

Preparation of Polysulfonebenzylthiourea-Reactive Ultrafiltration Plate Membranes and Their Rejection Properties for Heavy Toxic Metal Cations

Bing Wang, Fengyun Huangfu, Wei Liu

Key Laboratory of Hollow Fiber Membrane Material and Membrane Process (Ministry of Education),
School of Materials Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, China

Received 15 October 2007; accepted 19 January 2008

DOI 10.1002/app.28055

Published online 17 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The asymmetric membranes were prepared via phase inversion method, by using chloromethyl polysulfone as membrane materials, polyethylene glycol (PEG) as pore forming agent to improve the morphology and function of resultant membranes, *N,N*-dimethylacetamide as solvent, and water as the extraction solvent. Then the highly qualified polysulfonebenzylthiourea-reactive ultrafiltration plate membrane was prepared successively through the reactions between the chloromethyl polysulfone matrix membrane and thiourea. The thiourea-functionalized polysulfone plate reactive ultrafiltration membrane was used for the rejection of heavy toxic metal cations such as Cd^{2+} and Zn^{2+} through the coordination of the thiourea group and heavy toxic metal cations, in which the effects of the morphological and the structure of the

membrane on the rejection properties were investigated. The rejection conditions, including the concentration of heavy toxic metal cations, temperature and pH of the solution had significant effects on the rejection capacity of polysulfonebenzylthiourea-reactive ultrafiltration membrane. The reactive ultrafiltration membrane containing thiourea group can be conveniently recovered by dilute hydrochloric acid for coordination of heavy toxic metal cations, which would have wide application for the treatment of wastewater-containing heavy toxic metal cations. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 4014–4022, 2008

Key words: polysulfonebenzylthiourea; phase inversion; ultrafiltration membrane; heavy toxic metal cations; separation techniques

INTRODUCTION

Heavy toxic metal cations such as Cd^{2+} and Zn^{2+} can cause problems to people's health. The heavy toxic metal cations-containing industrial effluents that come from the plants that use or produce heavy toxic metal and heavy toxic metal compounds are the major resource of the heavy toxic metal pollution.¹ The reactive ultrafiltration membrane, which integrates the advantages of both reactive chromatography and modern membrane techniques, can be used to solve separation problems in a wide range of applications because its energy consumption is relatively low, it is simple to scale up, and its membrane properties can be kept under control easily.^{2–8} The reactive ultrafiltration membrane with definite micropores has reactive functional groups on its inner and outer surface as carrier of the reactive reagent. When the solution is filtered through the membrane, the target materials will quickly and effi-

ciently combine with the relevant functional groups of the reactive reagent. The materials captured on the reactive ultrafiltration membrane can be soon eluted when an eluent passes through the membrane.

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 $1050 \mu\text{g}/\text{cm}^2$ for mercury(II).⁹ In our previous work, we reported the synthesis of chloromethyl polysulfone from polysulfone by Friedel-Crafts reaction.¹⁰ Here, the homogeneous reactive ultrafiltration membrane with thiourea groups was obtained through the reaction between chloromethyl polysulfone matrix membrane and thiourea, and the rejection of heavy toxic metal cations were investigated.

EXPERIMENTAL

Materials

Dichloromethane, 2,2-dichloromethane, nitrobenzene, thiourea, and polyethylene glycol (PEG 600) were analytical grade and purchased from Tianjin Reagent Plant. Chloromethyl ether and ferriammonium sulfate were analytical grade and were purchased from Nan-

Correspondence to: B.Wang (bingwang666@yahoo.com.cn).

Contract grant sponsor: Natural Science Foundation of Tianjin; contract grant number: 05YFJMJC04200.

Journal of Applied Polymer Science, Vol. 108, 4014–4022 (2008)
© 2008 Wiley Periodicals, Inc.

kai University Chemical Plant. CdCl_2 and ZnCl_2 were purchased from Tianjin Chemical Reagent Plant as analytical grade. Sodium rhodanate was analytical grade and purchased from Tianjin Yaohua Chemical Plant.

Main apparatuses

XL30 ESEM (environmental scanning electron microscope) was made by PHILIPS. 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.

Synthesis of chloromethyl polysulfone

A given amount of dried polysulfone was dissolved in dichloromethane (or 1,2-dichloroethane) and the solution of anhydrous zinc chloride/chloromethyl ether was added dropwise. The reaction temperature was increased to 40°C slowly and the reaction was carried out at 40°C for 6 h. The solution was dropped into methanol slowly after the reaction system was cooled to room temperature. The chloromethyl polysulfone was precipitated from the system as lump and washed by hot distilled water repeatedly until no bubbles. The chloromethyl polysulfone was dried in vacuum oven at 60°C , and washed with distilled water for three times and dried in the vacuum oven at 50°C till constant weight.

Preparation of polysulfonebenzylthiourea-reactive ultrafiltration plate membrane

The matrix plate membranes were prepared by the phase inversion technology. The casting solution was formed after vacuum defoaming, using chloromethyl polysulfone as membrane materials, PEG as pore forming agent and DMAC as solvent with a certain ratio with heating to form a solution. The casting solution was poured onto a clear and smooth glass plate at predetermined temperature. The solution was cast into thin film using blade after the evaporation in the air for definite seconds and the glass plate was immersed in DMAC-water solution at a certain temperature to let it solidify into membrane. The matrix plate membranes were soaked in a thiourea of anhydrous ethanol solution and the reaction was carried out at 50°C for 8 h. The polysulfonebenzylthiourea plate reactive ultrafiltration membrane was afforded after taking the membrane stripe out of the solution and washed with distilled water repeatedly.

FTIR analysis of polysulfonebenzylthiourea-reactive ultrafiltration plate membrane

The polysulfonebenzylthiourea membranes were dried at $50\text{--}55^\circ\text{C}$ in vacuum oven. The dried mem-

brane 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 ultra-pure water was pumped from a 2000 mL of feed reservoir and returned 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 was calculated according to eq. (1):

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

where, V was the volume of transmitted liquid and t was the ultrafiltration time, and S was the effective surface area of the membrane.

Measurement of porosity

The porosity of membrane was determined by means of gravimetric method.¹¹ 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 . Then the wet membrane was dried in a vacuum oven till constant weight with the weight of dried membrane as W_d . The porosity of membrane Pr was calculated from eq. (2):

$$Pr = \frac{W_w - W_d}{S \cdot d \cdot \rho} \times 100\% \quad (2)$$

where, d was the average thickness of membrane and ρ was the density of glycerol, respectively.

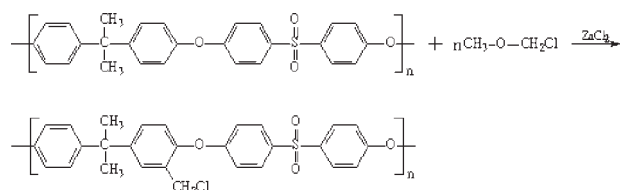
Measurement of membrane pore size

The membrane pore size was determined by means of filtering velocity method.¹¹ The membrane pore diameter r_f was calculated from eq. (3)

$$r_f = \sqrt{\frac{8 \times (2.90 - 1.75Pr) \cdot \mu \cdot L \cdot Q}{Pr \cdot \Delta P \cdot S}} \quad (3)$$

where, p_r was porosity, L was thickness of membrane, μ was viscosity of transmitted liquid, Q was flux, Δp was pressure and S was filtering area, respectively.

The ESEM characterization was performed on a coating film by ion-sputtering after the membrane



Scheme 1 The synthesis of chloromethyl polysulfone.

was frozen in liquid nitrogen and fasten on the sample table. The pore size and size distribution of the membrane was obtained from the observation of the morphological structure of the cross section of the matrix membrane with a XL30 ESEM

The determination of chloromethyl polysulfone chlorinity was performed by Woolhad method.¹¹

The concentration of Cd^{2+} and Zn^{2+} were determined with dithizone method.¹²

Rejection of polysulfonebenzylthiourea-reactive ultrafiltration plate membrane for Cd^{2+} and Zn^{2+}

The rejection of polysulfonebenzylthiourea-reactive ultrafiltration membrane for Cd^{2+} and Zn^{2+} were 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 rejection capacity of the membrane for Cd^{2+} and Zn^{2+} was calculated from eq. (4):

$$\Gamma = \frac{C_0 - C_t}{S} \quad (4)$$

where, C_0 is original concentration of Cd^{2+} and Zn^{2+} , C_t is the residual concentration of Cd^{2+} and Zn^{2+} after the Cd^{2+} and Zn^{2+} were through the membrane, and S was membrane area.

RESULTS AND DISCUSSION

Preparation of polysulfonebenzylthiourea-reactive ultrafiltration plate membrane

The chloromethyl polysulfone was afforded by Friedel-Crafts electrophilic substitution reaction under anhydrous conditions using polysulfone as starting material, dichloromethane as solvent, chloromethyl ether as chloromethyl reagent and anhydrous zinc chloride as catalyst. The specific reactions were as Scheme 1:

The reaction was carried out at 40°C for 5 h. It was observed that the amount of the catalyst had significant effect on the chloromethylation of polysulfone. The chlorinity of chloromethyl polysulfone increased considerably with the increase amount of zinc chloride. However, the reaction system would freeze if the amount of zinc chloride was in large

TABLE I
The Effect of the Concentration of Chloromethyl Polysulfone on the Properties of the Matrix Membrane

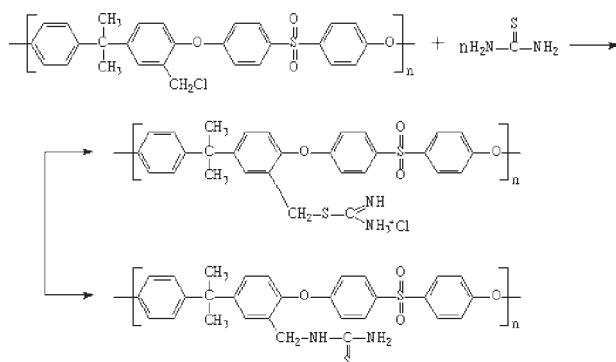
Chloromethyl polysulfone content (%)	Water flux ($\text{L}/\text{m}^2 \text{ h}$)	Pore diameter (nm)	Porosity (%)
10	64.2 ± 0.1	38.5 ± 0.2	61.3 ± 0.2
12	51.8 ± 0.2	31.2 ± 0.1	52.4 ± 0.1
14	45.3 ± 0.1	27.1 ± 0.1	48.4 ± 0.2
16	40.7 ± 0.2	23.2 ± 0.2	45.7 ± 0.1
18	37.6 ± 0.2	22.1 ± 0.1	43.2 ± 0.2
20	34.3 ± 0.1	20.6 ± 0.1	42.6 ± 0.2

excess. The chlorinity of chloromethyl polysulfone also increased with the increase amount of chloromethyl ether. The chloromethyl polysulfone matrix plate membranes were prepared via phase inversion method. The structure and property of membrane were determined not only by the nature of the membrane materials and membrane-forming process conditions but also by the thermodynamic conditions of casting solutions, such as concentration of polymer, the concentration of additive and temperature for casting solutions. Table I shows the relationship between chloromethyl polysulfone concentration and the properties of matrix membrane. It could be observed that water flux, pore size, and porosity of chloromethyl polysulfone matrix membrane all decreased significantly and the dense layer became more compact with increasing concentration of chloromethyl polysulfone in casting solution. Furthermore, as chloromethyl polysulfone concentration increased, the viscosity of casting solution increased, which caused to decrease the diffusion rate between solvent and coagulating agent and gradually to decrease the phase inversion rate and coagulating rate. Table II showed the effect of the concentration of the polymer additive PEG ($M_w = 600$) on matrix membrane structure. It could be observed that water flux, pore size, and porosity of matrix membrane all increased significantly with increase of the concentration of the polymer additive in casting solution.

The polysulfonebenzylthiourea-reactive ultrafiltration membrane was obtained through the reaction

TABLE II
The Effect of the Amount of Polymer PEG on the Properties of the Chloromethyl Polysulfone Matrix Membrane

PEG content (%)	Water flux ($\text{L}/\text{m}^2 \text{ h}$)	Pore diameter (nm)	Porosity (%)
0	41.2 ± 0.1	24.0 ± 0.2	46.3 ± 0.1
2	170.1 ± 0.2	34.8 ± 0.2	60.1 ± 0.2
4	180.4 ± 0.1	37.2 ± 0.1	61.3 ± 0.1
6	194.5 ± 0.2	38.4 ± 0.2	62.7 ± 0.3
8	201.1 ± 0.1	40.1 ± 0.2	65.7 ± 0.2
10	208.4 ± 0.2	42.1 ± 0.1	67.8 ± 0.1



Scheme 2 The synthesis of polysulfonebenzylthiourea.

between chloromethyl polysulfone matrix plate membrane and thiourea. The synthetic route was shown as in Scheme 2:

The polysulfonebenzylthiourea-reactive ultrafiltration membrane successively through the thiourea reaction to incorporate the thiourea groups were characterized with FTIR spectra as shown in Figure 1. The successful thiourea reaction was confirmed by the FTIR spectra in Figure 2(a,b) with complete disappearance of the peak at 1246 cm^{-1} corresponding to the stretching vibration of chloromethyl group for chloromethyl polysulfone matrix membrane and the presence of new peaks at 1402 cm^{-1} assigning to the vibration of C—S bond, 1640 cm^{-1} attributing to

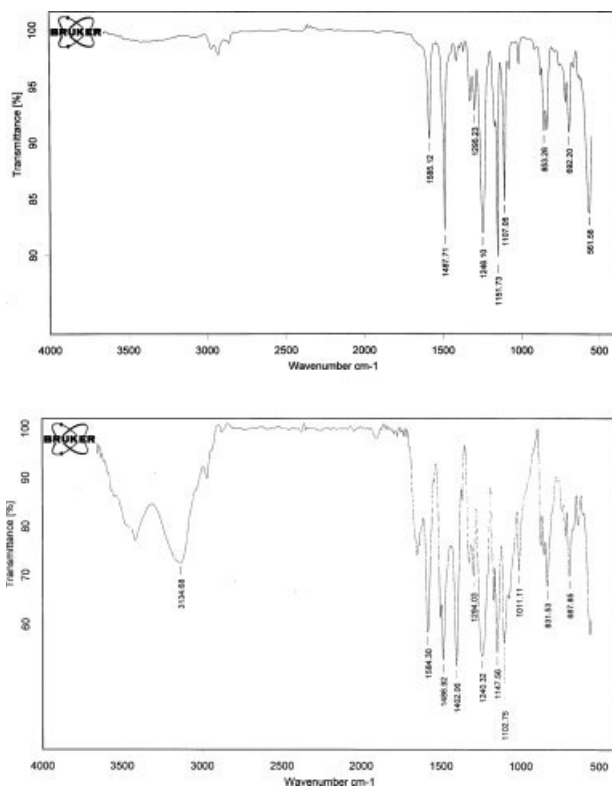


Figure 1 FTIR spectra of membrane. (a) Chloromethyl polysulfone; (b) Polysulfonebenzylthiourea.

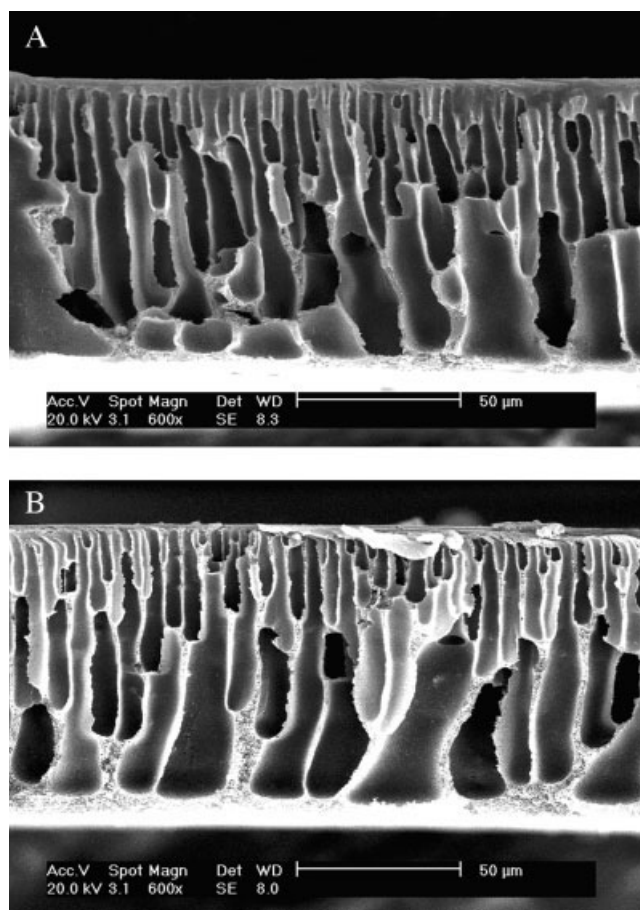


Figure 2 Scanning electron micrographs of the cross section of membranes with different concentration of PEG (M_w : 600). (a) PEG: 6%; (b) PEG: 4%.

the vibration of C=N, and the wide strong peak around 3134 cm^{-1} contributing to the NH_3^+ plus of the thiourea group on methyl(*iso*-thiourea) polysulfone plate (MTUPSF), respectively. In other words, the chloromethyl groups were quantitatively converted into the thiourea groups with estimation from the complete disappearance of peak at 1246 cm^{-1} of the chloromethyl group in the FTIR spectra.

Figure 2 was the ESEM of the cross section of the polysulfonebenzylthiourea-reactive ultrafiltration membrane with different concentration of PEG ($M_w = 600$). Figure 3 showed that the cross-section structure of the membrane changed from dense to loose gradually, the pore size of membrane increased considerably and the structure from compact to loose gradually while the amount of PEG increased. It was found from SEM micrograph of membrane that the pore size of the membrane increased, which was shown in Table II, with increase the concentration of polymer additive. This was attributed not only to the increase of pore size but also to the connection extent of the membrane pores. The formation process of micropore on the membrane was a liquid-liq-

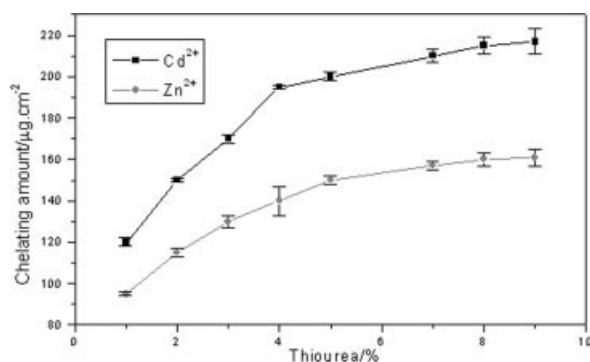


Figure 3 The effect of the loading of thiourea of polysulfonebenzylthiourea on the chelating capacity of polysulfonebenzylthiourea membrane.

uid phase inversion process. The structure of the membrane was mainly determined by the composition of the local field of the casting solution during the phase inversion. After the phase inversion of the casting solution, the rich phase of chloromethyl polysulfone was continuous and gelled, then solidified into a continuous membrane phase with micropores. When the solvent (DMAC) and the additive (PEG) scattering in the polymer as poor phase were washed away, the poor phase grew larger and larger and then intercrossed the micropores during casting. The prerequisite for the continuous growth of poor phase was that the vicinities could continuously provide solvent for poor phase before the solidification of the rich phase. In the casting system, when water was used as gel reagent, the diffusion rate of DMAC solvent towards water was faster than that of water to casting solution. The further the casting solution composition away from cloud point composition, the later the phase inversion occurred and the more the solvent (DMAC) overflowed. When the concentration of the additive PEG was low, the composition of the casting solution was far away from the cloud point and the overflowing amount of solvent was large. The chloromethyl polysulfone concentration was high before phase inversion to form a dense top layer structure and small pore size. The dense layers prevented the solvent DMAC from further interchanging with water, which was good for the formation of micropore with finger shape. With increase of the additive PEG concentration in the casting solution, the composition of the solution was approaching the cloud point. The rate of phase inversion increased and the solvent overflowed less before the phase inversion. The excessive amount of solvent was good for poor phase growth. The connections among membrane micropores increased to form a loose top layer. The hindrance of loose top layer to next layers decreased and formed an intercrossed finger shape structure. Although there was little change for pore sizes, the finger shape connections

were good, osmosis resistance decreased and flux of the membrane increased obviously.

Effect of the loading of thiourea groups on chelating capacity of polysulfonebenzylthiourea membranes

The chloromethyl polysulfone matrix membranes with different chlorinity were prepared with 4% PEG ($M_w = 600$) as pore forming agent and the entire solid content of 15% in the casting solution. Then the polysulfonebenzylthiourea-reactive ultrafiltration membrane with different amount of thiourea were prepared by the reaction between chloromethyl polysulfone matrix membrane and thiourea with the total conversion higher than 90% from chloromethyl group. The chelating capacity of polysulfonebenzylthiourea membrane for Cd^{2+} and Zn^{2+} were determined by soaking the membrane in 500 $\mu\text{g/mL}$ Cd^{2+} and Zn^{2+} solution at pH 2–5 for 24 h and the results were shown as in Figure 3. The results indicated that the chelating capacity of the polysulfonebenzylthiourea membranes increased rapidly with the increasing thiourea from 0 to 1%, and then increased considerably with the thiourea increasing further till 8%. The chelating capacity for Cd^{2+} and Zn^{2+} on polysulfonebenzylthiourea membranes increased with higher loading of thiourea groups. The polysulfonebenzylthiourea membrane with high thiourea loading (from the chlorinity of 5.4%) in the present work was utilized for investigation, as the chlorinity of chloromethyl polysulfone matrix material had little influence on the formation of chloromethyl polysulfone matrix membrane. These results further proved the successful incorporation of thiourea groups on the porous polymer membrane successively through the thiourea reaction.

Effect of the thiouriuming conditions on chelating capacity of polysulfonebenzylthiourea membranes

The chloromethyl polysulfone matrix membranes were soaked in saturate solution of thiourea in anhydrous ethanol for 5 h at different temperatures, i.e., 20, 30, 40, and 50°C to afford the polysulfonebenzylthiourea membranes. The effect of the thiouriuming temperature on the chelating properties of polysulfonebenzylthiourea membranes was shown in Figure 4. The results indicated that the chelating capacity increased considerable with the increasing reaction temperature, which was due to the higher conversion of methyl chloride to the methyl thiourium chloride under higher reaction temperature.

The chloromethyl polysulfone matrix membranes were soaked in saturate solution of thiourea in anhydrous ethanol for different time at room temperature to afford the polysulfonebenzylthiourea membranes. The effect of the thiouriuming time on the capacity of the polysulfonebenzylthiourea membrane was

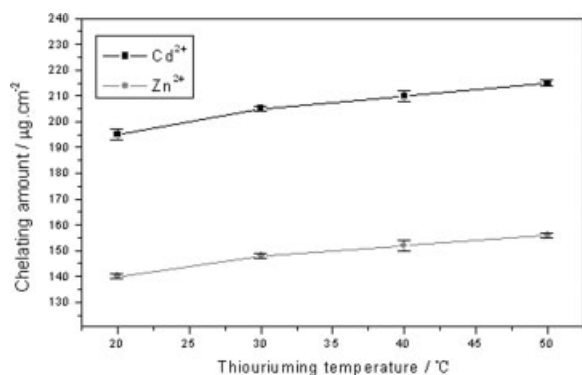


Figure 4 The effect of the thiouriuming temperature on the chelating properties of polysulfonebenzylthiourea membranes.

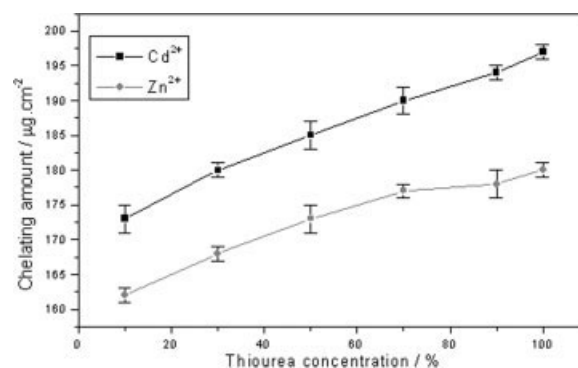


Figure 6 The effect of the thiourea concentration on the capacity of polysulfonebenzylthiourea membrane.

shown in Figure 5. The capacity of polysulfonebenzylthiourea with the pore size of 40 nm for Cd²⁺ and Zn²⁺ increased rapidly with the increasing thiouriuming time till 8 h and then leveled off at 12 h till a constant value. While the pore size was 35 nm, the capacity increased rapidly with the increasing thiouriuming time till 12 h and then leveled off at 16 h till a constant value. The results showed that the thiouriuming reaction of the chloromethyl polysulfone matrix membrane with bigger pore size was much faster than that of the membrane with the smaller size.

The effect of the thiourea concentration on the capacity of polysulfonebenzylthiourea membrane was shown in Figure 6. 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 saturated solution, respectively.

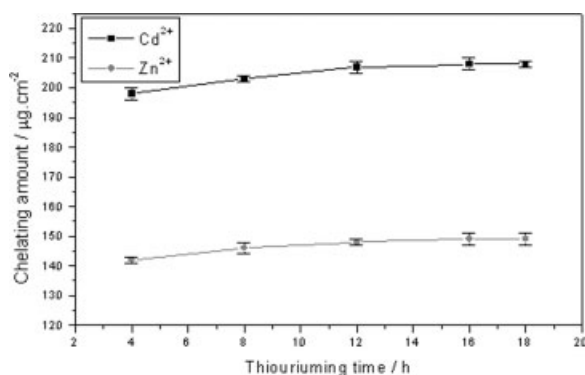


Figure 5 The effect of the thiouriuming time on the capacity of the polysulfonebenzylthiourea membrane.

Effects of the porosity and pore size on chelating capacity of polysulfonebenzylthiourea membranes

The chloromethyl polysulfone matrix membranes with different porosity and pore size were prepared by utilization of either different amount (2%, 4%, 6%, 8%) of PEG ($M_w = 600$) as the additive, while the total solid content in the casting solution was kept at 15%. The effects of the pore size and porosity on the chelating capacity of the polysulfonebenzylthiourea membranes for Cd²⁺ and Zn²⁺ were shown in Figure 7 and Figure 8, respectively. The results indicated that the chelating capacity of the polysulfonebenzylthiourea membranes increased both with the increasing pore size and porosity, which was originated either from the different amount of PEG additive. With bigger size and higher porosity, the area of the porous polymer polysulfonebenzylthiourea membrane increased and the fraction of the accessible thiourea groups on the wall of the membrane increased. In this way, the chelating capacity of the polysulfonebenzylthiourea membrane increased with larger pore size and porosity of the membrane.

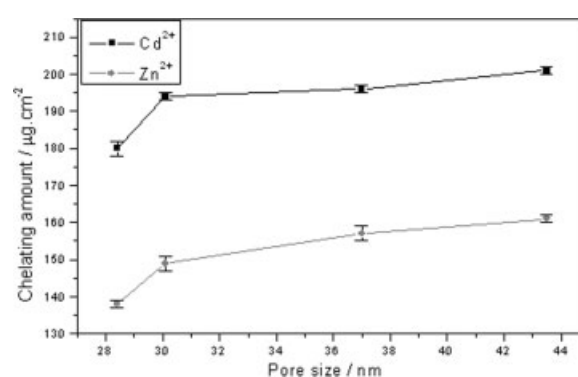


Figure 7 The effect of the pore size on the chelating capacity of polysulfonebenzylthiourea membrane.

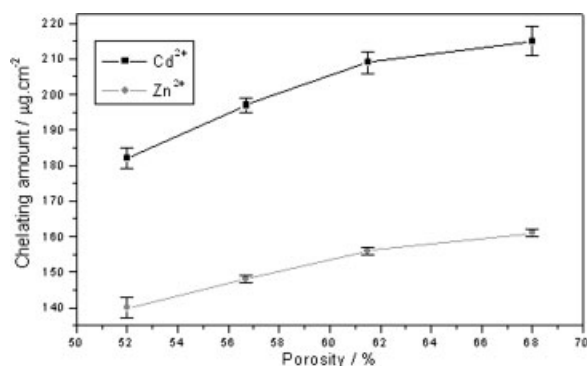


Figure 8 The effect of the porosity on the chelating capacity of polysulfonebenzylthiourea membrane.

Effect of pH of the Cd²⁺ and Zn²⁺ solution on chelating capacity of the polysulfonebenzylthiourea membranes

Figure 9 showed the effect of the pH of Cd²⁺ and Zn²⁺ solution on the chelating capacity of the polysulfonebenzylthiourea membranes. The results indicated that the capacity of the membrane was much high in the range of pH 2–5 and the capacity increased slightly with the increasing pH of Cd²⁺ and Zn²⁺ solution. However, the pH of the solution should be in acidic state because Cd²⁺ and Zn²⁺ react with hydroxide anion to precipitate from the solution under basic environment, which would cause it impossible to selective separation Cd²⁺ and Zn²⁺ from the pollution with the polysulfonebenzylthiourea membrane. Naturally, the low pH solution was not favorable for such chelating adsorption.

Effect of temperature on the chelating capacity of polysulfonebenzylthiourea membranes

Figure 10 showed the effect of the chelating temperature on the chelating capacity of the polysulfonebenzylthiourea membrane. The results indicated that the capacity increased slightly with increasing chelating temperature. The processes for the chelating adsorp-

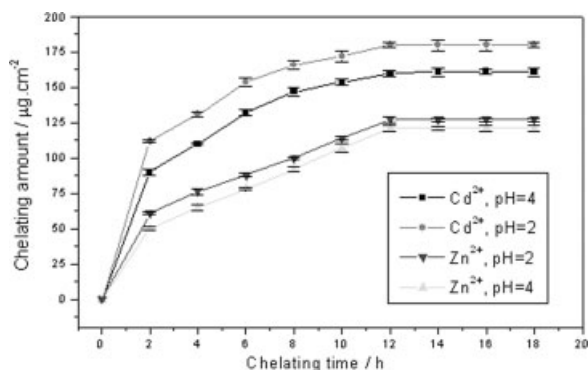


Figure 9 The effect of the pH of Cd²⁺ and Zn²⁺ solution on the chelating capacity of the polysulfonebenzylthiourea membrane.

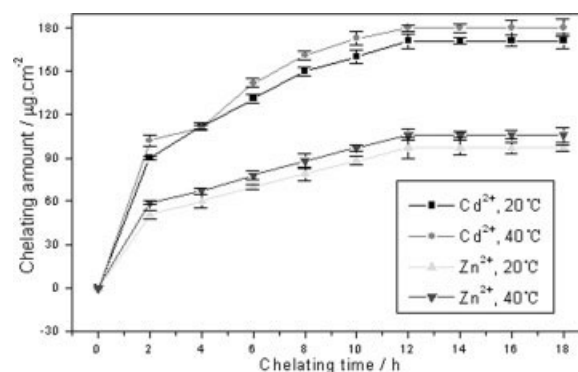


Figure 10 The effect of the chelating temperature on the chelating capacity of the polysulfonebenzylthiourea membrane.

tion of the polysulfonebenzylthiourea membrane for the metal cations included the following three steps: (i) The diffusion of the metal cations to the surface of the membrane; (ii) The diffusion of the metal cations in the pore of the membrane; (iii) Chemical adsorption through the ion-exchanges between the metal cations and the chelating groups on the membrane. The high temperature was good not only to the diffusion of the metal cations but also for the dissociation of the thiourea 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 polysulfonebenzylthiourea membrane and Cd²⁺ and Zn²⁺ with a little higher temperature.

Effect of concentration of Cd²⁺ and Zn²⁺ on the chelating properties of polysulfonebenzylthiourea membranes

The polysulfonebenzylthiourea membranes were soaked in 400, 800, 1000 μg/mL of Cd²⁺ and Zn²⁺ solution at pH 2–3 to determine the chelating capacity. The relationship between the chelating amount of the polysulfonebenzylthiourea membrane and the adsorption time was shown in Figure 11. The results indicated that the chelating amount increased rapidly in the first 3 h and then leveled off with the increasing adsorption further till a saturate value after 16 h for all the four samples. The saturate adsorption amount of the polysulfonebenzylthiourea membrane increased with the increasing concentration of Cd²⁺ and Zn²⁺ in the solution. The adsorption properties of the polysulfonebenzylthiourea 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.

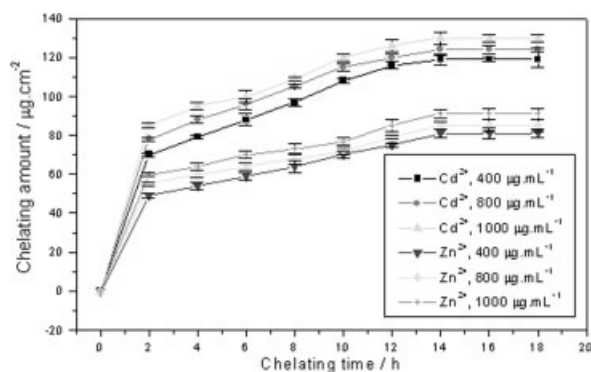


Figure 11 The relationship between the chelating amount of the polysulfonebenzylthiourea membrane and the adsorption time.

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

To determine the competitive coordination effect of the ligand on the chelating capacity, the chelating capacity of polysulfonebenzylthiourea 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 polysulfonebenzylthiourea membrane decreased significantly with the increasing concentration of EDTA in the solution. It is well known that EDTA has a strong chelating ability with Cd^{2+} and Zn^{2+} , which is much stronger than that between polysulfonebenzylthiourea membrane and Cd^{2+} and Zn^{2+} . Such competitive coordination prevented polysulfonebenzylthiourea chelating with Cd^{2+} and Zn^{2+} to decrease the capacity of the polysulfonebenzylthiourea membrane for Cd^{2+} and Zn^{2+} .

The rejection and the recycle of the polysulfonebenzylthiourea membrane

The rejection of polysulfonebenzylthiourea membrane was determined from the relationship between

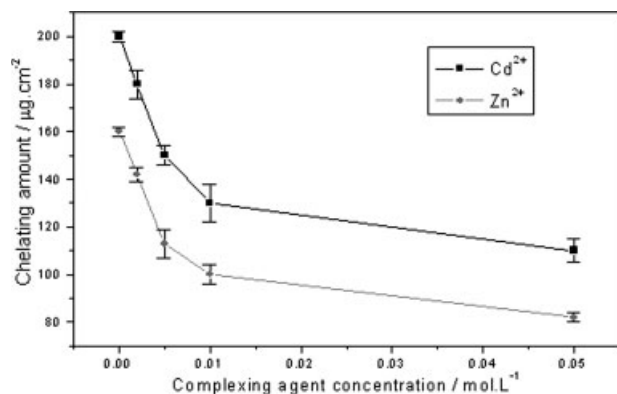


Figure 12 The chelating capacity of polysulfonebenzylthiourea membrane which was determined in the presence of reagent EDTA in the introductory solution.

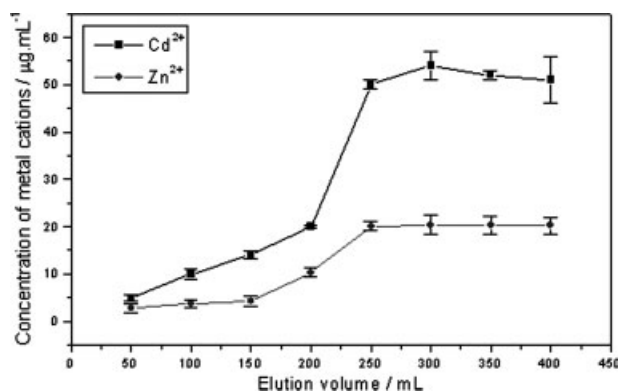


Figure 13 The dynamic rejection of polysulfonebenzylthiourea membrane.

the concentration of Cd^{2+} and Zn^{2+} in the eluted solution and the volume eluted through the membrane under 0.1 MPa with 100 $\mu\text{g/mL}$ of Cd^{2+} and Zn^{2+} as the elution, which was shown in Figure 13. The results indicated that the concentrations of Cd^{2+} and Zn^{2+} were below 30 $\mu\text{g/mL}$ in the initial 150 mL of eluted solution and then increased abruptly till the same level as the starting solution after eluted 200 mL and 230 mL of Cd^{2+} and Zn^{2+} . It meant that the chelating adsorption of the polysulfonebenzylthiourea membrane reached a saturate state after eluted 200–230 mL of the solution and the rejection capacity were 420 $\mu\text{g/cm}^2\text{-memb}$ for Cd^{2+} and 403 $\mu\text{g/cm}^2\text{-memb}$ for Zn^{2+} , which were much similar as the static adsorption capacity of 417 $\mu\text{g/cm}^2\text{-memb}$. for Cd^{2+} and 400 $\mu\text{g/cm}^2\text{-memb}$ for Zn^{2+} . The concentration of Cd^{2+} and Zn^{2+} in the eluted solution decreased slightly after the eluted volume larger than 300–310 mL and the eluted solution was a little turbid maybe due to the precipitation of Cd^{2+} and Zn^{2+} from the elution on the chelating membrane. The polysulfonebenzylthiourea membrane was recycled by soaking in 250 mL of 0.1M dilute HCl solution for 6–8 h at room temperature and the concentration of Cd^{2+} and Zn^{2+} in HCl was 30–32 $\mu\text{g/mL}$. The recycled polysulfonebenzylthiourea membrane was used to remove Cd^{2+} and Zn^{2+} and the rejection capacity was 310–315 $\mu\text{g/cm}^2\text{-memb}$, which was little smaller than that of the brand new membrane. This showed that the polysulfonebenzylthiourea membrane can be easily and conveniently recycled in dilute HCl solution, which will play an important roll for the utilization of such polysulfonebenzylthiourea plate reactive ultrafiltration membrane in the treatment of Cd^{2+} and Zn^{2+} in the industrial wasted-water.

CONCLUSIONS

The highly qualified polysulfonebenzylthiourea-reactive ultrafiltration membranes with high rejection

capacity for heavy toxic metal cations Cd^{2+} and Zn^{2+} were prepared through the reaction between the chloromethyl polysulfone matrix membrane and thiourea. The results indicated that the rejection capacity of polysulfonebenzylthiourea membrane with increasing the thiourea loading, the pore size and porosity due to the larger accessible number of thiourea groups for chelating adsorption. The chelating capacity of polysulfonebenzylthiourea membrane increased with increasing the reaction time, temperature, concentration of thiourea for the thiourium reaction. The chelating capacity also increased with the adsorption temperature, the concentration of Cd^{2+} and Zn^{2+} in the introductory solution and the adsorption time. The optimum pH for the adsorption of Cd^{2+} and Zn^{2+} is in the range of 4–5. The dynamic rejection capacity of the polysulfonebenzylthiourea-reactive ultrafiltration membrane for Cd^{2+} and Zn^{2+} was much the same as that of the static adsorption chelating capacity. The polysulfonebenzylthiourea-reactive ultrafiltration membrane can be

easily and conveniently by soaking in dilute HCl solution with high chelating capacity.

References

1. Volchek, K.; Krentsel, E.; Zhilin, Y.; Shtereva, D. *J Membr Sci* 1993, 79, 253.
2. Yamada, K.; Nagano, R.; Hirata, M. *J Appl Polym Sci* 2006, 99, 1895.
3. Ahmed, S. R.; Kelly, A. B.; Barbari, T. A. *J Membrane Sci* 2006, 280, 553.
4. Ruckenstein, E.; Guo, W. *J Membrane Sci* 2001, 193, 131.
5. Liu, J.; Chen, X.; Shao, Z.; Zhou, P. *J Appl Polym Sci* 2003, 90, 1108.
6. Kubota, N.; Nakagawa, Y.; Eguchi, Y. *J Appl Polym Sci* 1996, 62, 1153.
8. Yang, L.; Hsiao, W. W.; Chen, P. *J Membrane Sci* 2002, 197, 185.
9. Wang, B.; Cui, Y.; Du, Q.; Pei, G. *J Appl Polym Sci* 2003, 87, 908.
10. Wang, B.; Huang, W. *J Appl Polym Sci* 2005, 93, 990.
11. Gao, Y. X.; Ye, L. B. *Fundamental of Membrane Separation Technology*; Chinese Science Press: Beijing, 1989; p 173.
12. Marczenko, Z. *Spectrophotometric Determination of Elements*; Geologic Press: Beijing, 1983, p 303 (in Chinese).