

The Removal of Toxic Heavy Metal Cations by Polysulfonebenzylthiourea Reactive Hollow Fiber Ultrafiltration Membranes

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ABSTRACT: The hollow fiber asymmetric matrix membranes were prepared with phase inversion by utilization of the chloromethyl polysulfone/polyethylene glycol/DMAC casting solution and chloromethyl polysulfone as membrane materials. The effects of composition of spinning casting solution and process parameters of dry-wet spinning on the structure of hollow fiber matrix membrane were investigated. Through the reaction between matrix membrane and thiourea, the highly qualified polysulfonebenzylthiourea reactive hollow fiber ultrafiltration membranes were able to afford. The adsorption isotherms of the polysulfonebenzylthiourea hollow fiber membrane for Cd^{2+} and Zn^{2+} were determined and the effects of mobile phase conditions and the operating parameters on removal performance of the polysulfonebenzylthiourea hollow fiber membrane for Cd^{2+}

and Zn^{2+} were also investigated. The experimental results showed that adsorption isotherms of Cd^{2+} and Zn^{2+} could be described by the Langmuir isotherm, the polysulfonebenzylthiourea hollow fiber membrane could be operated at high feed flow rate, and a large-scale removal of Cd^{2+} and Zn^{2+} could be realized. According to required recovery of Cd^{2+} and Zn^{2+} and the saturation degree of polysulfonebenzylthiourea hollow fiber membrane, the optimum loading amount of Cd^{2+} and Zn^{2+} should be selected in the actual removal of Cd^{2+} and Zn^{2+} . © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1942–1953, 2009

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

INTRODUCTION

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 of its energy consumption is relatively low, it is simple to scale up and its membrane properties can be kept under control easily.^{1–6} 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 efficiently 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. There are ever increasing requirement for large amount of wastewater to be

purified within a reasonable time. Heavy toxic metal cations such as Cd^{2+} and Zn^{2+} can cause a problem to person's health. The heavy toxic metal cations containing industrial effluent that comes from the plants, which use or produce heavy toxic metal and heavy toxic metal compounds, are the major resource of the heavy toxic metal pollution.⁷ The heavy toxic ions can be adsorbed selectively on the membrane by introducing thiourea group in the matrix membrane. In our previous work,^{8–10} we reported that the mercapto chelating resin was used as a carrier of chelating affinity agent and blended with polysulfone to prepare a new type of heterogeneous hollow fiber affinity filter membrane for the removal of Hg^{2+} . Here, the highly qualified reactive hollow fiber ultrafiltration membranes with thiourea groups were obtained through the reaction between chloromethyl polysulfone matrix hollow fiber membrane and thiourea, and the rejection of heavy toxic metal cations were also investigated.

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EXPERIMENTAL

Materials and reagents

Dichloromethane, 2,2 dichloroethane, nitrobenzene, thiourea, and polyethylene glycol (PEG 600) were

analytical grade and purchase from Tianjin Reagent Plant. Chloromethyl ether and ferriammonium sulfate were analytical grade and were purchased from Nankai 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. The polysulfone (PSF), was purchased from Shanghai Shuguang Chemical Plant.

Main apparatuses

XL30 environmental scanning electron microscope (ESEM) was made by PHILIPS. Dry-Wet Spinning Equipment was made by Tianjin Polytechnic University, China. The retention measurement apparatus of membrane was made by Tianjin Polytechnic University, China. Model 7220 spectrophotometer was made in Beijing RuiLi Instrument Plant.

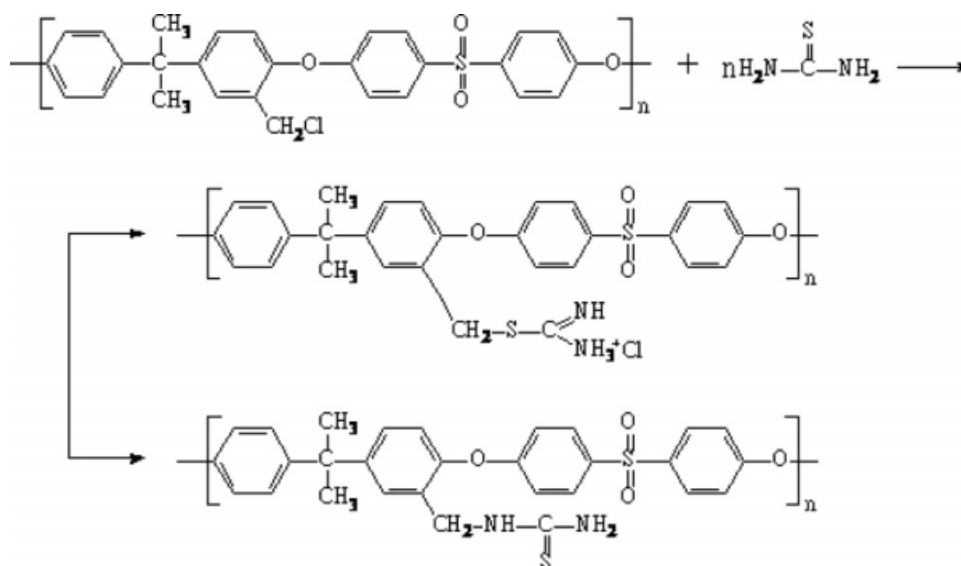
Preparation of polysulfonebenzylthiourea reactive hollow fiber ultrafiltration membranes

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, and the chloromethyl polysulfone was precipitated from the system as lump and washed by hot distilled water repeatedly until no bubbles. The dry-wet spinning method was adopted to prepare the hollow fiber matrix membrane in the spinning equipment. The chloromethyl polysul-

fone, the solvent *N,N*-dimethyl acetamide (DMAC) and additives PEG (molecular weight is 600, PEG600) were blended to a scale, and were stirred at given temperature until they were totally dissolved, then were stood still to put into use. Then 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 chloromethyl polysulfone casting solution that 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. Finally, 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 mold completely, by hot drawing and heat setting treatment, the hollow fiber matrix membrane would be prepared. The hollow fiber matrix membrane was soaked in a solution of thiourea in anhydrous ethanol and the reaction was carried out at 40°C for 10 h. The polysulfonebenzylthiourea reactive hollow fiber ultrafiltration membranes were afforded after taking the membranes out of the solution and washed with distilled water repeatedly. The synthetic route was shown as in Scheme 1:

The polysulfonebenzylthiourea reactive ultrafiltration plate membrane successively through the thiourea reaction to incorporate the thiourea groups were characterized with FTIR spectra as shown in Figure 1. In Figure 1(b), there is highly intense peak at 1240 cm^{-1} . It is a shift for the same band (1246 cm^{-1}) seen in Figure 1(a).

The successful thiourea reaction was confirmed by the FTIR spectra in Figure 1(a,b). The presence of new



Scheme 1 The synthetic route of the polysulfonebenzylthiourea ultrafiltration membranes.

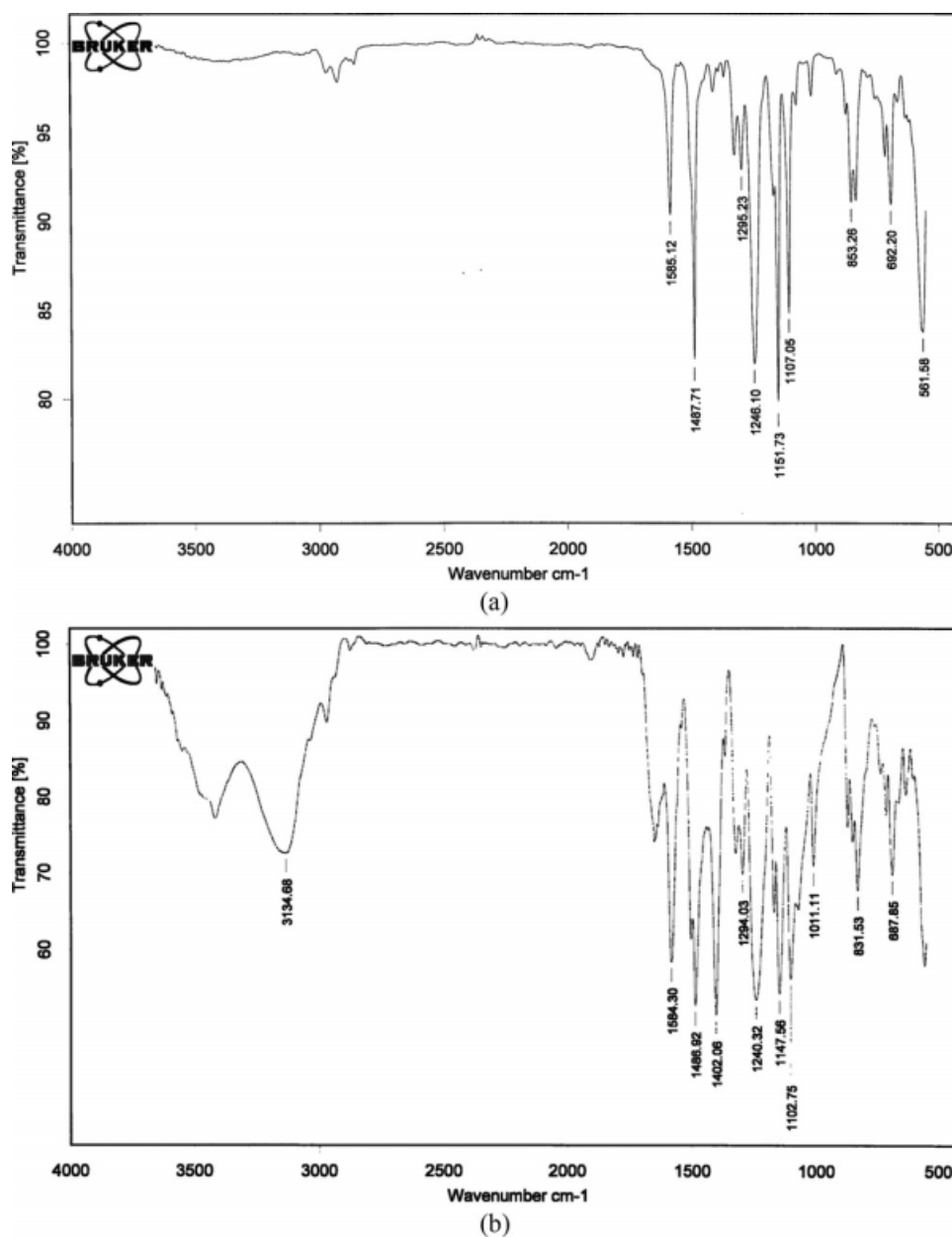


Figure 1 FTIR spectra of membrane (a) chloromethyl polysulfone and (b) polysulfonebenzylthiourea.

peaks at 1402 cm^{-1} assigning to the vibration of C—S bond, 1640 cm^{-1} attributing to the vibration of C=N, and the wide strong peak around 3134 cm^{-1} contributing to the NH^{3+} of the thiourea group on methyl(isothiourea) polysulfone plate (MTUPSF), respectively. In other words, the presence of the peak at 1402 cm^{-1} confirms the incorporation of thiourea groups to the membrane, and the chloromethyl groups were quantitatively converted into the thiourea groups.

Measurement of flux of the polysulfonebenzylthiourea hollow fiber membrane

The hollow fiber membrane was installed on the self-made hollow fiber membrane module, and

when the pure water permeated from outside into inside of the membrane under a given pressure of the circulating pump, the pure water volume that through given membrane area was noted in given time. The flux (permeate rate) could be calculated by eq. (1):

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

where Q is flux ($\text{L}/\text{m}^2\text{ h}$), V is the volume of the permeate liquid (L), S is the effective membrane area of external surface of the hollow fiber matrix membrane, and t is the ultra filtration time(s).

Measurement of porosity of the polysulfonebenzylthiourea hollow fiber membrane

The experiment was carried out by the gravimetric method while the glycerol was used as the soak solution of the hollow fiber membrane.¹¹ A piece of given area (S) hollow fiber hygrometric state membrane was sheared and weighed W_w (wet weight) after being wiped the glycerol off the membrane surface, then the membrane was moved into vacuum drying oven to a constant weight W_d (dry weight of the membrane), the porosity is calculated by eq. (2):

$$P_r(\%) = \frac{W_w - W_d}{s \cdot d \cdot \rho} \quad (2)$$

where d is the average thickness of the membrane (m), s is area (m^2), and ρ is the glycerol density (kg/m^3).

Measurement of pore size of the polysulfonebenzylthiourea hollow fiber membrane

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

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

where P_r is porosity(%); L is the membrane thickness, μ is the viscosity of the permeate liquid (Pa s), Q is the flux (m^3/s), ΔP is the pressure (Pa), and S is the permeated area of the external surface of the hollow fiber membrane (m^2).

ESEM of the polysulfonebenzylthiourea hollow fiber membrane

The hollow fiber membrane was immersed in 50% aqueous glycerol for 24 h. Then the membrane was taken out and the glycerol on its surfaces was wiped away. The membrane was dehydrated by immersing it in 50, 70, 90, and 100% ethanol, sequentially. The ESEM characterization was performed on a coating film by ion-sputtering after the membrane was frozen in liquid nitrogen and fastens on the sample table and the thickness was about 20 nm. The pore size and size distribution of the membrane was obtained from the observation of the morphological structure of the cross-section of the membrane with a XL30 ESEM.

Determination of chloromethyl polysulfone chlorinity

The determination of chloromethyl polysulfone chlorinity was performed by Woolhad method¹¹

Quantity measurement of Cd^{2+} and Zn^{2+}

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

Assemble of the modules of polysulfonebenzylthiourea hollow fiber membrane

The produce of polysulfonebenzylthiourea hollow fiber membrane filter was to cut the hollow fiber membrane into 19 cm length pieces, put these pieces together into bundling, then 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, and to cast the ringed section of the hollow fiber membrane nylon tube with the epoxy resin and curing agent with ratio of 4 : 1, then, to seal the other end and wait till it was cured. The membrane chromatography was obtained to put this hollow fiber membrane filter into the stainless steel sleeve whose shell pass is $V = 31.60$ (mL) in the experimental apparatus of the hollow fiber membrane chromatography for removal of Cd^{2+} and Zn^{2+} .

Removal of Cd(II) and Zn(II) in mobile phase with polysulfonebenzylthiourea hollow fiber membrane

The experiment was adopted the heavy toxic metal cations-removal experimental apparatus of the hollow fiber membrane, which was made by Tianjin Polytechnic University. The peristaltic pump extruded the solution into the polysulfonebenzylthiourea hollow fiber membrane. The solution went through the pores of the hollow fibemembrane by 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 removal capacity of the polysulfonebenzylthiourea hollow fiber membrane for heavy toxic metal cations, which was calculated from eq. (4):

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

where C_0 is original concentration of heavy toxic metal cations, C_t is the residual concentration of heavy toxic metal cations after the heavy toxic metal cations were through the membrane, and S was membrane area of the external surface of the hollow fiber membrane.

RESULTS AND DISCUSSION

Effect of PEG on the structure of polysulfonebenzylthiourea hollow fiber membrane

Table I shows the effect of additive PEG (molecular weight 600) concentration on the structure of polysulfonebenzylthiourea hollow fiber membrane. From

TABLE I
Effect of Additive PEG Concentration on the Structure of Polysulfonebenzylthiourea Hollow Fiber Membrane

PEG content (%)	Water flux (L/m ² h)	Pore diameter (nm)	Porosity (%)
0	39.1	23.1	46.1
2	167.3	32.4	57.3
4	176.2	35.7	61.0
6	189.5	37.1	62.3
8	199.8	39.5	64.0
10	203.4	43.0	66.2

Table I, it can be seen that the average pore size of membrane becomes larger, the porosity also shows the upward current with the increase of the content of the additive PEG (molecular weight 600), and the flux increases under the combined effects of pore size and porosity. When the content of PEG in the spinning liquid increases, the exchange rate of the solvent and the precipitant is expedited for the strong hydrophilic effect, and much more finger-like pores formed. The increase of the proportion of the finger-like pores appeared as the increase of the porosity and the pore size. Nevertheless, too much additives would deduce the intensity of membrane so that the viscosity of the spinning liquid is too high to spin.

Effects of the extrusion rate on structure of the polysulfonebenzylthiourea hollow fiber membrane

In the spinning process of the hollow fiber membrane, the factors that affect the quality and structure of the hollow fiber can be divided into two parts. One is the effect of composition of the spinning dope, such as the composition and dosage of the additives, and the content of the polymer. Another is the effect of the process conditions, such as the reeling velocity, the temperature of the spinning liquid, the pressure in the spinning process, the proportioning and the temperature of the core liquid, the temperature of the coagulating bath and the distance of the vaporizing part. The two factors both have restrict and relation with each other in the experimental and product procedure. Table II shows the effects of the volume flow rate of the extrusion on the membrane structure under other

constant spinning conditions, such as dry spinning line, the reeling velocity, and the flow rate of the core liquid. From Table II, it can be seen that when the volume flow rate increased, the external diameter, wall thickness and the porosity of the polysulfonebenzylthiourea hollow fiber matrix membrane all increased, whereas the pore size and flux decreased. With increasing of extrusion volume outflow, the amount of solvent of casting solution and the contact surface between coagulating agent and the spinning dope increased, and then the double diffusion rate between the solvent and coagulating agent accelerated. The fast speed of coagulation caused the membrane structure to become looser, thus causing the increasing trend of porosity of the membrane. The continuity condition of spinning process is expressed as follows¹³:

$$\rho\pi(R^2 - r^2)V = \rho\pi(R_0^2 - r_0^2)V_0 \quad (5)$$

where R and r are the external and internal diameter of hollow fiber matrix membrane respectively; R_0 and r_0 are the external and internal diameter of the spinning head respectively, ρ is the density of the jetting spinning dope; and V_0 and V are the extrusion rate and the movement velocity of the spinning dope, respectively. When the extrusion speed increases and the movement velocity of the spinning dope keeps invariable, to meet the continuity condition, the left term of the eq. (5) $\pi(R^2 - r^2)$ increases, that is, the wall thickness of the hollow fiber membrane increases. Because the core liquid and the flow rate are changeless, the internal diameter of the hollow fiber membrane keeps unaltered and the external diameter of the hollow fiber matrix membrane increases. The change of the flux, pore size and the porosity of the hollow fiber matrix membrane keep consistency with the results in literature,¹⁴ that is, the flux decreases with the increase of the wall thickness of the hollow fiber membrane. The reason that the pore size decreased was that the increase of the shearing rate caused the volume flow rate when the polymer solution flows in the spinning head. The increase of the shearing stress could enhance the degree of orientation of the molecular chain of the chloromethyl polysulfone make the array more compact, and lead the decreases of the porosity of the hollow fiber membrane.

TABLE II
The Effect of Extrusion Volume Outflow on the Structure of Polysulfonebenzylthiourea Hollow Fiber Membrane

Extrusion volume Outflow (mL min ⁻¹)	External diameter (mm)	Wall thickness (mm)	Water flux (L/m ² h)	Pore diameter (nm)	Porosity (%)
11.1	0.42	0.22	130.3	41.2	68.5
22.1	0.48	0.24	121.2	39.4	67.3
31.2	0.57	0.28	118.5	37.4	64.1
41.3	0.64	0.30	111.4	36.3	62.2

TABLE III
The Effect of Core Liquid Outflow on the Structure of the Polysulfonebenzylthiourea Hollow Fiber Membrane

Core liquid outflow (L h ⁻¹)	External diameter (mm)	Inner diameter (mm)	Wall thickness (mm)	Water flux (L/m ² h)	Pore diameter (nm)	Porosity (%)
0.45	0.48	0.25	0.23	120.8	38.9	64.1
0.50	0.49	0.28	0.21	134.1	42.3	68.3
0.56	0.55	0.35	0.20	139.9	46.1	70.2
0.58	0.59	0.40	0.19	148.3	50.3	74.3

Effects of flow rate of the core liquid on the structure of polysulfonebenzylthiourea hollow fiber membrane

The insert tube type spinning head of the hollow fiber was adopted, and the core liquid was passed over the inset tube on the one hand to offer a inside support for the fiber that just extruded, on the other hand to operate the inside coagulation effect. The effect of the flow rate of the core liquid on the structure of the hollow fiber membrane is shown on the Table III. It shows that with the increase of the flow rate of the core liquid, the internal and external diameter both increase, but the increase of the internal diameter is faster, and the wall thickness of the hollow fiber decreases, and the flux, pore size, and the porosity all increase. The reason is that with the increase of the flow rate of the core liquid, the acting force of the core liquid on the inner wall increases, and that results in the wall thickness of the spinning dope thinner; meanwhile, the increase of the flow rate of the core liquid make the increase of the diffusion velocity of the solvent in the spinning dope to the core liquid, and increase the differential concentration between the solvent and the coagulator on the interface of the membrane, then, the rate of the membrane forming is quickened, and the porosity, the pore size and the flux increase. But with the increase of the flow rate of the core liquid, the internal diameter and the external diameter of the membrane increase, then the wall thickness decreases rapidly, and the bearing capacity of the membrane decreases suddenly.

Effects of length of dry spinning line on structure of the polysulfonebenzylthiourea hollow fiber membrane

Table IV shows that the change of the structure of the polysulfonebenzylthiourea hollow fiber mem-

brane with the changing of the length of the dry spinning line at the constant reeling speed. From Table IV, it can be seen that the flux, pore size and porosity of the hollow fiber membrane increase with the increase of the dry spinning line, but the external diameter and the wall thickness decrease. The change of the dry spinning line affected the force on the spinning dope, hereby, it resulted the change of the shape of the spinning dope, then, resulted the change of the external diameter and wall thickness of the hollow fiber membrane. In the spinning process, the stresses applied on the spinning dope were mainly the following ones: (1) the extensional force F_t forced by the collecting device on the spinning dope; (2) the deadweight of the spinning dope; (3) the inertia force F_{in} to render the spinning accelerating; (4) the friction force F_f caused by the spinning dope and surrounding medium; (5) the surface tension F_s of the spinning dope; and (6) the rheological resistance F_R of the intermolecular chains in the spinning dope. The acting forces of any point in the spinning dope satisfied the equilibrium of the above forces¹³:

$$F_t + F_g = F_R + F_s + F_f + F_{in} \quad (6)$$

The exterior tension F_t caused by the winding equipment at L away from the spinning head could be expressed by the follow equation¹³:

$$F_t = P_{xx}^0(L) \cdot \pi R_L^2 \quad (7)$$

where P_{xx}^0 is the winding stress, and the equation of the gravity F_g is expressed as follows¹³:

$$F_g = (L - L_0) \pi R_L^2 g \left(1 - \frac{\rho^0}{\rho} \right) \cos \omega \quad (8)$$

The $\cos \omega$ value is relatable with the direction of motion. When the direction of spinning is upward

TABLE IV
The Effect of Dry Spinning Distance on the Structure of Polysulfonebenzylthiourea Hollow Fiber Membrane

Dry spinning distance (cm)	External diameter (mm)	Wall thickness (mm)	Water flux (L/m ² h)	Pore diameter (nm)	Porosity (%)
10	0.48	0.24	121.2	39.3	64.0
20	0.44	0.21	141.6	44.9	66.3
30	0.39	0.19	161.8	51.0	70.7

vertically, $\cos \omega = -1$; when horizontal, $\cos \omega = 0$; when downward vertically, $\cos \omega = 1$. In this study, the direction of the spinning in the dry spinning stage is downward vertically, so $\cos \omega = 1$. Where ρ^0 is the density of medium; ρ is the density of the spinning dope. The inertia force F_{in} is to render the spinning accelerating. The work applied by the outside forces on the spinning dope equals to the increase of its kinetic energy, and it could be calculated by the following equation¹³:

$$F_{in}(X_2 - X_1) = \frac{1}{2g}(mv_2^2 - mv_1^2) \quad (9)$$

$$F_{in}\Delta X = m(v_2^2 - v_1^2)/2g$$

where X_1 , X_2 are the distance of the two points on the nozzle plate respectively; v_1 , v_2 represent the movement velocity when the spinning dope at X_1 , X_2 ; and F_{in} is independent with the degree of the spinning. Rheological resistance F_R appears in the shear flow of the pore passages in the spinning head and is caused by the viscoelasticity normal stress passed by the winding equipment. It was decided by the rheological behavior of the spinning liquid, the flowing condition when passing the spinning head and the reeling velocity V_L [].

$$F_R = \pi R_0^2 P_{xx,0}^0 \quad (10)$$

The fiction resistance F_f refers to the skin fiction force of the spinning dope and the surrounding medium and its expression is¹³:

$$F_f = 2\pi(L - L_0)v^2 C_f / 2g \quad (11)$$

where v is the velocity; C_f is the coefficient of the friction resistance, which related with Reynolds criterion.¹³

$$\begin{aligned} C_f &= 0.68 \times Re^{-0.8} \\ Re &= Dv\rho^0/\mu \end{aligned} \quad (12)$$

where D is the external diameter of the spinning dope; ρ^0 is the medium density; μ is the medium viscosity, the following eq. (13) was obtained when eq. (12) was substituted into eq. (11)¹³:

$$F_f = \frac{0.68}{20.2g}(L - L_0)\pi R_L^2 \rho^0^{-0.8} V_L^{1.2} \mu^{0.8} \quad (13)$$

The eq. (13) shows that the fiction resistance not only will increase to 1.2 power of the reeling velocity, but also has relationship with the spinning line and the semidiameter of the spinning trick. The surface tension F_s on the spinning dope is so tiny that

could be ignored, then the eq. (6) transmutes to the following expression when F_s ignored¹³:

$$F_t = F_R + F_{in} + F_f - F_g \quad (14)$$

In eq. (14), only the fiction resistance term and the gravity term have relation with the spinning line. Combined F_f with F_g , the following eq. (15) was obtained¹³:

$$\begin{aligned} F_f - F_g &= \\ (L - L_0) &\left[\frac{0.68}{20.2} \pi R_L^2 \rho^0^{-0.8} V_L^{1.2} \mu^{0.8} - g\pi R_L^2 \left(1 - \frac{\rho^0}{\rho}\right) \cos \omega \right] \end{aligned} \quad (15)$$

Based on eq. (15), when the fiction resistance is greater than the gravity, that is,

$$\left[\frac{0.68}{20.2} \pi R_L^2 \rho^0^{-0.8} V_L^{1.2} \mu^{0.8} - g\pi R_L^2 \left(1 - \frac{\rho^0}{\rho}\right) \cos \omega \right] > 0$$

the spinning rate is high, and with the increase of the dry spinning line, the distance ($L - L_0$) between point L and the spinning head will increase, and the right term of (10) will increase. When the reeling velocity keeps constant, the left term F_t will be invariable. Hereby, to keep the stress balance of the spinning dope, that is, to set up eq. (14), the inertia force and rheological resistance must be reduced. The eq. (9) shows that the decrease of the inertia force will result in the decrease of movement velocity of the spinning dope. Learned from the equation of continuity, the decrease of the movement velocity of the spinning dope will enlarge the cross-section of the spinning dope, that is, the wall thickness of the spinning dope will increase, and the inside diameter of the spinning dope will be invariable with the constant flux of the core liquid. Therefore, when the spinning rate is large, the movement velocity of the spinning dope will decrease and the semidiameter of the spinning dope will increase with the increase of the dry spinning line. When the friction resistance is less than the gravity, that is $\left[\frac{0.68}{20.2} \pi R_L^2 \rho^0^{-0.8} V_L^{1.2} \mu^{0.8} - g\pi R_L^2 \left(1 - \frac{\rho^0}{\rho}\right) \cos \omega \right] < 0$, the spinning rate is less at this point, and the left term F_t of eq. (14) will decrease with the increase of the spinning line. When the reeling velocity is constant, F_t will be invariable, that is, when eq. (14) is set up, the inertia force and rheological resistance must be enlarged. The eq. (9) shows that the increase of the inertia force will result in the increase of the movement velocity of the spinning dope. Figure 2 is the ESEM photos of the cross-section of the hollow fiber membrane in different dry spinning lines. Based on the condition of continuity, the increase of the movement velocity of the spinning dope will result in the

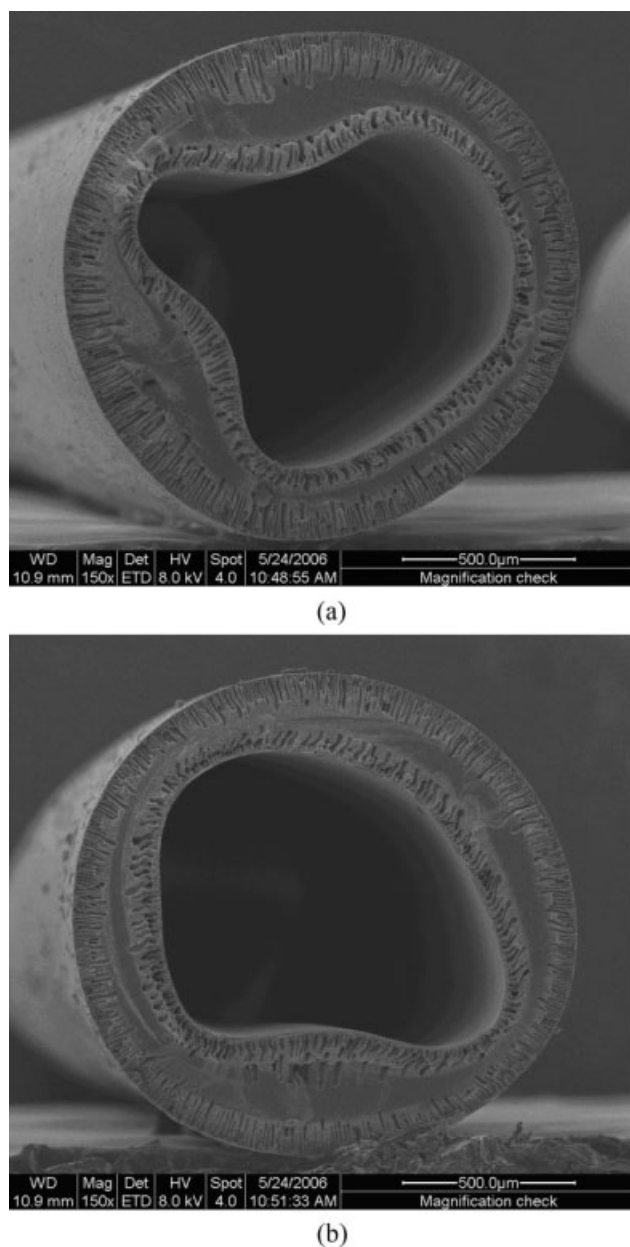


Figure 2 The ESEM of the cross-section of the polysulfonebenzylthiourea hollow fiber membrane with different dry spinning distance. (a) Dry spinning distance: 10 cm; and (b) dry spinning distance: 30 cm.

decrease of the cross-section of the spinning dope, that is, the external diameter of the spinning dope will decrease. Thus, when the reeling velocity is less, with the increase of the dry spinning line, the movement velocity will increase and the semidiameter of the spinning dope will decrease. In this study, with the increase of the dry spinning line, the velocity of the spinning dope increased, the diameter of the spinning dope decreased, the internal diameter was invariable and the wall thickness decreased. These results accord with the second situation discussed earlier. Therefore, the spinning process in this study

belongs to the low velocity spinning process. Because that the wall thickness of the spinning dope became thinner with the increase of the dry spinning line, the diffusional resistance of the solvent decreased and the residence time of the spinning dope in air got longer, the solvent in the spinning dope has diffused into the core liquid. That lead to the rich phase of chloromethyl polysulfone in the membrane center moving to the external surface, then, the thickness of the skin layer and density of the membrane increased; while because the fast solvent diffusion and low polymer concentration, the membrane beneath the skin layer formed many big interconnected finger like pores, the osmotic resistance was reduced greatly, and the porosity and pore size were elevated. In addition, the solvent volatilization can make the membrane surface compact, but DMAC was so easy to absorb the moisture in air that the coagulating concentration of the surface layer decreased and the coagulating course changed from the total wet double diffusion to gas phase coagulation partly. That resulted in the increase of the flux with the increase of the dry spinning line.

Isothermal adsorption equation of the polysulfonebenzylthiourea hollow fiber membrane for Cd^{2+} and Zn^{2+}

The adsorption isotherm is the relationship between the solution equilibrium concentration and the equilibrium adsorptive quantity of the membrane after the adsorption equilibrium. The adsorption isotherm can be determined at a static equilibrium condition or a dynamic equilibrium condition. In this study, the dynamic adsorption isotherm of the polysulfonebenzylthiourea hollow fiber membrane was determined to reflect the practical process of the Cd^{2+} and Zn^{2+} adsorption of the polysulfonebenzylthiourea hollow fiber membrane truly. The measuring method with the external pressure is shown as the following: the raw material solution of given concentration was extruded into the polysulfonebenzylthiourea hollow fiber membrane by the peristaltic pump, and the Cd^{2+} and Zn^{2+} in solution were absorbed by the thiourea chelating groups of the hollow fiber membrane; when the Cd^{2+} and Zn^{2+} concentration at the outlet of the polysulfonebenzylthiourea hollow fiber membrane did not vary with time, the Cd^{2+} and Zn^{2+} adsorption of the polysulfonebenzylthiourea hollow fiber membrane was saturated to reach to the balance; then the Cd^{2+} and Zn^{2+} adsorbed were dissociated by a given concentration of HCl solution, and the raw material concentration and the quality of Cd^{2+} and Zn^{2+} that dissociated were respectively as the equilibrium concentration of the solution and the equilibrium adsorption quantity of the polysulfonebenzylthiourea

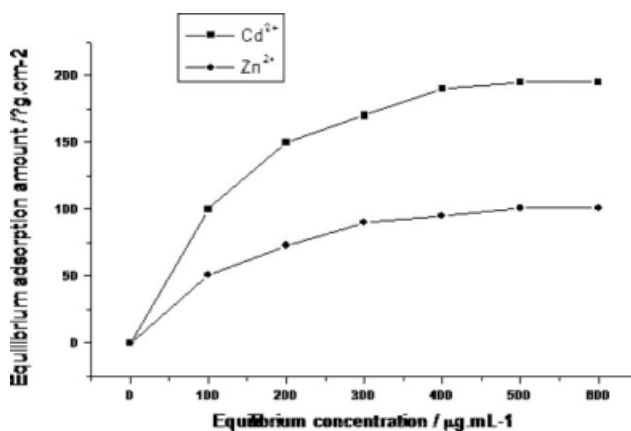


Figure 3 The adsorption isothermal curve of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺.

hollow fiber membrane. The dynamic adsorption experiment was carried out with a series of concentrations of the Cd²⁺ and Zn²⁺ solution at room temperature and the isothermal adsorption curve of the polysulfonebenzylthiourea hollow fiber membrane were obtained by plotting the equilibrium adsorption quantity versus equilibrium concentration of the solution, see Figure 3. For further investigating the isothermal adsorption of the polysulfonebenzylthiourea hollow fiber membrane, 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 polysulfonebenzylthiourea hollow fiber membrane, and these points are distributed uniformly, every adsorption point may be for nothing or adsorb a metal ion (that is the single molecule adsorption hypothesis), among them there are N_A adsorb the metal ion. Supposing the partition function of each metal ion is $q_0(T)$, from the knowledge of the quantum chemistry, the main partition function is¹⁵:

$$Q = \frac{N!}{N_A!(N - N_A)!} q_0^N(T) \quad (16)$$

According to the Stirling equation:

$$\begin{aligned} \ln Q = N \ln N - N_A \ln N_A - (N - N_A) \ln (N - N_A) \\ + N \ln q_0(T) \end{aligned}$$

Then the chemical potential of the metal ion on the polysulfonebenzylthiourea hollow fiber membrane is¹⁶:

$$\begin{aligned} \mu_a = RT \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T} \\ = RT \ln \left[\frac{N_A}{N - N_A} / q(T) \right] \end{aligned} \quad (17)$$

And the chemical potential of the metal ion in solution is¹⁶:

$$\mu_c = \mu_0 + RT \ln C \quad (18)$$

When the adsorption reaches to balance:

$$\mu_a = \mu_c$$

So

$$\frac{\theta}{1 - \theta} \frac{1}{q_0(T)} = \exp \left(\frac{\mu_0}{RT} \right) \quad (19)$$

Combined $q_0(T)$ with $\exp(\mu_0/RT)$ 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 obtained¹⁷:

$$\tau = \frac{\tau_m B(T) C}{1 + B(T) C} \quad (20)$$

Combined with the experiment, the isothermal adsorption equation that the Cd²⁺ and Zn²⁺ adsorption of the polysulfonebenzylthiourea hollow fiber membrane were associated as the following, respectively¹⁷:

$$\tau(\text{Cd}^{2+}) = \frac{2.1032C}{1 + 0.0021C} \quad (21)$$

$$\tau(\text{Zn}^{2+}) = \frac{1.7181C}{1 + 0.0013C} \quad (22)$$

From Figure 2, 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 metal ion adsorption of the polysulfonebenzylthiourea hollow fiber membrane was less. Therefore, this equation has a guiding significance for the magnified experiment and the commercial application of the removal Cd²⁺ and Zn²⁺ of the polysulfonebenzylthiourea hollow fiber membrane.

Effect of pH of the raw material solution on retention of the polysulfonebenzylthiourea hollow fiber membrane

In the exchange of the chelating ions, the pH value is the most important parameter to control the separation of the metal ions. The effect of the pH value on the retention of the polysulfonebenzylthiourea hollow fiber membrane is showed in Figure 4. In this experiment, the Cd²⁺ and Zn²⁺ were dissolved in different buffer solutions with different pH. From Figure 4, it can be found that with the increase of the pH value of the feed solution, the retention of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺ increased accordingly. The alternative thiourea

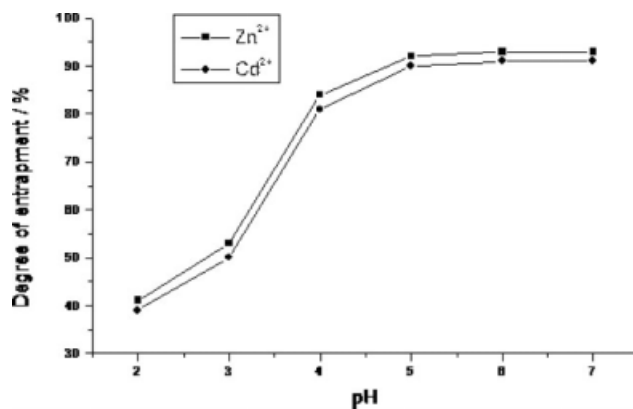


Figure 4 The effect of pH on the degree of entrapment of polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺.

groups of the polysulfonebenzylthiourea hollow fiber membrane create the stable compounds with Cd²⁺ and Zn²⁺. The thiourea chelating group on the hollow fiber membrane is subacidity group and had a strong affinity to H⁺. Therefore, the H⁺ concentration had an important effect on the chelates forming by thiourea and metal ions in the polysulfonebenzylthiourea hollow fiber membrane. The pH is one of the key factors that affect the chelating capacity of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺, the stronger the acidity, the more seriously decompose of chelates, the lower chelating capacity of the membrane for Cd²⁺ and Zn²⁺, and the chelating capacity could be enhanced by increasing the pH the mobile phase. But under the alkaline condition, Cd²⁺ and Zn²⁺ would hydrolyze and deposit and jam the membrane pores of the hollow fiber membrane. That resulted in the decrease of the flux and the retention.

Effects of ionic strength of the raw material solution on the retention of the polysulfonebenzylthiourea hollow fiber membrane

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 polysulfonebenzylthiourea hollow fiber membrane is shown in Figure 5. Figure 5 shows that when the NaCl concentration increases in raw solution, the retention of the hollow fiber membrane for Cd²⁺ and Zn²⁺ decrease a bit. 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 Cd²⁺ and Zn²⁺. Debye–Hückel limit formula is as follows¹⁸:

$$\lg \gamma_{\pm} = -AZ_{+}|Z_{-}|\sqrt{I} \quad (23)$$

$$A = \frac{(2\pi L\rho_A^*)^{1/2}e^3}{2.303(4\pi\epsilon_0\epsilon_r kT)^{3/2}}$$

where L is the Avogadro 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 γ_{\pm} is the mean activity coefficient of the ions. From the Debye–Hückel limit formula we learned that when the ionic strength increase, the ionic mean activity coefficient decrease, that is, the activity decrease; While with the increase of the NaCl concentration, the ionic strength increases either, therefore, the Cd²⁺ and Zn²⁺ activity decreased and made the chelating capacity of the hollow fiber membrane on Cd²⁺ and Zn²⁺ decreased.

Effects of operating rate on the retention of metal ions on the polysulfonebenzylthiourea hollow fiber membrane

Figure 6 shows the effect of the feeding rate on the retention of the polysulfonebenzylthiourea hollow fiber membrane under the condition of a given feeding amount and concentration of solution (the concentration of Cd²⁺ is 100 µg mL⁻¹, and the concentration of Zn²⁺ is 80 µg mL⁻¹). It can be concluded from Figure 6 that with the increase of the feeding rate, the retention of the hollow fiber membrane for Cd²⁺ and Zn²⁺ decreased a bit. The bond ability of Cd²⁺ and Zn²⁺ in the mobile phase with

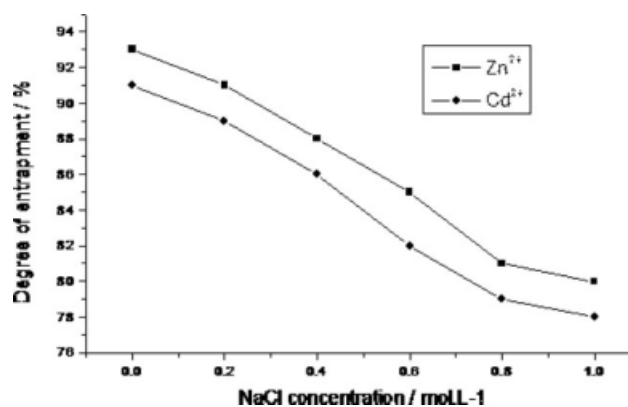


Figure 5 The effect of NaCl concentration on the degree of entrapment of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺.

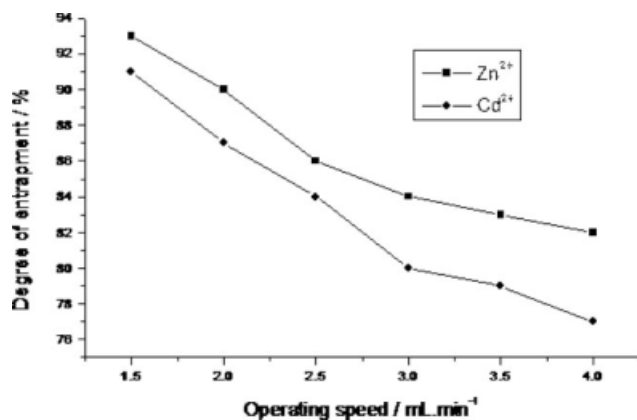


Figure 6 The effect of operating speed on the degree of entrapment of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺.

the thiourea group on the hollow fiber membrane was a little stronger and the bonding rate was also fast. The thiourea chelating group mostly bonded on the internal surface of the hollow fiber membrane. When the raw solution permeated through the hollow fiber membrane in convection way, the thiourea chelating group on the membrane could chelate with Cd²⁺ and Zn²⁺ soon. That is why the change of the feeding rate of the mobile phase had little effect on the retention of the polysulfonebenzylthiourea hollow fiber membrane. The fast bonding kinetics of the thiourea chelating group on the membrane with Cd²⁺ and Zn²⁺ permitted that the polysulfonebenzylthiourea hollow fiber membrane could be operated at a high feeding rate. At the same time, the Cd²⁺ and Zn²⁺ adsorption of the hollow fiber membrane fully used the high efficient and speedy bonding characters of the thiourea on the membrane with Cd²⁺ and Zn²⁺, and that could realize the fast separation and reclamation of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺ at a large scale. The fast feeding rate and the short separation period could make an industrial foundation of removal of Cd²⁺ and Zn²⁺ for the polysulfonebenzylthiourea hollow fiber membrane.

Effects of feeding ram on retention of the polysulfonebenzylthiourea hollow fiber membrane

The chelating capacity of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺ was a constant at a given concentration of the raw material solution. With increase of the feeding ram, the thiourea chelating groups unemployed on the hollow fiber membrane became less and less. When the feeding ram reached to a certain degree, the polysulfonebenzylthiourea hollow fiber membrane could not adsorb Cd²⁺ and Zn²⁺ and the adsorption reached to balance. The saturation of the polysulfonebenzylthiourea hollow fiber membrane became higher

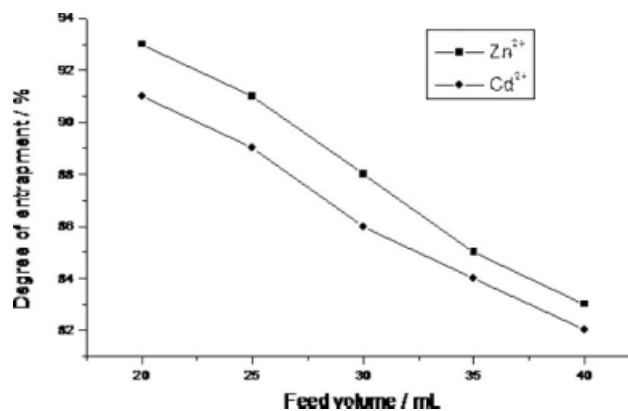


Figure 7 The effect of feed volume on the degree of entrapment of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺.

nebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺ is expressed as follows:

$$S = \frac{\tau}{\Gamma} \quad (24)$$

where S is saturation of the hollow fiber membrane, τ ($\mu\text{g cm}^{-2}$) is the quantity of Cd²⁺ and Zn²⁺ adsorbed by the hollow fiber membrane, and Γ ($\mu\text{g cm}^{-2}$) is the balance adsorption quantity of the hollow fiber membrane at the feeding concentration. Figure 7 shows the relationship between the feeding ram of the solution and the retention of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺; Figure 8 shows the relationship of the feeding ram of solution and the adsorption saturation of the hollow fiber membrane. It can be concluded from Figure 7 and Figure 8 that with the increase of the relative feeding ram, the retention of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺ decreased gradually, but the adsorption saturation of the polysulfonebenzylthiourea hollow fiber membrane became higher

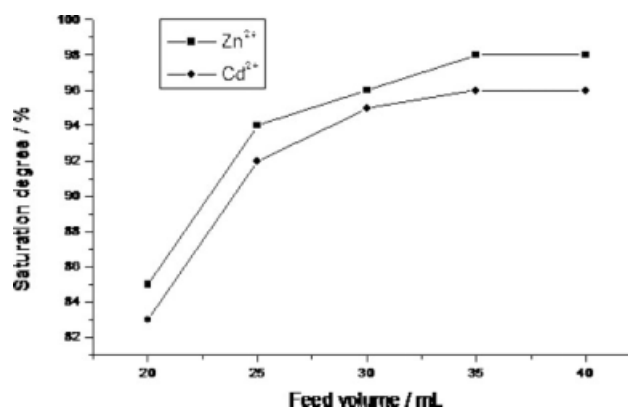


Figure 8 The effect of feed volume on the saturation degree of the polysulfonebenzylthiourea hollow fiber membrane for Cd²⁺ and Zn²⁺.

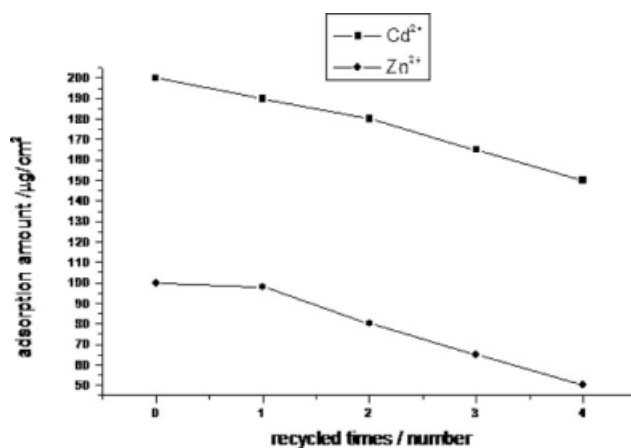


Figure 9 The trendline between recycled times and Cd²⁺/Zn²⁺ dynamic equilibrium adsorption amount.

and higher. Therefore, in the process of reclamation of Cd²⁺ and Zn²⁺, the retention and saturation of the hollow fiber membrane should be considered comprehensively. It should confirm the feeding rate of the raw solution based on the required production recovery and the saturation of the hollow fiber membrane. The polysulfonebenzylthiourea hollow fiber membrane was recycled by soaking in 600 mL of 0.1M dilute HCl solution for 10 h at room temperature and the concentration of Cd²⁺ and Zn²⁺ in HCl were 10 µg/mL and 8 µg/mL, respectively. The recycled polysulfonebenzylthiourea hollow fiber membranes were used to remove Cd²⁺ and Zn²⁺, respectively, and the dynamic equilibrium adsorption amount were 190 µg/cm²-memb and 98 µg/cm²-memb, which were little smaller than that of the brand new membrane. Figure 9 is the trendline between recycled times and Cd²⁺/Zn²⁺ dynamic equilibrium adsorption amount. This showed that the polysulfonebenzylthiourea hollow fiber membrane can be easily and conveniently recycled in dilute HCl solution, which will play an important roll for the utilization of such hollow fiber membrane in the treatment of Cd²⁺ and Zn²⁺ in the industrial wastewater.

CONCLUSION

The highly qualified polysulfonebenzylthiourea hollow fiber reactive ultrafiltration membranes with high rejection capacity for heavy toxic metal cations

Cd²⁺ and Zn²⁺ can be prepared through the reaction between the chloromethyl polysulfone hollow fiber matrix membrane and thiourea. The results indicated that the additive content, extrusion rate, flow rate of the core liquid, and the length of dry spinning line have significant effects on the structure of polysulfonebenzylthiourea hollow fiber membrane. The adsorption isotherms of Cd²⁺ and Zn²⁺ can be described by the Langmuir isotherm. The pH value had a great effect on the removal of heavy toxic metal cations, and the increase of the ionic concentration of the raw material solution was not favorable for the removal of heavy toxic metal cations of the polysulfonebenzylthiourea hollow fiber membrane. The polysulfonebenzylthiourea hollow fiber membrane could be operated at high feed flow rate, and a large-scale removal of heavy toxic metal cations could be realized.

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