Preparation, Characterization, and Adsorption Properties for Metal Ions of a Novel Chelating Resin Containing Sulfoxide and Diethylene Glycol

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ABSTRACT: A novel chelating resin containing sulfoxide and diethylene glycol, poly{4-vinylbenzyl-[2-2-(hydroxyethyl)ethoxyl]sulfoxide} (PVESO) was synthesized using chloromethylated polystyrene (PS-Cl) as material. Its structure was characterized by elemental analysis, infrared spectra, and scanning electron microscopy (SEM). The adsorption capacities of the resin for Hg^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} at various pH values were determined. The maximum adsorption capacities for Hg^{2+} and Ag^{+} were 1.56 and 0.75 mmol g^{-1} respectively. The resin had high selectivity for Hg^{2+} and Ag^{+} over the pH range 1.0–7.0. The adsorption capacities for Hg^{2+} and Ag^{+} under competitive condition were also determined by batch experiment method. In addition, the adsorption kinetics of the resin towards Hg^{2+} at different temperatures was also investigated. The results showed that the adsorption rate was governed by film diffusion at 20°C and 25°C, by particle diffusion at 30°C and 35°C. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 6054–6059, 2006

Key words: chelating resins; sulfoxide; adsorption kinetics; film and particle diffusion; metal ions

INTRODUCTION

It is well-known that ligands with ''soft'' type donors prefer interactions with ''soft,'' i.e., large and more easily polarizable, acceptors such as mercury, silver, and mercury.[1] High ligand affinity for these cations is used in the synthesis of selective extractions and resins. Chelating resins containing sulfur are highly efficient in the selective adsorption of precious metal ions.[2,3] Many attempts have been made to design new chelating resins containing sulfur atoms, such as thiol,[4–6] thiourea,[7,8], dithiazone,[9,10] and 2-mercaptobenzothiazole.[11] Recently, chelating resins bearing sulfoxide groups have been utilized in separating noble metal,[12,13] poisonous mercury,[14] rare earth,[15] and radioactive element uranium[16] from aqueous solution. In Ref. [17], the adsorption properties and mechanism of the resins containing sulfide, sulfone, and sulfoxide have been reported. The resin with sulfoxide presents a high capacity and good selectivity towards noble metal ions, especially for Au^{3+} and Pd^{2+}.

When chelating resins are used to remove and recover metal ions from aqueous solutions, hydrophilic resins are preferred over hydrophobic systems. The hydrophobicity of the resin sometimes makes it difficult for the metal ions to swell in water and to diffuse into the interior of the resin, which will limit the coordinating reaction between functional group and metal ions.[18] In Refs. 19 and 20, the hydrophilic chain of poly (ethylene glycol) has been introduced into the polymeric matrix. They conclude that the incorporation of hydrophilic group shows a remarkable influence in the coordinating reactions both increasing the affinity and the adsorption kinetic of the chelating groups.

Considering the above, we synthesized a novel chelating resin containing sulfoxide and diethylene glycol (PVESO). Its adsorption properties for Hg^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} were determined as a function of

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pH. The adsorption selectivity in several binary mixtures by the batch method and the adsorption kinetics for Hg^{2+} at different temperatures were also investigated.

EXPERIMENTAL

Materials

Chloromethylated polystyrene (PS-Cl, crosslinked with 10% DVB, 5.49 mmol/g Cl) was purchased from Chemical Factory of Nankai University of China. 2-(2-Chloroethoxy) ethanol was purchased from Aldrich Chemical and used as received. All other reagents for synthesis of the resin were analytical-grade and used without further purification. Stock solutions of Pb^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, and Ag^{+} were prepared by dissolving the appropriate amount of analytical grade nitrates in deionized H_2O respectively.

Instruments

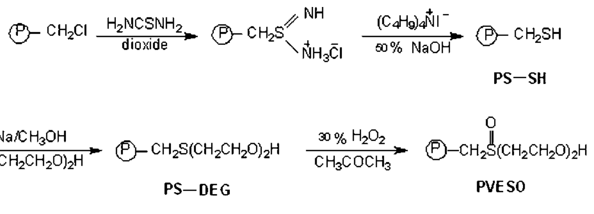
Elemental analysis was performed by a Elementar Analysensysteme Gmbh Varioel made in Germany. The infrared spectra were recorded on a Nicolet MAGNA-IR550 (series II) spectrometer; test condition: potassium bromide pellets, scanning 32 times, resolution 4 cm^{-1}. The surface morphology of the intermediates and PVESO were examined on a scanning electron microscope (SEM), JSF5610LV, JEOL. The surface area and average pore diameter were determined by ASAP 2020 V3.00 E (made in America). The concentration of metal ion in the solution was measured on a GBC-932 atomic absorption spectrophotometer (AAS) made in Australia. The adjustment of pH was done with a systronics digital pH meter (Model pH211, made in Australia).

Preparation of PVESO

The synthetic route of PVESO is described in Scheme 1.

Preparation of PS-SH

PS-Cl (5 g, ∼ 27.5 mmol Cl) and thiourea (8.5 g) were suspended in dioxide/ethanol (4 : 1, 75 mL) and the reaction was stirred at 85°C for 1 h. The resin was then filtered and washed with distilled water and benzene respectively, to remove all the excess soluble reagents and by-products. After this washing, the resin was suspended in benzene (60 mL) and a solution of 0.16 g of tetrabutyl ammonium iodide in 4 mL of distilled water and 3 g sodium hydroxide was added. The mixture was then refluxed under a nitrogen atmosphere for 48 h. After filtration, the resin was washed with THF, water, and methanol. Then the resin was moved to a Soxhlet's extraction apparatus for reflux-extraction in 95% ethanol for 4 h and finally was dried under vacuum at 50°C for 48 h. Then, 4.88 g of PS-SH was obtained.



Scheme 1 Synthetic route of PVESO

Preparation of PS-DEG

Sodium metal (0.72 g, 31.3 mmol) was added in small pieces to a mixture of ethanol (20 mL) and dioxide (20 mL). When all of the sodium had undergone reaction, PS-SH (4.64 g, ∼ 23.8 mmol SH) prepared earlier was added, and the suspension was shaken at room temperature overnight. Then, 2-(2-chloroethoxy) ethanol (5.83 g, 46.8 mmol) was added and the reaction was stirred at 50°C for 24 h. The product was filtered and washed with water and ethanol. The procedure of purification of PS-DEG was similar to that of PS-SH. Then, 6.33 g of PS-DEG was obtained.

Preparation of PVESO

PS-DEG (6.0 g, ∼ 23.9 mmol S) was suspended in acetone (50 mL), a mixture of 2.71 g of 30% hydrogen peroxide (23.9 mmol) and 10 mL of acetone was added dropwise to the stirred suspension at room temperature. After addition was complete, the reaction was stirred at room temperature for 6 h, then at 63°C for 2 h. The procedure of purification of PVESO was similar to that of PS-DEG. Then, 6.38 g of PVESO was obtained.

Water regain

Water regain was defined as the amount of water absorbed by 1 g of the resin. It was measured according to the following method: Approximately 1 g of resin was swollen in 50 mL of double distilled water for 48 h, and then filtered off by suction, weighed, dried at 80°C for 48 h. After cooling in a desiccator, the resin was reweighed. The water regain was calculated as $(m_w - m_d)/m_d$, where m_w is the weight of the water swollen resin, m_d is the dry weight of the resin.

Adsorption experiments

Adsorption capacities

About 50 mg of PVESO was added to 25 mL of metal ion solution adjusted to the desired pH and the mixture was shaken for 24 h at 25°C. The mixture was filtered off and the concentration of the solution was determined by atomic absorption spectrometry.

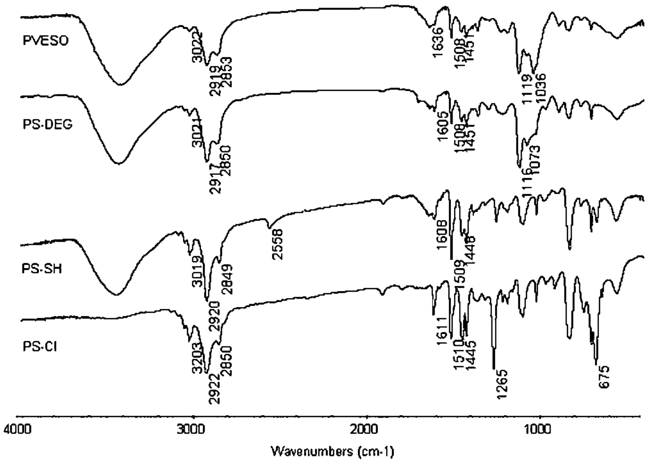


Figure 1 IR spectra of the intermediates and PVESO.

Adsorption capacity (Q) was calculated according to eq. (1):

$$Q(\text{mmol/g}) = \frac{(C_0 - C)V}{W} \tag{1}$$

where C_0 and C are the concentration of metal ions before and after sorption (mmol/mL), respectively; V is the volume of solution used for sorption (mL); and W is the weight of the resin (g).

Adsorption rate

In kinetic experiment, 50 mg of PVESO was added to 20 mL of $2 \times 10^{-3}M$ Hg^{2+} solution (pH 5.0). The mixture was shaken continuously at a definite temperature. At predetermined intervals, aliquots of 1 mL solution were withdrawn for analysis and the concentration of Hg^{2+} was determined by atomic absorption spectrometry.

Adsorption selectivity

To determine adsorption selectivity of PVESO under competitive condition, the resin was contacted with a binary mixture, in which the concentration of each metal ion was equal. The total concentration of the two kinds of metal ions was $5 \times 10^{-4}M$. Thus, 50 mg of PVESO was shaken with a solution of binary mixture for 24 h. Then, the resin was separated by filtration and the concentration of the metal ions in the binary mixture was determined by atomic absorption spectrometry.

The regeneration of PVESO

To assess the reusability of the resin, consecutive adsorption–desorption cycles were repeated five times using the same resin. The metal ions adsorbed on the resin were eluted with certain volume of desorbents, and the concentrations of the effluents were determined by atomic absorption spectrometry.

RESULTS AND DISCUSSIONS

Synthesis and characterization of PVESO and intermediates

PS-SH was characterized by the presence of a weak absorption band at 2558 cm^{-1} belonging to S—H group[21] and by the weakening of two strong absorption bands at 1265 and 675 cm^{-1} corresponding to the flexural vibration of C—Cl.[22] The percent conversion of C—Cl group calculated from the sulfur content in PS-SH was 92%. PS-DEG was characterized by the presence of new bands at 1116 cm^{-1} (stretching in the C—O group), 1073 cm^{-1} (bending in the O—H group) (Fig. 1). The content of sulfur in PS-DEG was 3.98 mmol g^{-1}, which meant that the reaction was not complete and the percent conversion of SH group in PS-SH was 78%. The water regain of PS-DEG was about twice as large as that of PS-SH (shown in Table I), which indicated that a considerable improvement on hydrophilicity was obtained after introducing hydrophilic chain of diethylene glycol into the polymeric matrix. In the synthesis of PVESO, we adopted the similar reaction condition described in the literature.[17] The structure of PVESO was conformed by the presence of strong adsorption band at

TABLE I
Elemental Analysis, Water Regain, and Functional Group Capacity of the Intermediates and PVESO

Resin	C%	H%	S%	Functional group capacity (mmol FG/g)	Water regain (mmol/g)
PS-SH	73.17	6.724	16.92	5.12	13.03
PS-DEG	66.75	7.284	12.75	3.98	29.19
PVESO	62.99	7.127	11.97	3.74	43.30

The functional group capacities were calculated from the content of S in the intermediates and PVESO.

BET surface area and BJH desorption average pore diameter of PVESO: 24.22 m^2/g and 42.04 nm, respectively.

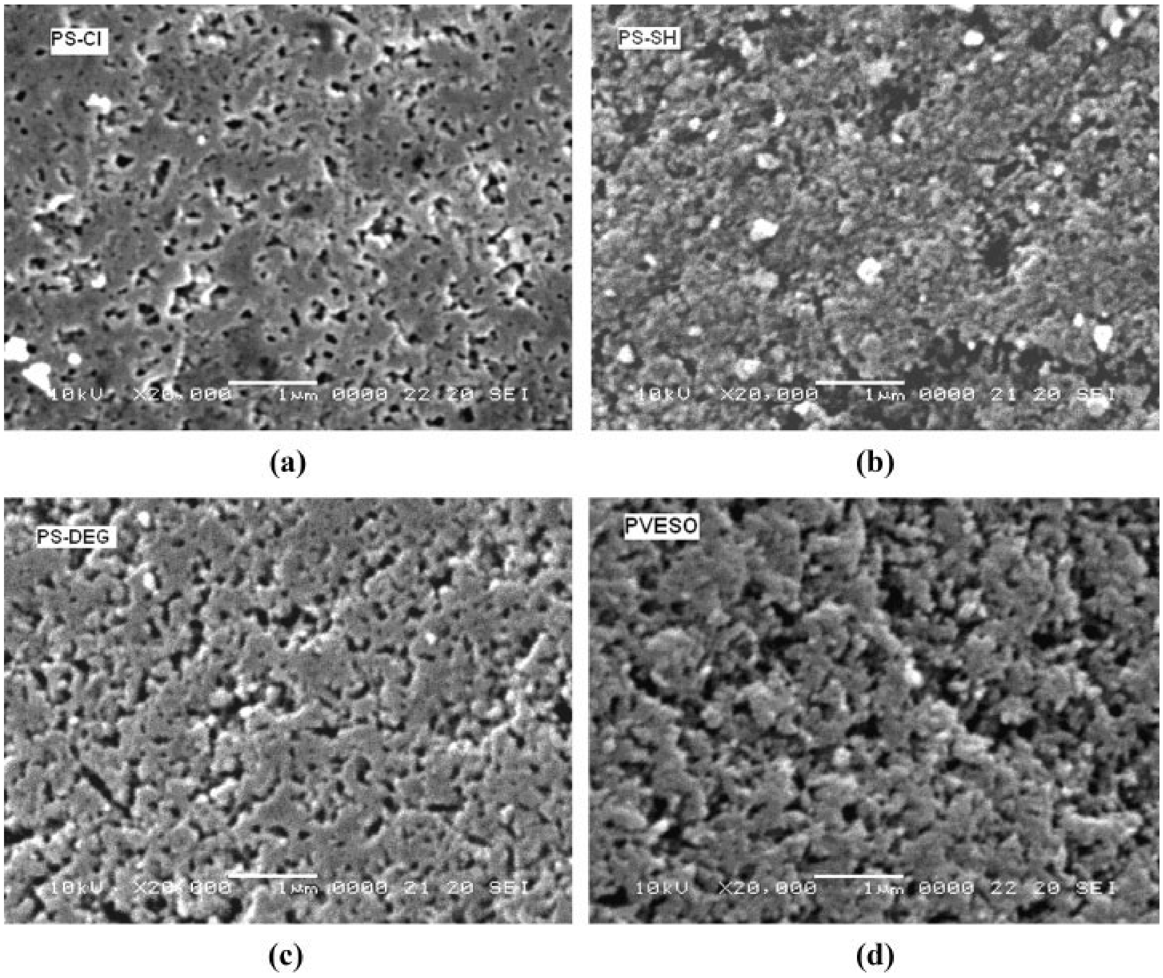


Figure 2 The SEM images of the intermediates and PVESO.

1036 cm^{-1} corresponding to the group of S=O.[21] The elemental results showed that the percent conversion of sulfide group was 94%. PVESO had a water regain of 43.30 mmol/g, which was much higher than that of PS-DEG. These experimental data indicated that the increase of hydrophilicity was not only by the introduction of diethylene glycol but also the oxidation of sulfur into sulfoxide.

To observe the surface morphology of the intermediates and PVESO, scanning electron micrographs of the gold-coated samples were taken with a SEM and the images are shown in Figure 2. Obviously, there were abundant pores distributed on the surface of PVESO, which indicated that the macroporous structure of PS-Cl had not been damaged after the reaction with thiurea, NaOH aqueous solution, sodium metal, 2-(2-chloroethoxy) ethanol, and further with 30% hydrogen peroxide solution.

Adsorption capacities of PVESO

The adsorption capacities of PVESO for Hg^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} at different pH values under noncompetitive conditions were investigated. The results are shown in Figure 3.

From Figure 3, it could be seen that PVESO exhibited high affinity towards Hg^{2+}, next for Ag^{+}, Cu^{2+},

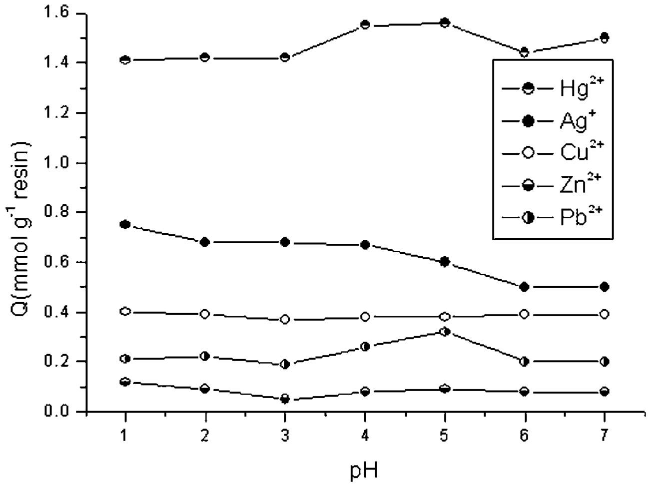


Figure 3 Adsorption capacity of PVESO for different metal ions versus pH.

TABLE II
The Adsorption Selectivity of PVESO in Binary Mixtures at 25°C

Systems	Metal ions	pH	Adsorption capacity (mmol g^{-1})	Selective coefficient
Hg^{2+}-Ag^{+}	Hg^{2+}	5.0	0.85	$\alpha_{Hg/Ag} = 42.5$
	Ag^{+}		0.02	
Hg^{2+}-Cu^{2+}	Hg^{2+}	5.0	1.46	$\alpha_{Hg/Cu} = \infty$
	Cu^{2+}		0	
Hg^{2+}-Zn^{2+}	Hg^{2+}	5.0	1.55	$\alpha_{Hg/Zn} = \infty$
	Zn^{2+}		0	
Hg^{2+}-Pb^{2+}	Hg^{2+}	5.0	1.63	$\alpha_{Hg/Pb} = \infty$
	Pb^{2+}		0	
Ag^{+}-Cu^{2+}	Ag^{+}	1.0	0.62	$\alpha_{Ag/Cu} = 5.2$
	Cu^{2+}		0.12	
Ag^{+}-Zn^{2+}	Ag^{+}	1.0	0.33	$\alpha_{Ag/Zn} = \infty$
	Zn^{2+}		0	
Ag^{+}-Pb^{2+}	Ag^{+}	1.0	0.31	$\alpha_{Ag/Pb} = \infty$
	Pb^{2+}		0	

Pb^{2+}, and Zn^{2+}. The maximum adsorption capacities of PVESO for Hg^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} were 1.56, 0.75, 0.39, 0.12, and 0.32 mmol g^{-1} respectively. The pH values had a slight effect on the adsorption capacities of the resin. The maximum adsorption capacities of the metal ions were obtained under the optimal pH 5 for Hg^{2+} and Pb^{2+}, 1 for Ag^{+}, Cu^{2+}, and Zn^{2+} in this study.

Adsorption selectivity of PVESO

The ability to selectively remove some particular metal ions from aqueous solution under competitive conditions is of utmost importance in designing chelating resins. The adsorption selectivity of PVESO for metal ions in a binary component system was investigated. The experimental results are shown in Table II.

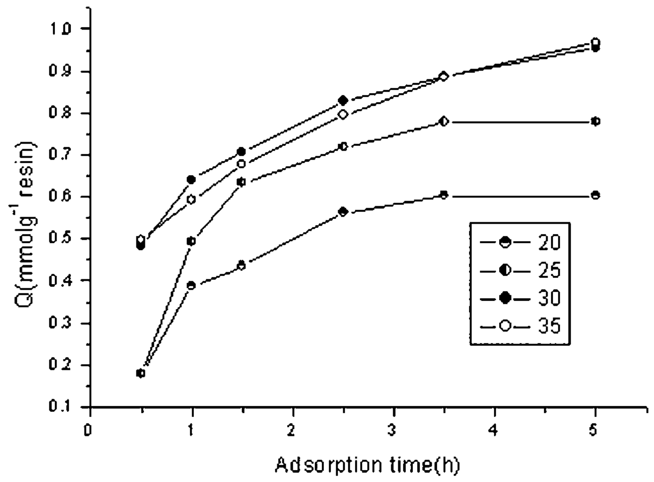


Figure 4 Adsorption rate curves of PVESO for Hg^{2+} at different temperatures (pH = 5.0).

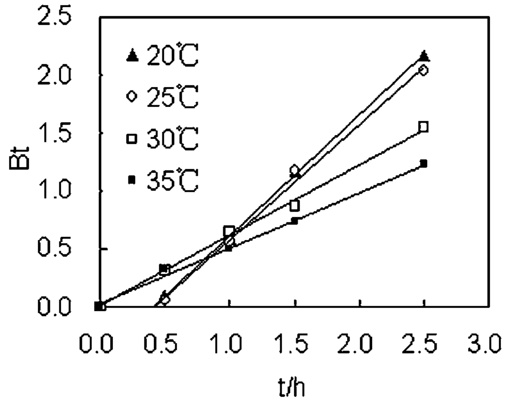


Figure 5 *Bt* versus time plots at different temperatures.

It could be seen that Hg^{2+} was prior to be adsorbed, and Cu^{2+}, Zn^{2+} and Pb^{2+} was not adsorbed completely by PVBSO in systems of Hg^{2+}-Cu^{2+}, Hg^{2+}-Zn^{2+} and Hg^{2+}-Pb^{2+}. A similar behavior was found for Ag^{+} in systems of Ag^{+}-Zn^{2+} and Ag^{+}-Pb^{2+}. When PVESO contacted with a solution of Hg^{2+}-Ag^{+} at pH 5.0, the adsorption capacities for Hg^{2+} and Ag^{+} were 0.85 and 0.02 mmol g^{-1} respectively, which were less than in the case of noncompetitive conditions. This corresponded to a selective coefficient of 42.5. In system of Ag^{+}-Cu^{2+}, the selective coefficient was 5.2. All the above-mentioned data implied that PVESO had good adsorption selectivity for Hg^{2+} and Ag^{+}, and it could be probably used in extracting and separating Hg^{2+} and Ag^{+} from multi-ionic system.

Adsorption kinetics of PVESO

Considering the high adsorption capacity and good selectivity of PVESO, Hg^{2+} was chosen to investigate the adsorption kinetics. The adsorption rate curves of PVESO for Hg^{2+} at different temperatures were shown in Figure 4. The results showed the adsorption capacity of PVESO increased with the increase of temperature, which was, higher temperature was more beneficial to adsorption. A possible explanation for this was that the resin was swollen more completely at higher temperature, which made it easier for Hg^{2+} to diffuse into the interior of the resin.

The adsorption procedure of adsorbent for metal ions was regarded as taking place through two mechanisms

TABLE III
The *Bt* Versus Time Linear Equations, Correlation Coefficients R^2, and Intercept Errors

Temperature (°C)	Linear equation	Correlation coefficient, R^2	Intercept errors
20	$Bt = 1.0412t - 0.4307$	0.9983	0.0387
25	$Bt = 0.9941t - 0.4137$	0.9945	0.0813
30	$Bt = 0.6089t + 0.005$	0.9977	0.0466
35	$Bt = 0.4777t + 0.0293$	0.9961	0.0291

TABLE IV
Desorption and Regeneration Data

Reuse times	Adsorption (mmol g^{-1})
1	1.56
2	1.55
3	1.53
4	1.52
5	1.5

of film diffusion and particle diffusion. The following equation derived by Boyd et al.[23] was employed to determine the adsorption mechanisms of the resin.

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp[-n^2Bt] \tag{2}$$

where F is the fractional attainment of equilibrium at time t and is obtained by the expression

$$F = \frac{Q_t}{Q_0} \tag{3}$$

where Q_t is the amount of adsorbent taken up at time t and Q_0 is the maximum equilibrium uptake.

Bt is obtained from the F value. Values of Bt for each F value are given by Reichenberg.[24] The results were plotted in Figure 5. If the plot of Bt versus time (having slope B) is a straight line passing through the origin, then the adsorption rate is governed by particle diffusion mechanism, otherwise it is governed by film diffusion. As shown in Figure 5, the straight lines at 30°C and 35°C passed through the origin, meaning that the rate controlling step of the adsorption process was particle diffusion, while at 20 and 25°C, the rate of adsorption was governed by film diffusion. The linear equations, correlation coefficients R^2 and intercept errors were listed in Table III.

The regeneration of the resin

In this study, 0.1M HNO_3 and 5% thiourea 0.1M $HClO_4$ was used for the desorbents of Hg^{2+}. The recoveries were found to be 89.1% and 98.4%, respectively. Therefore, 5% thiourea 0.1M $HClO_4$ was chosen to be used in the experiments of regeneration of the resin. The adsorption capacities of five adsorption–desorption cycles were listed in Table IV. It could be noted that there was almost no decrease in adsorption capacity under static conditions even after five cycles of operation. This meant that this resin could be used repeatedly.

CONCLUSIONS

A novel chelating resin containing sulfoxide and diethylene glycol was synthesized and characterized in this study. The water regain experiments showed that the introduction of diethylene glycol or sulfoxide into the polymeric matrix might increase the hydrophilicity effectively. The maximum adsorption capacities of the resin for Hg^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}were 1.56, 0.75, 0.40, 0.12, 0.32 mmol g^{-1}, respectively. The resin had good selectivity for Hg^{2+} and Ag^{+} under competitive conditions. The kinetics of the adsorption was governed by film diffusion at 20 and 25°C, by particle diffusion at 30 and 35°C.

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