Synthesis and Characterization of Polystyrene-Supported Glucosamine Resin and Its Adsorption Behavior for Au(III)

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ABSTRACT: A novel chelating resin, crosslinking polystyrene-supported glucosamine (PS-GA), was prepared and its structure was confirmed by FTIR, elemental analysis, and X-ray photoelectron spectroscopy. The adsorption properties of PS-GA for Au(III) were investigated. PS-GA resin possessed excellent enriching property to Au(III) ions and adsorption proportion $E\%$ could reach to about 90 shortly after 3 h. The adsorption dynamics of Au(III) showed that the adsorption was controlled by liquid film diffusion and the apparent activation energy E_a was 12.91 kJ mol^{-1}. Both Langmuir model and Freundlich model could describe the isothermal process of Au(III), and ΔG, ΔH, ΔS values were calculated. The mechanism of adsorption for Au(III) was confirmed by FTIR, SEM, and XPS. The results showed that redox reaction occurred and both coordination and ion-exchange existed simultaneously in the adsorption. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4581–4586, 2006

Key words: polystyrene-supported glucosamine; adsorption; Au(III)

INTRODUCTION

Selective adsorption by chelating resin 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. The design of chelating devices anchoring the active site to a solid support in a polymer matrix provide an immobilized active surface capable of selective and quantitative separation of cations from aqueous solution. This solid-phase extraction system can be operated indefinitely for the purification of water and industrial effluents etc. without loss of the expensive ligating group.[1–6]

Chitosan-containing biomaterials have been recognized as effective biosorbents for metal removal, and they are readily available, inexpensive, and nontoxic. Glucosamine is the hydrolysis product of chitosan and is 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 of the nitrogen atom and five oxygen atoms in it.[7,8] So, we prepared a novel chelating resin, polystyrene-supported glucosamine (PS-GA), by the reaction of chloromethylated polystyrene with glucosamine and studied its adsorption properties for heavy metal ions such as Cu^{2+}, Ni^{2+}, Hg^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+}.[9] According to Pearson's hard and soft acid–base concept, the promising selective sorbents toward noble metal ions are expected from the polymers containing functional groups with donor N atom. The chelating resins containing nitrogen atom possess excellent adsorption and selectivity properties for noble metal ions.[10–15] So, in this study, we further researched the adsorption of PS-GA for Au(III) and confirmed the adsorption mechanism by SEM, XPS, and FTIR. This study will provide a new approach to apply glucosamine derived from chitosan.

EXPERIMENTAL

Materials

Commercial macroporous chloromethylpolystyrene beads (chlorobeads, PS-Cl), chlorine content 19.85%, were purchased from Chemical Factory of Nankai University of China. Glucosamine hydrochlorate were provided by Qingdao Chemical (China). HAuCl$_4$·4H$_2$O

was purchased from Sigma-Aldrich Co., St. Louis, MO. Other reagents were analytical-grade chemical products and used without further purification.

Instruments

Infrared spectra were recorded on a Nicolet MAGNA-IR 550 (series II) spectrophotometer; test conditions: potassium bromide pellets, scanning 32 times, resolution is 4 cm^{-1}. The content of Cl and N elementary analyses were carried out by central laboratory of Elemental Research Institute of Nankai University. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI1600 ESCA system made under U.S. Test conditions were MgKα, 1253.6 eV; power, 200.0 W; and resolution, 187.85 eV. Quantitative and qualitative analysis were carried out by special data treatment software of the instrument. The concentration of Au(III) was online measured on a GBC-932 atomic absorption spectrophotometer (AAS) made in Australia.

Synthesis of PS-GA resin

The PS-GA resin was synthesized, according to our previous work.[9] Elemental analysis (%): Cl, 1.75; N, 3.87. FTIR: ν_{O-H} 3427 cm^{-1}, σ_{N-H}: 1636 cm^{-1}.

Adsorption kinetics

Batch tests were performed to determine adsorption kinetics. A typical procedure was as follows: 50-mL Pyrex glass tubes were prepared with the desired amounts of reagent solution (10 mL) and were placed in a thermostat-cum-shaking assembly. When the desired temperature was reached, a known amount of resin (0.05 g) was added into each tube, and the mixed solutions were mechanically shaken. At predecided intervals of time, the solutions in the specified tubes were separated from the adsorbent and the concentration of metal ions was determined by means of AAS. The adsorption amount and adsorption proportion were calculated according to the following eqs. (1) and (2), respectively.

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

$$E\% = \left(1 - \frac{C}{C_0}\right) \times 100 \tag{2}$$

where Q is the adsorption amount (mmol g^{-1}); E% is the adsorption proportion; C_0 and C are the initial concentrations and concentrations of metal ion in solution when the contact time is t (mmol mL^{-1}); V is the
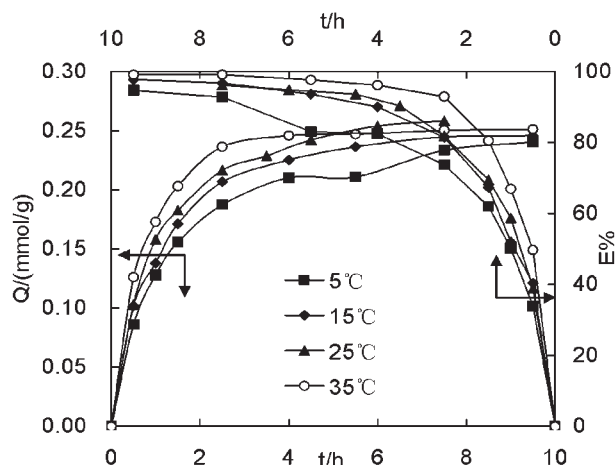

Figure 1 The adsorption kinetics of PS-GA for Au(III) (conditions: PS-GA resin, 0.05 g; initial Au(III) solution, 0.5 mM, 25 mL).

volume (mL); and W is the weight of the chelating resin (g).

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 concentrations and adjusted to the desired pH and temperature. A known amount of resin (about 0.05 g) was added into each test tube and agitated intermittently for the desired time periods. The adsorption capacities were also calculated by using Eq. (1), where C is the equilibrium concentration of metal ion in solution.

RESULTS AND DISCUSSION

Adsorption kinetics

Figure 1 shows the changes of adsorption capacity Q and adsorption proportion E% with the contact time of PS-GA for Au(III) at different temperatures. As shown in Figure 1, the adsorption capacities of Au(III) increased with prolonging of contact time and the adsorption equilibriums were established in about 6 h. Also, it could be seen that temperature had an effect on the adsorption speed, that is, the adsorption speed increased with the increasing of temperature. The possible explanations for this was can be given as follows: (1) the resin was swollen more completely at higher temperature, which made Au(III) ions diffused more easily into the inside of resin; (2) the adsorption was a endothermal process and high temperature was of benefit to the adsorption of PS-GA for Au(III). Another phenomenon that should be considered was that
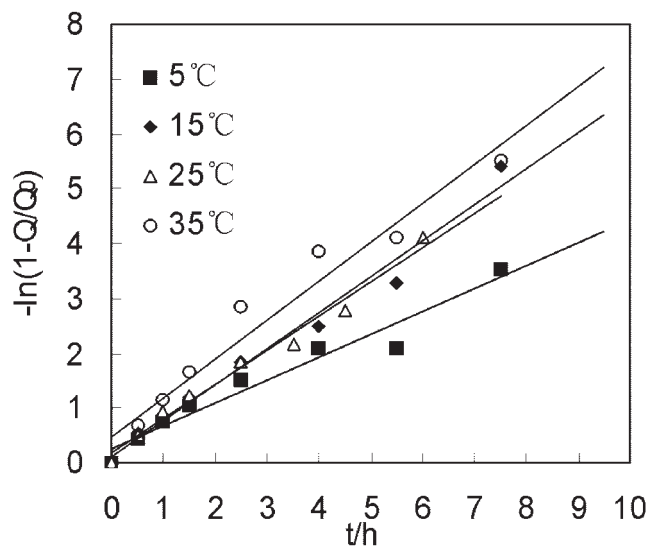
Figure 2 The relationship between $-\ln(1 - Q/Q_0)$ and t.

Figure 3 The relationship between $\ln k$ and $1/T$.

$E\%$ could reach to about 90 shortly after 3 h and reach to 99 after 7 h at 35°C, which implied that PS-GA resin possessed excellent enriching property to Au(III) ions. Experiment showed that the maximum adsorption capacity could reach to 1.032 mmol g^{-1} if the concentration of Au(III) was high enough (e.g., 5 mM).

Figure 2 was obtained by treating the data in Figure 1 with G. E. Boyd equation, $-\ln(1 - Q/Q_0) = kt$, where Q is the adsorption amount when the contact time is t; Q_0 is the maximum adsorption capacity; k is the constant rate of adsorption; and t is the adsorption time. Both the linear relationship between $-\ln(1 - Q/Q_0)$ and t shown in Figure 2 and $R^2 > 0.95$ shown in Table I indicated that the adsorption process of PS-GA for Au(III) could be approximatively described by G. E. Boyd equation, meaning that this adsorption may obey the mechanism of liquid film diffusion control.[16] From Table I, it could be seen that the k values increase with increase of temperature on the whole, indicating that the adsorption could proceed more easily at higher temperature. This result agreed with that of the aforementioned adsorption kinetics experiments.

According to Arrhenius equation, $\ln k = -E_a/RT + \ln A$ where k is the constant of adsorption, plotting $\ln k$ against $1/T$, Figure 3 was obtained. The apparent

activation energy of adsorption E_a calculated from the linear slope was 12.91 kJ mol^{-1}. This low activation energy as compared to these of typical chemical reaction of 65–250 kJ mol^{-1} implied that the adsorption of PS-GA for Au(III) was a facile procedure.

Isothermal adsorption

The adsorption isotherms of the Au(III) were presented in Figure 4 at four different temperatures. Analyzing the data in Figure 4 with Langmuir (3) and Freundlich (4) equations, respectively, Figures 5 and 6 were obtained.

$$\frac{C}{Q} = \frac{1}{bQ_0} + \frac{C}{Q_0} \qquad (3)$$

Figure 4 Adsorption isotherms of PS-GA for Au(III).

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

Temperature (°C)	Constant rate of adsorption k (10^{-4} s^{-1})	Correlation coefficients R^2
5	1.156	0.9555
15	1.826	0.9788
25	1.746	0.9842
35	1.968	0.9593

Figure 5 The Langmuir isotherms of PS-GA for Au(III).
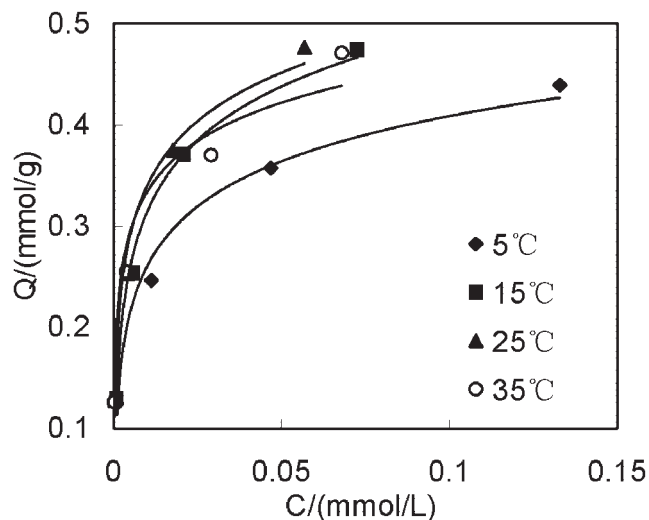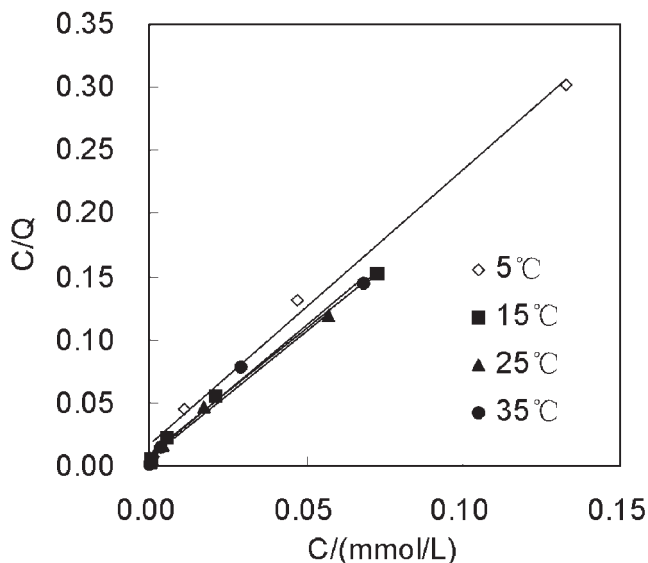
$$\ln Q = \ln K_F + \frac{1}{n}\ln C \qquad (4)$$

Where Q is the adsorption capacity (mmol g^{-1}); C is the equilibrium concentration of metal ions (mmol mL^{-1}); Q_0 is the maximum adsorption capacity (mmol g^{-1}); b is an empirical parameter; n is the Freundlich constant; and K_F is the binding energy constant reflecting the affinity of the resin to metal ions. Freundlich and Langmuir parameters are given in Table II. The correlation coefficients showed that both Langmuir model and Freundlich model could fit the results well, indicating that all adsorption processes could be described by Langmuir formula and Freundlich formula.
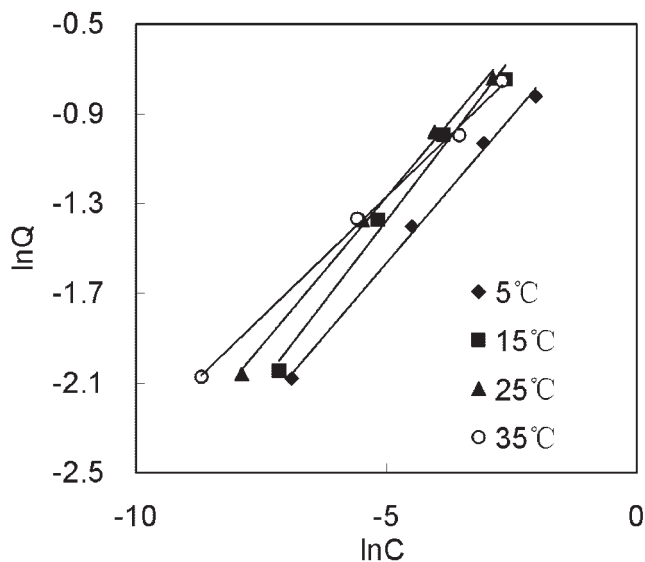

Figure 6 The Freundlich isotherms of PS-GA for Au(III).

TABLE II
Freundlich and Langmuir Constants for Au(III) Adsorption on PS-GA Resin at Different Temperatures

Temperature (°C)	Freundlich parameters			Langmuir parameters		
	K_F	$1/n$	R_F^2	Q_0 (10^3)	b	R_L^2
5	0.55	0.26	0.9962	458.9	126.68	0.9941
15	1.20	0.29	0.9878	500.6	208.07	0.9957
25	1.15	0.27	0.9963	498.1	295.24	0.9940
35	0.64	0.22	0.9972	480.4	298.24	0.9864

Thermodynamic parameters, namely, free energy (ΔG), enthalphy (ΔH), and entropy(ΔS) changes were also calculated using Eqs. (5)–(7)[17] and are given in Table III.

$$\Delta G = -RT\ln K \qquad (5)$$

$$\Delta H = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right)\ln\frac{K_2}{K_1} \qquad (6)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (7)$$

Where K, K_1, and K_2 are the Langmuir constants corresponding to temperatures at 5, 15, 25, and 35°C. A negativeΔG value confirmed the feasibility of the process and the spontaneous nature of adsorption. The ΔH being positive value justified that the adsorption of PS-GA for Au(III) was endothermal process, which was fitted to the deduction obtained from the adsorption kinetics.

The effect of acidity on the adsorption of PS-GA for Au(III)

The adsorption capacities of Au(III) and adsorption proportion $E\%$ as a function of acidity were determined and the results were presented in Figure 7. Both adsorption capacities and $E\%$ decreased with the increase of acidity, as seen in Figure 7. It was probably because the increase of acidity meant the increase of concentration of Cl^- in this system and Cl^- could

TABLE III
Thermodynamic Parameters for the Adsorption on PS-GA Resin

Temperature (°C)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
5	−11.20	29.03	144.6
15	−12.79		
25	−14.09		
35	−14.09		

compete with $[AuCl_4]^-$ to bind with protonized N atoms under acid conditions.

Adsorption mechanism of PS-GA for Au(III)

The SEM images of PS-GA resins before and after adsorption are shown in Figure 8. Obviously, there were a number of grains of elemental gold distributed on the surface of the resin after adsorption and most of them were nanosized. It was probably because that redox reaction occurred after adsorption and Au(III) ions were reduced to Au(0). Also, we could notice that there were few grain of Au(0) interior of PS-GA-Au, which indicated that redox reaction mainly occurred on the surface of the resin. Figure 9 shows the FTIR spectra of PS-GA and PS-GA-Au. By comparison with that of PS-GA, the characteristic peaks of carboxylic acid, C=O at 1720 cm^{-1} and O—H at 1400 cm^{-1}, appeared in the curve of PS-GA-Au, confirmed that the PS-GA resin were oxidized.

The XPS of PS-GA before and after adsorption for Au(III) was investigated and the binding energy data are listed in Table IV. A new 402.02 eV peak of N_{1s} binding energy appeared in PS-GA-Au in contrast to PS-GA and the binding energy value increased 2 eV, which demonstrated that electron donor nitrogen atom of PS-GA coordinated with Au(III) ions. Compared with PS-GA, the other 400.05 eV peak of N_{1s} binding energy that almost had no change probably represented the protonized N atom, and ion-exchange action maybe existed between —N^+H and $[AuCl_4]^-$. Correspondingly, there were two states of Cl, 198.33 and 201.37 eV, which represented the Cl^- ions in charge complex and chelate complex, respectively. So,
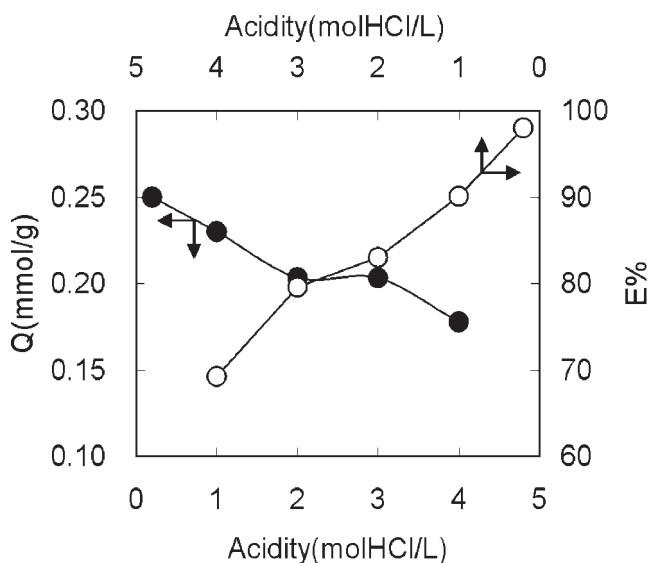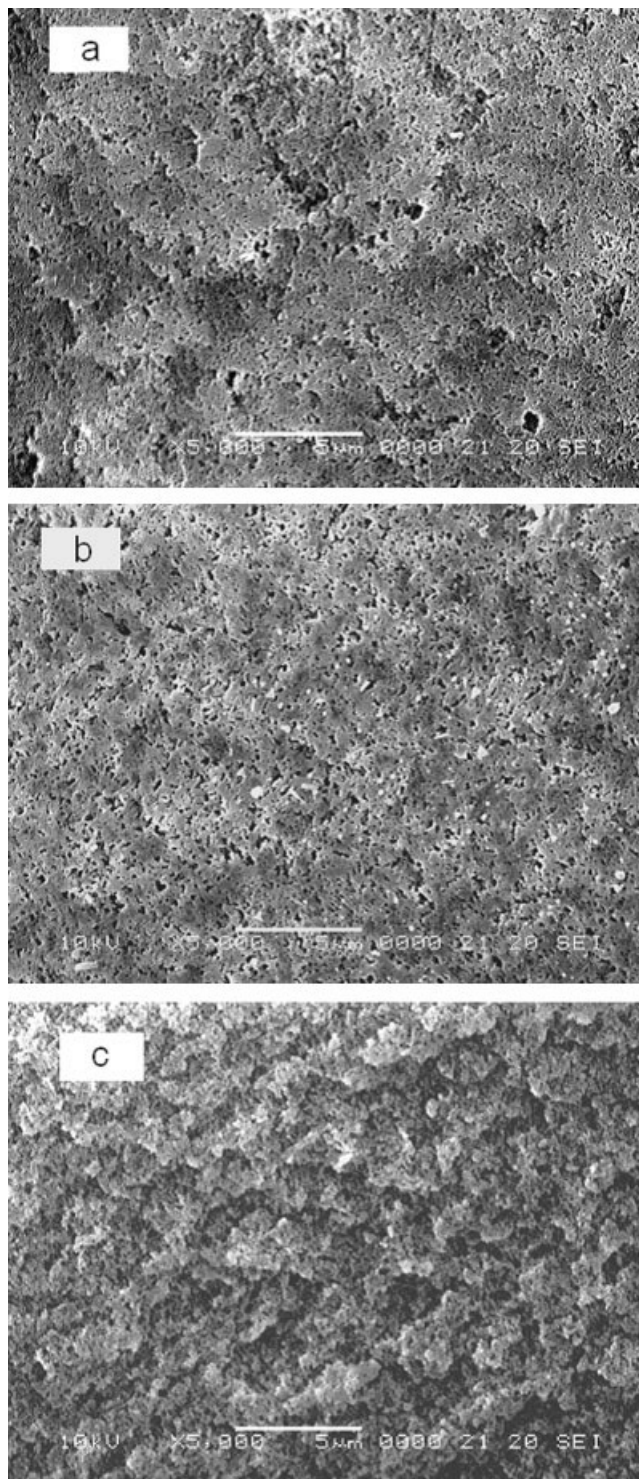

Figure 8 The SEM images of PS-GA and Au(III)-loading PS-GA (PS-GA-Au). (a) The surface of PS-GA, (b) the surface of PS-GA-Au, and (c) interior of PS-GA-Au.

Figure 7 The effect of acidity on adsorption of PS-GA for Au(III) at 25°C.

both coordination and ion-exchange existed simultaneously in the adsorption of PS-GA for Au(III).

The Au_{4f} binding energy of $AuCl_4^-$ adsorbed by PS-GA decreased obviously (-2.35 eV) in contrast to $HAuCl_4$. This meant that $AuCl_4^-$ was an electron acceptor.
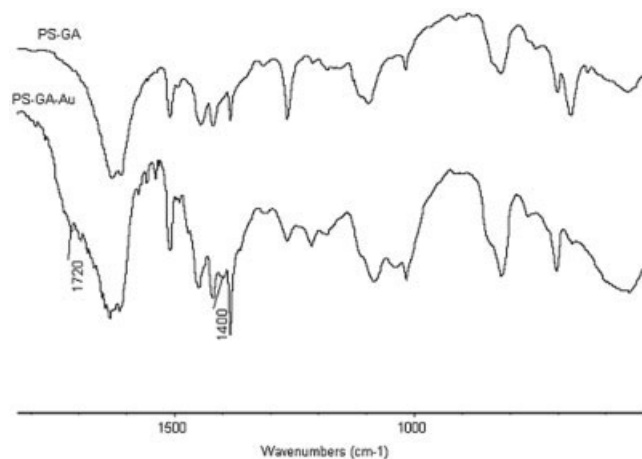
Figure 9 FTIR spectra of PS-GA and PS-GA-Au.

Figure 10 The adsorption of PS-GA for Au(III).

The O_{1s} and C_{1s} binding energy almost changed slightly after adsorption. From the data in Table IV, it could be seen that there were two different states of O atoms (—OH and C=O)and three different states of C atoms(—CH_2—, —CHOH, and C=O) in PS-GA and PS-GA-Au, indicating that a part of glucose rings were opened and existed as chain-typed structure. Redox reaction could occurred between —CH=O and Au(III). Based on all aforementioned results, the adsorption mechanism of PS-GA for Au(III) may be expressed as Figure 10.

CONCLUSIONS

A novel chelating resin crosslinking PS-GA was prepared from chloromethylpolystyrene and glucosamine hydrochlorate. Its structure was confirmed by FTIR, elemental analysis, and XPS.

The adsorption properties of PS-GA for Au(III) were investigated. PS-GA resin possessed excellent enriching property to Au(III) ions and adsorption proportion $E\%$ could reach to about 90 shortly after 3 h. The adsorption dynamics of Au(III) showed that the adsorption was controlled by liquid film diffusion and the apparent activation energy E_a was 12.91 kJ mol^{-1}.

TABLE IV
The Binding Energy (eV) of the Adsorption of PS-GA for Au(III)

Samples	N_{1s}	O_{1s}	C_{1s}	Cl_{2P}	Au_{4f}
PS-GA	400.02	531.49	284.74		
		532.78	286.64		
			288.34		
PS-GA-Au	400.05	531.49	284.76	198.33	84.98
	402.02	532.73	286.51	201.37	
			288.31		
$HAuCl_4$					87.33

Both Langmuir model and Freundlich model could describe the adsorption isothermal process of Au(III), and ΔG, ΔH, and ΔS values were calculated.

The mechanism of adsorption for Au(III) was confirmed by FTIR, SEM, and XPS. The results showed that both coordination and ion-exchange existed simultaneously in the adsorption. Some Au(III) ions were reduced to Au(0) and some —CHO groups in glucose chain were oxidized to —COOH groups.

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