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Synthesis of 2-phenoxyethanol/formaldehyde copolymer beads by dispersion polycondensation and their adsorption properties for copper ions after polyamine modification

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ABSTRACT

Two kinds of novel chelating resins were prepared by surface modification of 2-phenoxyethanol/formaldehyde copolymer beads (PB) with ethylenediamine (EA) and diethylenetriamine (DEA) (denoted as PB-EA and PB-DEA, respectively). The obtained resins were characterized by infrared spectra, scanning electron microscopy (SEM), and elemental analysis to demonstrate successful surface modification. The adsorption properties of the resins for metal ions are investigated. The results showed that the resins have higher adsorption capacities for Cu(II) than other metal ions such as Pb(II), Hg(II), Ag(I), Ni(II), Zn(II), Co(II), and Cr(III), with the maximum adsorption capacities of 0.15 mmol/g for PB-EA and 0.18 mmol/g for PB-DEA. Furthermore, the adsorption mechanism was studied in details. The adsorption processes of the resins for Cu(II) are governed by a film diffusion mechanism and follow the pseudo-first-order model well. The Langmuir model fits the equilibrium data better than the Freundlich isotherm. The adsorbed Cu(II) can be effectively desorbed with 1 M HNO_3 solution, and the resins can be used more than five adsorption–desorption cycles.

Keywords: Ethylene polyamine; 2-Phenoxyethanol/formaldehyde copolymer beads; Chelating resin; Adsorption; Copper

1. Introduction

The removal of heavy metals from wastewater is one of the most important issues due to the adverse effects of such metals on human health and the environment [1]. Traditional metal ion treatment methods mainly include precipitation, ion exchange, electrolysis, reverse osmosis, and adsorption. Among these treatment methods, adsorption is considered to be an excellent and promising method for the removal of heavy metals from wastewater [2–5]. Nowadays, most chelating resins developed for the removal of heavy metal ions rely on the complexation of the metal ions with the functional groups present in the chelating resins. Therefore, these groups play an important role in terms of the adsorption performance,

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including adsorption capacity, selectivity, and reusability. Amine groups have been found to be one of the most efficient functional groups for heavy metal ion removal, and various adsorbents have been developed by immobilizing the amine groups onto the surface of various matrix, such as polystyrene [6,7], polymethyl methacrylate [8,9], and silica [10,11]. Chelating resins are, as mentioned above, very useful in removing metal ions from wastewater, but they often suffer from insufficient adsorption rates, owing to the hydrophobic characteristic of the polymeric support. Furthermore, the hydrophobicity of polymeric backbone can limit the intrinsic chelating properties of the functional groups [12,13]. It is well known that, phenol-formaldehyde resins is one of the most widely applied chelating resins because of their low cost, easy processing, and high hydrophilicity of the polymeric backbone. Therefore, a lot of chelating resins were synthesized by the condensation of phenol or its derivatives with formaldehyde and used for the removal of metal ions [14–17].

In this article, 2-phenoxyethanol/formaldehyde copolymer beads were produced by dispersion polycondensation using polyvinyl pyrrolidone as a stabilizer. The obtained PB was subsequently modified with ethylenediamine and diethylenetriamine to obtained PB-EA and PB-DEA. The structures of PB-EA and PB-DEA were characterized by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, and scanning electron microscope (SEM). Furthermore, their adsorption properties including the adsorption equilibrium, kinetics, and thermodynamics were investigated in details.

2. Materials and methods

2.1. Materials

2-Phenoxyethanol (CR, 98%) and polyvinyl pyrrolidone (PVP) ($M_w = 40{,}000$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Formaldehyde solution (37–41% (w/w)), ethylenediamine, diethylene triamine, and formic acid (AR, 88% w/w) were obtained from Tianjin Regent Chemicals Co. Ltd. All the other chemical reagents used in this study were of analytical grade and used without further purification.

2.2. Instruments

The morphology of the 2-phenoxyethanol/formaldehyde copolymer beads and resins was determined using a scanning electron microscopy (JSM-5610LV, JEOL, Tokyo, Japan). infrared spectra (IR) were recorded on a Nicolet MAGNA-IR550 (serious II) spectrometer (Madison, WI, USA); test conditions: potassium bromide pellets, scanning 32 times, resolution 4 cm^{-1}. Elemental analysis was performed by an Elemental Analysensysteme Varioel (Hanau, Germay). A pH meter (Mettler-Toledo, LE438 pH, China) was used for the measurement of pH values. The concentrations of metal ions were measured on a GBC-932 atomic absorption spectrophotometer (AAS) (Victoria, Australia), equipped with an air-acetylene flame.

2.3. Preparation of PB-EA and PB-DEA

The synthesis of PB, PB-EA, and PB-DEA is shown schematically in Fig. 1, and described as follows:

2.3.1. Preparation of PB

11.1 g of PVP was added into a mixture of formic acid (88% w/w solution, 112.0 mL, 136.64 g), formaldehyde solution (37% w/w solution, 94 mL, 100.26 g), and 2-phenoxyethanol (70 mL, 77.67 g). After PVP was dissolved completely, sulfuric acid (18 mL) was then added dropwise into the solution over a period of 30 min. The resulting mixture was agitated at 700 rpm and allowed to polymerize at 70℃ for 10 h. The beads were collected by filtration, washed repeatedly with distilled water, and then immersed into an aqueous NaOH solution (5% w/w) for 48 h. After washing with distilled water and 95% ethanol, respectively, the beads were dried under vacuum at 50℃ for 48 h. 100–200 mesh of PB was gathered and used in the subsequent experiment.

2.3.2. Preparation of PB-CHO

PB-CHO was synthesized by adopting the method reported in the literature [18]. Thus, 5 g of PB was added to 3.73 g acetic anhydride in 100 mL dimethylsulfoxide and stirred for 24 h at room temperature. The beads were filtered, and then washed with

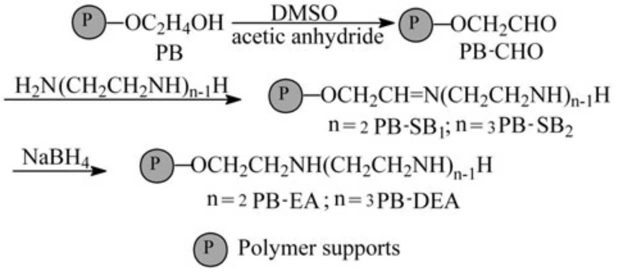

Fig. 1. The synthetic route sketch of the precursors, PB-EA, and PB-DEA.

distilled water and acetone, respectively. The beads were dried under vacuum at 50℃ for 48 h. 4.90 g of PB-CHO was obtained.

2.3.3. Preparation of PB-SB$_1$ and PB-SB$_2$

2.3.3.1. Preparation of PB-SB$_1$. PB-SB$_1$ was prepared according to a procedure described in the literature [19]. PB-CHO (30 g) was reacted with 2.62 g of glacial acetic acid and 22.92 g of EA in a mixture of 75 mL ethanol and 25 mL tetrahydrofuran (THF) at 90℃ for 48 h. The reaction mixture was filtered and washed with distilled water and methanol, respectively. Then, the polymeric beads were moved to a Soxhlet extraction apparatus for reflex in acetone for 4 h and finally dried under vacuum at 50℃ for 48 h. 30.74 g of PB-SB$_1$ was obtained.

2.3.3.2. Preparation of PB-SB$_2$. The reaction involved 30 g of PB-CHO, 2.62 g of glacial acetic, 39.11 g of DEA, 75 mL ethanol, and 25 mL THF. The procedure for the synthesis and purification of the product was similar to that of PB-SB1. 31.58 g of PB-SB$_2$ was obtained.

2.3.4. Preparation of PB-EA and PB-DEA

2.3.4.1. Preparation of PB-EA. PB-EA was prepared according to a procedure described in the literature [19]. PB-SB$_1$ (24.00 g) was reacted with 11.90 g of $NaBH_4$ in a mixture of 75 mL ethanol and 25 mL THF at ice-water bath. The reaction mixture was stirred at room temperature for 24 h. and then filtered and washed with distilled water and methanol, respectively. Then, the polymeric beads were moved to a Soxhlet extraction apparatus for reflex in acetone for 4 h and finally dried under vacuum at 50℃ for 48 h. 24.31 g of PB-EA was obtained. Anal. found (%): C, 69.33; H, 6.616; N, 1.389.

2.3.4.2. Preparation of PB-DEA. The reaction involved 25 g of PB-SB$_2$, 12.1 g of $NaBH_4$, 75 mL ethanol, and 25 mL THF. The procedure for the synthesis and purification of the product was similar to that of PB-SB1. 25.12 g of PB-DEA was obtained. Anal. found (%): C, 68.89; H, 6.730; N, 1.628.

2.4. Adsorption procedures

2.4.1. Adsorption capacity

The adsorption capacities of the resins for metal ions were determined according to the following procedure. 0.05 g of the resin was shaken with 20.0 mL of 0.2 mmol/L metal ion solution (pH 5.0) at room temperature for 24 h. Then, the resin was separated by filtration, and the metal ion concentration in the solution was determined by AAS. The adsorption capacity was calculated from the difference between amounts of metal ion in the solution and the starting solution according to Eq. (1).

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

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 mass of resins (g).

2.4.2. Adsorption kinetics

To obtain the data of adsorption kinetics, 50 mg of the resin was added to 20.0 mL of 0.002 mol/L metal ion solution (pH 5.0). The mixture was shaken continuously in a thermostat-cum-shaking assembly at a pre-determined temperature. Aliquots of 1 mL solution were withdrawn at pre-determined intervals, and the concentration of metal ion in the solution was determined by AAS. The adsorption capacity was calculated according to Eq. (1).

2.4.3. Adsorption isotherms

The isothermal adsorption was also investigated by batch tests. A typical procedure was as follows: A series of 100-mL test tubes were employed. Each test tube was filled with 50 mg of the resin and 20 mL of metal ion of varying concentrations and adjusted to pH 5.0 and the desired temperature. After a shaking time of 24 h, the solution was separated from the adsorbent and the residual concentration of metal ion was also determined by AAS. The adsorption capacities were calculated also according to Eq. (1), where C is the equilibrium concentration of metal ion in solution.

2.4.4. Adsorption selectivity

Several binary mixture systems were used to examine the adsorption selectivity of the resins for Cu(II). The adsorption selectivity of the resins was studied by batch tests. In the binary mixture systems, the concentration of each metal ion was equal (0.005 mol/L). A typical procedure was as follows:

50 mg of the resin was shaken with a solution of the binary mixture system at 25°C 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 the two kinds of metal ions in the binary mixture system.

2.4.5. Reusability of the resins

To test the reusability of the resins, adsorption–desorption cycles of PB-EA and PB-DEA for Cu(II) were repeated five times using the same resin. The solution of 1 mol/L HNO_3 were employed as the desorption medium. The resins-adsorbed Cu(II) were placed in 20 mL of desorbents and stirred for 10 h at room temperature. The final concentrations of Cu(II) were determined by AAS. The desorption ratio was calculated from the amount of Cu(II) adsorbed on the resin and the final concentration of Cu(II) in the desorption medium.

3. Results and discussion

3.1. Characterization of PB-EA, PB-DEA, and their precursors

The IR spectra of PB-CHO, PB-SB$_1$, PB-SB$_2$, PB-EA, and PB-DEA are shown in Fig. 2. The bands (1,610 and 1,499 cm^{-1}) in PB-CHO are assigned to the characteristic peaks of aromatic ring. The 1,247 cm^{-1} in PB-CHO is assigned to the aromatic ether, and the 1,029 cm^{-1} absorption band is attributed to the C–O–C stretching vibrations. These absorption bands are also observed in the spectra of PB-SB$_1$, PB-SB$_2$, PB-EA, and PB-DEA. In the spectra of PB-CHO, the strong stretching vibration (1,737 cm^{-1}) shows the presence of carbonyl group, which is obtained by the oxidation reaction of hydroxyl group in PB. The 1,638 cm^{-1} absorption bands in the spectra of PB-SB$_1$ and PB-SB$_2$ are attributed to the C=N group. The weak peaks near 1,288 cm^{-1} indicated the presence of C–N band in PB-SB$_1$, PB-SB$_2$, PB-EA, and PB-DEA. All the IR spectra, along with elemental analysis data of PB-EA and PB-DEA indicate that the modification of the PB with polyamine is successful. The morphology of the resins, including PB, PB-EA, and PB-DEA, is also observed by SEM (see Fig. 3). Obviously, PB-EA and PB-DEA still keep the regular spherical shape after being modified after the three-step successive reactions.

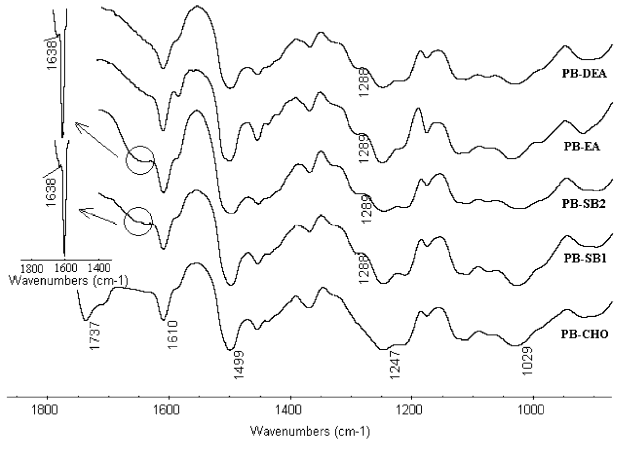

Fig. 2. The IR spectra of the precursors, PB-EA, and PB-DEA.

3.2. Adsorption capacities of the resins for metal ions

As is well known, pH value is a critical parameter in the adsorption process. Usually, at a high solution pH, copper ions may precipitate as $Cu(OH)_{2(s)}$, and the amount of copper species present in the aqueous solution in the forms of Cu(II), $Cu(OH)^+$, $Cu(OH)_2^0$, $Cu(OH)_3^-$, and $Cu(OH)_4^{2-}$ vary with the solution pH [20]. These copper ions, except Cu(II), interfere with the ability of PB-EA and PB-DEA to adsorb copper ions. Furthermore, the amine groups can be protonated at a low solution pH, the protonated amine groups cannot adsorb Cu^{2+}. In order to avoid the decrease of coordination capacity of PB-EA and PB-DEA due to the protonation of amine groups at lower pH and formation of precipitate of copper ions at high pH, pH 5 was selected for investigating the adsorption capacities of PB-EA and PB-DEA for Cu(II) [21]. The results are shown in Fig. 4. It is noted that the adsorption capacities of the resins for the metal ions follow the following order: Cu(II) > Pb(II) > Hg(II) > Ag(I) > Ni(II). The maximum adsorption capacities of PB-EA and PB-DEA for Cu(II) are 0.15 and 0.18 mmol/g, respectively. In addition, the resins show no affinity for Zn(II), Co(II), and Cr(III) at all. Therefore, the resins have good adsorption selectivity for Cu(II) over other metal ions such as Pb(II), Hg(II), Ag(I), Ni(II), Zn(II), Co(II), and Cr(III). The probable reason is interpreted as follows: According to the theory of soft and hard acids and bases (SHAB) [22], ligands with "borderline" or "hard" type donors prefer interactions with "borderline" or "hard" acceptors such as transition metal ions. In this study, the amino groups can be regarded as borderline bases, while the hydroxyl groups within the polymeric are hard bases. Therefore, the resins have higher adsorption capacities for

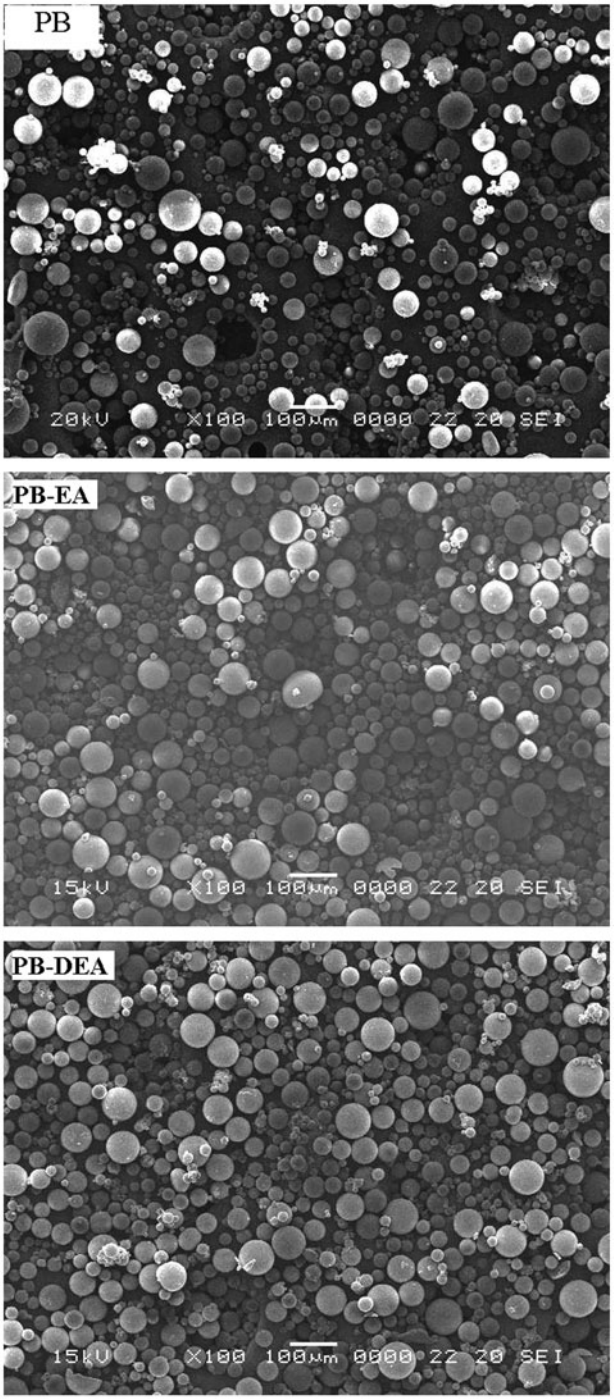

Fig. 3. The SEM images of PB, PB-EA, and PB-DEA.

Cu(II) over other metal ions such as Pb(II), Hg(II), Ag(I), Ni(II), Zn(II), Co(II), and Cr(III). Also, it can be noted that, for the same metal ion, the adsorption capacity of PB-DEA is higher than that of PB-EA, which can be attributed to the higher N content in PB-DEA as indicated by elemental analysis.

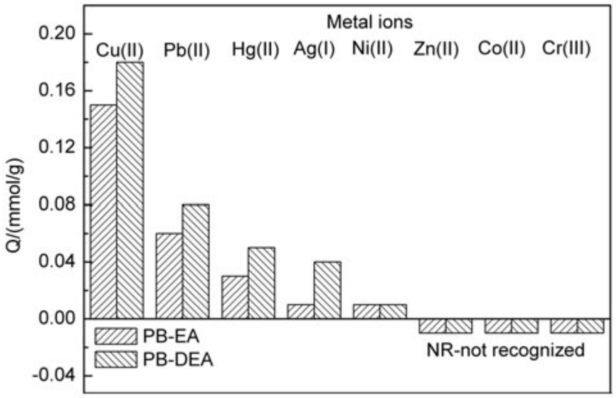

Fig. 4. The adsorption capacities of PB-EA and PB-DEA for metal ions (conc. of Cu(II): 2 mmol/L, pH 5.0, resin: 50 mg).

3.3. Adsorption kinetics

Fig. 5 shows the adsorption kinetics of PS-EA and PB-DEA for Cu(II) at different temperatures. It can be noted that the adsorption rates of PB-EA and PB-DEA for Cu(II) are fast within the first 30 min, and the adsorption equilibrium can be reached within 90 min. Furthermore, the results show that the adsorption capacities of PB-EA and PB-DEA increase with the increasing temperatures. We assume the resins swell more completely at higher temperatures, leading to higher diffusion rates of the metal ions into the interior of the resins.

The Boyd et al. [23] and Reichenberg [24] equations were used to clarify the adsorption kinetics of Cu(II) on the resins. The adsorption data in Fig. 5 were analyzed by the following equations:

$$F = 1 - \frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}\left[\frac{-D_i t\pi^2 n^2}{r_0^2}\right] \tag{2}$$

or

$$F = 1 - \frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}\exp\left[-n^2 Bt\right] \tag{3}$$

where F is the fractional attainment of equilibrium at time t and can be obtained by the following equation:

$$F = \frac{Q_t}{Q_0} \tag{4}$$

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

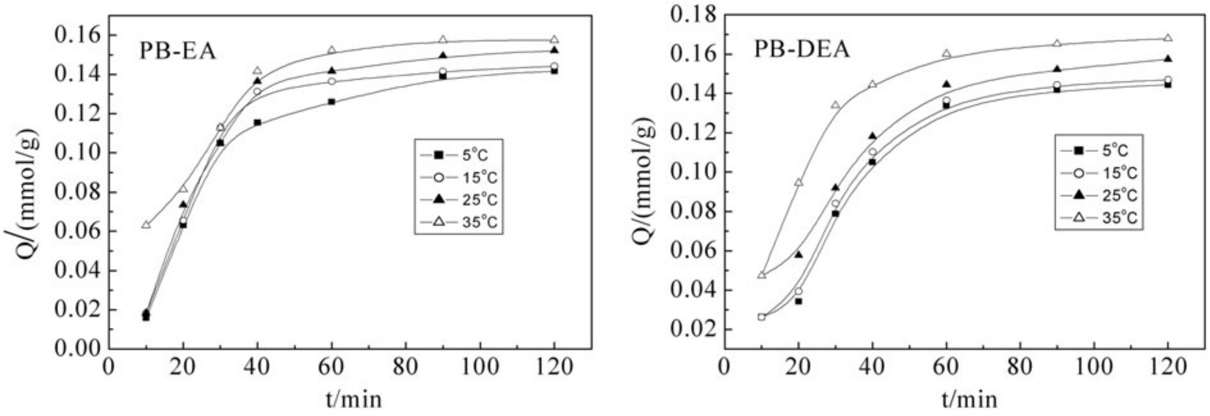

Fig. 5. Adsorption capacities of Cu(II) vs. time on PB-EA and PB-DEA at different temperatures (conc. of Cu(II): 2 mmol/L, pH 5.0, resin: 50 mg).

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \tag{5}$$

where D_i is the effective diffusion coefficient of the ion in the adsorbent phase; r_0 is the radius of the adsorbent particle, assumed to be spherical; and n is an integer that defines the infinite series solution.

Bt values were obtained for each observed value of F from Reichenberg's table, [24] and the results are plotted in Fig. 6. Generally, the adsorption process can be described by the following two mechanisms: film diffusion and particle diffusion. To distinguish these two mechanisms, a linearity test of *Bt* vs. time plots can be employed. If the plot is a straight line passing through the origin, the adsorption process is dominated by the particle diffusion mechanism, and otherwise it is governed by the film diffusion mechanism. Herein, the parameters of linear regression are given in Table 1. Fig. 6 shows that the four straight lines for each resin under different temperatures do not pass through the origin, indicating that the rate-controlling step is not particle diffusion mechanism, but film diffusion mechanism.

The adsorption kinetic data are also analyzed using two commonly used kinetic models, namely, the pseudo-first-order and pseudo-second-order models that can be expressed in their linearized forms as Eqs. (6) and (7), respectively.

$$\log(Q_0 - Q) = \log Q_0 - \frac{k_1}{2.303} t \tag{6}$$

$$\frac{t}{Q} = \frac{1}{k_2 Q_0^2} + \frac{1}{Q_0} t \tag{7}$$

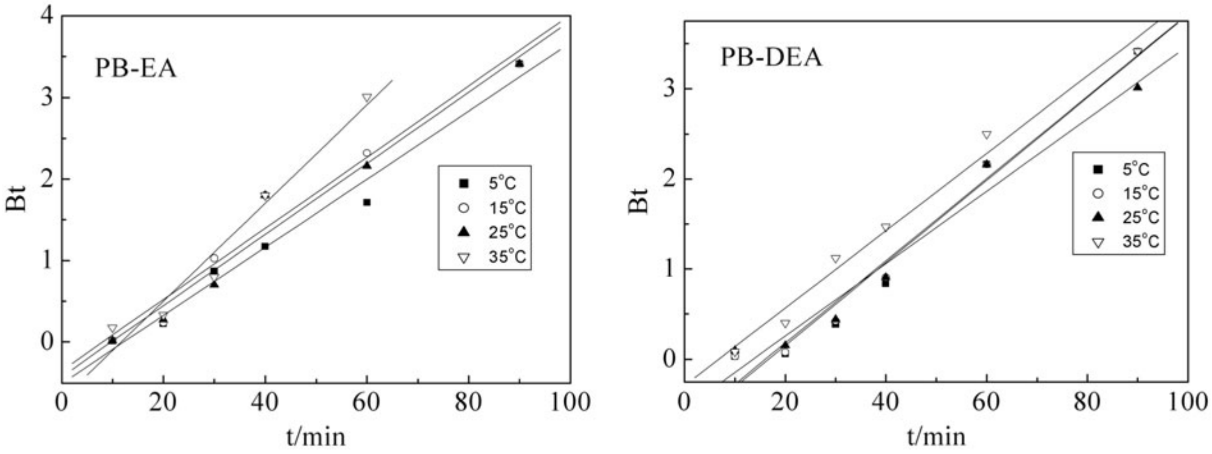

Fig. 6. *Bt* vs. time plots at different temperatures of PB-EA and PB-DEA for Cu(II).

Table 1
The Bt vs. time linear equations and coefficients R^2 and intercept errors

Resin	T (℃)	Linear equation	R^2	Intercept errors
PB-EA	5	$Bt = 0.0418t - 0.5085$	0.9810	0.0029
	15	$Bt = 0.0436t - 0.3491$	0.9659	0.0041
	25	$Bt = 0.0436t - 0.4247$	0.9642	0.0042
	35	$Bt = 0.0603t - 0.7054$	0.9803	0.0070
PB-DEA	5	$Bt = 0.0458t - 0.7648$	0.9715	0.0039
	15	$Bt = 0.0456t - 0.7348$	0.9766	0.0035
	25	$Bt = 0.0402t - 0.5504$	0.9676	0.0037
	35	$Bt = 0.429t - 0.2931$	0.9849	0.0027

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

Both of the models were used to fit the kinetics curves and the results are shown in Table 2. It is found that only the pseudo-first-order kinetic model provided a good fitting of the adsorption of Cu(II) onto the resins, which is shown in Fig. 7.

3.4. Adsorption isotherms

The adsorption isotherms of PB-EA and PB-DEA for Cu(II) were investigated at four different temperatures, and the experimental data were analyzed with the Langmuir (Eq. (8)) and Freundlich (Eq. (9)) equations, respectively. Then, Fig. 8 was obtained.

$$\frac{C}{Q} = \frac{1}{bQ_0} + \frac{C}{Q_0} \tag{8}$$

$$\ln Q = \ln K_{\mathrm{F}} + \frac{1}{n} \ln C \tag{9}$$

where Q is the adsorption capacity (mmol/g), C is the equilibrium concentration of metal ions (mol/L), Q_0 is the saturated adsorption capacity (mmol/g), b is an empirical parameter, n is the Freundlich constant, and K_{F} is the binding energy constant reflecting the affinity of the metal ions onto resin.

As is well known, the Langmuir model assumes that the adsorption takes place at specific homogeneous sites within the adsorbent and used successfully in many monolayer adsorption processes [25]. On the other hand, the Freundlich model can be applied for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. Table 3 shows the values of Q_0 and K_{L}, determined from the slopes and intercepts of the linear plots of C/Q vs. C, as well as the values of K_{F} and $1/n$, obtained from the slopes and intercepts of linear plot of $\ln Q$ vs. $\ln C$. The correlation coefficients for the two isotherms obtained from the experimental data were also presented in Table 3. It is found that the coefficients (R^2) of the Langmuir model are higher than those obtained from the Freundlich model, indicating that the Langmuir model can be used to describe the adsorption processes of Cu(II) on PB-EA and PB-DEA.

Table 2
The kinetic parameters of PB-EA and PB-DEA for Cu(II) at different temperatures

		Pseudo-first-order kinetics			Pseudo-second-order kinetics		
Resins	T (℃)	k_1 (min^{-1})	Q_0 (cal) (mmol/g)	R_1^2	k_2 (g/mmol/min)	Q_0 (cal) (mmol/g)	R_2^2
PB-EA	5	0.0462	0.15	0.9807	0.045	0.27	0.5065
	15	0.0485	0.18	0.9485	0.066	0.24	0.6188
	25	0.0489	0.19	0.9688	0.053	0.27	0.5822
	35	0.0616	0.22	0.9650	0.275	0.18	0.9862
PB-EA	5	0.0412	0.17	0.9847	0.037	0.29	0.6585
	15	0.483	0.20	0.9888	0.045	0.27	0.7558
	25	0.0508	0.25	0.9821	0.114	0.22	0.9578
	35	0.0509	0.26	0.9879	0.213	0.21	0.9749

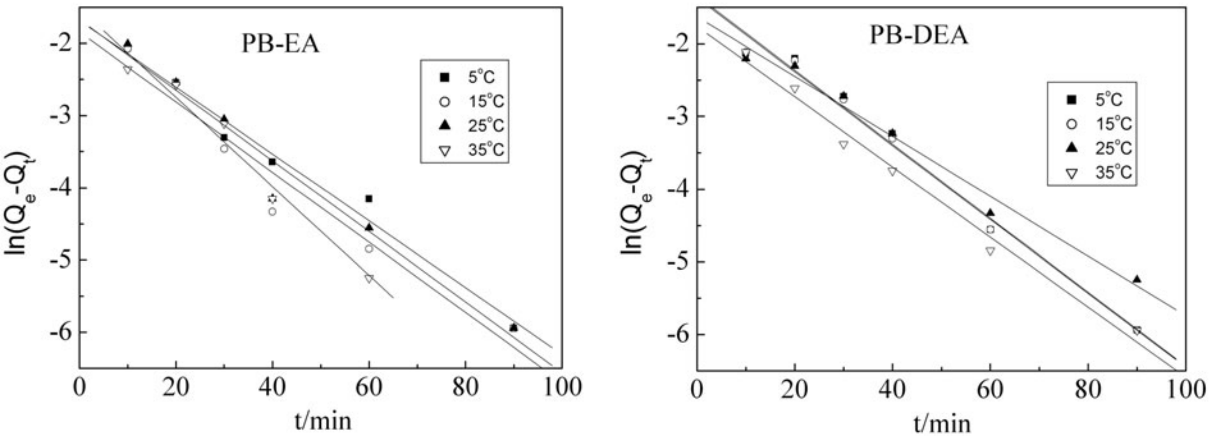

Fig. 7. The pseudo-first-order kinetic model of PB-EA and PB-DEA for Cu(II).

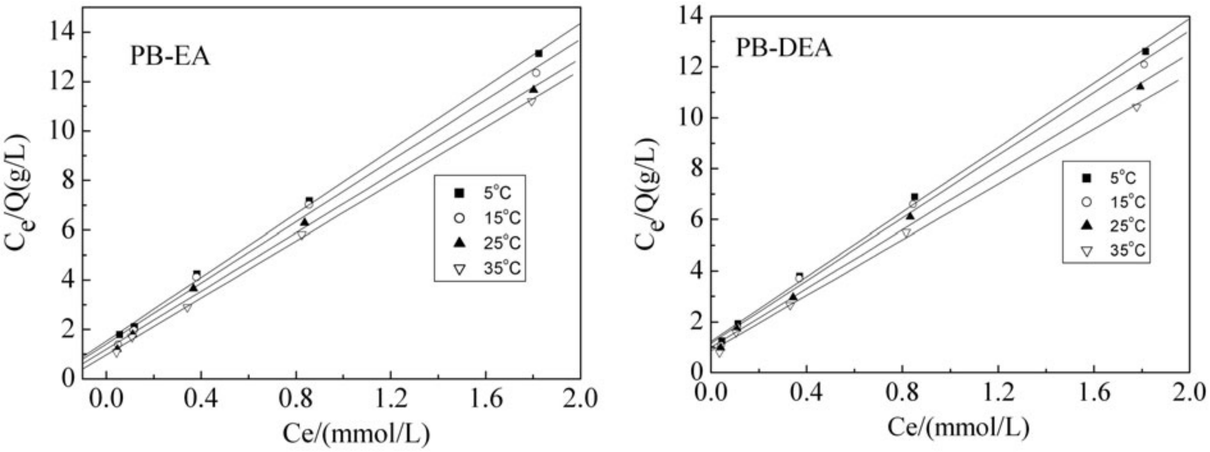

Fig. 8. The Langmuir isotherms of PB-EA and PB-DEA for Cu(II).

Table 3
The parameters in the Langmuir and Freundlich equations of PB-EA and PB-DEA for Cu(II)

		Langmuir parameters			Freundlich parameters		
Resins	T (°C)	Q_0 (mmol/g)	K_L (L/mmol)	R_L^2	n	K_F (mmol/g)	R_F^2
PB-EA	5	0.16	4.1878	0.9984	2.40	0.1217	0.9570
	15	0.16	4.3476	0.9945	2.58	0.1259	0.9807
	25	0.17	4.8955	0.9971	2.62	0.1361	0.9784
	35	0.17	5.9221	0.9993	2.63	0.1470	0.9513
PB-DEA	5	0.16	5.1927	0.9975	2.71	0.1272	0.9756
	15	0.16	5.3435	0.9963	2.81	0.1312	0.9839
	25	0.17	5.8550	0.9973	2.75	0.1439	0.9626
	35	0.18	6.3512	0.9975	2.82	0.1549	0.9625

3.5. Adsorption selectivity

The ability to selectively remove particular metal ions from aqueous solution under competitive conditions is important for chelating resins. The adsorption selectivity of the resins in binary mixture systems was also investigated. Table 4 shows the coefficients of adsorption selectivity of the resins under competitive conditions. In the systems of Cu(II)–Zn(II), Cu(II)–Co (II), and Cu(II)–Fe(III), the co-extensive metal ions such as Zn(II), Co(II), and Fe(III), do not affect the adsorption of the resins for Cu(II). For the other binary systems, the selectivity coefficients of PB-EA are 3.1 for Cu(II)–Pb(II), 6.7 for Cu(II)–Hg(II), 10.5 for Cu (II)–Ag(I), and 10.5 for Cu(II)–Ni(II). For PB-DEA, these values are 3.3, 1.6, 4.6, and 8. This indicated that the resins exhibit high adsorption selectivity for Cu(II) over the other metal ions investigated in this study.

3.6. Desorption and reusability

Such solutions as 0.1, 0.5, and 1.0 mol/L HNO_3 were chosen to desorb the metal ions adsorbed on the resin. The experimental result showed that rate of elution using the above-mentioned solutions were 87.1, 95.7, and 98.7%, respectively. Therefore, solution of 1 mol/L HNO_3 was employed as eluant to regenerate the resins. The results of five adsorption–desorption cycles are shown in Fig. 9. It can be noted that the resins can retain a high adsorption capacity after five adsorption–desorption cycles, suggesting that PB-EA

Table 4
The adsorption selective coefficients of PB-EA and PB-DEA for Cu(II) in binary mixture systems (conc. of metal ion: 2 mmol/L, pH 5.0, resin: 50 mg, temperature: 25˚C)

Resin	System	Metal ion	Adsorption capacity (mmol/g)	Selective coefficient
PB-EA	Cu(II)–Pb(II)	Cu(II)	0.19	$\alpha_{Cu(II)/Pb(II)} = 3.1$
		Pb(II)	0.06	
	Cu(II)–Hg(II)	Cu(II)	0.20	$\alpha_{Cu(II)/Hg(II)} = 6.7$
		Hg(II)	0.03	
	Cu(II)–Ag(I)	Cu(II)	0.21	$\alpha_{Cu(II)/Ag(I)} = 10.5$
		Ag(I)	0.02	
	Cu(II)–Zn(II)	Cu(II)	0.21	$\alpha_{Cu(II)/Zn(II)} = \infty$
		Zn(II)	0	
	Cu(II)–Ni(II)	Cu(II)	0.21	$\alpha_{Cu(II)/Ni(II)} = 10.5$
		Ni(II)	0.02	
	Cu(II)–Co(II)	Cu(II)	0.21	$\alpha_{Cu(II)/Co(II)} = \infty$
		Co(II)	0	
	Cu(II)–Cr(III)	Cu(II)	0.21	$\alpha_{Cu(II)/Cr(III)} = \infty$
		Cr(III)	0	
	Cu(II)–Fe(III)	Cu(II)	0.21	$\alpha_{Cu(II)/Fe(III)} = \infty$
		Fe(III)	0	
PB-DEA	Cu(II)–Pb(II)	Cu(II)	0.23	$\alpha_{Cu(II)/Pb(II)} = 3.3$
		Pb(II)	0.07	
	Cu(II)–Hg(II)	Cu(II)	0.23	$\alpha_{Cu(II)/Hg(II)} = 1.6$
		Hg(II)	0.15	
	Cu(II)–Ag(I)	Cu(II)	0.23	$\alpha_{Cu(II)/Ag(I)} = 4.6$
		Ag(I)	0.05	
	Cu(II)–Zn(II)	Cu(II)	0.25	$\alpha_{Cu^{2+}/Zn^{2+}} = \infty$
		Zn(II)	0	
	Cu(II)–Ni(II)	Cu(II)	0.24	$\alpha_{Cu(II)/Ni(II)} = 8$
		Ni(II)	0.03	
	Cu(II)–Co(II)	Cu(II)	0.25	$\alpha_{Cu(II)/Co(II)} = \infty$
		Co(II)	0	
	Cu(II)–Cr(III)	Cu(II)	0.25	$\alpha_{Cu(II)/Cr(III)} = 25$
		Cr(III)	0.01	
	Cu(II)–Fe(III)	Cu(II)	0.25	$\alpha_{Cu(II)/Fe(III)} = \infty$
		Fe(III)	0	

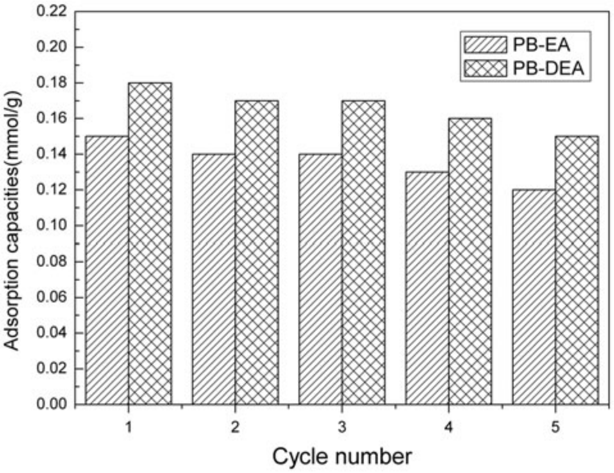

Fig. 9. Reusability of the resins with repeated adsorption–desorption cycle.

and PB-DEA exhibit good reusability and can be used for more than five adsorption–desorption cycles.

4. Conclusions

Two kinds of novel chelating resins were prepared by immobilizing ethylenediamine (EA) and diethylenetriamine onto the surface of the 2-phenoxyethanol/formaldehyde copolymer beads (PB). It was applied for the removal of Cu(II) from aqueous solutions, and was characterized by IR spectra, SEM, and elemental analysis. The adsorption capacities of PB-EA and PB-DEA are 0.15 and 0.18 mmol/g, respectively, and the adsorption kinetics follows a pseudo-first-order rate model. The isotherm adsorption equilibrium can be well described by Langmuir isotherm model. The resins exhibit higher selectivity for Cu(II) in binary mixture systems. Meanwhile, the adsorbed Cu(II) can be effectively desorbed in 1 M HNO_3 solution, and PB-EA and PB-DEA can be reused repeatedly.

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