

Preparation of a Heterogeneous Hollow-Fiber Affinity Membrane Having a Mercapto Chelating Resin and Its Recovery of Hg²⁺ Cations

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ABSTRACT: A kind of heterogeneous hollow-fiber affinity filter membrane with a high chelating capacity for Hg²⁺ was prepared by phase separation with blends of a mercapto chelating resin and polysulfone as the membrane materials, *N,N*-dimethylacetamide as the solvent, and water as the extraction solvent. The adsorption isotherms of the hollow-fiber affinity filter membrane for Hg²⁺ were determined. The heterogeneous hollow-fiber affinity filter membrane was used for the adsorption of Hg²⁺ cations through the coordination of the mercapto group and Hg²⁺ cations, and the effects of the morphology and structure of the affinity membrane on the chelating properties were investigated. The chelating conditions, including the chelating resin grain size, pH value, concentration of the metallic ion solution, mobile phase conditions, and

operating parameters, had significant effects on the chelating capacity of the hollow-fiber affinity filter membrane. The results revealed that the greatest chelating capacity of the hollow-fiber affinity filter membrane for Hg²⁺ was 1090 µg/cm² of membrane under appropriate conditions, and the adsorption isotherms of Hg²⁺ could be described by the Langmuir isotherm. The dynamic chelating experiments indicated that the hollow-fiber affinity membrane could be operated at a high feed flow rate and that large-scale removal of Hg²⁺ could be realized. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 501–508, 2008

Key words: adsorption; blending; fibers; membranes; separation techniques

INTRODUCTION

An affinity filter membrane with definite millipores has an affinity agent on its inner and outer surfaces as a carrier of the affinity agent, which integrates the advantages of both affinity chromatography and modern membrane techniques.^{1–6} When the solution is filtered through the affinity membrane, the target materials will quickly and efficiently combine with the relevant functional groups of the affinity reagent. The materials adsorbed on the affinity membrane can be soon desorbed when an eluent passes through the membrane. Poisonous mercury-containing industrial effluents, which come from the plants that use or produce mercury and mercury compounds, are the major sources of mercury pollution. Recently, we prepared highly qualified heterogeneous polysulfone (PSF) affinity plate filter membranes with chelating groups by phase separation with blends of a chelating resin and PSF, and the results revealed that the greatest chelating capacity of an affinity filter membrane for Hg²⁺ was 1050 µg/cm² of mem-

brane under appropriate conditions.^{7,8} As everyone knows, the loadability of the unit volume of a hollow-fiber membrane surface is much larger than that of a plate membrane, and the intensity of a hollow-fiber membrane is hard enough to support itself, whereas a plate membrane is not. In this study, a mercapto chelating resin was used as a carrier of a chelating affinity agent and blended with PSF to prepare a new type of heterogeneous hollow-fiber affinity filter membrane for the removal of Hg²⁺, and the greatest chelating capacity of Hg²⁺ reached 1090 µg/cm² of membrane.

EXPERIMENTAL

Materials and reagents

The mercapto chelating resin (D190; the structure was styrene–divinyl benzene (DVB)–SH, and the degree of crosslinking was 8%) used in this study was supplied by Nankai University Chemical Plant (Tianjin, China), PSF (intrinsic viscosity = 0.57) was obtained from Shanghai Shuguang Chemical Plant (Shanghai, China), and *N,N*'-dimethylacetamide (DMAC) and poly(ethylene glycol) (PEG; molecular weight = 1000) were obtained from Tianjin Chemical Reagent Plant (Tianjin, China). Sodium chloride was analytical grade and was purchased from Tianjin Yaohua Chemical Plant (Tianjin, China).

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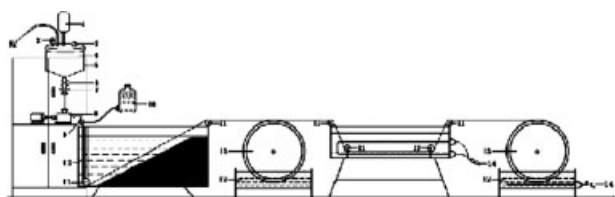


Figure 1 Schematic diagram of the wet-spinning apparatus: (1) motor agitator, (2) pressure gauge, (3) feed inlet, (4) kettle, (5) heating jacket, (6) shut-off valve, (7) blanket, (8) controlled volume pump, (9) spinning head, (10) bore liquid, (11) block, (12) water bath, (13) eling roll, and (14) heater.

Main apparatus and equipment

The XL30 environmental scanning electron microscope was made by Philips (Holland). The HD-201 electronic strand strength meter was made by Hongda Laboratory Apparatus, Ltd. (China). The wet-spinning equipment (see Fig. 1) was made by Tianjin Polytechnic University (Tianjin, China). The retention measurement apparatus for the membrane (see Fig. 2) was made by Tianjin Polytechnic University.

Preparation of the heterogeneous hollow-fiber affinity membrane having a mercapto chelating resin

Some PSF and PEG (content, 6%) were dissolved in DMAC to form a PSF solution of a certain concentration. Then, the quantitative mercapto chelating resin (D190), which was ground and sifted, was put into the PSF solution, and the solution of D190 and PSF was rigorously stirred for 8 h. Because D190 could not be dissolved in DMAC, the solution of D190 and PSF was heterogeneous. A certain composition of the heterogeneous D190/PSF spin-casting solution was obtained after vacuum deaeration. The wet-spinning method was adopted to prepare the heterogeneous hollow-fiber affinity membrane in the spinning equipment. The spin-casting solution was put into the storage tank and deaerated under negative pressure. High-pressure nitrogen was used as the pressure source to push out the spin-casting solution, which was 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 the head tank. Lastly, the 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 the mold completely by heat-drawing and heat-setting treatment, the heterogeneous hollow-fiber affinity membrane, modified with a mercapto chelating resin, was prepared. The heterogeneous hollow-fiber affinity

membrane modified with a mercapto chelating resin was preserved in a hygrometric state.

Assembly of the modules of the hollow-fiber affinity membrane having a mercapto chelating resin

To produce the hollow-fiber affinity membrane filter, the hollow-fiber membrane was cut into 19-cm-long pieces, these pieces were put together into a bundle, and one end of the bundle was invaginated into a nylon sleeve whose external diameter was 10 mm and length was 30 mm; the bundle reveal 20 mm, the ringed section of the hollow-fiber membrane nylon tube was cast with the epoxy resin and curing agent in a ratio of 4:1, the other end was sealed, and we waited until it was cured. The hollow-fiber membrane filter was put into a stainless steel sleeve, the shell pass of which was 31.60 mL, in the experimental apparatus of the hollow-fiber membrane for the removal of Hg^{2+} .

Removal of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} in the mobile phase

The experiment was adapted to the Hg^{2+} -removal experimental apparatus for the hollow-fiber membrane, which was made at Tianjin Polytechnic University. The peristaltic pump extruded the solution into the hollow-fiber affinity membrane. The solution went through the pores of the membrane in the external pressure mode and flowed out from the end of the hollow-fiber membrane module that was not sealed; then, the permeated liquid was collected by a collector. The properties of the membrane can be described by the adsorption amount of the membrane for Hg^{2+} (Γ), which was calculated as follows:

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

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

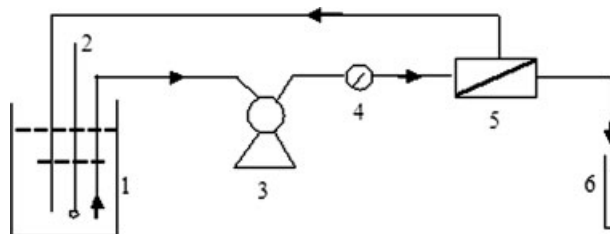


Figure 2 Schematic diagram of the retention measurement apparatus of the membrane: (1) reservoir, (2) thermometer, (3) water pump, (4) barometer, (5) plate membrane module, and (6) volumetric cylinder.

Quantity measurements of Hg^{2+}

The concentration of Hg^{2+} was determined with the dithizone method.⁹ In an acidic medium, Hg^{2+} reacted with an overdose of dithizone to form orange-yellow dithizonate [$\text{Hg}(\text{HDz})_2$], which could be dissolved in CCl_4 . The free dithizone was removed with a dilute NH_3 solution. At a maximum wavelength of 485 nm, the extinction of the $\text{Hg}(\text{HDz})_2$ solution was determined with a model 7220 spectrophotometer (Beijing RuiLi Instrument Plant, Beijing, China). Furthermore, the Hg^{2+} quantity with respect to the $\text{Hg}(\text{HDz})_2$ extinction could be determined.

RESULTS AND DISCUSSION

Optimal process to prepare the hollow-fiber affinity membrane having a mercapto chelating resin

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 at 20–30 m/min was appropriate. The temperature of the spinning dope should match other qualifications in the spinning process of the membrane. The viscosity of the spinning dope varied with changes in the contents of the additive PEG, mercapto chelating resin, and PSF. To increase the mobility of the spinning dope through an increase in the pressure blindly would have caused troubles in matching other conditions in the spinning. Therefore, the spinning temperature was fixed relatively for the special composition of the spin-casting dope. The spinning temperature of the blending hollow-fiber membrane was generally controlled between 25 and 35°C. The hollow-fiber membrane was easily off-center when the temperature of the raw solution was lower and the pressure was higher. An environmental scanning electron microscopy photograph is shown in Figure 3. Because of the difference in 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 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 just off the spinning head but also control the internal diameter of the hollow-fiber membrane; it also could change the composition of the wall of the hollow-fiber membrane that extruded from the porous area. When the as-formed fiber with some mobility went into the coagulating bath, the closer micelle could be frozen 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,

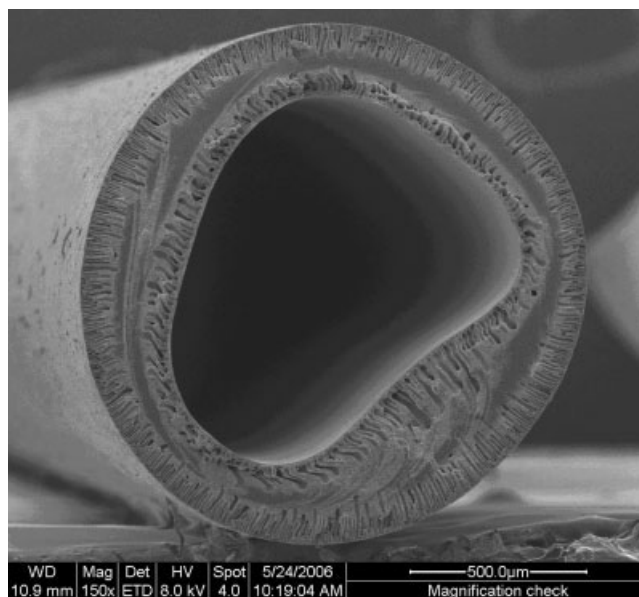


Figure 3 Environmental scanning electron microscopy photograph of a cross section of the hollow-fiber affinity membrane having a mercapto chelating resin.

the distances between micelles were relatively long, and so the resistance was little when the liquid flew through them. The thickness of the compact layer of the membrane had a close relationship with the permeating liquid; 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 had a relationship with the vaporization distance. The experiment proved that the longer the vaporization distance was, the thicker the compact layer was, and if the vaporization distance was less, the compact layer was thinner. In the spinning process of the blending hollow-fiber membrane, the vaporization distance was normally between 120 and 300 mm.

Isothermal absorption equation of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

The absorption isotherm is the relationship between the solution equilibrium concentration and the equilibrium adsorptive quantity of the membrane after the absorption equilibrium. In this study, the dynamic absorption isotherm of the affinity membrane was determined to reflect the practical process of the Hg^{2+} absorption of the membrane truly. The measuring method with the external pressure was as follows. A raw material solution of a given concentration was extruded into the membrane by the peristaltic pump, and the Hg^{2+} in solution was absorbed by the mercapto chelating groups of the membrane. When the Hg^{2+} concentration at the outlet of the hollow-fiber affinity membrane did not vary with

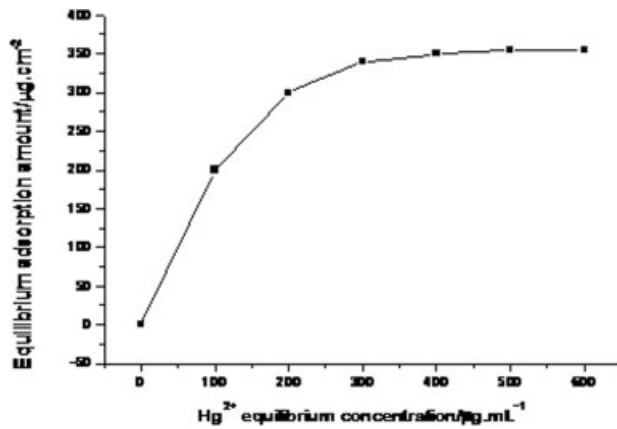


Figure 4 Adsorption isothermal curve of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; operation flow speed, 3.8 mL/min ; and feed volume, 20 mL).

time, the Hg^{2+} adsorption of the affinity membrane was saturated to reach the balance, and then the Hg^{2+} absorbed was dissociated by a given concentration of an HCl solution. The raw material concentration and the quantity of Hg^{2+} dissociated were the equilibrium concentration of the solution and the equilibrium adsorption quantity of the membrane, respectively. The dynamic absorption experiment was carried out with a series of concentrations of the Hg^{2+} solution at room temperature, and the isothermal adsorption curve of the membrane was obtained by the plotting of the equilibrium adsorption quantity versus the equilibrium concentration of the solution (see Fig. 4). If there are N chelating adsorption points on the surface of the membrane and these points are distributed uniformly, every adsorption point may be for nothing or absorb the metal ion Hg^{2+} (that is the single-molecule adsorption hypothesis; among them, there are N_A adsorbing the metal ion Hg^{2+}). If the partition function of each metal ion is $q_0(T)$, from knowledge of the quantum chemistry, the main partition function (Q) is given as follows:¹⁰

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

where Q is the main partition function.

According to the Stirling equation

$$\ln Q = N \ln N - N_A \ln N_A - (N - N_A) \ln(N - N_A) + N \ln q_0(T) \quad (3)$$

Then, the chemical potential of the metal ion Hg^{2+} on the membrane (μ_a) is

$$\mu_a = RT \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T} = RT \ln \left[\frac{N_A}{(N - N_A)q_0(T)} \right] \quad (4)$$

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

$$\mu_c = \mu_0 + RT \ln C \quad (5)$$

where C is the concentration and μ_0 is standard chemical potential.

When the adsorption reaches balance

$$\mu_a = \mu_c$$

Then

$$\frac{\theta}{1 - \theta} q_0(T) = \exp \left(\frac{\mu_0}{RT} \right) \quad (6)$$

where θ is the fraction of coverage.

When $q_0(T)$ is combined with $\exp(\mu_0/RT)$ to a temperature constant of $A(T) = q_0(T)\exp(\mu_0/RT)$, the theoretical maximum adsorption is Γ_m ; then, the isothermal adsorption equation is obtained:

$$\Gamma = \frac{\Gamma_m A(T)C}{1 + A(T)C} \quad (7)$$

Combined with the experiment, the isothermal adsorption equation for the Hg^{2+} adsorption of the membrane can be given as follows:

$$\Gamma = \frac{2.8305C}{1 + 0.0049C} \quad (8)$$

From Figure 4, it could be concluded that in relation to the experiment, the error of the adsorption quantity of the isothermal adsorption equation associated with describing the Hg^{2+} adsorption of the membrane was less.

Effect of the chelating resin grain size on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

The effect of the chelating resin grain size on the retention of the hollow-fiber affinity membrane for Hg^{2+} is shown in Table I. Table I indicates that the chelating resin grain size produced an effect on the retention of Hg^{2+} . The smaller the chelating resin grain size was, the greater the specific surface was of the chelating resin. It also means that both the sorption speed and saturated adsorption amount of Hg^{2+} increased with the decrease in the chelating resin grain size.

Effects of the raw solution concentration on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

Figure 5 shows the effect of the Hg^{2+} concentration of the raw solution on the retention of the membrane. When the concentration of the raw material

TABLE I
Effect of the Chelating Resin Grain Size on the Retention of the Hollow-Fiber Affinity Membrane Having a Mercapto Chelating Resin for Hg^{2+}

Grain diameter (μm)	Degree of entrapment (%)
125–147	93.4
97–105	94.7
74–88	95.8

Additive PEG content, 6%; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; operation flow speed, 3.8 mL/min ; and feed volume, 20 mL .

solution changed in the range of 100–600 $\mu\text{g}/\text{mL}$, the change of the retention of the membrane for Hg^{2+} was not too obvious. The adsorption of the hollow-fiber affinity membrane was based on the coordination between the mercapto chelating groups on the membrane with Hg^{2+} , and the coordination was highly efficient. When raw material solutions with different Hg^{2+} concentrations permeated the hollow-fiber membrane, the Hg^{2+} in solution could combine with mercapto ($-\text{SH}$) on the membrane abundantly, and the affinity was stronger. The membrane had preferable retention ability for solutions with different Hg^{2+} concentrations, and the effect of removing Hg^{2+} was good, but when the concentration of the raw material solution was very high, chelation of the membrane for Hg^{2+} could easily be saturated, and the retention would decrease distinctly.

Effect of the pH of the raw material solution on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

In the exchange of the chelating ions, the pH value of the raw material solution was the most important parameter to control the separation of metal ions. The effect of the pH value on the retention of the

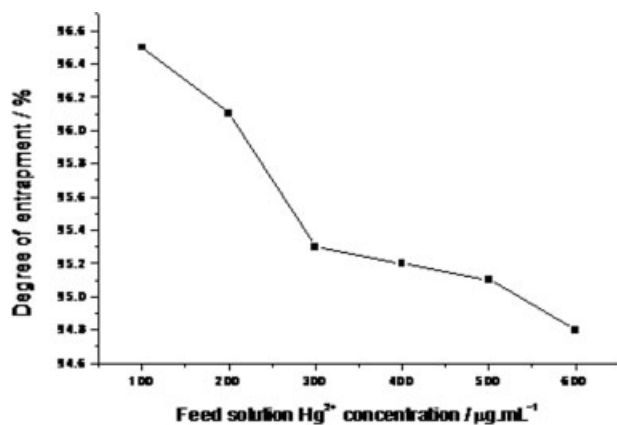


Figure 5 Effect of the feed-solution Hg^{2+} concentration on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; operating speed, 3.6 mL/min ; feed volume, 20 mL ; and pH, 7.0).

membrane for Hg^{2+} is shown in Figure 6. In this experiment, Hg^{2+} was dissolved in different buffer solutions with different pHs. With an increase in the pH value of the feed solution, the retention of the membrane for Hg^{2+} increased accordingly. The alternative mercapto groups of the membrane created stable compounds with Hg^{2+} . The mercapto groups on the membrane were subacidity groups and had a strong affinity to H^+ . Therefore, the H^+ concentration had an important effect on the chelates formed by $-\text{SH}$ and Hg^{2+} in the membrane. The pH was one of the key factors that affected the chelating capacity of the membrane for Hg^{2+} ; the stronger the acidity was, the greater the decomposition was of $\text{R}-\text{S}-\text{Hg}-\text{S}-\text{R}$ and the lower the chelating capacity was of the membrane for Hg^{2+} , and the chelating capacity could be enhanced by an increase in the pH in the mobile phase. However, under the alkaline condition, Hg^{2+} hydrolyzed, deposited, and jammed the membrane pores. This resulted in the decrease of the flux and the retention.

Effects of the ionic strength of a raw material solution on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

The mercapto chelating group on the membrane was a subacidity group, and its conjugate base formed a coordination bond with Hg^{2+} . Changes in the mobile phase such as the temperature, pH, and ionic strength directly affected the chelating affinity adsorption of the membrane for Hg^{2+} . The removal property of the membrane for Hg^{2+} can be expressed with retention as follows:

$$J = \frac{L_1}{L_2} \quad (9)$$

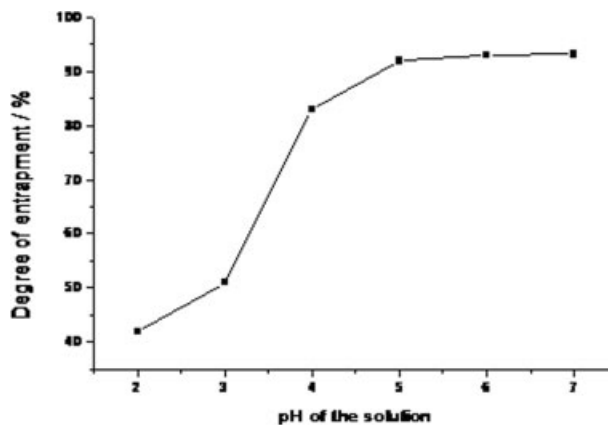


Figure 6 Effect of pH on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; operation flow speed, 3.8 mL/min ; and feed volume, 20 mL).

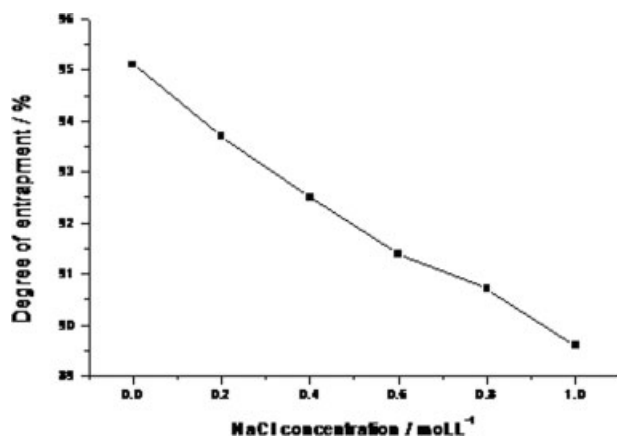


Figure 7 Effect of the NaCl concentration on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; operation flow speed, 3.8 mL/min ; and feed volume, 20 mL).

where J is the retention, L_1 is the elution amount, and L_2 is the feed amount. The most effective way to increase the ionic strength in the mobile phase is to add a common electrolyte to it, and these common electrolytes should be purified, have good solubility and low coordination ability, and not create an 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 is shown in Figure 7. When the NaCl concentration increased in the raw solution, the retention of the membrane for Hg^{2+} decreased a little. The ionic strength was one of the key factors affecting the physical properties of the raw material solution. Adding NaCl to the raw material solution could change the ionic strength. The change in the ionic strength affected the hydration layer and charge distribution around Hg^{2+} . The Debe-Hukele limit formula is as follows:¹¹

$$-\ln \gamma_{\pm} = C|z_+z_-|I^{1/2} \quad (10)$$

$$C = (2\pi L\rho_A^*)(e^2/4\pi\epsilon_0\epsilon_r kT)^{3/2}$$

where L is Avogadro's constant; ρ_A^* is the density of the pure solvent; e is the electrical voltage of an electron; ϵ_0 is the vacuum permittivity; ϵ_r is the relative permittivity of the solute; k is Boltzmann's constant; T is the thermodynamic temperature; z_+ and z_- are the charge numbers of positive and negative ions of the electrolyte, respectively; I is the ionic strength; and γ_{\pm} is the mean activity coefficient of the ions. From the Debe-Hukele limit formula, we learn that when the ionic strength increased, the ionic mean activity coefficient decreased, that is, the activity

decreased. However, with an increase in the NaCl concentration, the ionic strength increased, and so the Hg^{2+} activity decreased, and the chelating capacity of the membrane for Hg^{2+} decreased.

Effects of the operating rate on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

Figure 8 shows the effect of the feeding rate on the retention of the membrane under the condition of a given feeding amount. It can be concluded that with an increase in the feeding rate, the retention of the membrane for Hg^{2+} decreased a little. The bond ability of Hg^{2+} in the mobile phase with a mercapto group on the membrane was a little stronger, and the bonding rate was also fast. The chelating group mercapto ($-\text{SH}$) was mostly bonded on the internal surface of the hollow-fiber membrane. When the raw solution permeated through the membrane in a convection way, the chelating group mercapto ($-\text{SH}$) on the membrane could soon chelate with Hg^{2+} . That is why the change in the feeding rate of the mobile phase had little effect on the retention of the membrane. The fast bonding kinetics of the mercapto ($-\text{SH}$) chelating group on the membrane with Hg^{2+} permitted the hollow-fiber affinity membrane to be operated at a high feeding rate. At the same time, the Hg^{2+} adsorption of the hollow-fiber affinity membrane fully used the highly efficient and fast bonding characteristics of the mercapto ($-\text{SH}$) on the membrane with Hg^{2+} , and this could realize speedy separation and reclamation of the hollow-fiber affinity membrane for Hg^{2+} on a large scale. The fast feeding rate and short separation period could make an industrial foundation for the removal of Hg^{2+} for the membrane.

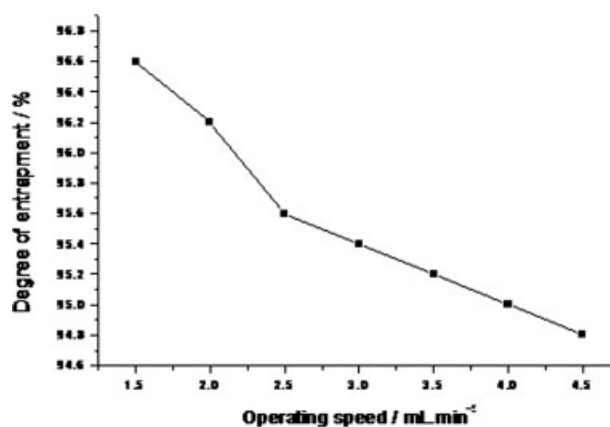


Figure 8 Effect of the operating speed on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; feed volume, 20 mL ; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; and pH, 7.0).

Effects of a raw material solution of a given concentration on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+}

The chelating capacity of the hollow-fiber affinity membrane for Hg^{2+} was a constant at a given Hg^{2+} concentration of the raw material solution. With an increase in the raw material solution of a given concentration, the mercapto ($-SH$) chelating groups unemployed on the affinity membrane became fewer and fewer. When the raw material solution of a given concentration reached a certain degree, the affinity membrane could not absorb Hg^{2+} , and the absorption reached a balance. The saturation of the membrane (S) for Hg^{2+} is expressed as follows:

$$S = \frac{\Gamma}{\Gamma_m} \quad (11)$$

where Γ is the Hg^{2+} quantity absorbed by the membrane and Γ_m is the balance absorption quantity of the membrane at the feeding concentration. Figure 9 shows the relationship between the raw material solution of a given concentration and the retention of the hollow-fiber affinity membrane for Hg^{2+} ; Figure 10 shows the relationship of the raw material solution of a given concentration and the absorption saturation of the hollow-fiber membrane. On the basis of the figures, it can be concluded that with an increase in the relative raw material solution of a given concentration, the retention of the hollow-fiber affinity membrane for Hg^{2+} decreased gradually, but the absorption saturation of the hollow-fiber affinity membrane became higher and higher. Therefore, in the process of reclamation of Hg^{2+} , the retention and saturation of the hollow-fiber affinity

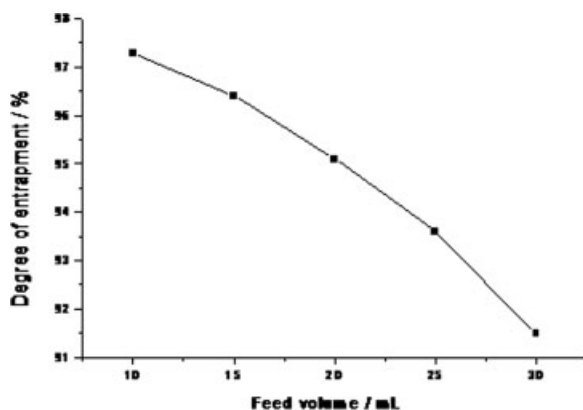


Figure 9 Effect of the feed volume on the retention of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; and operating speed, 3.8 mL/min).

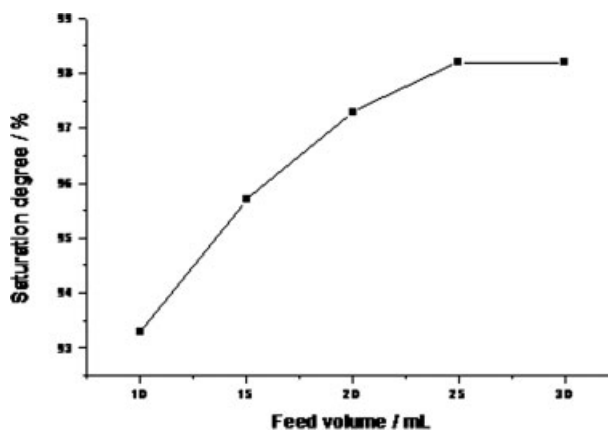


Figure 10 Effect of the feed volume on the saturation degree of the hollow-fiber affinity membrane having a mercapto chelating resin for Hg^{2+} (additive PEG content, 6%; feed-solution Hg^{2+} concentration, 400 $\mu\text{g}/\text{mL}$; and operating speed, 3.8 mL/min).

membrane should be considered comprehensively. It should confirm the raw material solution of a given concentration on the basis of the required production recovery and saturation of the membrane.

The affinity membrane was recycled through soaking in 500 mL of a 0.1M dilute HCl solution for 14 h at room temperature, and the concentration of Hg^{2+} in HCl was 13 $\mu\text{g}/\text{mL}$. The recycled affinity membrane was used to remove Hg^{2+} , and the dynamic adsorption capacity was 305 $\mu\text{g}/\text{cm}^2$ of membrane, which was a little lower than that of the brand new membrane. This shows that the affinity membrane can be easily and conveniently recycled in a dilute HCl solution, and this will play an important role in the utilization of such an affinity membrane in the treatment of Hg^{2+} in industrial wastewater.

CONCLUSIONS

Blends of a mercapto chelating resin and PSF can be used to prepare a high-quality, heterogeneous hollow-fiber affinity membrane with a high chelating capacity for Hg^{2+} by phase-separation technology, and the isothermal adsorption equation of the affinity membrane is set on the basis of the physical structure and the chemical equilibrium theory also. An increase in the ionic concentration of the raw material solution is not favorable for the removal of Hg^{2+} of the affinity membrane. The pH value has a great effect on the removal of Hg^{2+} . At a low pH value, the removal of Hg^{2+} decreases greatly, and the pH value of the raw material solution is appropriately 5–7. The concentration of the raw solution has little effect on the removal of Hg^{2+} at a given feeding rate of Hg^{2+} , and the membrane can be used to remove Hg^{2+} in a larger concentration range. The removal of Hg^{2+} decreases a bit with an increase in the feeding rate

when the feeding rate of Hg^{2+} does not vary; that is, the membrane can be operated to remove Hg^{2+} at a higher feeding rate on a large scale. With an increase in the feeding rate of Hg^{2+} , the recovery of Hg^{2+} decreases a bit, and the adsorption saturation of the membrane increases gradually. In the practical process of removal of Hg^{2+} , the feeding rate of the raw material solution should be confirmed on the basis of the required production recovery and the saturation of the hollow-fiber affinity membrane.

References

1. Li, J.; Che, H. L.; Chai, H. *Chem J Chin Univ* 1999, 20, 1322.
2. Petsch, D.; Beeskow, T. C.; Anspach, F. B. *J Chromatogr B* 1997, 693, 79.
3. Reif, O. W.; Volker, N.; Bahr, U. *J Chromatogr A* 1993, 654, 29.
4. Serfica, G. C.; Pimbley, J.; Belfort, G. *J Membr Sci* 1994, 88, 292.
5. Beeskow, T. C.; Kusharyoto, K.; Anspach, F. B. *J Chromatogr A* 1995, 715, 49.
6. Bao, S. X.; Shi, G. J.; Jiang, W. *J Chem Ind Eng (in Chinese)* 1995, 46, 15.
7. Wang, B.; Cui, Y. F.; Du, Q. Y. *J Appl Polym Sci* 2003, 87, 908.
8. Wang, B.; Huang, W.; Yang, X. *J Appl Polym Sci* 2005, 96, 2117.
9. Dranitskaya, R. M.; Gavrilchenko, A. I.; Okhitina, L. A. *Zh Anal Khim* 1970, 25, 1740.
10. Lu, P. *Chromatograph Theoretical Basis*; Science: Beijing, 1989; p 198.
11. Yupu, F. *Physical Chemistry*; Press of Dalian University of Technology: Dalian, China, 2004; p 455.