

# Preparation and Recovery of Polysulfone Affinity Membrane with Mercapto as Chelating Group for Hg<sup>2+</sup> Cations

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**ABSTRACT:** Highly qualified homogeneous poly(benzylsulfone) plate affinity membrane with mercapto group (PSF-SH) was prepared successively through reactions between chloromethyl polysulfone matrix membrane and thiourea, and then alkalic hydrolysis. The mercapto-functionalized polysulfone affinity membrane was utilized for the adsorption of Hg<sup>2+</sup> cations through the coordination of the mercapto group and Hg<sup>2+</sup> cations, in which the effects of the morphological and the structure of the affinity membrane on the chelating properties were investigated. The chelating conditions, including concentration of Hg<sup>2+</sup>, and temperature and pH of the introductory solution had significant influence on the chelating capacity of PSF-SH affinity membrane. The highest static and dynamic chelating capacity of

PSF-SH plate membrane for Hg<sup>2+</sup> cations were 398 and 403 μg/cm<sup>2</sup> per membrane, respectively, which demonstrated that the resultant polymer membrane was a highly efficient affinity chromatography for Hg<sup>2+</sup>. The affinity membrane containing mercapto group can be conveniently recovered by dilute hydrochloric acid for coordination of Hg<sup>2+</sup> cations, which would have wide application for the treatment of waste water containing heavy metal cations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2514–2522, 2007

**Key words:** adsorption; plate affinity membrane; chelating resin; chloromethyl polysulfone; chromatography; mercury(II); mercapto-modified polysulfone; separation technique

## INTRODUCTION

There are ever increasing requirement for large amount of waste water to be purified within a reasonable time.<sup>1,2</sup> Membrane material made of the functional polymer is one of the good candidates to eliminate the dissolved pollutant rapidly and efficiently from the waste water because the characteristics inherent in membrane provide rapid filtration with efficient adsorption and high selectivity. An affinity membrane can integrate the advantages of both affinity chromatography and modern membrane techniques.<sup>3–8</sup> The affinity membrane with definite micropores has an affinity functional group on its inner and outer surface as carrier of the affinity reagent. When the solution is filtered through the membrane, the aimed materials will quickly and efficiently combine with the relevant functional groups of the affinity reagent. The materials adsorbed on the membrane can

be soon desorbed when an eluent passes through the membrane. The ion-exchange membranes with thio-carbamide and iminodiacetic acid as chelating groups have been used for the removal of mercury(II), with chelating capacities of 600 μg/cm<sup>2</sup> per membrane and 92 mg/g per membrane, respectively.<sup>9,10</sup> Recently, we reported the highly qualified heterogeneous polysulfone plate filter membranes with amino group as chelating groups by phase separation with the blends of the chelating resin and polysulfone having the highest chelating capacity of 1050 μg/cm<sup>2</sup> per membrane.<sup>11</sup> The heavy metal ions can be adsorbed selectively on the membrane by introducing SH group in the matrix membrane due to the soft characters of both S and the heavy metal cations. In our previous work, we reported the synthesis of chloromethyl polysulfone from polysulfone (PSF) by Friedel–Crafts reaction and then the matrix membrane was prepared with CMPSF by phase inversion technology.<sup>12</sup> Here, the homogeneous polysulfone chelating plate affinity membrane modified with mercapto group was obtained through the methyl thiourium polysulfone chloride from CMPSF and then further hydrolyzed under alkaline conditions. The adsorption properties of such PSF-SH plate affinity membrane for Hg<sup>2+</sup> were investigated.

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## EXPERIMENTAL

### Materials and reagents

Dichloromethane, 2,2-dichloromethane, nitrobenzene, thiourea, and polyethylene glycol (PEG) were of analytical grade and purchased from Tianjin Reagent Plant. Chloromethyl ether and ferriammonium sulfate were of analytical grade and were purchased from Nankai University Chemical Plant. Mercury(II) nitrate ( $\text{Hg}(\text{NO}_3)_2$ ) was purchased from Tianjin Chemical Reagent Plant as analytical grade. Sodium rhodanate and sodium hydroxide were of analytical grade and purchased from Tianjin Yaohua Chemical Plant.

### Main apparatuses

VECTOR22 Fourier infrared spectrometer (with ART appendix) was made by Bruker Corp., Germany. The retention measurement apparatus of membrane was made by Tianjin Polytechnic University, China.

### Preparation of homogeneous polysulfone affinity membrane modified with mercapto

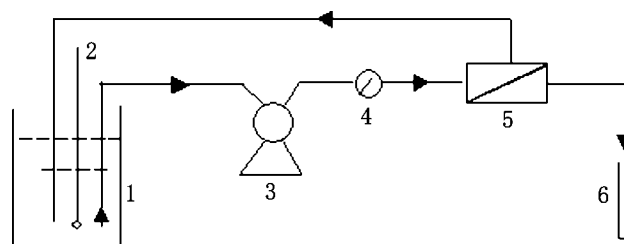
The preparation of plate of chloromethyl polysulfone (CMPSF) matrix membrane was reported in detail in our previous work.<sup>12</sup> The CMPSF plate was soaked in a thiourea of anhydrous ethanol solution and the reaction was carried out at 50°C for 8 h. The methyl(isothiourium) polysulfone (MTUPSF) plate membrane was afforded after taking the membrane stripe out of the solution and washing with distilled water repeatedly and then it was hydrolyzed in 1 mol/L of sodium hydroxide solution at 80°C for 10 h with stirring to form polysulfone modified with mercapto. The hydrolyzed stripe was washed with distilled water till the pH of the filtrate was 7 and then potched with 0.05 mol/L of hydrochloride solution twice to afford the homogeneous polysulfone affinity membrane modified with mercapto group (PSF-SH). The obtained PSF-SH membrane was preserved in the wet state until further use.

### FTIR analysis of polysulfone membrane modified with mercapto

The CMPSF, MTUPSF, and PSF-SH membranes were dried at 50–70°C in vacuum oven. The dried membrane was directly placed on the ART crystal and fastened firmly with clips. The metal peg should be firmly screwed when fastening. The FTIR spectra of ART annex fastened with plate membrane were determined on a VECTOR Fourier infrared spectrometer.

### Measurement of water flux

The schematic diagram of experimental apparatus for measurement of water flux is shown in Figure 1. The



**Figure 1** Schematic diagram of the retention measurement apparatus of membrane: 1, reservoir; 2, thermometer; 3, water pump; 4, barometer; 5, plate membrane module; 6, volumetric cylinder.

ultrapure water was pumped from a 2000-mL feed reservoir and returned to the feed reservoir after passing through the plate membrane module. The volume of the water filtered through the membrane was measured by a volumetric cylinder. The operation pressure was 0.1 MPa. The water flux  $Q(\text{L}/\text{m}^2 \text{ h})$  was calculated according to eq. (1)

$$Q = \frac{V}{St} \quad (1)$$

where  $V(\text{L})$  was the volume of transmitted liquid and  $t(\text{h})$  was the ultrafiltration time and  $S(\text{m}^2)$  was the effective surface area of the membrane.

### Porosity measurement

The porosity of the membrane was determined by means of gravimetric method.<sup>13</sup> Glycerol was used as saturate and a definite area of wet membrane was sheared. The glycerol on the surface of membrane was wiped away to obtain the wet membrane with the weight as  $W_w(\text{g})$ . Then the wet membrane was dried in a vacuum oven till constant weight with the weight of dried membrane as  $W_d(\text{g})$ . The porosity of membrane  $P_r$  was calculated from eq. (2)

$$P_r = \frac{W_w - W_d}{sd\rho} \times 100\% \quad (2)$$

where  $d(\text{cm})$  is the average thickness of membrane,  $S(\text{cm}^2)$  is the effective surface area of the membrane, and  $\rho(\text{g}/\text{cm}^3)$  is the density of glycerol.

### Membrane pore size measurement

The membrane pore size was determined by means of filtering velocity method.<sup>13</sup> The membrane pore diameter  $r_f$  was calculated from eq. (3)

$$r_f = \sqrt{\frac{8 \times (2.90 - 1.75P_r)\mu LQ}{P_r \Delta P S}} \quad (3)$$

where  $p_r$  is the porosity,  $L(\text{cm})$  the thickness of membrane,  $\mu$  the viscosity of transmitted liquid,  $Q(\text{L}/\text{m}^2 \cdot \text{h})$

the flux,  $\Delta P(\text{Pa})$  the pressure, and  $S(\text{cm}^2)$  the filtering area.

### Quantity measurement of $\text{Hg}^{2+}$

The concentration of  $\text{Hg}^{2+}$  was determined with dithizone method<sup>14</sup> and the detailed procedure is as follows: a piece of membrane ( $S = 25 \text{ cm}^2$ ) was immersed into 500 mL of mercury nitrate ( $\text{Hg}(\text{NO}_3)_2$ ) solution with the initial concentration of  $100 \mu\text{g}/\text{mL}$ , and  $\text{Hg}^{2+}$  concentration in the residual solution was determined after the immersion.

The  $\text{Hg}^{2+}$  concentration was determined by atomic absorption spectroscopy (AAS) in the presence of EDTA.

### Determination of the rejection of homogeneous polysulfone chelating affinity membrane modified with mercapto groups for $\text{Hg}^{2+}$

The rejection of homogeneous polysulfone chelating affinity membrane modified with mercapto groups for  $\text{Hg}^{2+}$  was determined with the experimental apparatus for measurement of water flux (made in Tianjin Polytechnic University, China). The properties of the membrane can be described by the adsorption capacity of the membrane for  $\text{Hg}^{2+}$ , which was calculated from eq. (4)

$$\Gamma = (C_0 - C_t)/S \quad (4)$$

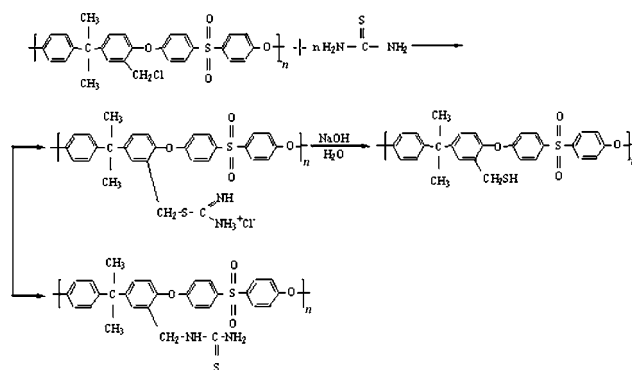
where  $C_0(\mu\text{g}/\text{mL})$  is original concentration of  $\text{Hg}^{2+}$ ,  $C_t(\mu\text{g}/\text{mL})$  is the residual concentration of  $\text{Hg}^{2+}$  after the  $\text{Hg}^{2+}$  solution was through the membrane, and  $S(\text{cm}^2)$  was membrane area.

## RESULTS AND DISCUSSION

### Synthesis of PSF-SH affinity membrane

In our previous work, we reported the effects of various aspects, such as species and contents of additives, CMPSF content in casting solution, and temperature of solution, on the morphology of the affinity membrane, including the pore size, porosity, and water flux of the membrane.<sup>10</sup> Polysulfone affinity membrane modified with mercapto groups (PSF-SH) was obtained through the reaction between CMPSF and thiourea and further alkaline hydrolysis. The synthesis route is shown as in Scheme 1.

The modification of the polymer affinity membranes successively through the thiourium reaction and the alkalic hydrolysis to incorporate the mercapto groups was characterized with FTIR spectra as shown in Figure 2. The successful thiourium reaction was confirmed by the FTIR spectra in Figures 2(a) and 2(b), with complete disappearance of the peak at  $1246 \text{ cm}^{-1}$  corresponding to the stretching vibration of



**Scheme 1** The synthesis of PSF-SH plate affinity membranes.

chloromethyl group for CMPSF matrix membrane and the presence of new peaks at  $1402 \text{ cm}^{-1}$  assigned to the vibration of C—S bond,  $1640 \text{ cm}^{-1}$  attributed to the vibration of C=N, and the wide strong peak around  $3134 \text{ cm}^{-1}$  ascribed to the  $\text{NH}_3^+$  of the thiourium group on MTUPSF plate. In other words, the chloromethyl groups were quantitatively converted into the thiourium groups with estimation from the complete disappearance of peak at  $1246 \text{ cm}^{-1}$  of the chloromethyl group in the FTIR spectra [Fig. 2(a)]. The peaks of FTIR spectra of MTUPSF at  $1402$ ,  $1640$ , and  $3134 \text{ cm}^{-1}$  due to the vibrations of the thiourium groups almost disappeared and a novel strong peak at around  $2580 \text{ cm}^{-1}$  was attributed to mercapto groups in mercapto-functionalized polysulfone membrane (PSF-SH), which was much similar to that of mercapto group reported in the literature.<sup>15</sup> The conversion of the thiourium group to mercapto groups was estimated to be higher than 90% because of the absence of the absorption peaks of the thiourium group in the FTIR spectra after alkalic hydrolysis [Fig. 2(c)].

### Effect of the properties of PSF-SH affinity membrane on the chelating capacity for $\text{Hg}^{2+}$

Effect of the loading of mercapto groups on the chelating capacity of PSF-SH affinity membranes

The CMPSF matrix membranes with different chlorinity were prepared with 4% PEG ( $M_w = 10,000$ ) as additive and the entire solid content of 15% in the casting solution.<sup>12</sup> Then PSF-SH affinity membranes with different amount of mercapto were prepared by the reaction between CMPSF matrix membrane and thiourea and then the alkaline hydrolysis with the total conversion higher than 90% from chloromethyl group. The chelating capacity of PSF-SH affinity membrane for  $\text{Hg}^{2+}$  was determined by soaking the membrane in  $1000 \mu\text{g} \text{ Hg}^{2+}/\text{mL}$  solution at pH 2–3 for 24 h and the results are shown as in Figure 3. The results indicated that the chelating capacity of the PSF-SH affinity membranes increased rapidly with increasing mercapto from 0 to 1%, and then increased consider-

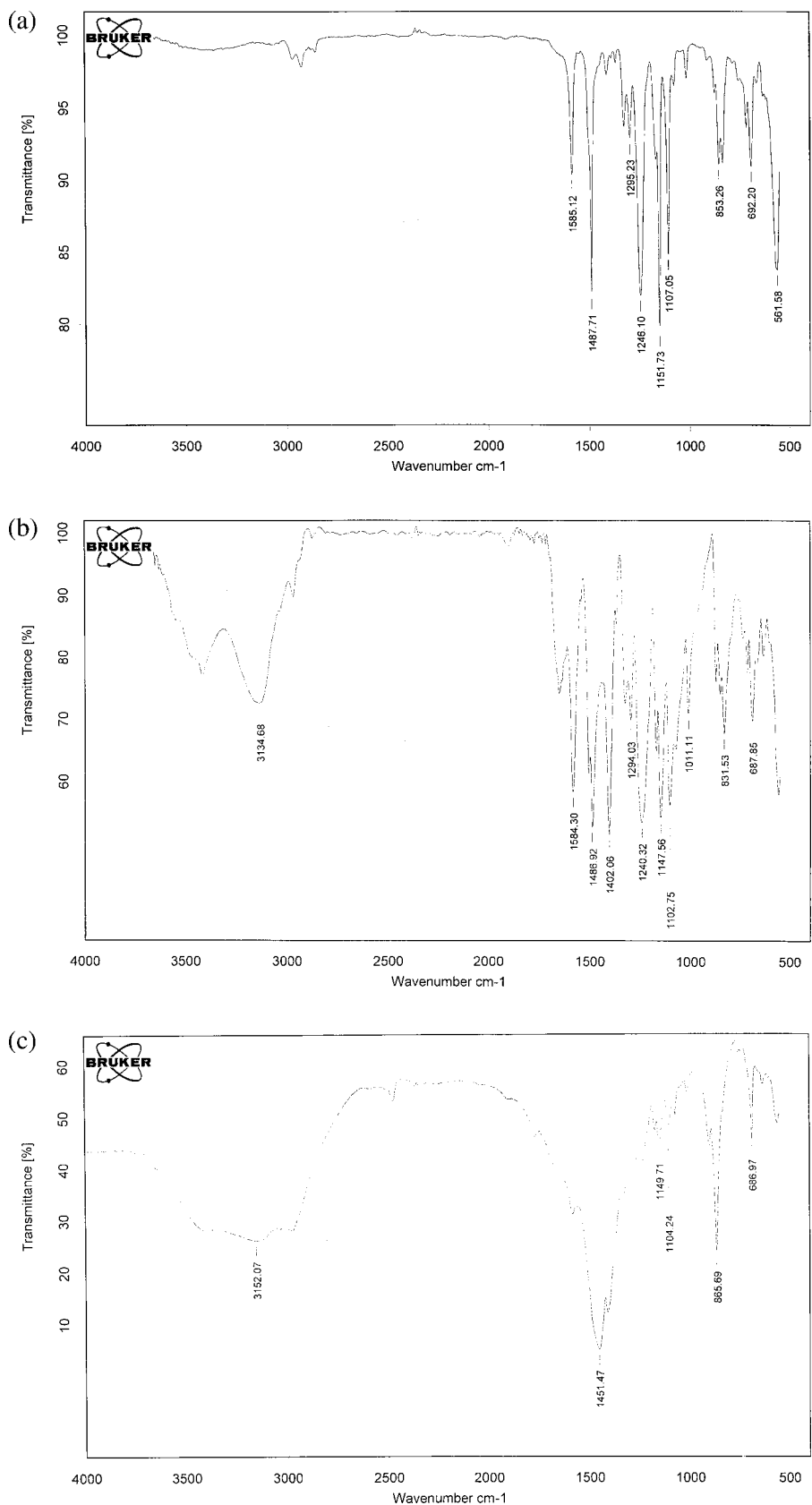
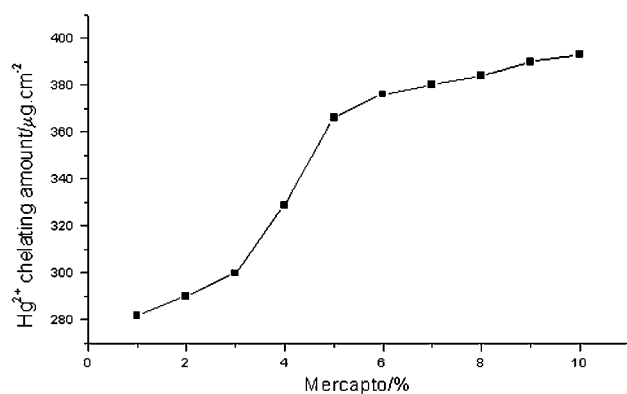


Figure 2 FTIR spectra of membrane: (a) CMPSF, (b) MTUPSF, (c) PSF-SH.

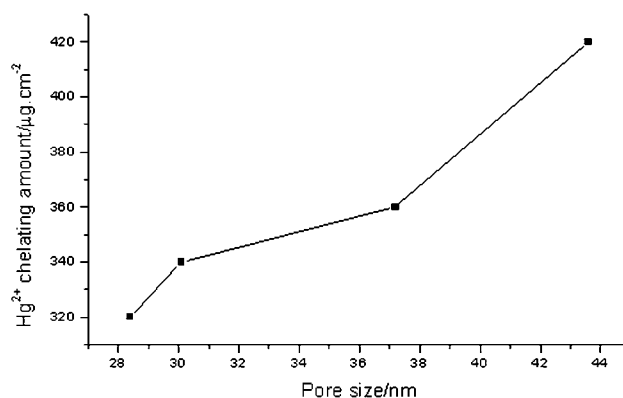


**Figure 3** The effect of the loading of mercapto of PSF-SH on the chelating capacity of PSF-SH affinity membrane: pore size, 37.2 nm; porosity, 61.3%.

ably with the mercapto increasing further till 11%. The chelating capacity for mercury(II) on PSF-SH affinity membranes increased with higher loading of mercapto groups. The PSF-SH with high mercapto loading (from the chlorinity of 5.34%) in the present work was utilized for investigation, as the chlorinity of CMPSF matrix material had little influence on the formation of CMPSF matrix membrane.<sup>12</sup> These results further proved the successful incorporation of mercapto groups on the porous polymer membrane successively through the thiourium reaction and alkalic hydrolysis.

Effects of the porosity and pore size on the chelating capacity of PSF-SH affinity membrane for Hg<sup>2+</sup>

The CMPSF matrix membranes with different porosity and pore size were prepared by utilization of either different amounts (2, 4, 6, 8%) of PEG ( $M_w = 10,000$ ) or 4% of PEG with different molecular weights ( $M_w = 600, 10,000, 20,000$ ) as the additive, while the total solid content in the casting solution was kept at 15%.<sup>12</sup> PSF-SH affinity membranes with different porosity and pore size were prepared from such CMPSF matrix membranes according to the procedures mentioned in our previous work.<sup>12</sup> The effects of the pore size and porosity on the capacity of the affinity membranes for Hg<sup>2+</sup> are shown in Figures 4 and 5, respectively. The results indicated that the chelating capacity of the membranes increased both with the increasing pore size and porosity, which was originated either from the different amounts of PEG additive or from the different molecular weights of PEG as additive (only with the later data as samples). With bigger size and higher porosity, the area of the porous polymer affinity membrane increased and the fraction of the accessible mercapto groups on the wall of the membrane increased. In this way, the chelating capacity of the PSF-SH affinity membrane increased with larger pore size and porosity of the membrane.

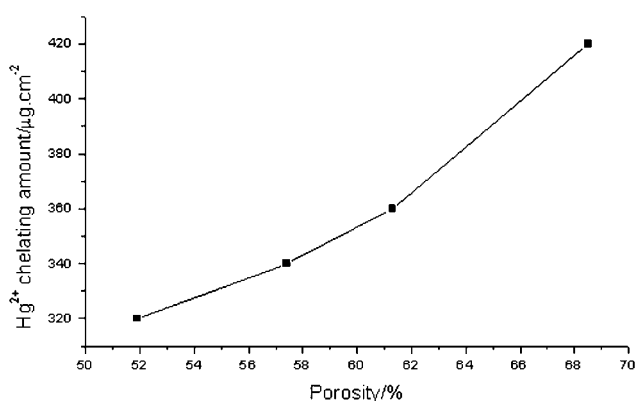


**Figure 4** The effect of the pore size on the chelating capacity of PSF-SH affinity membrane with different molecular weights of PEG (4 wt %; chlorinity, 5.34%) as additive.

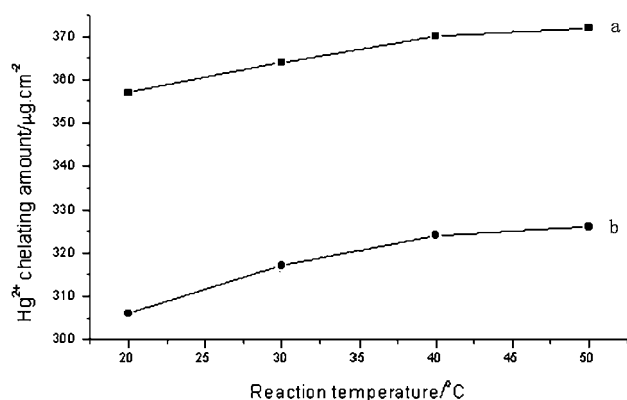
### Effect of the thiouriuming conditions on the chelating capacity of PSF-SH affinity membranes for Hg<sup>2+</sup>

The thiouriuming temperature

The CMPSF matrix membranes were soaked in saturate solution of thiourea in anhydrous ethanol for 5 h under different temperatures, i.e., 25, 35, 45, and 55°C to afford the MTUPSF membranes. Then PSF-SH affinity membranes were prepared and the chelating capacity of the affinity membranes was determined according to the methods mentioned in Effect of the Loading of Mercapto Groups on the Chelating Capacity of PSF-SH Affinity Membranes. The effect of the thiouriuming temperature on the chelating properties of PSF-SH affinity membranes is shown in Figure 6. The results indicated that the chelating capacity increased considerably with the increasing reaction temperature, which was due to the higher conversion of methylchloride to the methylthiourium chloride under higher reaction temperature. The dif-



**Figure 5** The effect of the porosity on the chelating capacity of PSF-SH affinity membrane with different molecular weights of PEG (4 wt %; chlorinity, 5.34%) as additive.



**Figure 6** The effect of thiouriuming temperature on the chelating capacity of PSF-SH affinity membrane: (a) pore size, 37.2 nm; porosity, 61.3%. (b) Pore size, 28.4 nm; porosity, 51.9%.

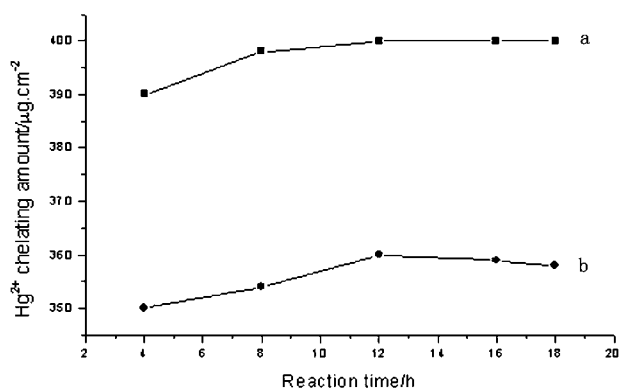
ference in the capacity between the affinity membranes with different pore sizes was due to the effect of the pore size as discussed in Effects of the Porosity and Pore Size on the Chelating Capacity of PSF-SH Affinity Membrane for  $\text{Hg}^{2+}$ .

#### The thiouriuming time

The CMPSF matrix membranes were soaked in saturate solution of thiourea in anhydrous ethanol for different durations at room temperature to afford the MTUPSF membranes. Then the preparation of PSF-SH affinity membranes and the determination of the capacity of the affinity membranes were carried out using the same procedures as those mentioned in Effect of the Loading of Mercapto Groups on the Chelating Capacity of PSF-SH Affinity Membranes. The effect of the thiouriuming time on the capacity of the affinity membrane is shown in Figure 7. The capacity of PSF-SH with the pore size of 40.1 nm for  $\text{Hg}^{2+}$  increased rapidly with increasing thiouriuming time till 8 h and then leveled off at 12 h till a constant value of 400  $\mu\text{g Hg}^{2+}/\text{cm}^2$ . While the pore size was 34.8 nm, the capacity increased rapidly with increasing thiouriuming time till 12 h and then leveled off at 16 h till a constant value of 360  $\mu\text{g Hg}^{2+}/\text{cm}^2$ -membrane. The results showed that the thiouriuming reaction of the CMPSF matrix membrane with bigger pore size was much faster than that of the membrane with the smaller size.

#### The concentration of thiourea

The CMPSF matrix membranes were soaked in different concentrations of thiourea in anhydrous ethanol at room temperature for 4 h to afford the MTUPSF membranes. The preparation of PSF-SH affinity membranes and the determination of the capacity of the



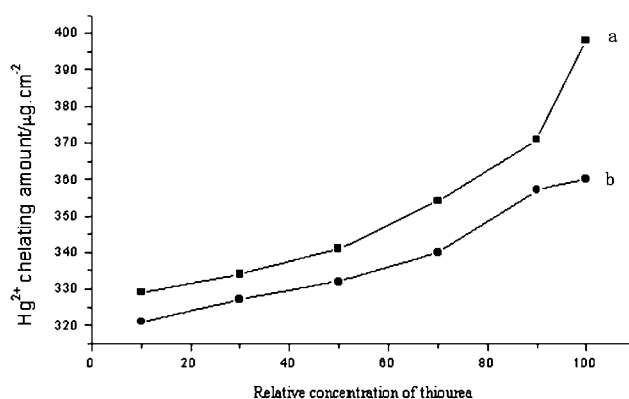
**Figure 7** The effect of thiouriuming time on the chelating capacity of PSF-SH affinity membrane with different molecular weights of PEG as additive (4 wt %; chlorinity, 5.34%): (a) pore size, 40.1 nm; porosity, 65.7%. (b) Pore size, 34.8 nm; porosity, 60.1%.

affinity membranes were carried out by the same procedures as those in Effect of the Loading of Mercapto Groups on the Chelating Capacity of PSF-SH Affinity Membranes. The effect of the thiourea concentration on the capacity of PSF-SH affinity membrane is shown in Figure 8. The results indicated that the chelating capacity increased considerably with increasing the concentration of thiourea during the thiouriuming reaction.

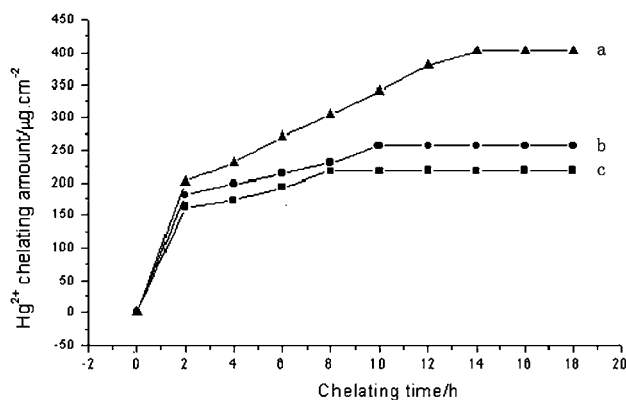
All these results demonstrated that the best thiouriuming temperature was 50°C, the best thiouriuming time was 12 h, and the best concentration of thiourea was a saturated solution.

#### Effect of the thickness of PSF-SH affinity membranes on the chelating capacity

Figure 9 shows the effect of the thickness of PSH-SH affinity membrane on the chelating capacity with the adsorption time in 1000  $\mu\text{g Hg}^{2+}/\text{mL}$  solution. The



**Figure 8** The effect of the concentration of thiourea on the chelating capacity of PSF-SH affinity membrane: (a) pore size, 40.1 nm; porosity, 65.7%. (b) Pore size, 34.8 nm; porosity, 60.1%.



**Figure 9** The effect of the thickness of the PSF-SH affinity membrane on the chelating capacity: pore size, 37.2 nm; porosity, 61.3%. (a) Membrane thickness, 0.14 mm; (b) membrane thickness, 0.19 mm; (c) membrane thickness, 0.24 mm.

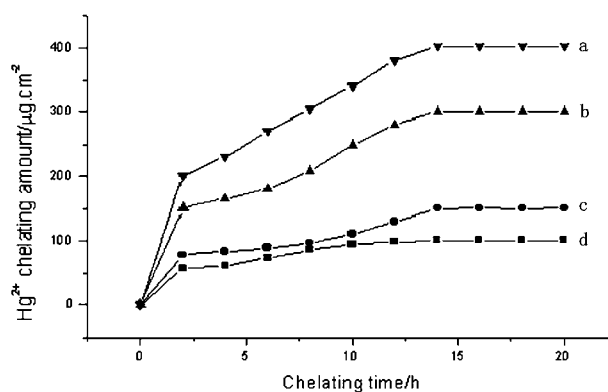
results showed that the chelating capacity increased quickly during the first 2 h and then leveled off with increasing the chelating adsorption time further. The chelating capacities of the affinity membranes reached plate-saturate values of 175, 200, 400  $\mu\text{g}/\text{cm}^2$  at 8, 10, 14 h for the thickness of 0.14, 0.19, 0.24 mm, respectively. These indicated that the chelating adsorption of  $\text{Hg}^{2+}$  occurred at the surface of the affinity membrane at the initial stage with a much higher rate and then took place inside the PSF-SH membrane with a lower rate because of the diffusion hindrance for  $\text{Hg}^{2+}$ .

#### The effect of the chelating conditions on the chelating properties of the affinity membranes

The PSF-SH affinity membranes were prepared according to the methods described in Effect of the Loading of Mercapto Groups on the Chelating Capacity of PSF-SH Affinity Membranes from CMPSF matrix membrane with the pore size of 37.2 nm and the porosity of 61.3%, which was obtained with 4% of PEG ( $M_w = 10,000$ ) as the additive and the total solid content of 15% CMPSF.

#### Effect of the concentration of mercury(II) on the chelating properties of the affinity membranes

The PSF-SH affinity membranes were soaked in 100, 400, 800, 1000  $\mu\text{g}/\text{mL}$  of  $\text{Hg}^{2+}/\text{mL}$  solution at pH 2–3 to determine the chelating capacity. The relationship between the capacity of the affinity membrane and the adsorption time is shown in Figure 10. The results indicated that the chelating amount increased rapidly in the first 2 h and then leveled off with the increasing adsorption further till a saturate value after 14 h for all the four samples. The saturate adsorption amount

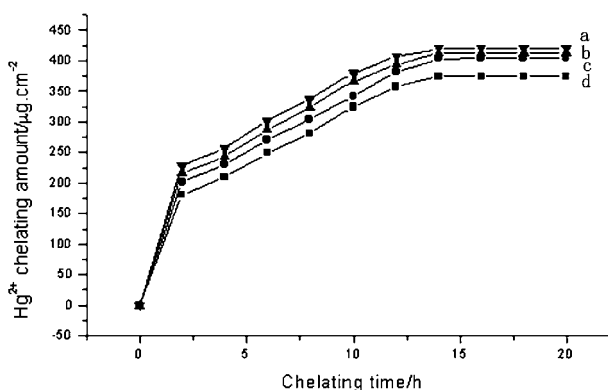


**Figure 10** The effect of concentration of  $\text{Hg}^{2+}$  in the elution on the chelating capacity of PSF-SH affinity membrane: pore size, 37.2 nm; porosity, 61.3%. (a)  $\text{Hg}^{2+}$  concentration, 100  $\mu\text{g}/\text{mL}$ ; (b)  $\text{Hg}^{2+}$  concentration, 400  $\mu\text{g}/\text{mL}$ ; (c)  $\text{Hg}^{2+}$  concentration, 800  $\mu\text{g}/\text{mL}$ ; (d)  $\text{Hg}^{2+}$  concentration, 1000  $\mu\text{g}/\text{mL}$ .

of the affinity membrane increased with the increasing concentration of  $\text{Hg}^{2+}$  in the solution. The times of half saturate-adsorption amount ( $T_{1/2}$ ) were 25, 35, 70, and 76 min for the different concentrations of  $\text{Hg}^{2+}$  at 100, 400, 800, 1000  $\mu\text{g}/\text{mL}$  respectively. The adsorption properties of the chelating affinity membrane for metal cations were mainly determined by the nature of the chelating groups on the membrane and the electronic structure of the metal cations. The PSF-SH affinity membranes had a selective adsorption for  $\text{Hg}^{2+}$  because of the soft Lewis base of  $-\text{SH}$  and the soft acid of  $\text{Hg}^{2+}$ .

#### Effect of the chelating temperature on the chelating capacity of the affinity membrane

Figure 11 shows the effect of the chelating temperature on the chelating capacity of the PSF-SH affinity

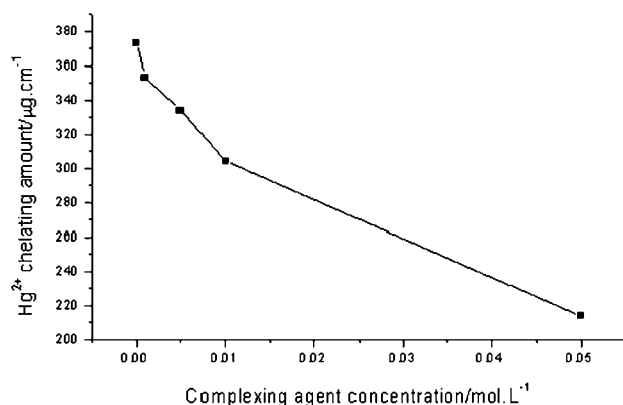


**Figure 11** The effect of the chelating temperature on the capacity of PSF-SH affinity membrane: pore size, 37.2 nm; porosity, 61.3%. (a) Salt solution temperature, 20°C; (b) salt solution temperature, 30°C; (c) salt solution temperature, 40°C; (d) salt solution temperature, 50°C.

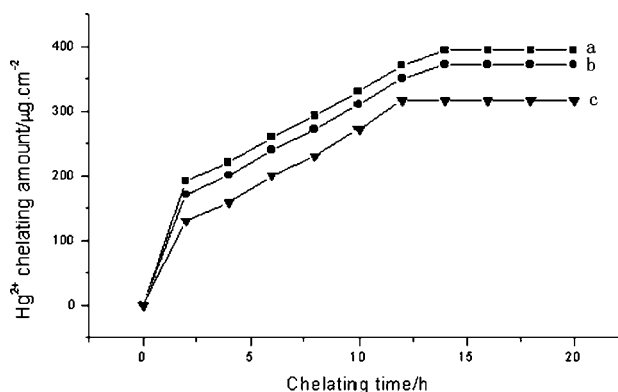
membrane. The results indicated that the capacity increased slightly with increasing chelating temperature. The processes for the chelating adsorption of the affinity membrane for the metal cations included the following three steps: (i) The diffusion of the metal cations to the surface of the homogeneous affinity membrane; (ii) the diffusion of the metal cations in the pore of the affinity membrane; and (iii) chemical adsorption through the ion-exchanges between the metal cations and the chelating groups on the affinity membrane. The high temperature was good not only for the diffusion of the metal cations but also for the dissociation of the mercapto group to chelate with the metal cations. The mobility of the metal cations increased with higher chelating temperature to overcome the hindrance of the membrane to enhance the chelating rate and the chelating capacity. Therefore, it was better to perform the chelating adsorption between PSF-SH affinity membrane and  $Hg^{2+}$  at a slightly higher temperature.

Effect of the chelating reagent in the solution on the chelating capacity of the affinity membrane

To determine the competitive coordination effect of the ligand on the chelating capacity, the chelating capacity of PSF-SH membrane was determined in the presence of reagent EDTA in the introductory solution as shown in Figure 12. The results indicated that the chelating capacity of the affinity membrane decreased significantly with the increasing concentration of EDTA in the solution. It is well known that EDTA has a strong chelating ability with  $Hg^{2+}$ , which is much stronger than that between PSF-SH affinity membrane and  $Hg^{2+}$ . Such competitive coordination prevented PSF-SH from chelating with  $Hg^{2+}$ , decreasing the capacity of the affinity membrane for  $Hg^{2+}$ .



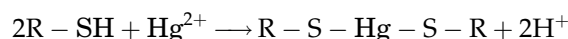
**Figure 12** The effect of the chelating reagent EDTA on the chelating capacity of PSF-SH affinity membrane: pore size, 37.2 nm; porosity, 61.3%. (a) Salt solution temperature pH = 5; (b) salt solution temperature pH = 4; (c) salt solution temperature pH = 2.



**Figure 13** The effect of the pH of the elution on the chelating capacity of PSF-SH affinity membrane: pore size, 37.2 nm; porosity, 61.3%. (a) pH = 5; (b) pH = 4; (c) pH = 2.

Effect of the pH of the  $Hg^{2+}$  solution on the chelating capacity of the PSF-SH affinity membrane

Figure 13 showed the effect of the pH of  $Hg^{2+}$  solution on the chelating capacity of the PSF-SH affinity membranes. The results indicated that the capacity of the affinity membrane was much high in the range of pH 2–5 and the capacity increased slightly with the increasing pH of  $Hg^{2+}$  solution. However, the pH of the solution should be in acidic state because mercury(II) reacts with hydroxide anion to precipitate from the solution under basic environment, which would make it impossible to selectively separate  $Hg^{2+}$  from the pollution with the affinity membrane. The chelating adsorption reaction between the PSF-SH affinity membrane with mercury(II) was as follows:



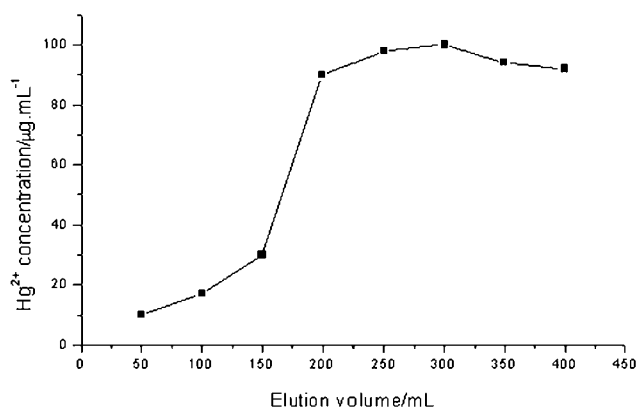
Naturally, the low pH solution was not favorable for such chelating adsorption.

Dynamic adsorption and the recycle of the homogeneous PSF-SH affinity membrane

The dynamic adsorption of PSF-SH affinity membrane was determined from the relationship between the concentration of  $Hg^{2+}$  in the eluted solution and the volume eluted through the membrane under 0.1 MPa with  $100 \mu g Hg^{2+}/mL$  as the elution, which is shown in Figure 14. The results indicated that the concentration of  $Hg^{2+}$  was below  $30 \mu g/mL$  in the initial 150 mL of eluted solution and then increased abruptly till the same level as the starting solution after eluted 200 mL of  $Hg^{2+}$ .

It meant that the chelating adsorption of the affinity membrane reached a saturate state after eluting 200 mL of the solution and the dynamic adsorption capacity was  $403 \mu g/cm^2$ -membrane, which was much similar as the static adsorption capacity of  $398 \mu g/cm^2$ -membrane.

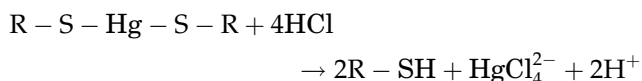




**Figure 14** The dynamic adsorption of PSF-SH affinity membrane.

The concentration of  $\text{Hg}^{2+}$  in the eluted solution decreased slightly after the eluted volume was larger than 300 mL, and the eluted solution was a little turbid, which maybe due to the precipitation of  $\text{Hg}^{2+}$  from the elution on the chelating membrane.

The PSF-SH affinity membrane was recycled by soaking in 250 mL of 0.1M dilute HCl solution for 6 h at room temperature and the concentration of  $\text{Hg}^{2+}$  in HCl was 30.4  $\mu\text{g}/\text{mL}$ . The recycled affinity membrane was used to remove  $\text{Hg}^{2+}$  and the dynamic adsorption capacity was 315  $\mu\text{g}/\text{cm}^2$ -membrane, which was a little lower than that of the brand new membrane. This showed that the PSF-SH affinity membrane can be easily and conveniently recycled in dilute HCl solution, which will play an important role in the utilization of such affinity membrane in the treatment of  $\text{Hg}^{2+}$  in the industrial waste-water. The possible mechanism for the recycled procedure is as follows:



## CONCLUSIONS

A homogeneous phase mercapto modified polybenzylsulfone (PSF-SH) plate affinity membrane with high chelating capacity for  $\text{Hg}^{2+}$  was prepared through the

reaction between the CMPSF matrix membrane and thiourea and then the alkaline hydrolysis. The results indicated that the chelating capacity of PSF-SH affinity membrane increased with increasing the mercapto loading, due to pores of membrane which had the larger accessible number of mercapto groups for chelating adsorption. The chelating capacity of PSF-SH membrane increased with increasing the reaction time, temperature, and concentration of thiourea for the thiourium reaction. The chelating capacity also increased with the adsorption temperature, the concentration of  $\text{Hg}(\text{II})$  in the introductory solution, and the adsorption time. The optimum pH for the adsorption of  $\text{Hg}(\text{II})$  is in the range of 4–5. The dynamic adsorption chelating capacity of the homogeneous PSF-SH phase plate affinity membrane for  $\text{Hg}^{2+}$  was much the same as that of the static adsorption chelating capacity. The PSF-SH affinity membrane can be regenerated easily and conveniently by soaking in dilute HCl solution with high chelating capacity.

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