

Synthesis, Characterization, and Properties for Hg^{2+} of New Chelating Resin Containing Sulfoxide and 3-Aminopyridine

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ABSTRACT: A new chelating resin (PVESO-AP) containing sulfoxide and 3-aminopyridine (AP) was synthesized by using chloromethylated polystyrene-*co*-divinylbenzene (PS-Cl) as material. Its structure was characterized by infrared spectra and elemental analysis. The adsorption capacities of the newly formed resin for Hg^{2+} , Ag^+ , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Ni^{2+} were determined at pH 2 and 5. In addition, the adsorption selective coefficients for Hg^{2+} in several binary mixture systems were investigated by batch experiment method. The results showed that this resin had high adsorption selectivity for Hg^{2+} . The

adsorption kinetics and isothermal of PVESO-AP for Hg^{2+} at different temperatures were also investigated. The adsorption kinetics showed that the apparent activation energy E_a was 13.71 kJ/mol. The results also showed that the Langmuir model was better than the Freundlich model to describe the isothermal process of PVESO-AP resin for Hg^{2+} . © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2144–2149, 2008

Key words: chelating resin; 3-aminopyridine; sulfoxide; adsorption; metal ion

INTRODUCTION

Much attention has been drawn to the synthesis of chelating resins and to the investigation of their adsorption behaviors for metal ions owing to their triple function of ion exchange, chelate formation, and physical adsorption. In general, the adsorption selectivity of chelating resins has been reported to be dependent mainly on the chelate forming properties of functional groups chemically bonded on the supports such as silica gel, cellulose, and macroporous copolymers.¹ Chelating resins with covalently bonded heterocyclic functional groups possess excellent adsorption and selectivity properties for metal ions, especially for heavy metal ions. Such heterocyclic functional groups as pyridine,^{2,3} imidazole,^{4,5} thiodiazole,^{6,7} 2-mercaptobenzothiazole,^{8,9} etc., have been introduced into polymeric matrix. Among the aforementioned heterocyclic functional groups, aminopyridine receives a lot of attention because of its

strong affinity for noble and heavy metal ions. The earlier reports^{10,11} has investigated the adsorption properties of the chelating resins anchoring aminopyridine to polymeric support for metal ions. It has been found that these resins containing aminopyridine as functional group have high affinity and good adsorption selectivity for mercury.¹¹

Recently, chelating resins bearing sulfoxide groups have been synthesized for separating noble and heavy metal ions from aqueous solution.^{12,13} The adsorption properties of the resins containing sulfide, sulfone, and sulfoxide for metal ions have been reported in the literatures.^{14,15} It has been shown that the resin with sulfoxide presents a high capacity and good selectivity toward noble and heavy metal ions.

Considering the above, we synthesized a novel chelating resin bearing sulfoxide and 3-aminopyridine (3-AP). Its adsorption properties for Hg^{2+} , Ag^+ , Cu^{2+} , Ni^{2+} , Cd^{2+} , and Zn^{2+} were determined. The adsorption kinetics and isotherms for Hg^{2+} at different temperatures were investigated. The adsorption selectivity in several binary mixture systems by batch method was also studied.

EXPERIMENTAL

Materials

Commercial chloromethylated polystyrene-*co*-divinylbenzene beads (PS-Cl, with a degree of cross-linking 10% DVB, chlorine content 19.85%, 30–40

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mesh, BET surface area 31.85 m²/g) was obtained from Chemical Factory of Nankai University of China. 2-Mercaptoethanol, tetrabutyl ammonium bromide, benzenesulfonyl chloride (BsCl), 3-aminopyridine (AP), and other reagents, solvents were purchased from Tianjin Resent Chemicals Co. These analytical-grade chemical products were used without further purification. Stock solutions of all the metal ions were prepared by dissolving appropriate amounts of analytical grade nitrates in distilled water. The buffer solutions were prepared by addition of dilute NH₄OH or HNO₃ to 0.1M ammonium acetate solution.

Instruments

Infrared spectra were recorded on a Nicolet MAGNA-IR550 (series II) spectrometer; test conditions: potassium bromide pellets, scanning 32 times, resolution is 4 cm⁻¹. The content of S and N elementary analyses were carried out by central laboratory of Shandong University. The concentration of metal ions was determined on a GBC-932 atomic absorption spectrophotometer. The adjustment of pH was made on microprocessor pH meter (Model pH211).

Preparation of PVESO-AP

The synthetic route of PVESO-AP was shown in Scheme 1.

Synthesis of PSM

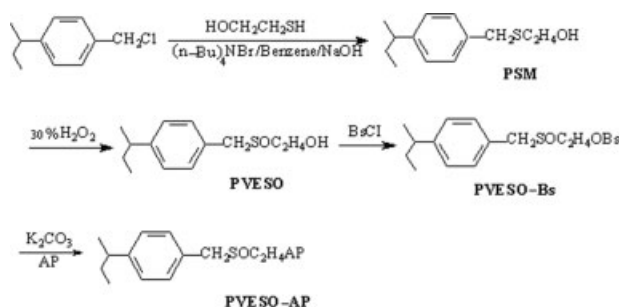
PS-Cl (10 g) was suspended in benzene (120 mL) and 68 mL of 2-mercaptoethanol, 12.6 g of sodium hydroxide, and 1.06 g of tetrabutyl ammonium bromide were added. The mixture was stirred at room temperature under a nitrogen atmosphere for 19 h. After filtration the resin was washed with THF, water, and ethanol. 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. 12.28 g of PSM was obtained. Elemental analysis (%): S 13.84.

Synthesis of PVESO

A suspension of 8.0 g of PSM, 4.53 g of hydrogen peroxide, and 70 mL of acetone were stirred at room temperature for 10 h and another 2 h at refluxed temperature. The reaction was filtered and moved to Soxhlet's extraction apparatus for reflux-extraction in 95% ethanol for 4 h. After drying under vacuum at 50°C for 48 h, 8.01 g of PSM was obtained. Elemental analysis (%): S 13.03.

Synthesis of PVESO-Bs

A mixture of 8.5 g of PVESO and 100 mL of pyridine was cooled in an ice-water bath, and 18.0 mL of



Scheme 1 Synthetic route of the intermediates and PVESO-AP.

BsCl was added dropwise. The mixture was stirred at room temperature for 24 h. After filtration and washing with distilled water and ethanol, the resin was dried under vacuum at 50°C for 48 h. 9.45 g of PVESO-Bs was obtained. Elemental analysis (%): S 12.32.

Synthesis of PVESO-AP

PVESO-Bs (6.0 g), 3-aminopyridine (7.69 g), and K₂CO₃ (3.76 g) were suspended in 100 mL of DMF; the reaction was stirred at 90°C for 24 h. After the reaction was then filtered off and thoroughly washed with distilled water and ethanol, the product dried under vacuum at 50°C for 48 h. 5.21 g of PVESO-AP was obtained. Elemental analysis (%): N 2.90, S 11.57.

Adsorption capacity

Fifty milligram of PVESO-AP 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. Adsorption capacity (*Q*) was calculated according to eq. (1):

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

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 kinetic

The adsorption kinetics at different temperatures was determined according to the following procedure: 20 mL of metal ion solution (5 × 10⁻³ mol/L) was shaken (110 rpm) with 30 mg of the resin at the preconditioned temperature. At predetermined intervals, aliquots of 1 mL solution were withdrawn for

analysis and the concentration of metal ion was determined by atomic absorption spectrometry.

Isothermal adsorption

The isothermal adsorption was also investigated by batch studies. A typical procedure was as follows: A series of 50-mL test tubes were employed. Each test tube was filled with 10 mL of metal ion solution of varying concentration and adjusted to the desired pH. A known amount of PVESO-AP (30 mg) was added into each test tube and agitated intermittently for 24 h at the preconditioned temperature. The concentration of metal ions after sorption was determined by atomic absorption spectrometry. The adsorption capacities were also calculated by using eq. (1), where C was the equilibrium concentration of metal ion in solution.

Adsorption selectivity¹⁴

To determine adsorption selectivity of PVESO-AP 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 5×10^{-4} mol/L. Fifty milligram of PVESO-AP 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 coefficients of adsorption selectivity were calculated as the ratio of the adsorption capacities of two kind of metal ions in binary mixture.

RESULTS AND DISCUSSIONS

Characterization of the intermediates and PVESO-AP

Infrared spectra of the intermediates and PVESO-AP were recorded in KBr matrices and showed in Figure 1.

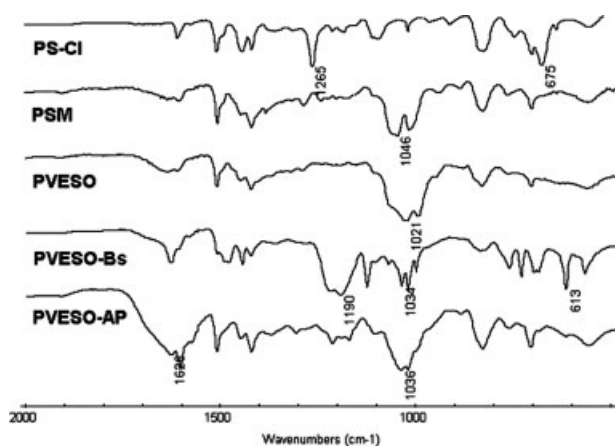
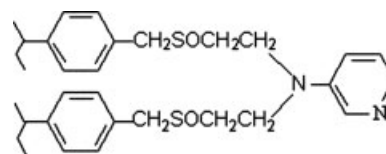


Figure 1 IR spectra of the intermediates and PVESO-AP.



Scheme 2 The crosslinked form in PVESO-AP.

PSM was confirmed by the presence of a strong band at 1046 cm^{-1} belonging to the characteristic peak of C—O band, and by the absence of two strong bands at 1275 and 675 cm^{-1} belonging to C—Cl group.¹⁶ After the thioether band in PSM was oxidized into sulfoxide, the characteristic peak of S=O in PVESO at 1021 cm^{-1} was observed.¹⁷ The structure of PVESO-Bs was confirmed by the presence of two new absorption bands at 1190 cm^{-1} (stretching in the $-\text{SO}_2-$ group) and 613 cm^{-1} (bending in the $-\text{SO}_2-$ group).¹⁷ However, these bands had disappeared in the infrared spectrum of PVESO-AP and a strong band corresponding to the breathing vibration of pyridyl ring at 1626 cm^{-1} was observed, which indicated that 3-aminopyridine had been introduced into the polymeric matrix.¹⁸ The nitrogen content found by elemental analysis in PVESO-AP was 2.07 mmol/g, which was much lower than its theoretical value 8.14 mmol/N/g. This indicated that a part of AP in PVESO-AP resin existed as a crosslinked form (Scheme 2).

Adsorption of PVESO-AP for metal ions

The adsorption capacities of PVESO-AP for metal ions were determined at pH 2 and 5. The results were shown in Figure 2. From Figure 2, it could be noted that the adsorption capacities of PVESO-AP for the metal ions decreased in the following order: $\text{Hg}^{2+} > \text{Ag}^+ > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.

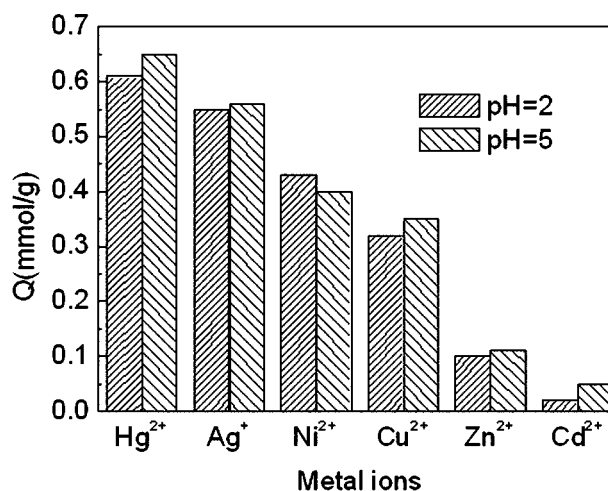


Figure 2 Adsorption capacities of PVESO-AP for different metal ions at pH 2 and 5.

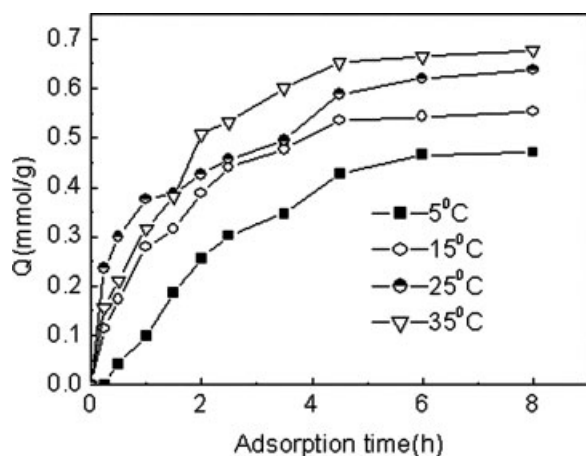


Figure 3 The adsorption kinetics of PVESO-AP for Hg^{2+} .

PVESO-AP had high affinity for Hg^{2+} . The highest adsorption capacity was 0.65 mmol/g. These results could be interpreted as follows: according to the theory of soft and hard acids and bases (SHAB), ligands with “soft” type donors prefer interactions with “soft,” i.e., large and more easily polarizable, acceptors such as noble and heavy metal ions.¹⁹ The functional groups of sulfoxide and 3-aminopyridine presented in PVESO-AP belong to soft bases, thus this resin have higher adsorption capacities for Hg^{2+} and Ag^+ than that for Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} , which are base metal ions.

As could be seen in Figure 2, the adsorption capacities of PVESO-AP for the investigated metal ions increased with the increase of the pH. The reason of this phenomenon could be ascribed to the protonation of the functional group under lower pH value, which decreased the number of available amino groups, thus lowering adsorption capacities. Considering the high adsorption capacity, Hg^{2+} was chosen to investigate the adsorption kinetics, isother-

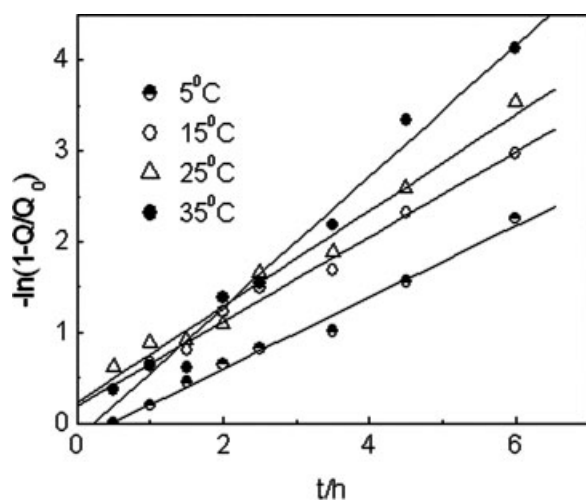


Figure 4 The relationship between $-\ln(1-Q/Q_0)$ and t .

TABLE I
The Constants of Adsorption k
and Correlation Coefficient R^2

Temperature (°C)	Adsorption rate constant $k \times 10^{-4}$ (s^{-1})	Correlation coefficient R^2
5	1.074	0.9794
15	1.362	0.9950
25	1.491	0.9691
35	2.156	0.9635

mal adsorption, and adsorption selectivity coefficients under competitive condition in the following experiment.

Adsorption kinetics

Plots of PVESO-AP adsorption kinetics for Hg^{2+} at different temperatures are shown in Figure 3. It could be seen that the equilibriums were all established within 6 h. Therefore the contact period was 8 h in all equilibrium tests. From Figure 3, it could be noted that the adsorption rates increased with the increase of the temperature. A possible explanation for this was that the diffusion rates of Hg^{2+} were enhanced by increasing temperature, so Hg^{2+} could approach and contact with PVESO-AP much faster at higher temperatures.

According to Boyd equation,²⁰ the adsorption rate constant could be calculated from:

$$-\ln(1-F) = kt \quad (2)$$

where $F = Q/Q_0$; Q and Q_0 were the adsorption amounts at sorption time t and at equilibrium, respectively. The slope of straight line that made by plotting $-\ln(1-F)$ versus t , yielded the sorption rate k . Both the linear relationship between $-\ln(1-F)$ and t shown in Figure 4 and $R^2 > 0.9635$ shown in Table I indicated that the adsorption process of PVESO-AP for Hg^{2+} could be described by Boyd equation,

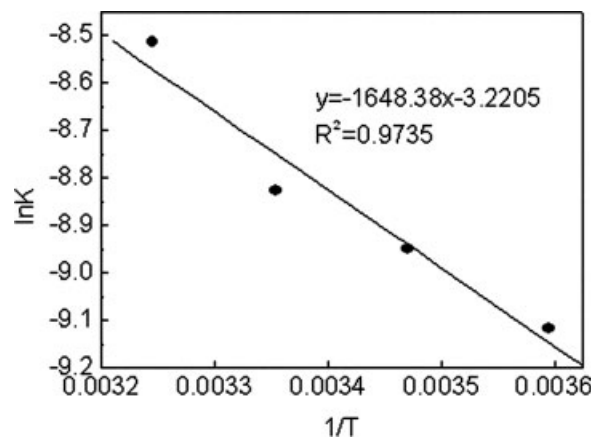


Figure 5 The relationship between $\ln k$ and $1/T$.

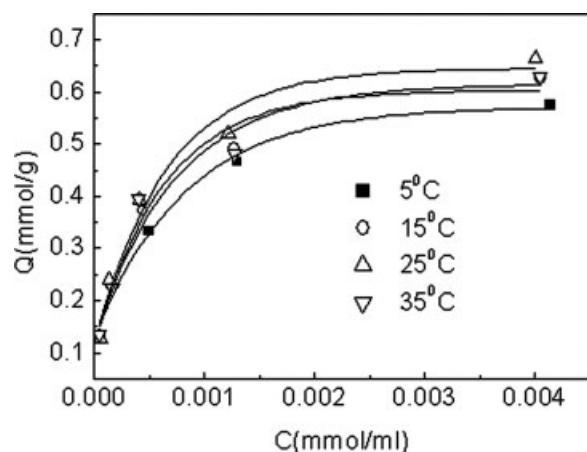


Figure 6 The adsorption isotherms of PVESO-AP for Hg^{2+} .

meaning that this adsorption might obey the mechanism of liquid film diffusion control. From Table I, it also could be seen that the k values increased with the increase of temperature on whole, indicating that the adsorption could process more easily at higher temperature. This result agreed with that of the aforementioned adsorption kinetics experiments.

According to Arrhenius equation,

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (3)$$

where k is the constant of adsorption. Plotting $\ln k$ against $1/T$, Figure 5 was obtained. The apparent activation energy of adsorption E_a calculated from the linear slope was 13.71 kJ/mol. In general, film diffusion is the rate-limiting step in systems, which have (1) poor mixing; (2) dilute concentration of adsorbate; (3) small particle size; and (4) high affinity of adsorbate for adsorbent.²¹ In this article, the low activation energy of the resin for Hg^{2+} might ascribed to the faster shaking rate (110 rpm) in the

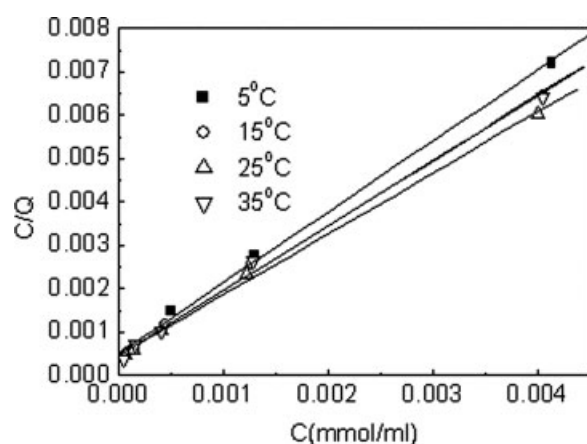


Figure 7 The Langmuir isotherms of PVESO-AP for Hg^{2+} .

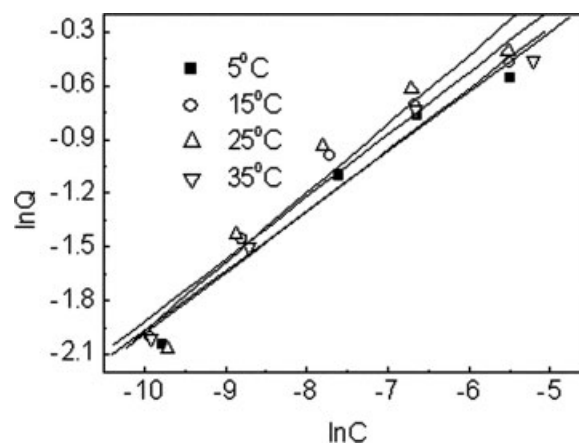


Figure 8 The Freundlich isotherms of PVESO-AP for Hg^{2+} .

determination of adsorption kinetics. The low activation energy implied that, the adsorption of PVESO-AP for Hg^{2+} was a facile procedure.

Isothermal adsorption

The adsorption isotherms of Hg^{2+} at different temperatures (pH = 5) are presented in Figure 6. Analyzing the data in Figure 6 with Langmuir (4) and modified Freundlich (5) equations, respectively, Figures 7 and 8 were obtained.

$$\frac{C}{Q} = \frac{C}{Q_0} + \frac{1}{bQ_0} \quad (4)$$

$$\ln Q = \ln K_F + \frac{1}{n} \ln C \quad (5)$$

where Q is the adsorption capacity (mmol/g); C is the equilibrium concentration of metal ions (mmol/g); Q_0 is the saturated adsorption capacity; b is the adsorption/desorption equilibrium constant; K_F is Freundlich constant; n is constant representing the adsorption intensity of adsorption. Freundlich and Langmuir parameters were given in Table II. According to the correlation coefficients in Table II, it could be concluded that the Langmuir model fit the result better than the Freundlich model, indicating that the isothermal adsorption process of the resin can be described by Langmuir formula.

TABLE II
Freundlich and Langmuir Constants

Temperature (°C)	Freundlich parameters			Langmuir parameters		
	K_F	$1/n$	R^2_F	Q_0	b (10^3)	R_L
5	4.20	0.34	0.9812	0.70	3.21	0.9993
15	4.79	0.35	0.9837	0.77	3.26	0.9996
25	6.56	0.39	0.9654	0.84	3.07	0.9973
35	3.95	0.33	0.9900	0.78	3.19	0.9967

TABLE III
The Adsorption Selective Coefficients of PVESO-AP in Binary Mixtures System at 25°C

Systems	Metal ions	pH	Adsorption capacity (mmol/g)	Selective Coefficients ^a
Hg ²⁺ -Ag ⁺	Hg ²⁺	5.0	0.27	$\alpha_{\text{Hg/Ag}} = 1.29$
	Ag ⁺		0.21	
Hg ²⁺ -Ni ²⁺	Hg ²⁺	5.0	0.25	$\alpha_{\text{Hg/Cu}} = 3.13$
	Cu ²⁺		0.08	
Hg ²⁺ -Zn ²⁺	Hg ²⁺	5.0	0.23	$\alpha_{\text{Hg/Zn}} = \infty$
	Zn ²⁺		0.09	
Hg ²⁺ -Cu ²⁺	Hg ²⁺	5.0	0.22	$\alpha_{\text{Hg/Ni}} = 3.67$
	Ni ²⁺		0.06	
Hg ²⁺ -Cd ²⁺	Hg ²⁺	5.0	0.23	$\alpha_{\text{Hg/Cd}} = \infty$
	Cd ²⁺		0	

^a The selective coefficients were the ratio of adsorption capacities of metal ions in binary mixture.

Adsorption selectivity of PVESO

The ability to remove some particular metal ions selectively from aqueous solution under competitive conditions is of utmost importance in designing chelating resins. The adsorption selectivity coefficients of PVESO-AP for Hg²⁺ in binary mixture system were investigated. The experimental results were tabulated in Table III. It could be seen that Hg²⁺ was prior to be adsorbed, and Zn²⁺ and Cd²⁺ was not adsorbed completely by PVESO in systems of Hg²⁺-Zn²⁺ and Hg²⁺-Cd²⁺. When PVESO-AP contacted in binary mixture systems of Hg²⁺-Ag⁺, Hg²⁺-Ni²⁺, and Hg²⁺-Cu²⁺, the adsorption selective coefficients were 1.29, 3.13, and 3.67, respectively. All the above-mentioned data implied that PVESO-AP had good adsorption selectivity for Hg²⁺, and it could be probably used in extracting and separating Hg²⁺ from multi-ionic system.

CONCLUSIONS

A novel chelating resin with sulfoxide and 3-amino-pyridine was prepared by using chloromethylated polystyrene as material. Its adsorption capacities for Hg²⁺, Ag⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Ni²⁺ were investigated. The experimental results showed that PVESO-AP exhibited good adsorption selectivity for Hg²⁺ and could adsorb Hg²⁺ selectively from such binary ions system as Hg²⁺-Ag⁺, Hg²⁺-Ni²⁺, Hg²⁺-Cu²⁺, Hg²⁺-Zn²⁺, and Hg²⁺-Cd²⁺. The process of adsorption for Hg²⁺ was controlled by liquid film diffusion. The adsorption activation energy (E_a) was 13.71 kJ/mol. Increasing temperature was beneficial to adsorption. The Langmuir adsorption model was much better than the Freundlich model for describing the isothermal process.

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