Preparation of Polysulfone Hollow Fiber Affinity Membrane Modified with Mercapto and Its Recovery Properties. II. Preparation of PSF-SH Hollow Fiber Affinity Membrane for Recovery of Hg^{2+}

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ABSTRACT: A high qualified polysulfone hollow fiber affinity membrane modified with mercapto as chelating groups was prepared by phase inversion technology using chlormethyl polysulfone (CMPSF) as membrane matrix materials, through the reaction between thiourea and CMPSF hollow fiber matrix membrane to afford the methyl isothiourium polysulfone and was then alkaline hydrolyzed. The adsorption isotherms of the hollow fiber affinity membrane chromatography for Hg^{2+} were determined, and the effects of mobile phase conditions and the operating parameters on removal performance of the hollow fiber affinity membrane chromatography for Hg^{2+} were also investigated. The experimental results showed that adsorption isotherms of Hg^{2+} could be described by the Langmuir isotherm. Addition of NaCl into feed solution for the increase of ionic strength was harmful for the removal of Hg^{2+}. The recovery of Hg^{2+} decreased at low pH and the optimum range of pH was from 5.0 to 7.0. The feed concentration had a remote effect on recovery of Hg^{2+} at the specified loading amount of Hg^{2+}, and the Hg^{2+} could be removed from different concentration feed solution by the hollow fiber affinity membrane chromatography. The increase of feed flow rate led to slight decrease of recovery of Hg^{2+} at the specified loading amount of Hg^{2+}. The hollow fiber affinity membrane chromatography could be operated at height feed flow rate and a large scale removal of Hg^{2+} could be realized. With the increase of load amount, Hg^{2+} recovery decreased, but the saturation degree of hollow fiber affinity membrane chromatography increased. According to required recovery of Hg^{2+} and the saturation degree of membrane chromatography, the optimum loading amount of Hg^{2+} should be selected in the actual removal of Hg^{2+}. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4795–4803, 2006

Key words: adsorption; membranes; matrix; fibers; separation technique

INTRODUCTION

The affinity membrane chromatography is a technique for the purification and separation of the biomacromolecule that was developed in recent decade.[1–6] On one hand, it overcomes the limitation of the diffusion of the microballoon stuffing in the axial direction in the traditional column chromatography, and mainly purifies and separates the biomacromolecule rapidly by the convective mass transfer mode to boost the activity yield; on the other hand, this technique simplifies the equipments and the purification steps, cuts the cost, and also the high purified objective outcome could be obtained through only one affinity purification step besides the separation of a large scale is easy to come true. At present, the study on the separation of the organic molecule and the metal ion is not much, and still less on the phase of the plate affinity purification membrane chromatography. Many chelating stationary phases with functional group for ion exchange could be used to separate and enrich the precious metallic ions, but little could be used to carry on the efficient chelating ion chromatography separation. The reason is that the reaction rate of some chelating exchanges is so slow that it cannot meet the needs in the separation process. The mercapto-chelating group has favorable chelating adsorbability and high selectivity for Hg^{2+}; at the same time, the mercapto chelates of Hg^{2+} will dissociate under the action of HCl. In our previous article,[7] the high quality heterogeneous polysulfone affinity plate filter membranes with chelating groups were prepared by phase separation

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by using blends of the chelating resin and polysulfone. Then, PSF was used as the starting materials to synthesize chloromethyl polysulfone (CMPSF) with Friedel-Crafts reaction and converted CMPSF into membrane using phase inversion technology.[8] The CMPSF matrix membrane reacted with sulfocarbamide and was then hydrolyzed under alkaline conditions to afford the mercapto-modified polysulfone as homogeneous chelating affinity plate membrane and its adsorption properties for Hg^{2+} were determined. Meanwhile, we have prepared the CMPSF hollow fiber membrane, which could be utilized as reactive matrix membrane materials of chelating hollow fiber affinity membrane modified with mercapto, based on the chelating plate membrane. In this study, it's the first time that the chelating hollow fiber affinity membrane chromatography was prepared by the chemical modification to link the mercapto chelating group with the CMPSF hollow fiber membrane, which was used as matrix, and the removal of Hg^{2+} behavior of the membrane chromatography was also investigated.

EXPERIMENTAL

Materials and reagents

Dichloromethane, 2,2-dichloromethane, nitrobenzene, thiourea, and polyethylene glycol (PEG) were analytical grade and were purchased from Tianjin Reagent Plant (Tianjin, China). Chloromethyl ether and ferriammonium sulfate were analytical grade and were purchased from Nankai University Chemical Plant (Tianjin, China). Sodium rhodanate and sodium hydroxide were analytical grade and were purchased from Tianjin Yaohua Chemical Plant.

Main apparatus and equipment

The retention measurement apparatus of membrane was made by Tianjin Polytechnic University, China.

Synthesis of chloromethyl polysulfone

A given amount of dried PSF was dissolved in dichloromethane (or 1,2-dichloroethane) and the solution of anhydrous zinc chloride/chloromethyl ether was added dropwise. The reaction temperature was slowly increased to 40°C 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. CMPSF was precipitated from the system as lump and washed by hot distilled water repeatedly until no bubbles appeared. The rough chloromethyl polysulfone (CMPSF) was dried in vacuum oven between 60 and 70°C. Then, the rough CMPSF was sheared into small pieces and dissolved in DMAC. The solution was poured into the distilled water of 70–80°C with stirring to get the white stripe or floc precipitate. The refined CMPSF was filtered and washed with distilled water for three times and dried in the vacuum oven at 60–70°C till constant weight was reached.

Preparation of the CMPSF hollow fiber matrix membrane

The dry–wet spinning method was adopted to prepare the hollow fiber matrix membrane in the spinning equipment. The CMPSF, the solvent (DMAC), and additives were blended to a scale, were stirred at given temperature until they were totally dissolved, were made to stand still, and then used. The spinning casting solution was put into the storage tank and deaerated under negative pressure. The high pressure nitrogen as the pressure source to push out the CMPSF casting solution had been measured from the spinning head; at the same time, the core liquid went from the central cavity of the spinning head into the hollow fiber cavity as its supporter and inner coagulum medium under the pressure of head tank. Lastly, the CMPSF spinning dope went away from the spinning head, passing the air clearance between the spinning head and coagulating bath tank, into the coagulating bath tank; when it had been coagulated into mold completely, by hot drawing and heat setting treatment, the hollow fiber matrix membrane would be prepared. The CMPSF hollow fiber matrix membrane should be preserved in hygrometric state.

Preparation of polysulfone hollow fiber affinity membrane modified with mercapto

The CMPSF hollow fiber membrane 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) hollow fiber membrane was afforded after taking the membrane stripe out of the solution and washed 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 afford polysulfone modified with mercapto. The hydrolyzed stripe was washed with distilled water till the pH of the filtrate reached 7 and then potched with 0.05 mol/L of hydrochloride solution twice to afford the homogeneous polysulfone hollow fiber affinity membrane modified with mercapto group (PSF-SH). The obtained PSF-SH hollow fiber affinity membrane was preserved in the wet state before utilization.

Quantity measurement of Hg^{2+}

The concentration of Hg^{2+} was determined with dithizone method.[9]

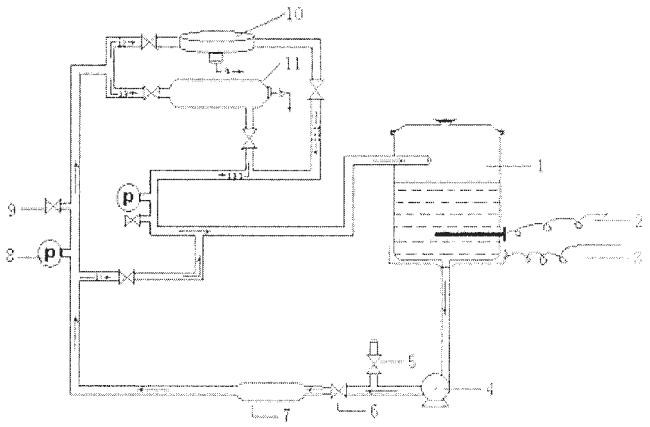

Figure 1 Schematic diagram of Hg^{2+} removing measurement apparatus of hollow fiber affinity membrane chromatography (1) impounding reservoir, (2) heating bar, (3) thermal barrier, (4) recirculating pump, (5) outlet, (6) shutoff valve, (7) buffer vessel, (8) pressure gauge (9) regulating valve, (10) plate module, and (11) hollow fiber module.

Assemble of the modules of polysulfone hollow fiber affinity membrane modified with mercapto

To produce polysulfone hollow fiber affinity membrane filter modified with mercapto, the hollow fiber membrane was cut into 19-cm length pieces, these pieces were put together into bundling, invaginate one end of the bundle into a nylon sleeve whose external diameter is 10 mm and length is 30 mm while the bundle basseted 20 mm, cast the ringed section of the hollow fiber membrane nylon tube with the epoxy resin and curing agent with ratio of 4 : 1, seal the other end, and wait till it was cured. The membrane chromatography was used in which this hollow fiber membrane filter was put into the stainless steel sleeve whose shell pass is $V = 31.60$ (mL) in the experimental apparatus of the hollow fiber membrane chromatography for the removal of Hg^{2+}.

Removal of polysulfone hollow fiber affinity membrane modified with mercapto for Hg^{2+} in mobile phase

The experiment adopted the Hg^{2+}-removal experimental apparatus of the hollow fiber membrane chromatography, which was made by Tianjin Polytechnic University. Figure 1 is the schematic diagram of Hg^{2+} removing measurement apparatus of hollow fiber affinity membrane chromatography. The peristaltic pump extruded the solution into the hollow fiber affinity chromatography. The solution went through the pores of membrane chromatography by the external pressure mode and flowed out from the end of the hollow fiber membrane module that was not sealed, and then the permeated liquid was collected by a collector. The properties of the membrane can be described by the adsorption capacity of the membrane chromatography for Hg^{2+}, which was calculated from eq. (1):

$$\Gamma = (C_0 - C_t)/S \quad (1)$$

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

RESULTS AND DISCUSSION

Optimal process to prepare polysulfone hollow fiber affinity membrane chromatography modified with mercapto

The synthesis of CMPSF and preparation of polysulfone hollow fiber matrix membrane were reported in detail in our previous work.[10] The polysulfone hollow fiber affinity membrane chromatography modified with mercapto was prepared by the thiourea reaction of the CMPSF hollow fiber matrix membrane and hydrolyzed with heat under the alkaline condition. The spinning of the CMPSF hollow fiber matrix membrane with good performances is the key to prepare the chelating hollow fiber affinity membrane chromatography. In the spinning process of the CMPSF hollow fiber matrix membrane, the thickness of the fiber membrane could be controlled by the change of the reeling rate. When other conditions were kept constant, thinner hollow fiber matrix membrane can be obtained through the increase of the reeling velocity, and the membrane wall was thinner with tiny compact layer on the surface; however, the results would be reverse if the reeling velocity decreased. It is a necessary technical process to control the reeling velocity in the spinning process. After trial and error, the results showed that the velocity controlled in 20–40 m/min was appropriate. The spinning temperature is referred to the temperature at which the spinning dope went off the spinning head. The temperature of the spinning dope should match with other qualifications in the spinning process of the hollow fiber membrane. The viscosity of the spinning dope varied with the change of the contents of the additive PEG and CMPSF. Therefore, the temperature of the spinning dope changed as well. In general, the higher the viscosity of the spinning dope, the higher is the spinning temperature. If the temperature was too high, the configuration of the sponging would be not good enough, and if the temperature was too low, the mobility of the spinning dope was relatively poor and the induction to the pressure was relatively blunt. To increase the mobility of the spinning dope through the increase of the pressure blindly would cause troubles in matching other conditions in the spinning. Thereby,

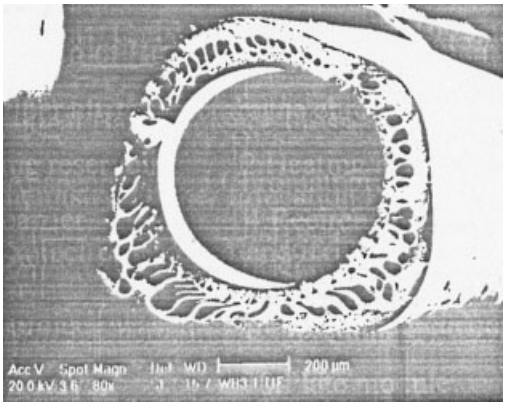

Figure 2 The ESEM of the cross section of the CMPSF hollow fiber matrix membrane.

the spinning temperature was fixed relative for the special composition of the spinning casting dope. The spinning temperature of the CMPSF hollow fiber membrane was generally controlled between 20 and 50°C. The pressure applied on the raw solution should be corresponded with the reeling velocity and the temperature of the spinning dope in the spinning process. The hollow fiber membrane was easy off center when the temperature of the raw solution was lower and the pressure was higher. The ESEM photograph is shown in Figure 2. Because of the difference of the thickness of the hollow fiber wall, the decentralized hollow fiber membrane was breached at the thin wall point for the yield stress under the effect of the external pressure and that appeared as the bearing capacity decreased and the use of the membrane was affected. The core liquid could not only provide the internal support for a small section of the hollow fiber membrane structure that just off the spinning head but also control the internal diameter of the hollow fiber membrane, and also could change the composition of the wall of the hollow fiber membrane that extruded from the porose area. As the matrix membrane of the chelating hollow fiber membrane chromatography, it should be avoided from the densification of the surface layer of the hollow fiber membrane in spinning process so as to cut down the fluid permeating resistance, increase the flux and decrease the operation pressure. The coagulating bath at lower temperature had some effect on the skin layer of the as formed hollow fiber membrane. When the as formed fiber with some mobility went into the coagulating bath, the closer micelle could be froze at its point for the low temperature of the coagulating bath, and prevent the further densification of the hollow fiber membrane before the skin layer reached its maximum density. In this way, the distances between micelles were relatively long, and so the resistance was little when the liquid flew through. If the hollow fiber was put into the coagulating with high temperature, the distances between the micelles were shorter and the skin layers got densified. The thickness of the compact layer of the membrane had a close relationship with the liquid permeating; if the compact layer was thicker, the flux was less, and if the compact layer was thinner, the flux was more. The thickness of the compact layer has relationship with the vaporization distance. The experiment proved that the longer the vaporization distance, the thicker is the compact layer, and if the vaporization distance was less, the compact layer was thinner. In the spinning process of the CMPSF hollow fiber, the vaporization distance is normally between 100 and 400 mm. The polysulfone hollow fiber affinity membrane chromatography modified with mercapto was prepared by the thiourea reaction of the CMPSF hollow fiber matrix membrane and hydrolyzed with heat under the alkaline condition. In the study of the homogeneous phase polysulfone plate affinity membrane chromatography modified with mercapto, it was found that the properties of the CMPSF matrix membrane such as the chloric content of the CMPSF, the pore size, and the porosity of the CMPSF plate membrane had a large effect on the chelating amount of the CMPSF plate membrane chromatography; the conditions such as the temperature, time, and concentration of the thiourea also had some effect on the chelating amount of the CMPSF plate membrane chromatograph. The hydrolytic temperature of the thiourea membrane had a visible effect on the chelating amount of the CMPSF plate membrane chromatography under the alkaline condition.[10] The experiment showed that the hydrolytic temperature was appropriate at about 80°C. In the preparation of the hollow fiber affinity membrane chromatography, first the appropriate chloric content of the CMPSF should be considered. The larger the chloric content, the more is the mercapto groups on the hollow fiber affinity membrane chromatography after the thiourea and hydrolysis, but too high chloric content was unfavorable for the spinning of the CMPSF hollow fiber. The experiment showed that the chloric content was appropriate from 7 to 10%. To make the hollow fiber affinity membrane chromatography have a good mechanical property and chelating affinity property, the reaction conditions should be as genial as possible and the reaction time should be as shorter as possible; and the hollow fiber affinity membrane chromatography modified with mercapto should be preserved in hygrometric state to pretend the contraction of the membrane chromatography.

Isothermal adsorption equation of the polysulfone hollow fiber affinity membrane modified with mercapto for Hg^{2+}

The Hg^{2+}adsorption of the chelating affinity chromatography is a dynamic reversible process. The isother-

mal adsorption is an important character of the adsorption system. The adsorption isotherm is the relationship between the solution equilibrium concentration and the equilibrium adsorptive quantity of the membrane chromatography after the adsorption equilibrium. The adsorption isotherm is the direct reflection of the adsorption property of the affinity membrane chromatography. The adsorption isotherm can be determined at a static equilibrium condition or at a dynamic equilibrium condition. In this study, the dynamic adsorption isotherm of the affinity membrane chromatography was determined to reflect the practical process of the Hg^{2+} adsorption of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto. The measuring method with the external pressure is given as follows: the raw material solution of given concentration was extruded into the hollow fiber affinity membrane chromatography by the peristaltic pump, and the Hg^{2+} in solution was absorbed by the mercapto chelating groups of the hollow fiber affinity membrane chromatography. When the Hg^{2+} concentration at the outlet of the hollow fiber affinity membrane chromatography did not vary with time, the Hg^{2+} adsorption of the affinity membrane chromatography was saturated to reach to the balance, and then the Hg^{2+} adsorbed was dissociated by a given concentration of HCl solution. The raw material concentration and the quality of Hg^{2+} dissociated were as the equilibrium concentration of the solution and the equilibrium adsorption quantity of the membrane chromatography, respectively. The dynamic adsorption experiment was carried out with a series of concentrations of the Hg^{2+} solution at room temperature and the isothermal adsorption curve of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto was obtained by plotting the equilibrium adsorption quantity versus equilibrium concentration of the solution (see Fig. 3). For further investing the isothermal adsorption of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto, the isothermal adsorption equation could be set up from the material structure and the basic principle of the chemical equilibrium. Supposing there are N chelating adsorption points on the surface of the chelating hollow fiber affinity membrane chromatography, and these points are distributed uniformly, every adsorption point may be for nothing or adsorb a metal ion Hg^{2+} (that is the single molecule adsorption hypothesis), among them there are N_A adsorb the metal ion Hg^{2+}. Supposing the partition function of each metal ion is $q_0(T)$, from the knowledge of the quantum chemistry, the main partition function[11] is given as

$$Q = \frac{N!}{N_A!(N - N_A)} q_0^N(T) \tag{2}$$

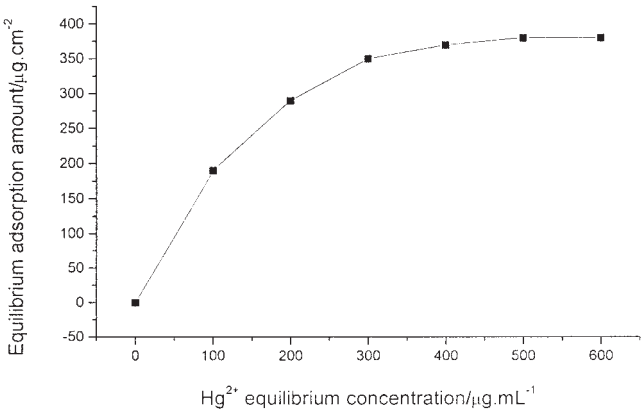

Figure 3 The adsorption isothermal curve of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; feed solution Hg^{2+} concentration, 400 μg/mL; operation flow speed, 3.8 mL/min; and feed volume, 20 mL).

According to the Stiring equation,

$$\ln Q = N\ln N - N_A \ln N_A - (N - N_A)\ln(N - N_A) + N\ln qo(T)$$

Then, the chemical potential of the metal ion Hg^{2+} on the chelating hollow fiber affinity membrane chromatography is

$$\mu_a = RT\left(\frac{\partial ln Q}{\partial N}\right)_{v,T} \tag{3}$$

$$RT\ln\left[\frac{N_A}{N - N_A}/q(T)\right]$$

The chemical potential of the metal ion Hg^{2+} in solution is

$$\mu_c = \mu_0 + RT\ln C \tag{4}$$

When the adsorption reaches to balance,

$$\mu_a = \mu_c$$

So

$$\frac{\theta}{1 - \theta}\frac{1}{q_0(T)} = \exp\left(\frac{\mu_0}{RT}\right) \tag{5}$$

Combined $q_0(T)$ with $\exp(\mu_o/RT)$ to a temperature constant $B(T) = q_0(T)$*$\exp(\mu_0/RT)$, the theoretical maximum adsorption was τ_m then the isothermal adsorption equation was obtained.

$$\tau = \frac{\tau_m B(T)C}{1 + B(T)C} \quad (6)$$

Combined with the experiment, the isothermal adsorption equation for the Hg^{2+} adsorption of the hollow fiber affinity membrane chromatography was given as

$$\tau = \frac{2.8188C}{1 + 0.0048C} \quad (7)$$

From Figure 3 the result could be concluded that in relation to the experiment the error of the adsorption quantity of the isothermal adsorption equation associated to describe the Hg^{2+} adsorption of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto was less. Therefore, this equation has a guiding significance for the magnified experiment and the commercial application of the removal Hg^{2+} of the hollow fiber affinity membrane chromatography.

Effects of ionic strength of the raw material solution on the retention of the membrane chromatography

The mercapto chelating group on the polysulfone hollow fiber affinity membrane chromatography modified with mercapto is a subacidity group and its conjugate base formed a coordination bond with Hg^{2+}. The changes of the mobile phase such as the temperature, pH, and ionic strength directly affected the chelating affinity adsorption of the membrane chromatography for Hg^{2+}. For this reason, the effects of the ionic strength and pH of the raw solution on the hollow fiber affinity membrane chromatography were considered in this study. The removal property of the chelating hollow fiber affinity membrane for Hg^{2+} could be expressed with the retention. The retention of the membrane chromatography for Hg^{2+} is expressed as follows:

$$R = \frac{Q_1}{Q_2} \quad (8)$$

where R is the retention, Q_1 is the elution amount, and Q_2 is the feed amount. The most effective way to increase the ionic strength in the mobile phase is to add the common electrolyte in it and these common electrolytes should be purified, have good solubility, low coordination ability, and not create insolubility outcome. In this study, NaCl was used to adjust the ionic strength and other parameters were constant when the effect of the ionic strength was considered. The effect of the NaCl concentration on the retention of the membrane chromatography is shown in Figure 4. Figure 4 shows that when the NaCl concentration increases in raw solution, the retention of the membrane chromatography for Hg^{2+} decreases a little. The ionic strength is one of the key factors affecting the physical properties of the raw material solution. Adding NaCl in the raw material solution changed the ionic strength. The change of the ionic strength affected the hydration layer and the charge distribution around Hg^{2+}. Debe-Hukele limit formula is as follow[12]:

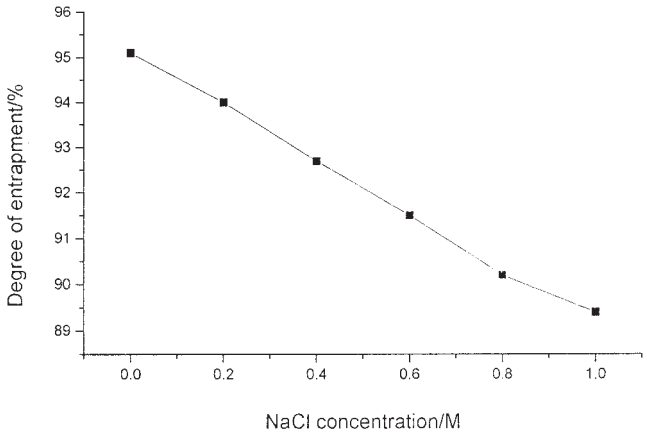

Figure 4 The effect of NaCl concentration on the degree of entrapment of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; feed solution Hg^{2+} concentration, 400 μg/mL; operation flow speed, 3.8 mL/min; and feed volume, 20 mL).

$$\log \gamma_{\pm} = -AZ_+|Z_-|\sqrt{I}$$

$$A = \frac{(2\pi L\rho_A^*)^{1/2}e^3}{2.303(4\pi\varepsilon_0\varepsilon_r kT)^{3/2}} \quad (9)$$

where L is the Avogadros constant; ρ_A^* is the density of the pure solvent; e is the electrical voltage of electron; ε_0 is the vacuum permittivity; ε_r is the relative permittivity of the solute; k is the Boltzmann's constant (J K^{-1}); T is the thermodynamic temperature; Z_+, Z_- is the charge number of the positive and negative ions of the electrolyte; I is the ionic strength; and $\gamma_{\pm}$ is the mean activity coefficient of the ions. From the Debe-Hukele limit formula, we learned that when the ionic strength increases, the ionic mean activity coefficient decreases, that is, the activity decreases, while with the increase of the NaCl concentration, the ionic strength increases either, and therefore, the Hg^{2+} activity decreases and makes the chelating capacity of the membrane chromatography on Hg^{2+} to decrease.

Effect of pH of the raw material solution on retention of the membrane chromatography

In the exchange of the chelating ions, the pH value is the most important parameter to control the separa-

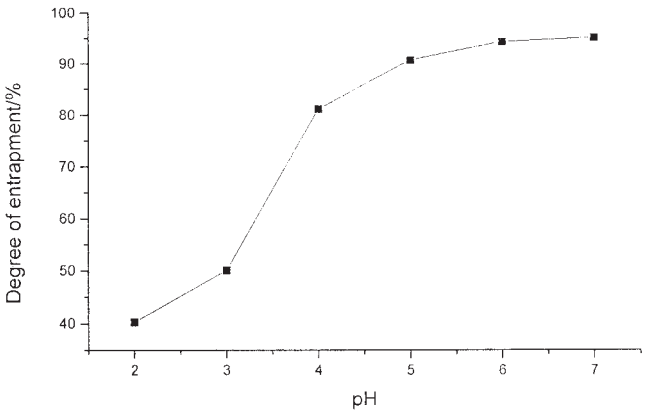

Figure 5 The effect of pH on the degree of entrapment of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; feed solution Hg^{2+} concentration, 400 μg/mL; operation flow speed, 3.8 mL/min; and feed volume, 20 mL).

tion of the metal ions. The effect of the pH value on the retention of the membrane chromatography is shown in Figure 5. In this experiment, the Hg^{2+} was dissolved in different buffer solutions with different pH. From Figure 5 it can be found that with the increase of the pH value of the feed solution, the retention of the hollow fiber affinity membrane chromatography for Hg^{2+} increased accordingly. The alternative mercapto groups of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto create the stable compounds with Hg^{2+}. The mercapto chelating group on the membrane chromatography is subacidity group and had a strong affinity to H^+. Therefore, the H^+ concentration had an important effect on the chelates forming by —SH and Hg^{2+} in the polysulfone hollow fiber affinity membrane chromatography modified with mercapto. The pH is one of the key factors that affect the chelating capacity of the membrane chromatography for Hg^{2+}; the stronger the acidity, the more is the decomposition of R—S—Hg—S—R and the lower is chelating capacity of the membrane for Hg^{2+}, and the chelating capacity could be enhanced by increasing the pH the mobile phase. But under the alkaline condition, Hg^{2+} would hydrolyze and deposit and would jam the membrane pores of the hollow fiber membrane chromatography. This resulted in the decrease of the flux and the retention.

Effects of the raw solution concentration on the retention of the membrane chromatography

Figure 6 showed the effect of the Hg^{2+} concentration of the raw solution on the retention of the membrane chromatography. It can be found from Figure 6 that when the concentration of the raw material solution changes in the range of 100–600 μg/mL, the change of the retention of the membrane for Hg^{2+} is not too obvious. The adsorption of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto was based on the coordination between the mercapto chelating group on the membrane chromatography with Hg^{2+}, and the coordinate was highly efficient. When the raw material solutions with different Hg^{2+} concentration permeated the hollow fiber membrane chromatography, the Hg^{2+} in solution could combine with mercapto (—SH) on the membrane chromatography abundantly and the affinity was stronger; the membrane chromatography had preferable retention ability for solutions with different Hg^{2+} concentration and the effect of removing Hg^{2+} was good, but when the concentration of the raw material solution was very high, the chelating of the membrane chromatography for Hg^{2+} can easily to saturate and the retention would decrease distinctly.

Effects of operating rate on the retention of the membrane chromatography

Figure 7 shows the effect of the feeding rate on the retention of the membrane chromatography under the condition of a given feeding amount. It can be concluded from Figure 7 that with the increase of the feeding rate, the retention of the membrane chromatography for Hg^{2+} decreased a little. The bond ability of Hg^{2+} in the mobile phase with the mercapto group on the membrane chromatography was a little stronger and the bonding rate was also fast. The chelating group mercapto (—SH) were mostly bonded on the internal surface of the hollow fiber membrane. When the raw solution permeated through the membrane chromatography in convection way, the chelating

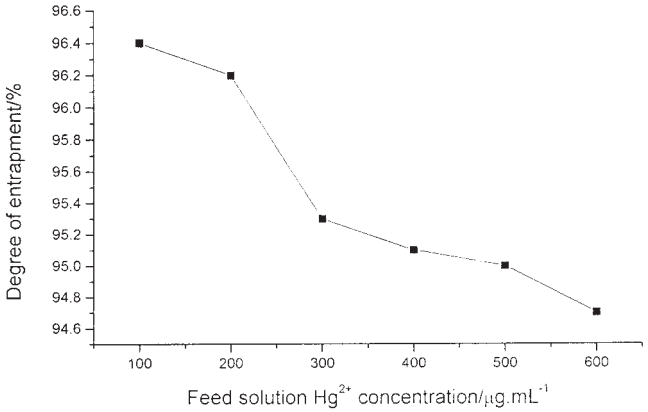

Figure 6 The effect of feed solution Hg^{2+} concentration on the degree of entrapment of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; operating speed, 3.6 mL/min; feed volume, 20 mL; and pH, 7.0).

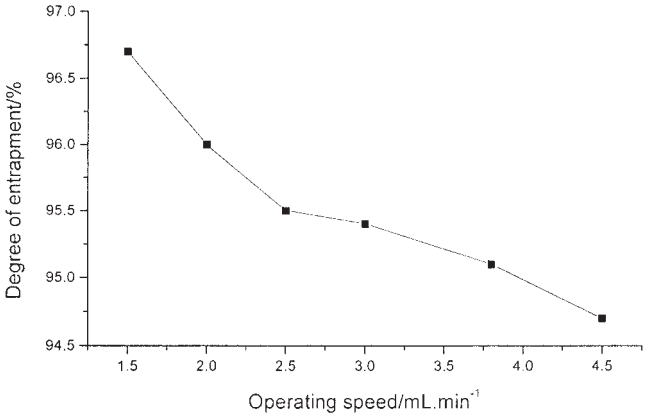

Figure 7 The effect of operating speed on the degree of entrapment of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; feed volume, 20 mL; feed solution Hg^{2+} concentration, 400 μg/mL; and pH, 7.0).

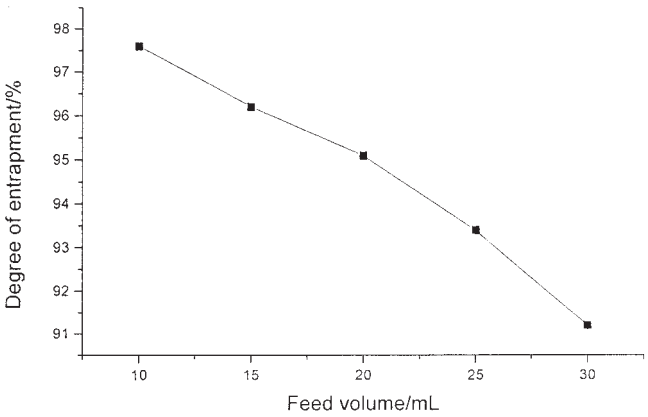

Figure 8 The effect of feed volume on the degree of entrapment of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; feed solution Hg^{2+} concentration, 400 μg/mL; and operating speed, 3.8 mL/min).

group mercapto (—SH) on the membrane chromatography could soon chelate with Hg^{2+}. That is why the change of the feeding rate of the mobile phase had little effect on the retention of the membrane chromatography. The fast bonding kinetics of the mercapto (—SH) chelating group on the membrane chromatography with Hg^{2+} permitted that the hollow fiber affinity membrane chromatography could be operated at a high feeding rate. At the same time, the Hg^{2+} adsorption of the hollow fiber affinity membrane chromatography fully used the highly efficient and speedy bonding characters of the mercapto (—SH) on the membrane chromatography with Hg^{2+}, and this could realize the speedy separation and reclamation of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto for Hg^{2+} at a large scale. The fast feeding rate and the short separation period could make an industrial foundation of removal of Hg^{2+} for the membrane chromatography.

Effects of feeding ram of Hg^{2+} on retention of the membrane chromatography

The chelating capacity of the hollow fiber affinity membrane chromatography for Hg^{2+} was a constant at a given Hg^{2+}concentration of the raw material solution. With increase of the feeding ram of the Hg^{2+} solution, the mercapto (—SH) chelating groups unemployed on the affinity membrane chromatography became lesser and lesser. When the feeding ram of the Hg^{2+} solution reached a certain degree, the affinity membrane chromatography could not adsorb Hg^{2+} and the adsorption reached a balance. The saturation of the membrane chromatography for Hg^{2+} is expressed as follows:

$$S = \frac{\tau}{\Gamma} \tag{10}$$

where S is the saturation of the membrane chromatography, τ is the Hg^{2+} quantity adsorbed by the membrane, and Γ is the balance adsorption quantity of the membrane chromatography at the feeding concentration. Figure 8 shows the relationship between the feeding ram of the Hg^{2+} solution and the retention of the hollow fiber affinity membrane chromatography for Hg^{2+}; Figure 9 shows the relationship of the feeding ram of the Hg^{2+} solution and the adsorption saturation of the hollow fiber membrane chromatography. It can be concluded from Figures 8 and 9 that with the increase of the relative feeding ram, the re-

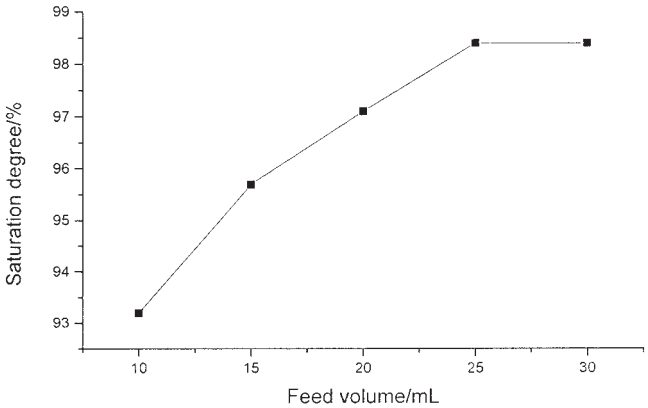

Figure 9 The effect of feed volume on the saturation degree of mercapto chelating hollow fiber affinity membrane chromatography for Hg^{2+} (chlorinity, 7.31%; additive PEG molecular weight, 10,000; additive PEG content, 6%; feed solution Hg^{2+} concentration, 400 μg/mL; and operating speed, 3.8 mL/min).

tention of the hollow fiber affinity membrane chromatography for Hg^{2+} decreased gradually, but the adsorption saturation of the hollow fiber affinity membrane chromatography became higher and higher. Therefore, in the process of reclamation of Hg^{2+}, the retention and saturation of the hollow fiber affinity membrane chromatography should be considered comprehensively. It should confirm the feeding ram of the raw solution based on the required production recovery and the saturation of the membrane chromatography.

The PSF-SH hollow fiber affinity membrane was recycled by soaking in 500 mL of 0.1*M* dilute HCl solution for 12 h at room temperature and the concentration of Hg^{2+} in HCl was 12 μg/mL. The recycled hollow fiber affinity membrane was used to remove Hg^{2+} and the dynamic equilibrium adsorption amount was 300 $\mu g/cm^2$, which was a little smaller than that of the brand new membrane. This showed that the PSF-SH hollow fiber affinity membrane can be easily and conveniently recycled in dilute HCl solution, which will play an important roll for the utilization of such hollow fiber affinity membrane in the treatment of Hg^{2+} in the industrial waste water.

CONCLUSIONS

A homogeneous phase mercapto modified polybenzylsulfone (PSF-SH) hollow fiber affinity membrane with high chelating capacity for Hg^{2+} was prepared through the reaction between the CMPSF hollow fiber matrix membrane and thiourea and then was alkaline hydrolyzed. The isothermal adsorption equation of the polysulfone hollow fiber affinity membrane chromatography modified with mercapto that was set up based on the physical structure and the chemical equilibrium theory is as follows:

$$\tau = \frac{\tau_m B(T)C}{1 + B(T)C}$$

Combined with the experiment, the adsorption isotherm of the chelating hollow fiber affinity membrane chromatography for Hg^{2+} is as follows:

$$\tau = \frac{2.8188C}{1 + 0.0048C}$$

The increase of the ionic concentration of the raw material solution was not favorable for the removal of Hg^{2+} of the chelating hollow fiber affinity membrane chromatography. The pH value had a great effect on the removal of Hg^{2+}. At low pH value, the removal of Hg^{2+}decreased greatly and the pH value of the raw material solution was appropriate from 5.0 to 7.0. The concentration of the raw solution had little effect on the removal of Hg^{2+} at a given feeding ram of Hg^{2+}. The polysulfone hollow fiber affinity membrane modified with mercapto could be used to remove Hg^{2+} in a larger concentration range. The removal of Hg^{2+} decreased a little with the increase of the feeding rate when the feeding ram of Hg^{2+} did not vary. The polysulfone hollow fiber affinity membrane modified with mercapto could be operated to remove Hg^{2+} at a higher feeding rate in a large scale. With the increase of feeding ram of Hg^{2+}, the recovery of Hg^{2+} decreased a little and the adsorption saturation of the polysulfone hollow fiber affinity membrane modified with mercapto increased gradually. In the practical process of removal of Hg^{2+}, the feeding ram of the raw material solution should be confirmed on the base of the required production recovery and the saturation of the membrane chromatography.

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