

Synthesis of Polystyrene-Supported Glucosamine Resin and Its Adsorption Properties for Metal Ions

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Received 23 February 2004; accepted 21 July 2004

DOI 10.1002/app.21271

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel chelating resin polystyrene-supported glucosamine was prepared by the reaction of chloromethylated polystyrene with glucosamine hydrochlorate, using anhydrous potassium carbonate as catalyst and dimethylformamide as solvent. Infrared spectra and elementary analysis were used to confirm its structure. The adsorption of the resin for Cu^{2+} , Ni^{2+} , Hg^{2+} , Co^{2+} , Cd^{2+} , and Pb^{2+} was investigated, as well as various factors affecting the adsorption such as time, temperature, ion concentration, and pH. The results showed that the resin had good adsorption

capacities for Cu^{2+} , Ni^{2+} , and Hg^{2+} . The adsorption was controlled by liquid film diffusion and adsorption isothermal data could be well interpreted by the Freundlich equation. Values of adsorption activation energy and adsorption Gibbs free energy were calculated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 890–896, 2005

Key words: polystyrene-supported glucosamine (PS-GA); adsorption; metal ions; activation energy; resins

INTRODUCTION

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. The removal of these metal ions from industrial effluents, water supplies, as well as mine waters is an important challenge to avoid one of the major causes of water and soil pollution. Various methods^{1–3} have been proposed to remove heavy metal ions from industrial effluents using ion-exchange, reverse osmosis, and electrodialysis techniques, which are efficient but expensive. Chemical precipitation can be envisaged, but the generation of bulky precipitated hydroxides and colloidal particles is often a major disadvantage.

Selective adsorption is an economical and efficient method to remove heavy metal ions and it has generated much interest among researchers and practitioners of environmental engineering and science. Furthermore, numerous investigations have proved the feasibility of use of agricultural products and byproducts, industrial waste biomass, and natural substances to absorb and accumulate heavy metals.^{4–7} These materials are also readily available and inexpensive.

Therefore, the adsorption phenomenon is still economically appealing for the removal of toxic metals from wastewater by choosing some adsorbents under optimum operation conditions.

Glucosamine is the hydrolysis product of chitosan and easily available. It has been proved that glucosamine can form various complexes with many metal ions such as Cu^{2+} , Ni^{2+} , Fe^{2+} , and Zn^{2+} because it contains a nitrogen atom and five oxygen atoms.^{8,9} Thus we can expect that, if a glucosamine group were introduced into polystyrene, the obtained hydrophilic resin would express excellent adsorption properties to many toxic metal ions. For this purpose, we prepared a novel chelating resin by the reaction of chloromethylated polystyrene with glucosamine and studied its adsorption property for Cu^{2+} , Ni^{2+} , Hg^{2+} , and so forth, and report results of our investigation in this article.

EXPERIMENTAL

Materials

Commercial macroporous chloromethyl polystyrene beads (chlorobeads, PS-Cl, chlorine content 19.85%) were purchased from Chemical Factory of Nankai University of China. Glucosamine hydrochlorate was provided by Qingdao Chemical Co. (China). Other reagents were analytical-grade chemical products and used without any further purification. Aqueous solutions containing metal ions at various concentrations (10^{-2} – 10^{-3}M) were prepared from metal salts and

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Contract grant sponsor: Nature Science Foundation of Shandong Province; contract grant number: Q99B15.

Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 29906008.

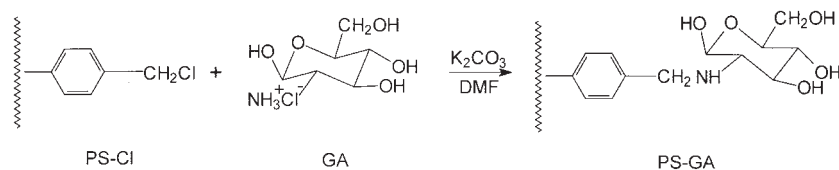


Figure 1 Reaction scheme for the synthesis of PS-GA.

controlled by titration with a standard EDTA solution. The pH of the solutions was adjusted with different buffer solutions as follows: HCOOH–NaOH (3.7), NH₄Ac–HAc (4.5), NaAc–HAc (5.0), hexamethylenetetramine–HNO₃ (5.4).

Instruments

Infrared spectra were recorded on a Nicolet Magna-IR 550 spectrophotometer (series II; Nicolet Analytical Instruments, Madison, WI). Test conditions: potassium bromide pellets, scanning 32 times, resolution at 4 cm⁻¹.

The content of Cl and N elementary analyses were carried out by the central laboratory of Elemental Research Institute of Nankai University.

Preparation of polystyrene-supported glucosamine resin (PS-GA)

Figure 1 shows a schematic representation of the preparation of PS-GA. The PS-Cl beads (1.0 g) were swollen in 20 mL dimethylformamide (DMF) in a three-neck flask for more than 2 h, and then GA (2.4 g) and K₂CO₃ (2.3 g) powder were added. With magnetic

stirring, the mixture was refluxed for 8 h to obtain the product with a light coffee color. The product was filtered off, washed with excess distilled water, and then moved to a Soxhlet's extraction apparatus for reflux-extraction in 95% ethanol for 10 h. Finally, the product was dried under vacuum at 50°C over 48 h. Elemental analysis (%): Cl, 1.75; N, 3.87.

Adsorption experiments

In a thermostat-*cum*-shaking assembly, batch adsorption experiments were carried out by shaking 0.1 g of PS-GA with 20 mL of an aqueous solution of metal ions of the desired concentration, pH, and temperature in a 50-mL Pyrex glass tube. At predetermined time intervals, the solutions in the specified tubes were separated from the adsorbent. The concentration of metal ions was determined by the titration method. The adsorption amounts and the coefficient of distribution for the metal ion were calculated, respectively, according to the following equations:

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

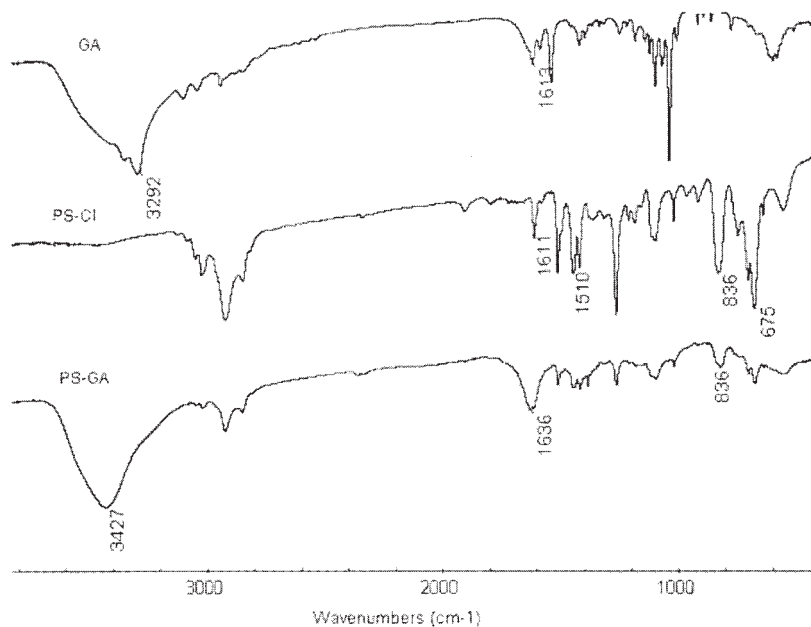


Figure 2 IR spectra of GA, PS-Cl, and PS-GA.

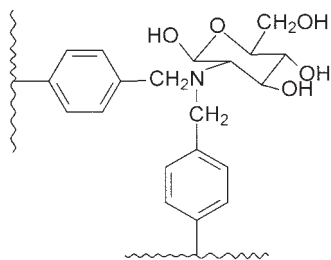


Figure 3 PS-GA structure crosslinked by GA.

$$D = \frac{V}{W} \left(\frac{C_0}{C} - 1 \right) \quad (2)$$

where Q is the adsorption amount (mmol/g); C_0 and C are the initial concentrations and the concentrations of metal ions in solution, respectively, when the contact time is t (mmol/mL); V is the volume (mL); W is the weight of PS-GA beads (g); and D is the coefficient of distribution (mL/g).

RESULTS AND DISCUSSION

Infrared spectra characterization

Figure 2 shows the infrared spectra of GA, PS-Cl, and PS-GA. By comparison with the curve of PS-Cl, the characteristic peak of C-Cl at 675 cm^{-1} apparently weakens in the curve of PS-GA, and a series of new peaks involved in the GA curve appears at 3427 and 1636 cm^{-1} , corresponding to the stretching vibration of O-H bonds and the overlapping of the bending vibration of N-H bonds and benzene ring backbone vibration in PS-Cl, which indicate that the GA group was successfully introduced into the polymeric matrix. Besides, the peak at 836 cm^{-1} , caused by the bending vibration of C-H in the benzene ring, indicates that PS-GA resin contains benzene structure.

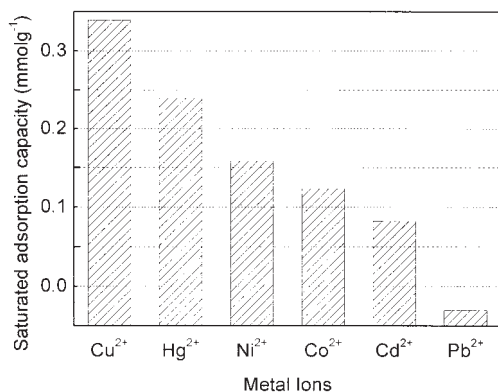


Figure 4 Saturated adsorption capacities of PS-GA for different metal ions at pH = 5.4 and 25°C with 0.01 mol/L metal ions (the saturated sorption time is 6 h; see Figs. 6, 8, and 10).

TABLE I
Coefficient of Distribution for Cu²⁺, Hg²⁺, Ni²⁺, Co²⁺, Cd²⁺, and Pb²⁺ at pH = 5.4 and 25°C with 0.01 mol/L Metal Ions (Saturated Sorption Time is 6 h)

Coefficient of distribution D , mL/g	Metal ions					
	Cu ²⁺	Hg ²⁺	Ni ²⁺	Co ²⁺	Cd ²⁺	Pb ²⁺
	22.16	15.51	11.05	9.67	5.37	1.03

According to the mass percentage of nitrogen (3.87%) and chlorine (1.75%) in PS-GA, determined by elemental analysis, the value of the degree of substitution (DS) can be calculated by eqs. (3) and (4), respectively.

$$DS (\%) = \frac{N\%}{n_{\text{Cl}}^0 [M_{\text{N}} - N\% (M_{\text{GA}} - M_{\text{Cl}})]} \times 100 \quad (3)$$

$$DS (\%) = \frac{\text{Cl}^0\% - \text{Cl}\%}{n_{\text{Cl}}^0 [\text{Cl}\% (M_{\text{GA}} - M_{\text{Cl}}) + M_{\text{Cl}}]} \times 100 \quad (4)$$

where $N\%$ and $\text{Cl}\%$ are the mass percentage of nitrogen and chlorine in PS-GA, respectively, determined by elemental analysis; $\text{Cl}^0\%$ is the mass percentage of Cl in PS-Cl; n_{Cl}^0 is the amount of Cl in 1 g of PS-Cl, mol; M_{N} and M_{Cl} are the atomic weight of nitrogen and chlorine, respectively; M_{GA} is the molecular weight of the GA group.

The DS obtained by eq. (3) (81.55%), which is smaller than that (85.19%) obtained by eq. (4), is probably explained by the fact that there are two active H atoms in $-\text{NH}_2$ group of GA and one $-\text{NH}_2$ group can react with two Cl atoms to form a crosslinked structure (Fig. 3). Therefore, the DS calculated according to $N\%$ is smaller than that calculated according to $\text{Cl}\%$. The result obtained from elementary analysis indicates that there is less than 20% residual chlorine in PS-GA resin.

TABLE II
Constants of Adsorption k and Correlation Coefficient R^2

	Temperature (°C)		
	25	35	45
Cu ²⁺			
k , s ⁻¹	1.33×10^{-4}	1.55×10^{-4}	1.75×10^{-4}
R^2	0.9807	0.9525	0.9388
Hg ²⁺			
k , s ⁻¹	1.14×10^{-4}	1.34×10^{-4}	1.81×10^{-4}
R^2	0.9424	0.9687	0.9109
Ni ²⁺			
k , s ⁻¹	1.01×10^{-4}	1.16×10^{-4}	1.42×10^{-4}
R^2	0.9430	0.9530	0.9912

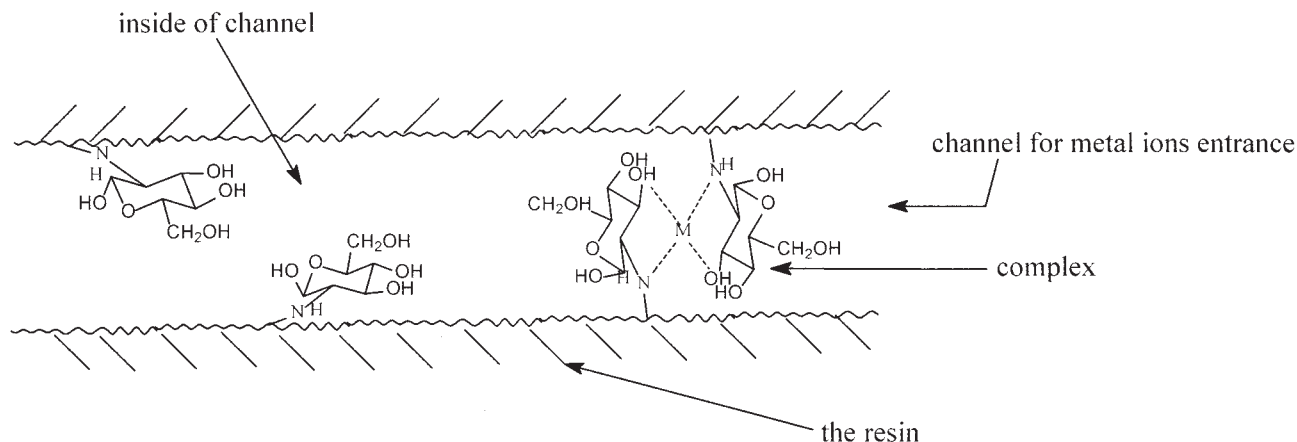


Figure 5 Scheme of crosslinking structure of metal ions.

Adsorption of PS-GA for metal ions

Figure 4 shows the saturated adsorption capacities of PS-GA for Cu^{2+} , Hg^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , and Pb^{2+} . Table I shows the values of coefficient of distribution for the six metal ions. Obviously PS-GA has good adsorption capacities for Cu^{2+} , Ni^{2+} , and Hg^{2+} , so we studied the adsorption kinetics and isothermal adsorption for the three metal ions in the following experiments.

Adsorption kinetics

Plots of PS-GA adsorption kinetics for Cu^{2+} , Hg^{2+} , and Ni^{2+} at different temperatures are shown in Figures 6, 7, and 8, respectively, which demonstrate that the equilibria are all established within 6 h. Therefore the contact period was 6 h in all equilibrium tests. Also it can be seen from the three figures that the adsorption capacities do not increase with increasing temperature, as we expected, whereas the adsorption rates for the three metal ions increase with increasing temperature (see the values of k in Table II). A possible

explanation for this is that the diffusion rates of metal ions are enhanced by increasing temperature, so metal ions can approach and contact with the resin much faster at higher temperature. Consequently, the complexes quickly formed on the surface and outer layer of the resin at high temperature prevent the metal ions from diffusing into the inside of the resin, so the values of adsorption capacities at high temperature are not the largest (see Fig. 5).

The data in Figures 6, 7, and 8 were respectively treated with the Boyd equation, $-\ln[1 - (Q/Q_0)] = kt$, where Q is the adsorption amount when the contact time is t ; Q_0 is the saturated adsorption capacity; k is the constant rate of adsorption; and t is the adsorption time. The excellent linear relationship between $-\ln[1 - (Q/Q_0)]$ and t ($R^2 > 0.91$ as shown in Table II) indicates that the adsorption processes of PS-GA for Cu^{2+} , Ni^{2+} , and Hg^{2+} can be precisely described by the Boyd equation, meaning that the adsorptions obey the mechanism of liquid film diffusion control.¹⁰

According to the Arrhenius equation, $\ln k = -E_a/RT + \ln A$, where k is the constant of adsorption. Figure 9 shows the results of plotting $\ln k$ against $1/T$. The values of adsorption apparent activation en-

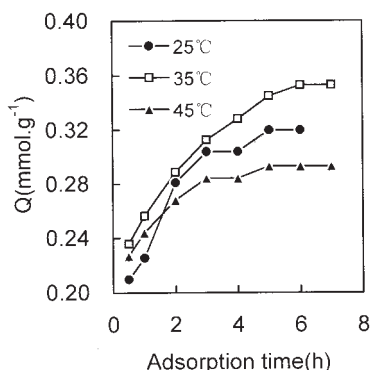


Figure 6 Adsorption kinetics of PS-GA for Cu^{2+} (pH = 5.4, $[\text{Cu}^{2+}] = 0.010 \text{ mol/L}$).

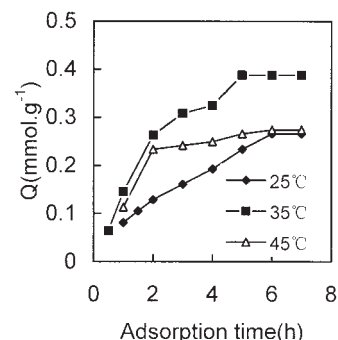


Figure 7 Adsorption kinetics of PS-GA for Hg^{2+} (pH = 5.4, $[\text{Hg}^{2+}] = 0.010 \text{ mol/L}$).

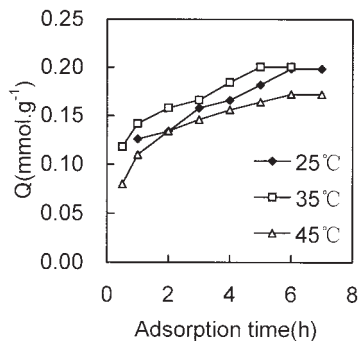


Figure 8 Adsorption kinetics of PS-GA for Ni²⁺ (pH = 5.4, [Ni²⁺] = 0.010 mol/L).

ergy (E_a), calculated from the linear slopes, are 10.38, 13.12, and 17.68 kJ mol⁻¹ for Cu²⁺, Ni²⁺, and Hg²⁺, respectively. These low values of E_a compared to those of typical chemical reactions of 65–250 kJ mol⁻¹, imply that the adsorptions of PS-GA for the three ions are facile procedures.

Adsorption isotherms

The adsorption isotherms of Cu²⁺, Hg²⁺, and Ni²⁺ at pH 5.4 are presented in Figures 10, 13, and 14, respectively. Figures 11 and 12 show the results of analyzing the data in Figure 10 with Langmuir [eq. (5)] and Freundlich [eq. (6)] equations, respectively.

$$\frac{C}{Q} = \frac{1}{bQ_0} + \frac{C}{Q_0} \tag{5}$$

$$\ln Q = \ln k + \frac{1}{n} \ln C \tag{6}$$

where Q is the adsorption capacity (mmol/g); C is the equilibrium concentration of metal ions (mmol/mL); Q_0 is the saturated adsorption capacity (mmol/g); b is

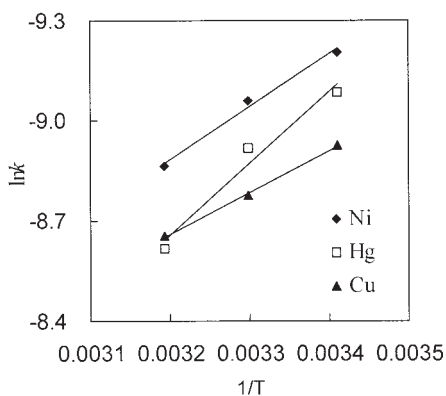


Figure 9 Relationship between $\ln k$ and $1/T$ for Cu²⁺, Hg²⁺, and Ni²⁺.

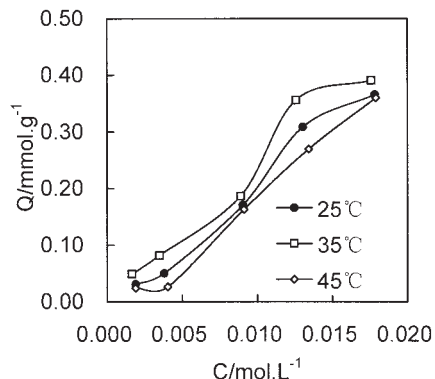


Figure 10 Adsorption isotherms of PS-GA for Cu²⁺ at pH 5.4.

an empirical parameter; n is the Freundlich constant; and k is the binding energy constant, which reflects the affinity of the resin to metal ions.

It is obvious that the Langmuir isotherms for Cu²⁺ (Fig. 11) are not linear, whereas the relationship between $\ln C$ and $\ln Q$ in the Freundlich isotherms (Fig. 12) express excellent linearity, indicating that all adsorption processes can be described by the Freundlich formula. The values of k and $1/n$ are equal to the intercept and slope of the Freundlich isotherm, respectively. By analyzing the data in Figures 13 and 14 with

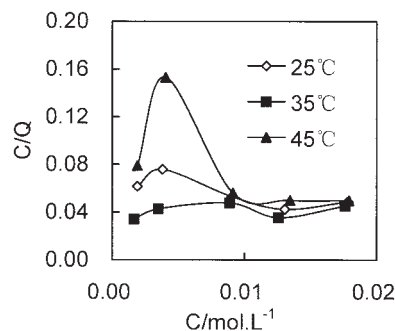


Figure 11 Langmuir isotherms of PS-GA for Cu²⁺ at pH 5.4.

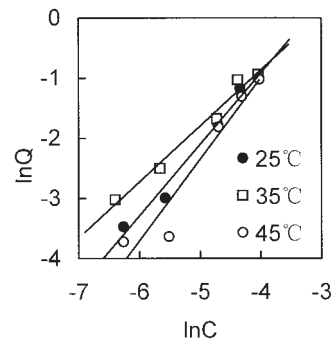


Figure 12 Freundlich isotherms of PS-GA for Cu²⁺ at pH 5.4.

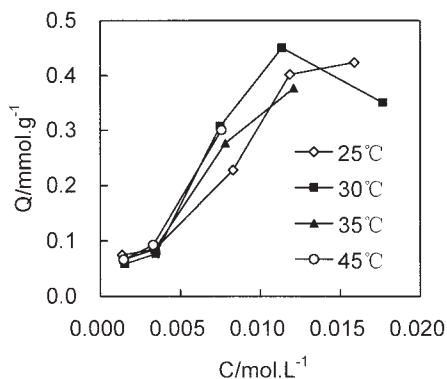


Figure 13 Adsorption isotherms of PS-GA for Hg²⁺ at pH 5.4.

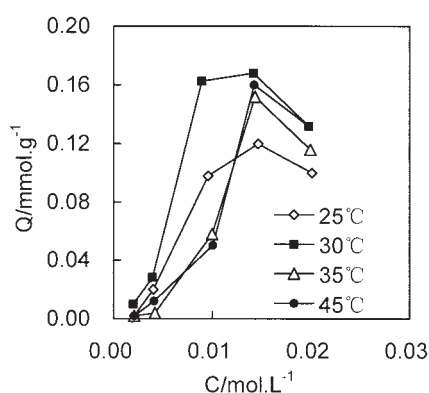


Figure 14 Adsorption isotherms of PS-GA for Ni²⁺ at pH 5.4.

the same method, similar conclusions can be obtained. All the parameters in the Freundlich equations for Cu²⁺, Hg²⁺, and Ni²⁺ are listed in Tables III, IV and V, respectively.

The following equation expresses adsorption Gibbs free energy (ΔG)¹¹:

$$\Delta G = - RT \int_0^a N \frac{da}{a} \tag{7}$$

which, at a low concentration, can be recast into

$$\Delta G = - RT \int_0^x q \frac{dx}{x} \tag{8}$$

TABLE III
Parameters in Freundlich Equations and the ΔG for Cu²⁺

Temperature (°C)	1/n	k	R ²	ΔG (kJ/mol ⁻¹)
25	1.1905	45.6635	0.9826	-2.09
35	0.9259	17.2446	0.9792	-2.76
45	1.3514	82.0969	0.9263	-1.96

TABLE IV
Parameters in Freundlich Equations and the ΔG for Hg²⁺

Temperature (°C)	1/n	k	R ²	ΔG (kJ/mol ⁻¹)
25	0.7937	11.1184	0.9163	-3.12
30	0.8850	18.9253	0.8708	-2.90
35	0.9091	17.9340	0.9313	-2.78
45	0.9174	22.9519	0.9081	-2.89

TABLE V
Parameters in Freundlich Equations and the ΔG for Ni²⁺

Temperature (°C)	1/n	k	R ²	ΔG (kJ/mol ⁻¹)
25	1.7544	177.0797	0.8772	-1.42
30	1.2658	32.3852	0.8733	-1.99
35	2.0833	693.1871	0.9436	-1.22
45	1.9608	403.8324	0.9652	-1.36

By associating eq. (8) with the Freundlich equation, another expression of ΔG is obtained,¹² as follows:

$$\Delta G = - nRT \tag{9}$$

where ΔG is Gibbs free energy and n is Freundlich constant. The calculated values of ΔG are also listed in Tables III–V. The negative ΔG values imply that the adsorption of PS-GA for Cu²⁺, Hg²⁺, and Ni²⁺ are spontaneous processes.

Effect of solution pH

The effect of the solution pH on the adsorption of Cu²⁺, Ni²⁺, and Hg²⁺ ions on PS-GA is presented in Figure 15. The solution pH is an important controlling parameter in the adsorption process, and thus the role of hydrogen ion concentration was examined from solutions at pH 3.5–6.0. Figure 15 shows that the pH of solution has only a slight effect on the adsorption of PS-GA for Cu²⁺ and Ni²⁺, but it substantially affects the adsorption for Hg²⁺. The possible explanation for

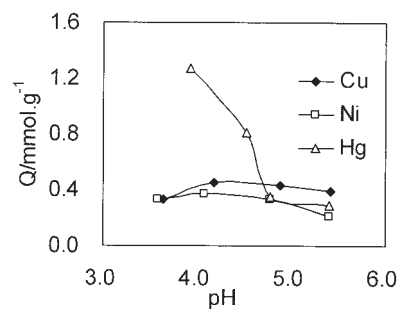


Figure 15 Effect of pH on adsorption of PS-GA for Cu²⁺, Ni²⁺, and Hg²⁺ at 25°C with 0.01 mol/L metal ions.

this is that the main contributor for chelating Cu^{2+} and Ni^{2+} in PS-GA is the nitrogen atom, which cannot be protonized under this experimental condition. With respect to Hg^{2+} , we have not yet found a reasonable interpretation for the phenomenon. Perhaps the acidity of the solution has a great effect on the oxidizability of Hg^{2+} and it becomes stronger at low pH; thus more side reactions appear and more Hg^{2+} metals are consumed.

CONCLUSIONS

A novel chelating resin PS-GA was prepared by the reaction of chloromethylated polystyrene with glucosamine. It has good adsorption capacities for Cu^{2+} , Ni^{2+} , and Hg^{2+} ions. The adsorption processes are dependent on time, concentration, temperature, and pH and follow Freundlich isothermal adsorption. The low values of E_a imply that the adsorptions of PS-GA for the three ions are facile procedures, and the negative ΔG values indicate that the adsorptions of PS-GA for the above-mentioned metal ions are spontaneous processes.

The authors are grateful for the financial support by the Nature Science Foundation of Shandong Province (Grant Q99B15) and the National Nature Science Foundation of China (Grant 29906008).

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