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Preparation and adsorption properties of chelating resins containing 3-aminopyridine and hydrophilic spacer arm for Hg(II)

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ABSTRACT

Two novel chelating resins, denoted as PS-DEG-3-AP and PS-TEG-3-AP, were obtained by inserting spacer ethylene oxide and ethylene sulfide, respectively, with 3-aminopyridine (3-AP) into polystyrene-*co*-divinylbenzene. Fourier transform-infrared spectra (FTIR) and elemental analysis were employed to characterize their structures. The adsorption properties of the resins for Hg(II), Ag(I), Fe(III), Pb(II), Co(II), Cu(II), Ni(II), Cd(II) and Zn(II) had been studied, and the results revealed that the resins had higher adsorption capacities and adsorption selectivity for Hg(II). The adsorption kinetics and adsorption isotherms of the resins for Hg(II) were also investigated. The adsorption data of Hg(II) on the resins were fitted well by the pseudo second-order kinetics. Langmuir and Freundlich models were used to describe Hg(II) adsorption isotherms on both resins. The adsorption mechanisms of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) were confirmed by X-ray photoelectron spectroscopy (XPS). Furthermore, five consecutive sorption–desorption cycles demonstrated that the resins were suitable for repeated use without considerable change in adsorption capacity.

1. Introduction

Water pollution has received increasing attention for several decades because of the higher and higher requirement for the environment and the health of human beings, which are threatened by the various contaminants, such as organic pollutants and metal ions in water. Heavy metal ions, such as Hg(II), Cd(II), Ni(II), As(III), and Pb(II), are the major metal ion contaminants in water [1–3]. Among them, Hg(II) is considered as one of the most harmful metal ions to the environment. The Word Health Organization (WHO) has announced a maximum Hg(II) uptake of 0.3 mg per week and a maximum acceptable Hg(II) concentration of 1 μg/L in drinking water [4]. Hence, it is required to remove mercury from industrial watery discharges.

A number of approaches have been suggested for the removal of heavy metal ions from aqueous solution. The techniques include chemical precipitation, ion exchange, solvent extraction, biosorption and adsorption [5–10], etc. Of these, chelating resins with high adsorption selectivity has been widely used for the removal of mercury from aqueous solutions [11–15]. In general, the adsorption selectivity of chelating resins mainly depends on the chelate forming properties of functional groups chemically bonded to the supports such as silica gel, cellulose and styrene–divinylbenzene copolymers. Owing to the high adsorption selectivity of heterocyclic functional groups for heavy and noble metal ions, numerous studies have been concerned with the synthesis of chelating resins with heterocyclic functional groups such as pyridine [16,17], imidazole [18–22], and thiazole [23]. Among those heterocyclic functional groups, aminopyridine has drawn most attention due to its strong affinity for heavy and noble metal ions and the wide range of potential applications [24,25].

Recently developed chelating resins with hydrophilic spacer arms, such as ethylene oxide [26–29], ethylene sulfide [30], and ethylene imine [31], which are located between the polymeric matrix and functional groups, have made it possible to increase the adsorption capacity and the adsorption rate of the resins, as well as the adsorption selectivity. However, to the best of our knowledge, no study has been reported so far on the synthesis of chelating resins containing 3-aminopyridine functional groups, which are incorporated via spacer arms of ethylene oxide and ethylene sulfide.

In the present paper, we synthesize two novel chelating resins containing 3-aminopyridine and hydrophilic spacer arms and investigate the adsorption properties for metal ions. The action of the spacer arm and 3-aminopyridine in the coordination with Hg(II) is confirmed by XPS.

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2. Experimental

2.1. Materials and methods

PS-DEG-Bs and PS-TEG-Bs (shown in Scheme 1), with sulfur contents 11.93 and 12.15%, respectively, were used as raw materials. The synthesis and characterization of PS-DEG-Bs and PS-TEG-Bs were reported in our previous work [32]. 3-Aminopyridine was purchased from Tianjin Resent Chemicals Co. and used as received. Other reagents and solvents were of analytical grade and used without further purification. Stock solutions of the metal ions (0.1 mol/L each) were prepared by dissolving appropriate amounts of analytical grade nitrates in distilled water, and further diluted prior to use. Buffer solutions were prepared by adding dilute nitric acid or liquid ammonia to 0.1 mol/L ammonium acetate solutions.

Infrared spectra were recorded on a Nicolet MAGNA-IR550 (series II) spectrometer (Madison, WI); test conditions: potassium bromide pellets, scanning 32 times, resolution 4 cm^{-1}. Elementary analysis was performed by an Elementar Analysensysteme Varioel made in Hanau, Germany. XPS spectra were collected on PHI 1600ESCA system, PerkinElmer Co., USA, test conditions: MgK_α (1253.6 eV), power 200.0 W, resolution 187.85 Ev. The concentrations of metal ions were measured on a GBC-932 atomic absorption spectroscopy (AAS) (Victoria, Australia), equipped with air–acetylene flame.

2.2. Synthesis of PS-DEG-3-AP and PS-TEG-3-AP

The synthetic route of PS-DEG-3-AP and PS-TEG-3-AP was shown in Scheme 1.

The synthesis procedure of PS-DEG-3-AP was as following: under a nitrogen atmosphere, a mixture of 3.0 g of PS-DEG-Bs, 1.0 g of 3-AP, 0.5 g of K_2CO_3 and 80 mL of DMF was stirred at 358 K for 24 h. After filtration and washing with water and ethanol subsequently, the sample was moved to a Soxhlet's extraction apparatus for reflux-extraction in an ethanol solvent for 7 h, and then dried under vacuum at 323 K for 48 h. 2.78 g of PS-DEG-3-AP was obtained. Elemental analysis (%): N, 2.14; S, 10.90.

The preparation of PS-TEG-3-AP involved 3.0 g of PS-TEG-Bs, 1.0 g of 3-AP, 0.5 g of K_2CO_3 and 80 mL of DMF. The procedure of synthesis and purification of PS-TEG-3-AP was similar to that of PS-DEG-3-AP. 2.54 g of PS-TEG-3-AP was obtained. Elemental analysis (%): N, 1.85; S, 10.87.

2.3. Adsorption procedures

2.3.1. Adsorption capacity

Adsorption capacities of the resins for different metal ions were determined by batch tests according to the following procedure. 30 mg of the resin was added to 20.0 mL of 0.005 mol/L metal ion solution (pH = 4.0) in a 100-mL glass bottle with a stopper. After being shaken at 298 K for 24 h, the solution was separated from the resin. The concentration of metal ions in the solution was determined by AAS. The adsorption capacity was calculated according to Eq. (1).

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

where Q is the adsorption capacity (mmol/g); C_0 and C are the initial concentration and the concentration at any time t, respectively, of metal ion in solution (mmol/mL); V is the solution volume (mL); and W is the dry weight of resins (g). Each determination in the adsorption procedures was repeated three times and the results were given as average values. The error bars were also indicated wherever necessary.

2.3.2. Adsorption kinetics

To obtain the data of adsorption kinetics, 30 mg of the resin was added to 20.0 mL of 0.005 mol/L metal ion solution (pH = 4.0). The mixture was shaken continuously in a thermostat-cum-shaking assembly at a pre-determined temperature. Aliquots of 1 mL solution were withdrawn at desirable intervals and the concentration of metal ions in the solution was determined by AAS. The adsorption capacity of the resin was calculated according to Eq. (1).

2.3.3. Isothermal adsorption

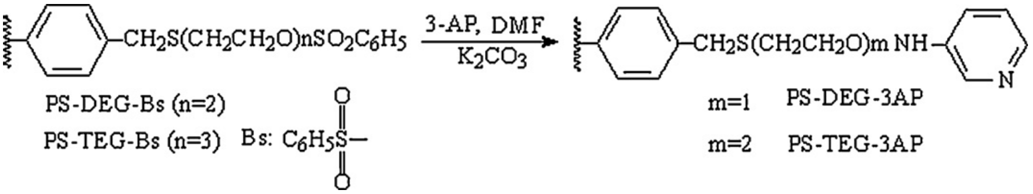
The isothermal adsorption property of the resins was investigated also by batch tests. In a typical procedure, a series of 100-mL tubes were used. Each tube was filled with 30 mg of the resins and 20 mL of metal ion solution of varying concentrations and adjusted to pH 4.0 and desired temperature. The mixture was shaken for 24 h. The adsorption capacities were calculated also by using Eq. (1), where C is the equilibrium concentration of Hg(II) in solution.

2.3.4. Adsorption selectivity

A binary mixtures system was used to examine the adsorption selectivity of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II). In the binary mixture system, the concentration of each metal ion was equal (0.005 mol/L). 30 mg of PS-DEG-3-AP or PS-TEG-3-AP was shaken with a solution of the binary mixture system for 24 h. Then the resin was separated by filtration and the concentration of the metal ions in the binary mixture was determined by AAS. The coefficients of adsorption selectivity were calculated as the ratio of the adsorption capacities of two kind of metal ions in the binary mixture system.

2.4. Desorption and reusability studies

To assess the reusability of PS-DEG-3-AP and PS-TEG-3-AP, consecutive adsorption–desorption cycles were repeated five times using the same resin. The solution of 3% thiourea in 0.1 mol/L HNO_3 was employed as the desorption medium. The Hg(II)-loaded PS-DEG-3-AP or PS-TEG-3-AP was placed in this medium, and then the mixtures were shaken for 60 min at room temperature (primary experiments indicated that Hg(II) adsorbed on the resin was almost desorbed completely when the contact time of Hg(II)-loaded PS-DEG-3-AP or PS-TEG-3-AP with this medium was about 40 min). The final concentration of Hg(II) in the aqueous phase was determined by AAS. After determination of metal content of the final solutions, the resin was washed with excess of the base solution and distilled water in order to reuse for next experiment.



Scheme 1. The synthetic route of PS-DEG-3-AP and PS-TEG-3-AP.

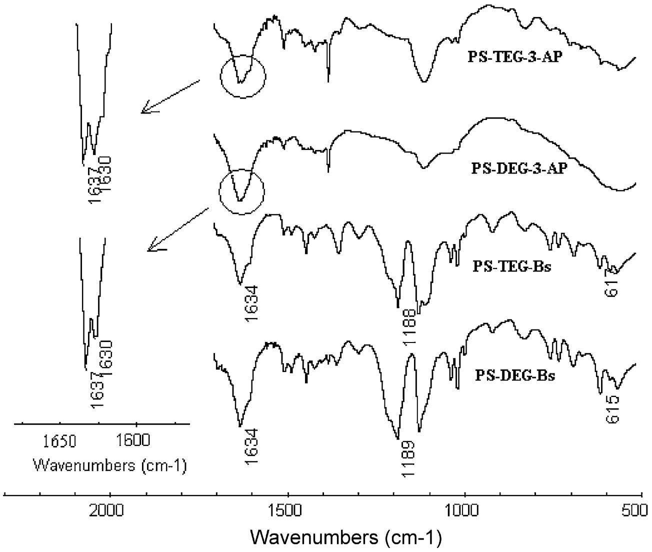


Fig. 1. FT-IR spectra of PS-DEG-Bs, PS-TEG-Bs, PS-DEG-3-AP and PS-TEG-3-AP.

3. Results and discussion

3.1. Characterization of the resins

Fig. 1 showed the infrared spectra of PS-DEG-Bs, PS-TEG-Bs, PS-DEG-3-AP and PS-TEG-3-AP. The bands at 1189 and 615 cm^{-1} for PS-DEG-Bs and at 1188 and 617 cm^{-1} for PS-TEG-Bs were assigned to the characteristic absorption peaks of PhSO_3^-. In the infrared spectra of PS-DEG-3-AP and PS-TEG-3-AP, the disappearance of the absorption peaks belonging to PhSO_3^- and the appearance of strong bands at 1630 cm^{-1} belonging to the breathing vibration of pyridyl ring [33] indicated that 3-AP had been incorporated into the polymeric matrix successfully. In addition, the existence of sulfur and nitrogen in PS-DEG-3-AP and PS-TEG-3-AP further demonstrated that 3-AP had been introduced via hydrophilic spacer arms of ethylene oxide and ethylene sulfide.

3.2. Adsorption capacity

To investigate the affinity of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II), Ag(I), Fe(III), Pb(II), Co(II), Cu(II), Ni(II), Cd(II) and Zn(II), an experiment was conducted at pH 4.0 by batch tests. The results were tabulated in Table 1. From Table 1, it could be note that, the resins had highest adsorption capacities for Hg(II). The adsorption capacities of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) were 0.96 and 1.04 mmol/g, respectively. The adsorption capacities of PS-DEG-3-AP and PS-TEG-3-AP for the investigated metal ions decreased in the following orders: Hg(II) > Ag(I) > Pb(II) > Fe(III) > Cu(II) > Co(II) > Ni(II); Hg(II) > Ag(I) > Fe(III) = Pb(II) > Cu(II) > Ni(II) > Co(II), respectively. PS-DEG-3-AP had no affinity for Ni(II), Cd(II) and Zn(II). In case of PS-TEG-3-AP, Cd(II) and Zn(II) could not be absorbed at all. These orders were in according with the characteristic of 3-AP and sulfur atom existed in the resins, which prefer interaction with large and more easily polarizable metal ions such as Hg^{2+} and Ag^{+} [34]. On the other hand, one could note that the adsorption capacities of PS-TEG-3-AP for each metal ion investigated in this paper were higher than that of PS-TEG-3-AP, which meant that the adsorption capacity increased with the increase of the length of the spacer arm. A reasonable explanation for this was that the increase of spacer arm might increase the flexibility of the functional group, which would be beneficial for the functional group to coordinate with metal ion [28]. Owing to the resins had highest capacity for Hg(II), thus, the adsorption of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) was selected to be studied in detail in the following part.

Table 1
Adsorption capacities of PS-DEG-3-AP and PS-TEG-3-AP for metal ions.

Metal ions[a]	Adsorption capacity[b] (mmol/g)	
	PS-DEG-3-AP	PS-TEG-3-AP
Hg(II)	0.96	1.04
Ag(I)	0.21	0.30
Fe(III)	0.15	0.19
Pb(II)	0.17	0.19
Co(II)	0.08	0.11
Cu(II)	0.10	0.13
Ni(II)	–	0.02
Cd(II)	–	–
Zn(II)	–	–

[a] The concentration of each metal ion in solution: 0.005 mol/L.

[b] Adsorption conditions: pH 4.0, quantities of resins: 30 mg, temp.: 298 K. "–": no affinity for metal ions.

Table 2
Comparison of adsorption capacities (*Q*) of chelating resins with different functional groups based on macroporous divinylbenzene–styrene copolymers.

Ligand	Q (mmol/g)	pH	Reference
Sulfur and 2-amino-pyridine	2.76	3.0	[10]
Imidazolyl azo group	0.62	4.0–6.0	[12]
Benzimidazolylazo	0.83	6.0	[13]
Bis(2-benzimidazolylmethyl)amine	0.20	6.0	[15]
1,4-Bis(imidazolylazo)benzene	0.11	5.5	[22]
Imidazolylazobenzene	0.25	5.0	[22]
2,5-Dimercapto-1,3,4-thiodiazole	0.67	2.0	[23]
Thiol	0.10	5.5	[26]
6-Mercaptopurine	1.74	6.0	[35]
1,2-Bis(o-aminophenylthio)ethane	0.38	5.0	[36]
Acrylamide	0.10	5.0	[37]
Spacer arm (DEG) and 3-amino-pyridine	0.96	4.0	Present study
Spacer arm (TEG) and 3-amino-pyridine	1.04	4.0	Present study

The adsorption of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) at pH 1–6 was studied at 298 K. With pH 1–4, the adsorption capacities increased with the increasing pH value. Its probably because that the N atoms in 3-aminopyridine could easily be protonized at lower pH condition and thus lose coordination ability. Also, the experiments showed that at higher pH condition (>4), the adsorption capacities decreased with the increasing pH value. The reason for this might ascribe to the formation of soluble hydroxilated complexes of Hg(II) at higher pH condition. According to these results, the pH in the solution would be kept at 4.0 in the subsequent experiments.

On the other hand, Table 2 presented the comparison of adsorption capacities (mmol/g) of chelating resins for Hg(II) based on macroporous divinylbenzene–styrene copolymers. The adsorption capacities of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) were higher than that of the majority of the other resins listed in Table 2. Therefore, it could be noteworthy that the resins had a considerable potential for the removal of Hg(II) from aqueous solution.

3.3. Adsorption kinetics

Figs. 2 and 3 showed the plots of adsorption capacities of PS-DEG-3-AP and PS-TEG-3-AP toward Hg(II) versus the contact time at different temperatures, respectively. The data in Figs. 2 and 3 were modeled by the Lagergren's pseudo first-order and pseudo second-order rate equation given below as Eqs. (2) and (3), respectively.

$$\log(Q_0 - Q) = \log Q_0 - \frac{k_1}{2.303}t \qquad (2)$$

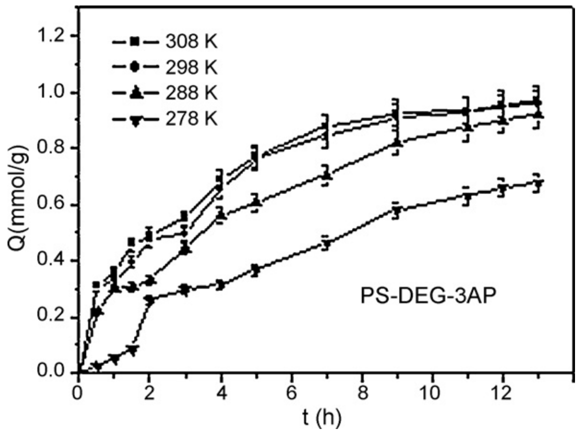


Fig. 2. Adsorption capacities of Hg(II) versus time on PS-DEG-3-AP at different temperatures (conc. of Hg^{2+}: 0.005 mol/L, pH 4.0, resin: 30 mg).

$$\frac{t}{Q} = \frac{1}{k_2 Q_0^2} + \frac{1}{Q_0} t \tag{3}$$

where k_1 is the rate constant of pseudo first-order adsorption (h^{-1}); k_2 is the rate constant of pseudo second-order adsorption (g/mmol); Q_0 and Q are the adsorption uptake at equilibrium and at time t, respectively (mmol/g).

Both the models were used to fit the kinetics curves and the results showed that pseudo second-order model was more suitable since the values of R^2 could be regarded as a measure of the goodness-of-fit of experimental data on the kinetic models [38]. The straight-lines of pseudo second-order kinetic model were shown in Figs. 4 and 5. The corresponding parameters calculated according to the models were tabulated in Table 3. It could be seen that: (1) For PS-DEG-3-AP or PS-TEG-3-AP, the adsorption rates increased with the increasing temperature (see the values of k_2 in Table 3), while the saturation adsorption capacities did not increase with the increasing temperature as we expected. A possible explanation for this was that the diffusion rate of Hg(II) was enhanced by increasing temperature, so Hg(II) could 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 Hg(II) from diffusing into the inside of the resin, so the value of adsorption capacities at highest temperature was not the largest. (2) At the same temperature, the adsorption rates of PS-TEG-3-AP were higher than those of PS-DEG-3-AP for Hg(II). This result illustrated that the increase in length of the spacer arm containing ethylene oxide could increase the hydrophilicity of the polymeric matrix further, which was beneficial for Hg(II) to contact and complex with the functional groups. Thus, the value of adsorption rate increased with the increase of the length of the spacer arm.

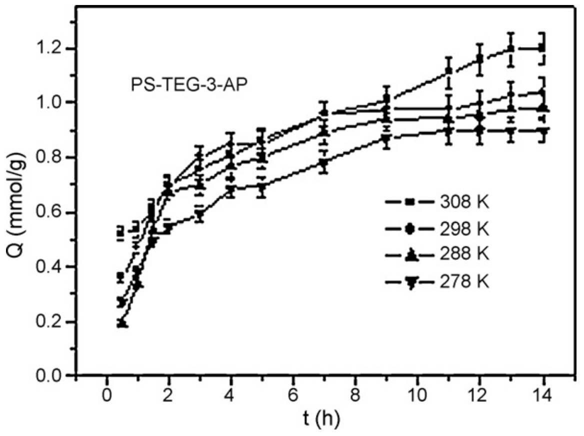


Fig. 3. Adsorption capacities of Hg(II) versus time on PS-TEG-3-AP at different temperatures (conc. of Hg^{2+}: 0.005 mol/L, pH 4.0, resin: 30 mg).

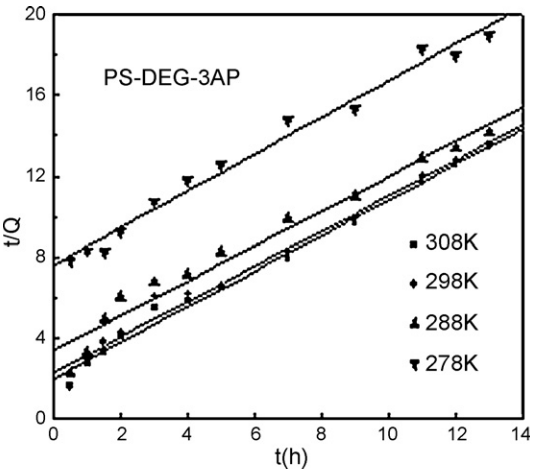


Fig. 4. The pseudo second-order kinetic model of PS-DEG-3AP for Hg(II).

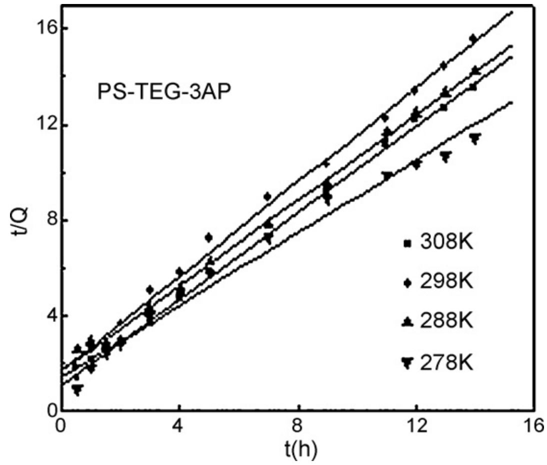


Fig. 5. The pseudo second-order kinetic model of PS-TEG-3AP for Hg(II).

According to Arrhenius equation, $\ln k_2 = -E_a/RT + \ln A$, plotting $\ln k_2$ against $1/T$, two straight lines could be obtained (see Fig. 6). The apparent activation energies of adsorption E_a calculated from

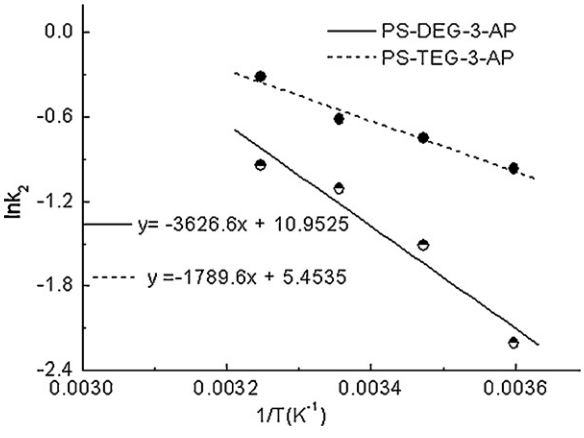


Fig. 6. lg k_2 versus $1/T$ plots for the adsorption of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II).

Table 3
The kinetic parameters of Hg(II) adsorption on PS-DEG-3-AP and PS-TEG-3-AP at different temperatures.

Resins	T (K)	Pseudo first-order model			Pseudo second-order model		
		k_1 (h^{-1})	Q_0 (mmol/g)	R^2	k_2 (g/mmol/h)	Q_0 (mmol/g)	R^2
PS-DEG-3-AP	308	0.23	1.14	0.9891	0.38	1.13	0.9908
	298	0.33	0.96	0.9747	0.33	1.15	0.9836
	288	0.27	0.98	0.9399	0.22	1.16	0.9664
	278	0.28	0.89	0.8471	0.11	1.10	0.9837
PS-TEG-3-AP	308	0.22	0.57	0.9383	0.73	1.11	0.9986
	298	0.45	1.08	0.9288	0.54	1.02	0.9963
	288	0.28	0.72	0.9761	0.47	1.12	0.9968
	278	0.16	0.84	0.9745	0.38	1.33	0.9825

the linear slopes for PS-DEG-3-AP and PS-TEG-3-AP were 30.15 and 14.88 kJ/mol, respectively. These low activation energies as compared to these of typical chemical reaction of 65–250 kJ/mol implied that the adsorption of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) was a facile procedure.

3.4. Adsorption isotherm

The adsorption isotherms of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) were investigated at four different temperatures and the data were analyzed with Langmuir (4) and Freundlich (5) equations, respectively. Then, Figs. 7 and 8 were obtained.

$$\frac{C}{Q} = \frac{1}{bQ_0} + \frac{C}{Q_0} \tag{4}$$

$$\ln Q = \ln K_F + \frac{1}{n} \ln C \tag{5}$$

where Q is the adsorption capacity (mmol/g), C the equilibrium concentration of metal ions (mol/L), Q_0 the saturated adsorption capacity (mmol/g), b an empirical parameter, n the Freundlich constant, and K_F the binding energy constant reflecting the affinity of the resin for metal ions. As we known, the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each sorbate molecule on to the surface had equal adsorption activation energy. While, the Freundlich equation is employed to described heterogenous systems and reversible adsorption and is not restricted to the formation of monolayer.

The parameters for the two isotherms models obtained from Figs. 7 and 8 were summarized in Table 4. It was found that the regression coefficients R^2 obtained from Langmuir or Freundlich models were greater than 0.9504, which implied that both Langmuir and Freundlich models could be used to describe the adsorption isotherms of Hg(II) on PS-TEG-3-AP and PS-DEG-3-AP at the temperature range of 278–308 K. In addition, the values of n varied in the range between 1 and 10. This demonstrated that Hg(II) was easily adsorbed on the two resins [39].

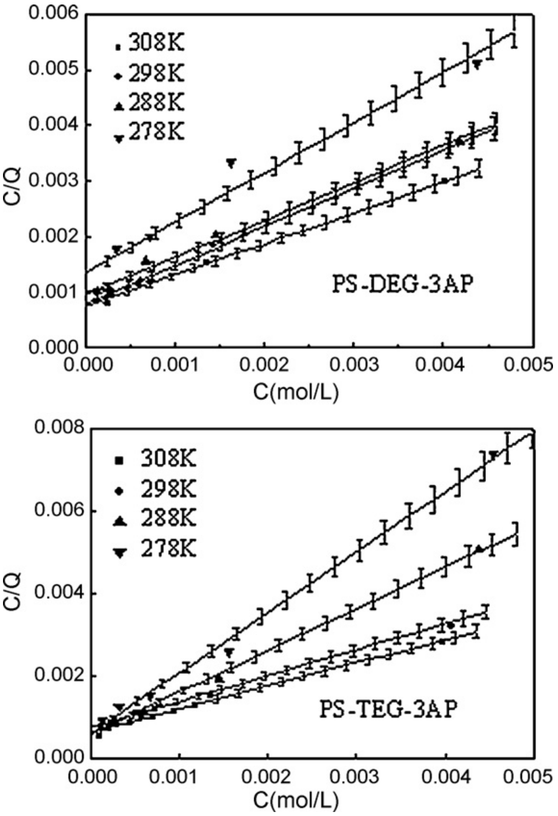


Fig. 7. The Langmuir isotherms of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) (pH: 4.0, resin: 30 mg).

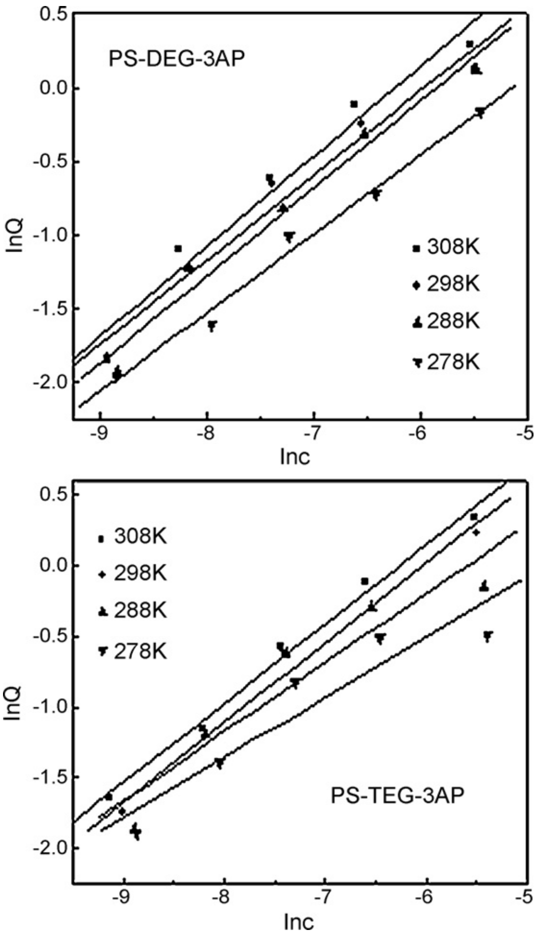


Fig. 8. The Freundlich isotherms of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) (pH: 4.0, resin: 30 mg).

Table 4
Langmuir and Freundlich parameters of Hg(II) adsorption on PS-DEG-3-AP and PS-TEG-3-AP at different temperatures.

Resins	T (K)	Q_0 (mmol/g)	b	R_L^2	$1/n$	K_F	R_F^2
PS-DEG-3-AP	308	1.77	775.54	0.9955	1.6362	45.15	0.9643
	298	1.45	884.33	0.9987	1.7466	30.27	0.9710
	288	1.49	715.28	0.9881	1.6872	32.14	0.9740
	278	1.10	685.23	0.9504	1.8730	15.49	0.9877
PS-TEG-3-AP	308	1.79	856.48	0.9864	1.7659	1.00	0.9955
	298	1.6	813.42	0.9764	1.4450	1.00	0.9987
	288	0.99	1664.03	0.9962	1.4851	1.01	0.9881
	278	0.68	2346.01	0.9940	1.0973	1.00	0.9504

Table 5
The adsorption selective coefficients of adsorption of PS-DEG-3-AP and PS-TEG-3-AP in binary mixtures systems at 298 K.

Systems[a]	Metal ions	PS-DEG-3-AP		PS-TEG-3-AP	
		Adsorption capacity (mmol/g)	Selective coefficients[b]	Adsorption capacity (mmol/g)	Selective coefficients
Hg(II)–Ag(I)	Hg(II)	0.86	8.6	0.96	8.00
	Ag(I)	0.10		0.12	
Hg(II)–Pb(II)	Hg(II)	1.05	52.5	1.20	40.0
	Pb(II)	0.02		0.03	
Hg(II)–Cu(II)	Hg(II)	1.03	∞	1.14	∞
	Cu(II)	0		0	
Hg(II)–Ni(II)	Hg(II)	1.02	∞	1.22	∞
	Ni(II)	0		0	
Hg(II)–Zn(II)	Hg(II)	1.02	∞	1.23	∞
	Zn(II)	0		0	
Hg(II)–Fe(III)	Hg(II)	0.99	49.5	1.19	39.7
	Fe(III)	0.02		0.03	

[a] Concentration of the metal ion: 0.005 mol/L. pH: 4.0. Resin: 30 mg.

[b] The selective coefficients were the ratio of adsorption capacities of metal ions in binary mixture system.

3.5. *Adsorption selectivity in binary metal ion mixture systems*

The adsorption selectivity of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) in binary metal ion mixture systems was studied at 298 K by batch tests. One of the following metal ions such as Ag(I), Pb(II), Fe(III), Cu(II), Ni(II) and Zn(II) was chosen as co-existence metal ion in binary mixture systems. The results were listed in Table 5. In the systems of Hg(II)–Cu(II), Hg(II)–Ni(II), and Hg(II)–Zn(II), three metal ions including Cu(II), Ni(II) and Zn(II) were not adsorbed at all by PS-DEG-3-AP or PS-TEG-3-AP. When PS-DEG-3-AP contacted in the systems of Hg(II)–Ag(I), Hg(II)–Fe(III), and Hg(II)–Pb(II), the selective coefficients for Hg(II) were 8.6, 49.5 and 52.5, respectively. In the case of PS-TEG-3-AP, the selective coefficients for Hg(II) in the above-mentioned mixture systems were 8.0, 39.7 and 40.0, respectively. All these experimental data implied that PS-DEG-3-AP and PS-TEG-3-AP had good adsorption selectivity for Hg(II), and the resins could be potentially used in extracting and separating Hg(II) from multi-ionic systems.

3.6. *Adsorption mechanism of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II)*

The results of XPS of PS-DEG-3-AP and PS-TEG-3-AP before and after adsorption of were investigated. The binding energy data of several elements were listed in Table 6. It could seen that the N_{1s} binding energies of PS-DEG-3-AP and PS-TEG-3-AP increased from 399.85 to 401.13 and 399.96 to 401.18 eV, respectively, after the adsorption for Hg(II), meaning that N was an electron donor. The binding energies of S_{2p} in the resins of PS-DEG-3-AP and PS-TEG-3-AP increased by 0.71 and 1.03 eV, respectively, after adsorption, showing that S atoms existed in the spacer arm was also involved in coordinating with Hg(II). Meanwhile, the decrease values of the binding energies of Hg_{4f} after adsorption for PS-DEG-3-AP and PS-TEG-3-AP were 2.72 and 2.58 eV, respectively, indicating that Hg atom was an electron acceptor. From the XPS results it also could be seen that there were little changes in the O_{1s} binding energies of PS-DEG-3-AP and PS-TEG-3-AP after adsorption of Hg(II). This meant that O atom did not take part in the coordination with Hg(II) and the existence of it in spacer arm only increased the hydrophilicity of PS-DEG-3-AP and PS-TEG-3-AP.

3.7. *Desorption efficency and reusability*

Four different desorption agents such as 0.1 M HNO_3, 1% thiourea in 0.1 M HNO_3, 3% thiourea in 0.1 M HNO_3 and 3% thiourea solution were chosen to be eluents in the desorption of Hg(II) adsorbed in resin. The elution values of the above-mentioned solutions were 40.5, 95.7, 100 and 59.8%, respectively. Thus, 3% thiourea in 0.1 M HNO_3 was selected as desorption agent for Hg(II) due to the attaining the best regeneration using this solution. The results of five consecutive adsorption–desorption cycles were shown in Fig. 9. The lost in the adsorption capacity of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) were determined to be 5.3 and 3.8%, respectively. This might be due to the ignorable partial plug of pore canals during the adsorption–desorption process. These results indicated that the

Table 6
The binding energy (eV) of the adsorption of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II).

	C_{1s}	N_{1s}	O_{1s}	S_{2p}	Hg_{4f}
PS-DEG-3-AP	284.72 286.34 288.22	399.85	531.72 533.26	167.85	
PS-DEG-3-AP-Hg	284.72 286.34 288.33	399.78 401.13	531.97 533.39	168.56	101.28
PS-TEG-3-AP	284.72 286.24 288.09	399.96	531.83 533.43	167.56	
PS-TEG-3-AP-Hg	284.72 286.24 288.38	399.97 401.18	531.98 533.47	168.59	101.42
Hg(II)					104.0 [40]

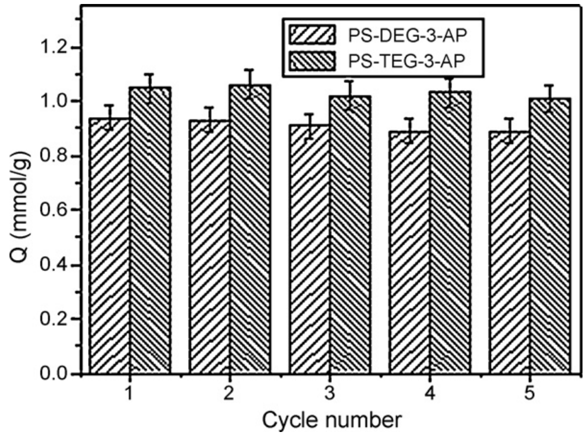


Fig. 9. Reusability of PS-DEG-3-AP and PS-TEG-3-AP with repeated sorption–desorption cycle (conc. of Hg^{2+}: 0.005 mol/L, pH 4.0, resin: 30 mg).

resins were suitable for repeated use without considerable change in adsorption capacity.

4. Conclusions

Novel chelating resins containing 3-aminopyridine and hydrophilic spacer arm (PS-DEG-3-AP and PS-TEG-3-AP) were prepared using PS-DEG-Bs and PS-TEG-Bs as materials. Elemental analysis and FTIR were employed to characterize their structures. The resins had higher capacity and selectivity for Hg(II). The adsorption kinetics and adsorption isotherms of PS-DEG-3-AP and PS-TEG-3-AP for Hg(II) were investigated. The results showed that the adsorption kinetics of the resins could be modeled by the pseudo second-order rate equation. The existence of the hydrophilic spacer was beneficial to enhance the hydrophilicity of the resins and then increase the adsorption rate. Langmuir and Freundlich equations could well interpret the adsorption of the resins for Hg(II). The XPS results showed that not only 3-aminopyridine but also S atoms existed in the spacer arm could take part in the coordination with Hg(II). The resins could be regenerated by 3% thiourea in 0.1 M HNO_3 with higher effectiveness. Five adsorption–desorption cycles demonstrated that the resins could be used repeatedly without considerable change in adsorption capacity.

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