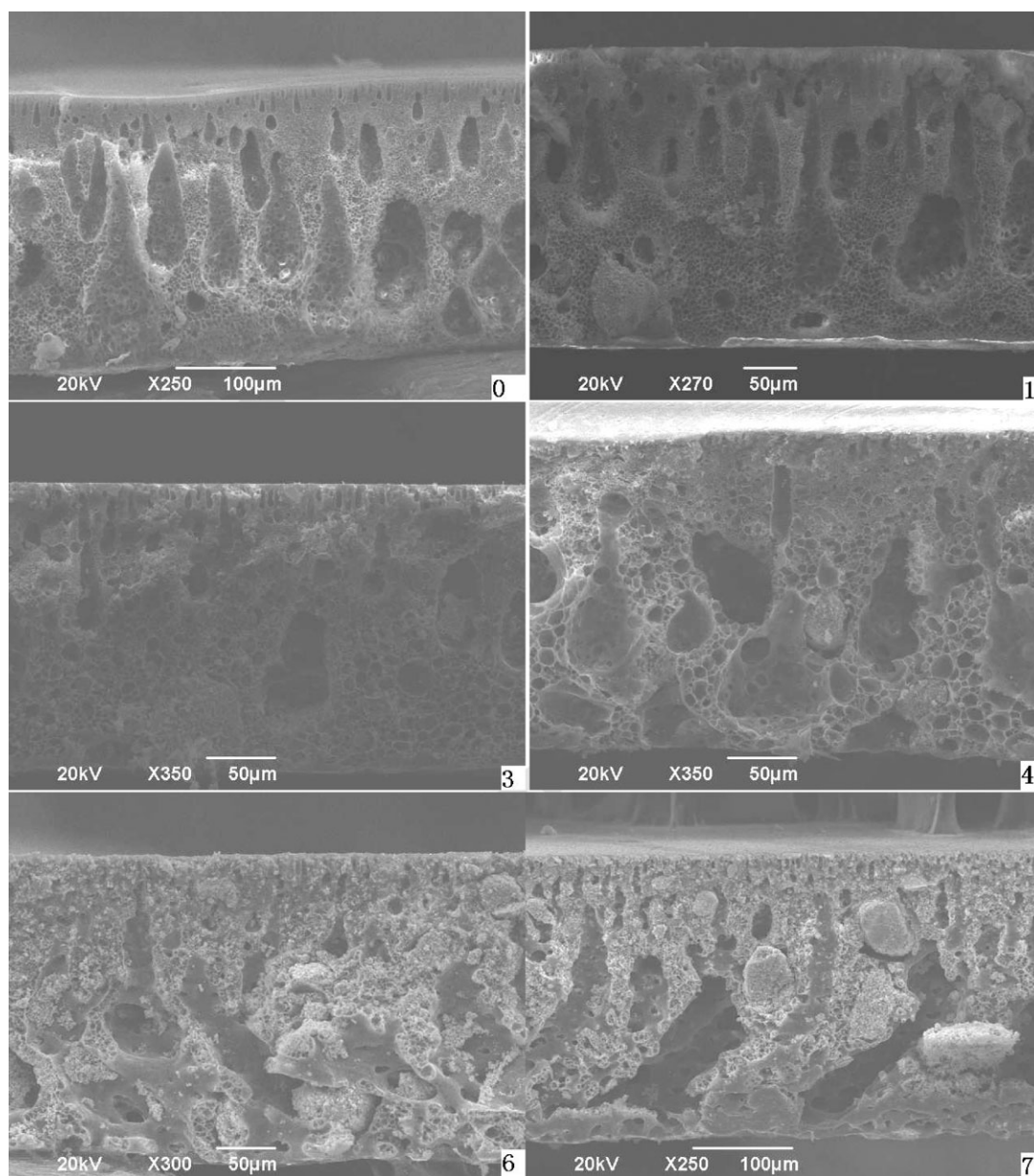
Figure 2. The cross-sectional structures of membranes: numbers from "0" to "7" represent no. of membrane.

had a good absolute antifouling ability. Usually, the antifouling ability of a membrane depends on many factors such as the surface roughness, the surface pore size and its distribution, the hydrophilic performance of a membrane surface, the concentration of BSA aqueous solution, and the conditions of test. Figure 7 indicates that the contact angle dropped from 85.9° to 78.6° with the change of Fe_3O_4/PAA mass ratio from 5:1 to 13:1. A small water contact angle indicates a good hydrophilic performance of membrane surface, which will improve the antifouling ability of membrane. However, the water contact angle only had a change of 7°, which indicated that the hydrophilic performance of membrane had no dramatic change. In addition, the roughness of organic-inorganic membrane rised with increase of inorganic filler particle,[13] which might reduce the antifouling ability of membrane. So many factors such as the surface rough-

ness, the surface pore size and its distribution, the hydrophilic performance of a membrane surface, the concentration of BSA aqueous solution, and the condition of test may have a comprehensive influence on the antifouling ability of membrane.

The relative flux (J_r) is usually used for the comparison of relative membrane antifouling performance since initial molecular weight cutoff and pure water flux of membranes are different. A high relative flux results in stronger relative antifouling ability. Figure 8 indicates that membranes had a 20–30% reduction of water flux. The relative fluxes of membrane only had a 10% difference with the change of the Fe_3O_4/PAA mass ratio. The surface pore size of membrane had little difference due to the close rejection. The surface roughness and the surface hydrophilicity rised with increase of the Fe_3O_4/PAA mass ratio. An increasing
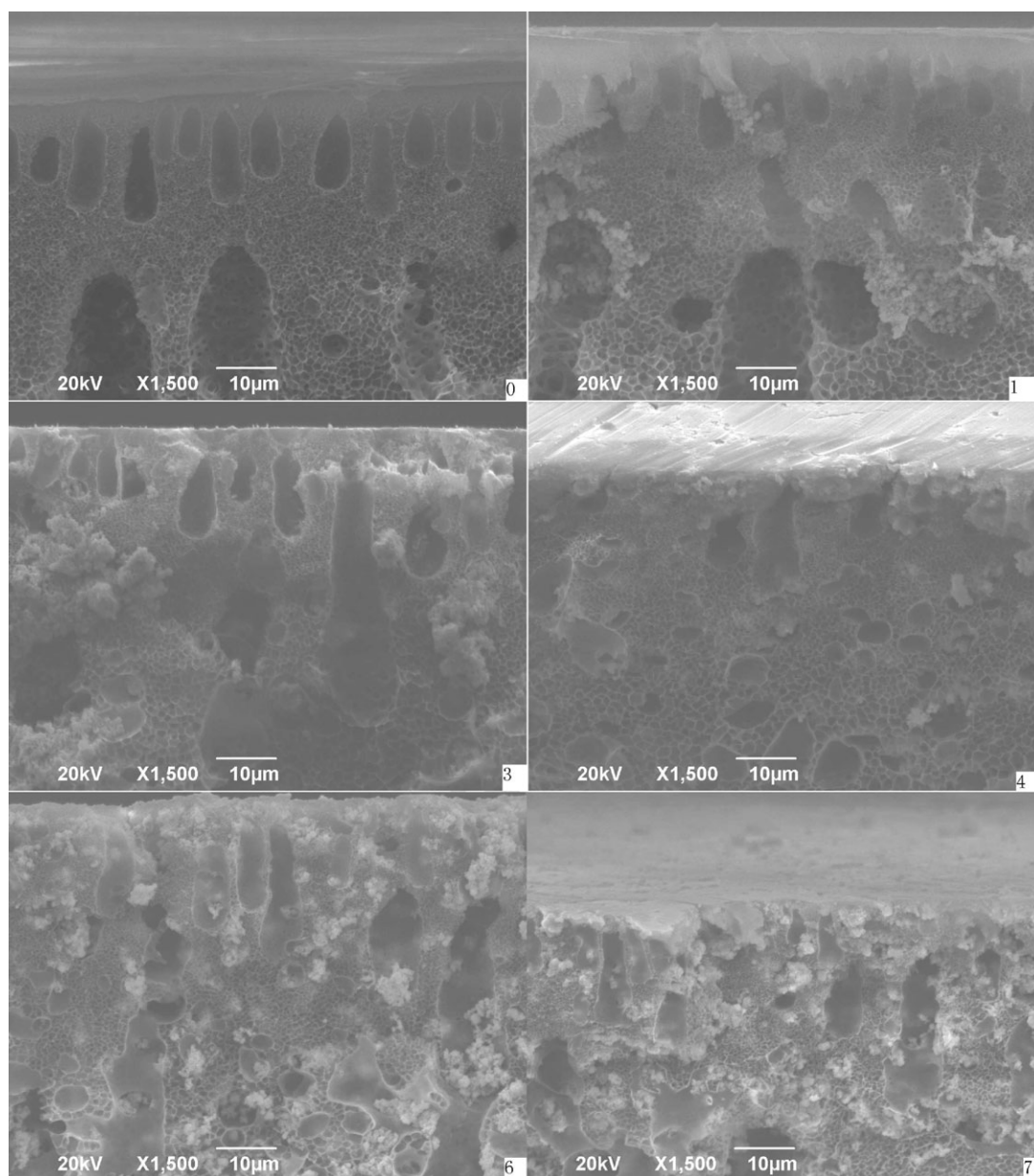
Figure 3. The magnification micrographs of cross-sectional structures near the top layer: numbers from "0" to "7" represent no. of membrane.

surface roughness will reduce antifouling ability, but an increasing surface hydrophilicity will improve antifouling ability. Two factors might result in stronger relative antifouling ability, when the Fe_3O_4/PAA mass ratio was between 3:1 and 7:1.

Effect of the Fe_3O_4/PAA Mass Ratio on the Extractive Amount of Fe_3O_4 During Membrane Formation

An interesting phenomenon was observed during the membrane formation. Some black Fe_3O_4 grains were extracted into water coagulation bath during the formation of No.1 to No.7 membrane. Table II indicates that the residual Fe_3O_4 content rised with increase of the Fe_3O_4/PAA mass ratio. However, the extractive amount of Fe_3O_4 during membrane formation was between 2.8 g and 4.0 g, when the Fe_3O_4/PAA mass ratio changed. Fe_3O_4 grains are insoluble in water and cannot be extracted into water

during the membrane formation. Nevertheless, the extractive Fe_3O_4 grains had the same FTIR spectra as the bare Fe_3O_4 grains.

Figure 9 shows the FTIR spectra for the membrane surfaces of No. 0 and No. 7. Both No. 0 membrane and No. 7 membrane samples had the same FTIR spectra, which had no peaks above 1600 cm^{-1}. This result indicated that PAA molecules did not exist in final membrane samples. Because PAA molecules is soluble in water and have a weak interaction with PES molecules, all PAA molecules diffused into the water coagulation bath during the formation of membrane.

Wu et al.[28] found that PAA could act as dispersant of alpha-alumina grains in DMF, since a bidentate chelate compound was formed between PAA molecules and alumina grains. Fe_3O_4
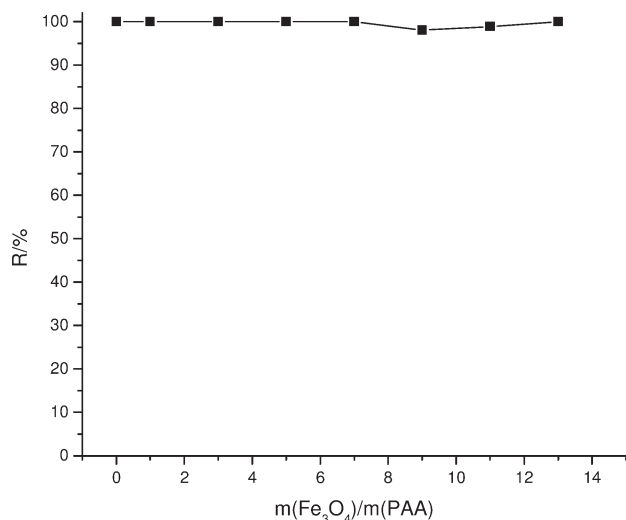
Figure 4. The rejections of membranes.

Figure 6. The pure water fluxes of fouled membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecules have some unoccupied orbits and can form a chelate compound with PAA molecules. PAA molecules is soluble in water and have a weak interaction with PES molecules, so PAA molecules chelating Fe_3O_4 grains will diffuse into water. PAA molecules have a strong interaction with water molecules and form hydrogen bond. PAA molecules will be desorbed from Fe_3O_4 grains, so the extractive Fe_3O_4 grains have the same FTIR spectra as the bare Fe_3O_4 grains. Although the Fe_3O_4/PAA mass ratio changed in casting solutions, PAA had an invariable addition of 3.0 g in the casting solution. The constant mass of PAA only can chelate a constant mass of Fe_3O_4 grains, so the extractive amount of Fe_3O_4 during membrane formation nearly keep a constant between 2.8 g and 4.0 g.

This result is very important for us to solve problems from the template leaching method. If the Fe_3O_4/PAA mass ratio is controlled in a suitable value, All Fe_3O_4 grains modified by PAA
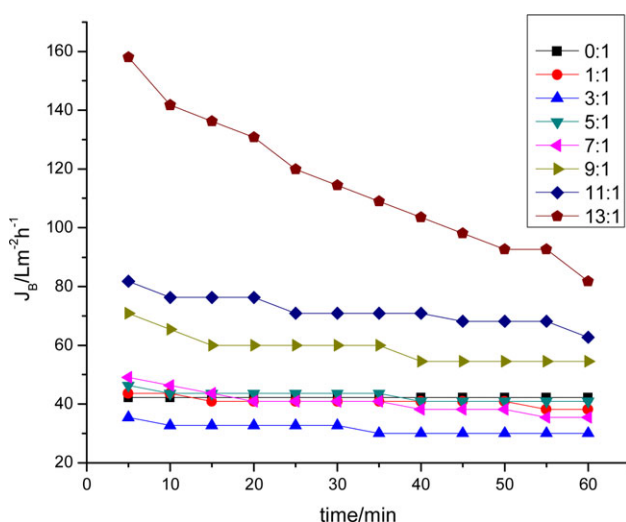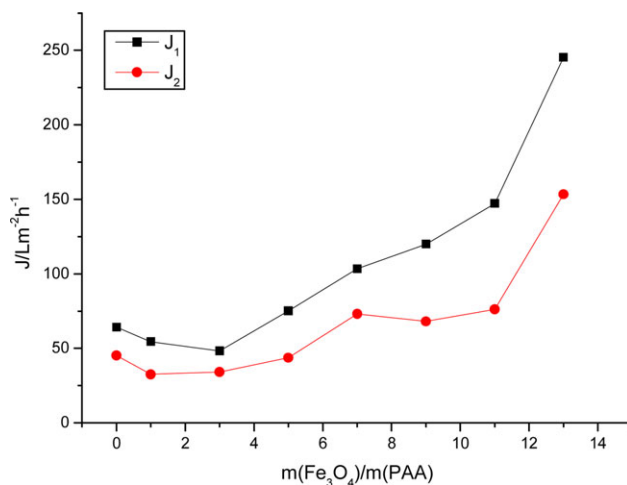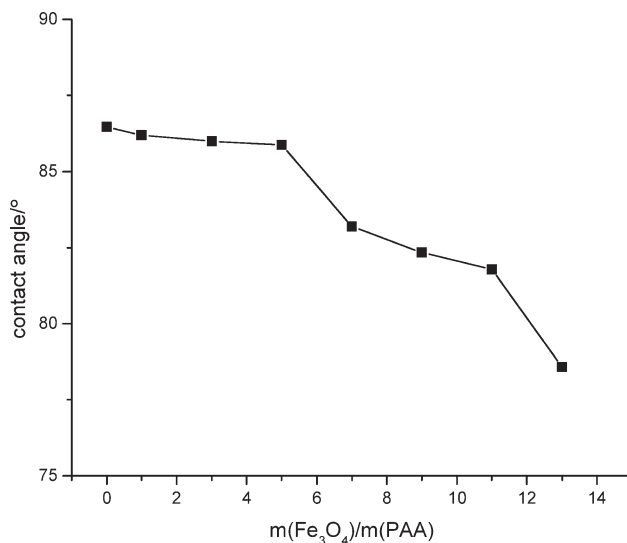

Figure 7. Water contact angles of membranes.

Figure 5. The BSA solution fluxes of membranes vs. time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
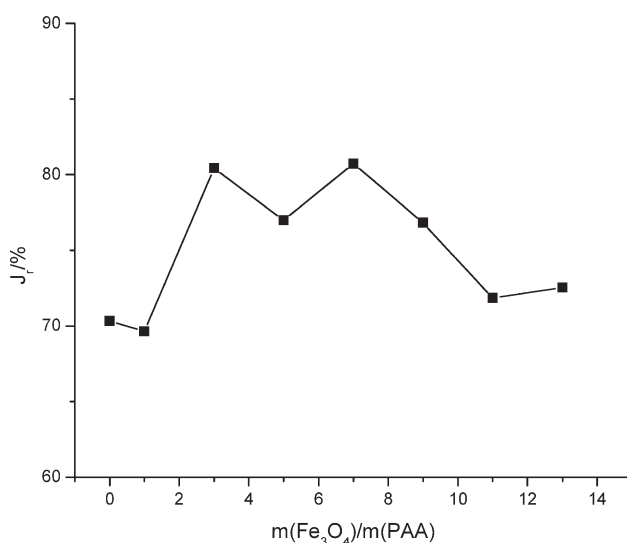

Figure 8. The relative fluxes of membranes.

Table II. The Content of Residual Fe_3O_4 Particles in the Membranes and the Extractive Mass of Fe_3O_4 Particles

No.	Fe_3O_4 (residual)/ (PES+Fe_3O_4) (wt %)	Fe_3O_4 (initial)/ (PES+Fe_3O_4) (wt %)	Fe_3O_4 (extractive)/ (PES+Fe_3O_4) (wt %)	Fe_3O_4 (extractive) (g)
1	1.0	15.0	14.0	2.8
2	20.7	34.6	13.9	3.6
3	34.3	46.9	12.6	4.0
4	47.6	55.3	7.7	2.9
5	53.3	61.4	8.1	3.6
6	58.6	66.0	7.4	3.7
7	62.8	69.6	6.8	3.8

will diffuse into the water coagulation, and Fe_3O_4 grains modified by PAA can act as a pore-forming agent without use of acids and bases. The template leaching method may be used to prepare porous inorganic and organic membranes. Nevertheless, the template leaching method usually needs to leach the fillers from the template by using acids and bases, which may pollute the environment and reduce the strength of membrane.

CONCLUSIONS

From the findings of this study, the following statements may be concluded:

(1) The Fe_3O_4/PAA mass ratio had little effect on the rejection of membranes to BSA. However, the pure water flux had a slight decline and then rised rapidly with the increase of Fe_3O_4/PAA mass ratio. The increase of Fe_3O_4/ PAA mass ratio improved the absolute antifouling ability of membranes and had no obvious effect on the relative antifouling ability of membranes.

(2) An interesting phenomenon observed was that the Fe_3O_4 particles modified by PAA could diffuse into the nonsolvent bath during the formation of membrane, and the

amount of Fe_3O_4 extracted into the nonsolvent bath nearly kept a constant mass ratio to PAA, even if the Fe_3O_4/PAA mass ratio was changed.

NOMENCLATURE

List of Symbols

A	Membrane area (m^2)
C_f	Concentration of feed (mg L^{-1})
C_P	Concentration of permeate (mg L^{-1})
Jr	Relative water flux (%)
J_B	BSA solution flux (L m^{-2} h^{-1})
J_1	Initial pure water flux (L m^{-2} h^{-1})
J_2	Pure water flux through a fouled membrane (L.m^{-2}. h^{-1})
R	Rejection (%)
t	Filtration time (h)
V	Permeate volume (L)

REFERENCES

1. Yan, L.; Hong, S.; Li, M. L.; Li, Y. S. *Sep. Purif. Technol.* **2009**, *66*, 347.

2. Maximous, N.; Nakhla, G.; Wong, K.; Wan, W. *Sep. Purif. Technol.* **2010**, *73*, 294.

3. Liu, F.; Abed, M. R. M.; Li, K. *J. Membr. Sci.* **2011**, *366*, 97.

4. Abedini, R.; Mousavi, S. M.; Aminzadeh, R. *Desalination* **2011**, *277*, 40.

5. Wei, Y.; Chu, H. Q.; Dong, B. Z.; Li, X.; Xia, S. J.; Qiang, Z. M. *Desalination* **2011**, *272*, 90.

6. Oh, S. J.; Kim, N.; Lee, Y. T. *J. Membr. Sci.* **2009**, *345*, 13.

7. Hamid, N. A. A.; Ismail, A. F.; Matsuura, T.; Zularisam, A. W.; Lau, W. J.; Yuliwati, E. *Desalination* **2011**, *273*, 85.

8. Arthanareeswaran, G.; Sriyamuna Devi, T. K.; Raajenthiren, M. *Sep. Purif. Technol.* **2008**, *64*, 38.

9. Yu, S. L.; Zuo, X. T.; Bao, R. L.; Xu, X.; Wang, J.; Xu, J. *Polymer* **2009**, *50*, 553.

10. Arthanareeswaran, G.; Thanikaivelan, P. *Sep. Purif. Technol.* *74* (**2010**) 230.

11. Shen, J. N.; Ruan, H. M.; Wu, L. G.; Gao, C. J. *Chem. Eng. J.* **2011**, *168*, 1272.

12. Maximous, N.; Nakhla, G.; Wan, W.; Wong, K. *J. Membr. Sci.* **2010**, *352*, 222.

13. Zhang, Y. Z.; Li, H.; Lin, J.; Li, R.; Liang, X. P. *Desalination* **2006**, *192*, 198.

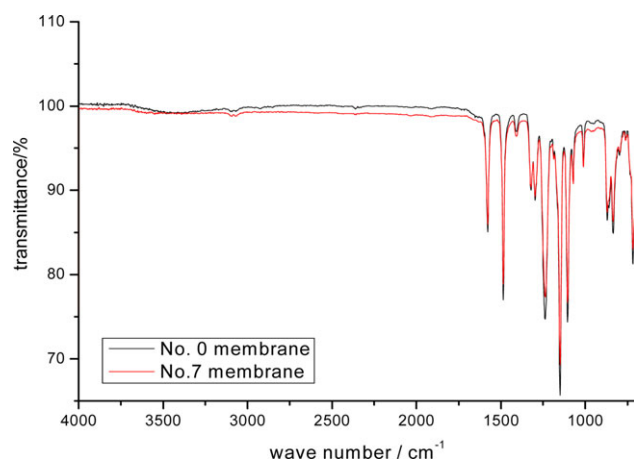14. Jian, P.; Yahui, H.; Yang, W.; Linlin, L. *J. Membr. Sci.* **2006**, *284*, 9.

Figure 9. The FTIR spectra for the membrane surfaces of No.0 and No.7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

15. Huang, Z. Q.; Chen, L.; Chen, K.; Zhang, Z.; Xu, H. T. *J. Appl. Polym. Sci.* **2010**, *117*, 1960.

16. Huang, Z. Q.; Chen, K.; Li, S. N.; Yin, X. T.; Zhang, Z.; Xu, H. T. *J. Membr. Sci.* **2008**, *315*, 164.

17. Wang, X. M.; Li, X. Y.; Shih, K. *J. Membr. Sci.* **2011**, *368*, 134.

18. Liu, X. J.; Peng, Y. L.; Ji, S. L. *Desalination* **2008**, *221*, 376.

19. Li, J. H.; Xu, Y. Y.; Zhu, L. P.; Wang, J. H.; Du, C. H. *J. Membr. Sci.* **2009**, *326*, 659.

20. Luo, M. L.; Zhao, J. Q.; Tang, W.; Pu, C. S. *Appl. Surf. Sci.* **2005**, *249*, 76.

21. Kukizaki, M. *J. Membr. Sci.* **2010**, *360*, 426.

22. Sa-nguanruksa, J.; Rujiravanit, R.; Supaphol, P.; Tokura, S. *Polym. Test.* **2004**, *23*, 91.

23. Kellenberger, C. R.; Luechinger, N. A.; Lamprou, A.; Rossier, M.; Grass, R. N.; Stark, W. J. *J. Membr. Sci.* **2012**, *387*, 76.

24. Genné, I.; Kuypers, S.; Leysen, R. *J. Membr. Sci.* **1996**, *113*, 343.

25. Genné, I.; Doyen, W.; Adriansens, W.; Leysen, R. *Filtr. Sep.*, **1997**, *34*, 964.

26. Tong, P. S.; Barbano, D. M.; Rudan, M. A. *J. Dairy Sci.* **1988**, *71*, 604.

27. Jaffrin, M. Y.; Ding, L. H.; Defossez, M.; Laurent, J. M. *Chem. Eng. Sci.* **1995**, *6*, 907.

28. Wu, L.; Huang, Y.; Wang, Z.; Liu, L. *J. Eur. Ceram. Soc.* **2010**, *30*, 1327.