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Preparation of thiacalix[4]arenetetrasulfonate-modified D201 resin and its adsorption of heavy metal ions

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ABSTRACT

A thiacalix[4]arenetetrasulfonate-modified resin has been prepared by loading thiacalix[4]arenetetrasulfonate onto resins for the adsorption of heavy metal ions. Various factors affecting the adsorption capacities such as different resins, resin size, pH, contact time, and temperature were investigated by batch adsorption experiments, and the adsorption isotherms, thermodynamics, kinetics, selectivity, and regeneration were also studied. It was found that the loading capacity of the D201 resin (macroporous strong basic anion exchange resin) for thiacalix[4]arenetetrasulfonate was substantially higher than those of the D301 (macroreticular weak basic styrene anion exchange resin) and the 717 (strong base styrene anion exchange resin) resins and increased with decreasing particle size of the D201 resin. The adsorption kinetics followed the pseudo-second-order rate law for heavy metal ions, indicating that chemical sorption is the rate-limiting step of the adsorption mechanism. The adsorption of heavy metal ions onto the thiacalix[4]arenetetrasulfonate-modified resin was analyzed and was found to fit better to the Langmuir isotherm than to the Freundlich isotherm, and the maximum adsorption capacities were 78.1, 65.8, 54.3, and 49.8 mg/g for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions, respectively. The prepared modified resin has high adsorption selectivity for heavy metal ions under the co-occurrence of alkali metal and alkaline earth metal ions. The regeneration efficiencies still exceed 90% after five cycles, indicating that the thiacalix[4]arenetetrasulfonate-modified resin could be favorably recycled.

Keywords: Thiacalix[4]arenetetrasulfonate; D201 resin; Adsorption; Heavy metal ions; Regeneration and recycle

1. Introduction

Removal of heavy metal ions from wastewater and drinking water is of great importance because of their high toxicities. Zinc and lead are classified as hazardous materials due to their accumulative character and high toxicities in living organism [1] and could cause many diseases such as hypertension, nephritis, developmental defects, and language difficulties. Cadmium is considered to be one of the most toxic metal ions when its concentration in water exceeds 0.01 mg/L, which is the permissible limit for human consumption [2]. Although copper is considered an essential element for human life and is widely used, it is potentially toxic under certain concentrations like

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any other heavy metal and can cause kidney failure and lung cancer by accumulating in the human body through drinking water [3]. Many separation methods such as chemical reduction, membrane separation, adsorption, precipitation, ion exchange, and biological treatment have been used to remove heavy metal ions from wastewater [4–7]. Among those methods, adsorption has been demonstrated to be one of the most simple, easily implemented, and highly efficient methods for the removal of heavy metal ions from polluted water [8,9]. Until recently, many types of novel adsorbents have been prepared and used to remove those heavy metal ions that are harmful to human health from wastewater such as agricultural wastes [10], modified clay materials [11], chelating resins [12–18], and biological-based materials [19].

Thiacalix[4]arenes are a class of important receptor compounds that have been extensively investigated in the fields of water treatment of heavy metal pollution [20] and are made up of four phenol units linked via sulfur bridges. The thiacalix[4]arenes have outstanding selective recognition abilities for heavy metal ions from the cooperative coordination of the bridging sulfur atom and adjacent phenoxy groups [21,22], and have no interaction with alkali metal and alkaline earth metal ions, such as K^+, Na^+, Ca^{2+}, and Mg^{2+} [23]. Several researchers have prepared excellent selective adsorbents for metal ions by immobilizing thiacalix[4]arenes or its similar compounds onto proper solid materials [24–28]. Kikuchi and Suzuki have prepared an adsorbent named p-tert-butylthiacalix[4]arene-impregnated silica and conducted an investigation on its adsorption capacity for americium in radioactive liquid waste [29]. Matsumiya et al. immobilized thiacalix[4]arene onto a resin and found by column adsorption experiments that the resulting resin had excellent selective adsorption capacities for heavy metal ions [30]. Nie et al. prepared a p-tert[(dimethylamino)methyl]-calix[4]arene-functionalized aminopropylpolysiloxane resin for selective solid-phase extraction and preconcentration of metal ions [31]. Recently, we also prepared a thiacalix[4]arene-loaded resin by immobilizing thiacalix[4]arenetetrasulfonate (Fig. 1) onto 717 resin and investigated its adsorption isotherms, kinetics, and thermodynamics in relation to heavy metal ions [32]. It was also found that the selective adsorption capacities of the thiacalix[4]arene-loaded resin are mainly attributed to complexation of the loaded thiacalix[4]arenetetrasulfonate with heavy metal ions. Therefore, the loading capabilities of the resin for thiacalix[4]arene would play an important role in the adsorptive removal of heavy metal ions, and selection of an optimal resin for the loading of thiacalix[4]arenetetrasulfonate will be helpful to improve the adsorption capacities of this adsorbent to heavy metal ions.

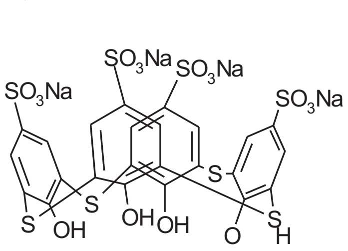

Fig. 1. The structure of thiacalix[4]arenetetrasulfonate.

In this work, thiacalix[4]arenetetrasulfonate was immobilized onto several different resins, and an optimal resin was selected for the preparation of thiacalix[4]arenetetrasulfonate-modified resin. Several factors effecting the adsorption of heavy metal ions by the thiacalix[4]arenetetrasulfonate-modified resin, such as resin size, pH value, contact time, and temperature were investigated, and the adsorption isotherms, thermodynamics, kinetics, selectivity, and regeneration were also studied.

2. Experimental

2.1. Materials

D201, 717, and D301 anion exchange resins were purchased from Kerry chemical industry Co., Ltd in Hebei province, China. Thiacalix[4]arenetetrasulfonate was synthesized in our laboratory as described in the literature [33]. All reagents and solvents used in this work were of analytical grade. $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, KNO_3, $NaNO_3$, $Ca(NO_3)_2{\cdot}4H_2O$, and $Mg(NO_3)_2{\cdot}6H_2O$ were, respectively, used for Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, K^+, Na^+, Ca^{2+}, and Mg^{2+} ions. Deionized water was prepared from water purification systems (Model AHL-0502-Pt, Aquapro) and used throughout this study.

A thermostatic water bath shaker (Model SHA-2, Changzhou Sino Instrument Co., LTD) was used in all of the adsorption experiments. Atomic absorption spectrometer (Model Spectr AA220, Varian USA) was used to measure the concentrations of metal ions.

2.2. Preparation of thiacalix[4]arenetetrasulfonate-modified resin

D301, 717, and D201 anion exchange resins were selected to load thiacalix[4]arenetetrasulfonate for the optimal carrier. The loading method of thiacalix[4]arenetetrasulfonate onto the resins was the same as the reported method [32]. The concentrations of thiacalix[4]arenetetrasulfonate were 1, 5, 10, 20, 40, 60, and 80 mmol/L, respectively. The concentrations of thiacalix[4]arenetetrasulfonate in solution were measured with a UV–Vis spectrophotometer (Varian Cary 50 UV–Vis spectrometer). The equilibrium loading quantity is calculated by the following equation:

$$q_e = \frac{(c_0 - c_e) \times V}{m} \qquad (1)$$

where q_e is the equilibrium loading quantity (mg/g), c_0 is the initial concentration of adsorbate (mg/L), c_e is the equilibrium concentration of adsorbate (mg/L), V is the volume of solution (L), and m is the mass of adsorbent (g).

D201 resin was ground and sieved to pass through 60, 80, 100, and 120 mesh sizes. The sieved resins were thoroughly washed with hydrochloric acid, sodium hydroxide, and deionized water. Thiacalix[4]arenetetrasulfonate was loaded onto resins of different mesh sizes by putting 0.1 g of resin into 5 mL water solutions with different concentrations of thiacalix[4]arenetetrasulfonate and stirring for 24 h. The resin was filtered off, washed with deionized water, and dried in an oven for the following experiments.

2.3. Characterization of thiacalix[4]arenetetrasulfonate-loaded resin

The thiacalix[4]arenetetrasulfonate content of thiacalix[4]arenetetrasulfonate-modified resin was determined by measuring the absorbance change at the maximal absorbing wavelength of the thiacalix[4]arenetetrasulfonate aqueous solution before and after soaking. The particle size distribution of the resin was investigated with a Malvern Mastersizer 2000 Laser Particle Size Analyzer. FT-IR spectra of thiacalix[4]arenetetrasulfonate-modified resin, blank resin, and thiacalix[4]arenetetrasulfonate were recorded on a Varian 3100 spectrometer.

2.4. Batch adsorption experiments

Adsorption experiments were carried out with thiacalix[4]arenetetrasulfonate-modified resin (0.1 g) in 25 mL (10 mg/L) of metal ion solutions under controlled pH value at 25℃. The solutions used for adjusting the pH value were aqueous solutions of hydrochloric acid and sodium hydroxide. The adsorption isotherm experiments were performed at temperatures of 15, 25, and 35℃, the initial heavy metal ions concentrations were set from 1 to 15 mg/L, and the pH values of solutions were set at 6.0. After equilibrium, the residual concentrations of heavy metal ions were determined. The equilibrium adsorption capacity q_e was also determined by Eq. (1).

2.5. Regeneration experiments

For regeneration, 0.1 g of used thiacalix[4]arenetetrasulfonate-modified resin was soaked in 25 mL of 0.50% HNO_3 solution for 120 min, and then washed with deionized water and dried in an oven at 50℃. The adsorption experiments were carried out with the regenerated thiacalix[4]arenetetrasulfonate-modified resin (0.1 g) in 25 mL (10 mg/L) of metal ion solutions for 120 min under pH 6.0 at 25℃.

3. Results and discussion

3.1. Preparation and characterization of thiacalix[4]arenetetrasulfonate-modified resin

The negative thiacalix[4]arenetetrasulfonate could be fixed on the surface of anion exchange resins by virtue of electrostatic interaction [32]. The loading capability of the anion exchange resin for thiacalix[4]arenetetrasulfonate is an important factor that affects the removal efficiency of the thiacalix[4]arenetetrasulfonate-modified resin to heavy metal ions. Three types of anion exchange resins, i.e. D301, 717, and D201, were investigated for their loading capability for thiacalix[4]arenetetrasulfonate under different thiacalix[4]arenetetrasulfonate concentrations. As shown in Fig. 2, the loading quantities of three resins all increased with the increase in the thiacalix[4]arenetetrasulfonate concentrations from 1 to 80 mmol/L. The loading quantities of D201 resin were substantially higher than those of D301 and 717 resins under all thiacalix[4]arenetetrasulfonate concentration values, with that of 717 resin

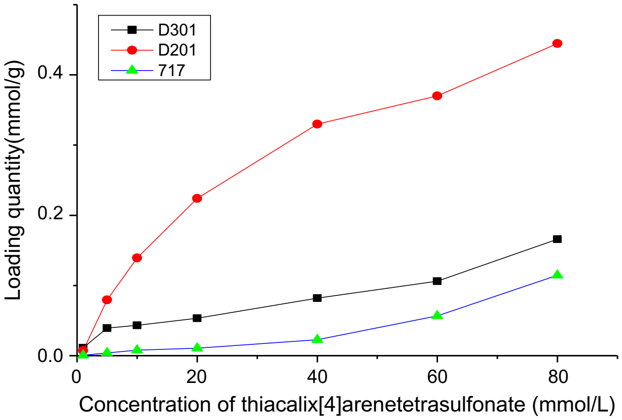

Fig. 2. Loading capacities of three resins to thiacalix[4]arenetetrasulfonate.

being the lowest, which illustrated that the D201 resin could be the optimal carrier for the loading of thiacalix[4]arenetetrasulfonate among the three resins. Furthermore, there was almost no desorbed thiacalix[4]arenetetrasulfonate from the surface of D201 resin detected in the subsequent adsorption experiments, which indicated that the combination of thiacalix[4]arenetetrasulfonate and D201 resin is very steady.

In the preparation of thiacalix[4]arenetetrasulfonate-modified resin, D201 resin was ground into small particles and sieved to pass through meshes of different sizes. The particle size distributions of these resin particles with different mesh sizes were analyzed. As shown in Fig. 3, the particle size distribution of these little particles ranged from 10 to 1,000 μm, and the volume mean particle sizes of the resin particles with 60, 80, 100, and 120 mesh sizes were 361, 219, 149, and 113 μm, respectively. Thiacalix[4]arenetetrasulfonate was loaded onto these resin particles with different volume mean particle sizes. Fig. 4 shows that the loading quantities of thiacalix[4]arenetetrasulfonate increased with the decrease in the volume mean particle size, with the order of the loading quantities being 113, >149, >219, >361 μm. D201 resin particles with a volume mean particle size of 113 μm were selected for the maximal loading capability of thiacalix[4]arenetetrasulfonate.

FT-IR spectra (Fig. 5) of thiacalix[4]arenetetrasulfonate, blank resin (D201 resin) and thiacalix[4]arenetetrasulfonate-modified resin were recorded to characterize the immobilization of thiacalix[4]arenetetrasulfonate onto D201 resin. In the IR spectrum of thiacalix[4]arenetetrasulfonate (Fig. 5(a)), the absorption band near 3,462 cm^{-1} is assigned to $\upsilon_{\text{O-H}}$ of thiacalix[4]arenetetrasulfonate, and two absorption peaks near 1,197 and 1,050 cm^{-1} are ascribed to the $\upsilon_{\text{-SO3}}$. The IR spectrum (Fig. 5(c)) of thiacalix[4]arenetetrasulfonate-modified resin is similar to that of blank resin (Fig. 5(b)). The only difference between the two spectra is that two new absorption peaks near 1,189 and 1,037 cm^{-1} are observed in the spectrum of thiacalix[4]arenetetrasulfonate-modified resin, which are assigned to the $\upsilon_{\text{-SO3}}$ of thiacalix[4]arenetetrasulfonate, confirming the immobilization of thiacalix[4]arenetetrasulfonate onto D201 resin.

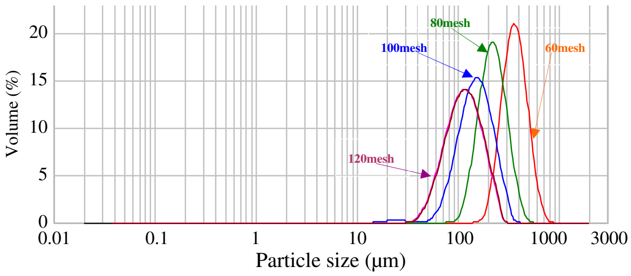

Fig. 3. Particle size distribution of the resin particles with different mesh sizes.

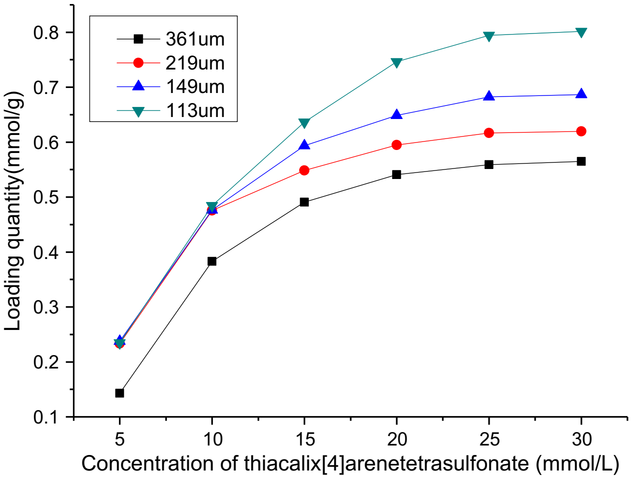

Fig. 4. Loading capacities of D201 resins of different sizes to thiacalix[4]arenetetrasulfonate.

3.2. Batch adsorption experiments

3.2.1. Effect of pH

The pH of aqueous solutions is one of the most important variables governing the adsorption capacity of adsorbents for heavy metal ions. The effect of pH on the adsorption of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} ions by thiacalix[4]arenetetrasulfonate-modified resin is shown in Fig. 6. The adsorption capacity of four heavy metal ions all increased sharply with the increase in the solution pH from 3 to 6. The highest adsorption capacities were observed at pH 6.0, which indicated that the adsorption capacities of thiacalix[4]arenetetrasulfonate-modified resin for heavy metal ions in weakly acidic solutions are stronger than those in strongly acidic solutions. The reason for this is that the adsorption capacity of thiacalix[4]arenetetrasulfonate-modified resin is mainly ascribed to the complex of the loaded thiacalix[4]arenetetrasulfonate with heavy metal ions by the cooperative coordination of the bridging sulfur atom and two adjacent phenoxide O^{-} moieties [22,23]. The phenolic hydroxy groups of thiacalix[4]arenetetrasulfonate remain protonated in strongly acidic solutions, which is unfavorable for the cooperative coordination of the bridging sulfur atom and two adjacent phenoxide O^{-}, leading to lower adsorption capacities of heavy metal ions under strong

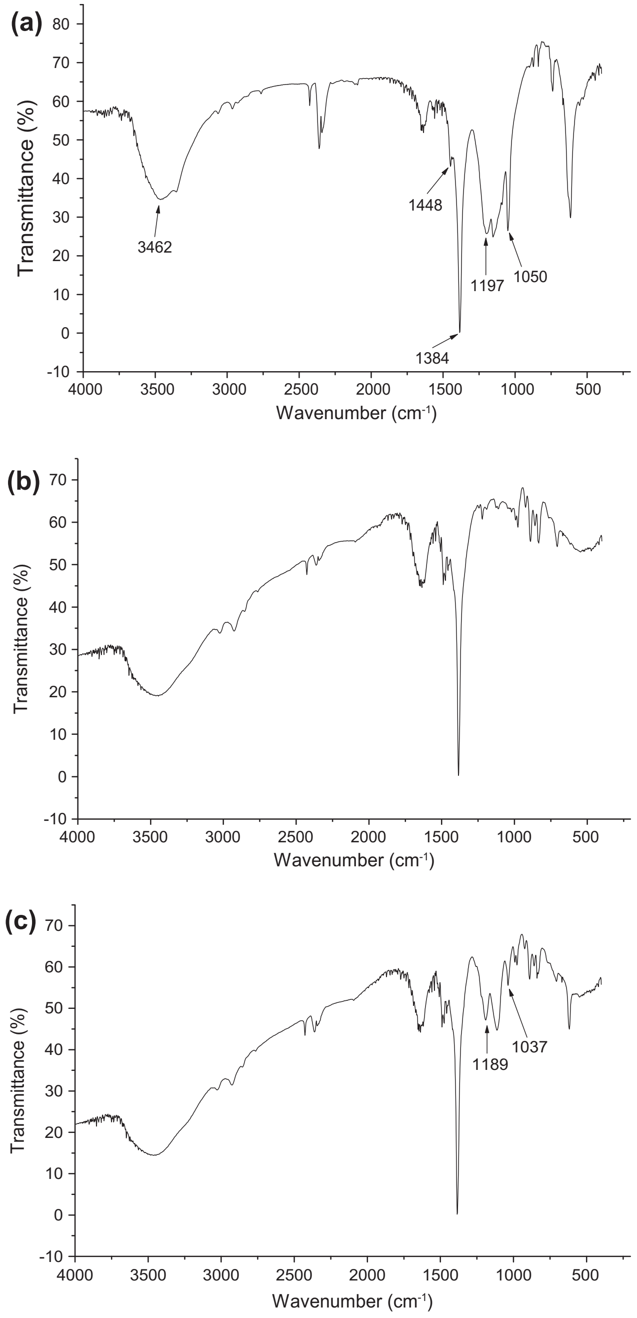

Fig. 5. FT-IR Spectra of thiacalix[4]arenetetrasulfonate (a), blank resin (b), and thiacalix[4]arenetetrasulfonate-modified resin (c).

acidic conditions [32]. Therefore, the optimal pH value of 6.0 was chosen for the adsorption of heavy metal ions by thiacalix[4]arenetetrasulfonate-modified resin in the following experiments. Experiments were not carried out at pH values above 6 because metal precipitation occurs at higher pH values.

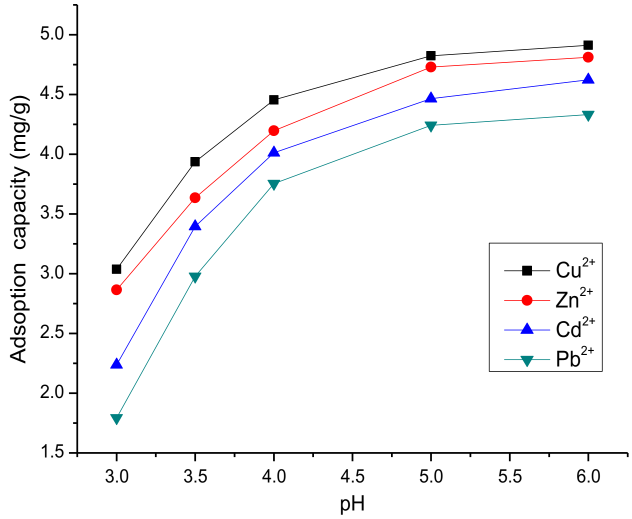

Fig. 6. Effect of pH value on the adsorption capacities of heavy metal ions.

3.2.2. Effect of contact time and adsorption kinetics

The influence of contact time on the adsorption capacities of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions by thiacalix[4]arenetetrasulfonate-modified resin were investigated at three temperatures, i.e. 288, 298, and 308 K, and the results were shown in Fig. 7. For all of the adsorption experiments, the adsorption capacities of heavy metal ions increased quickly with time and then slowly reached equilibrium after 120 min at all three temperatures. Thus, 120 min is selected as the equilibrium contact time for subsequent studies. The adsorption amounts at equilibrium (q_e) of thiacalix[4]arenetetrasulfonate-modified resin all increase slightly with the increase in temperature for the four heavy metal ions, which indicated that increased temperature could enhance the adsorption of heavy metal ions.

To investigate the adsorption rate of heavy metal ions onto thiacalix[4]arenetetrasulfonate-modified resin, pseudo-first-order and pseudo-second-order rate models were employed to interpret the adsorption experimental data. The Lagergren's first-order model [34] has been used for reversible reactions with equilibrium, and its rate equation is expressed as follows:

$$\ln(q_1 - q_t) = \ln q_1 - k_1 t \tag{2}$$

where q_t is the adsorption capacity of a heavy metal ion at time t (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}), and q_1 is the adsorption capacity of the heavy metal ion at equilibrium (mg/g). The k_1 and q_1 can be determined by the linear plot of $\ln(q_1 - q_t)$ vs. t.

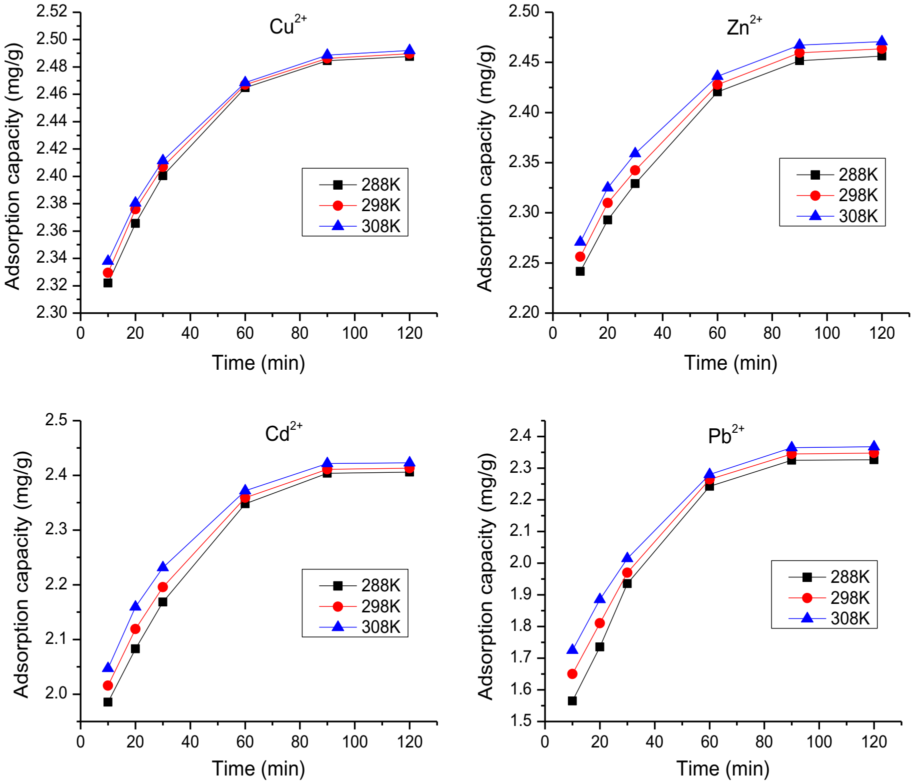

Fig. 7. Adsorption capacity of metal ions by thiacalix[4]arenetetrasulfonate-modified resin.

The pseudo-second-order kinetics model [35] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{q_2}t + \frac{1}{k_2 q_2^2} \tag{3}$$

where k_2 is the adsorption rate constant of the pseudo-second-order model (g/(mg min)). Data of k_2 and q_2 can be obtained from the plot of t/q_t against t.

The kinetic parameters for the adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions by thiacalix[4]arenetetrasulfonate-modified resin were reported in Table 1. In most situations, the pseudo-first-order kinetics model cannot apply to the entire adsorption process and is generally suitable for the initial 30 min. The pseudo-second-order kinetics model is based on the assumption that chemical adsorption may be the rate-limiting step [36]. Based on the determination of coefficients, the R^2 values for the pseudo-second-order kinetics model are all greater than 0.999, indicating that the pseudo-second-order kinetics model is more suited to the adsorption kinetics process than the pseudo-first-order kinetics model for the adsorption of heavy metal ions, and suggesting that chemical adsorption is the rate limiting step [37]. The k_2 value increased with a rise in temperature, which could be explained by the fact that increasing temperature results in a rise in diffusion rates of heavy metal ions across the external boundary layer.

The effect of temperature on the rate constant k_2 has been represented by the Arrhenius equation [32]:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{4}$$

where A is the adsorption frequency of the adsorbent (g/(mg min)), E_a is the activation energy of the adsorption reaction (kJ/mol), R is the universal gas constant (8.314 J/(mol K)), and T is the absolute temperature of the adsorption reaction. A and E_a are determined, respectively, from the intercept and the slope of each regression straight line, which is obtained by plotting $\ln k_2$ against the reciprocal of absolute temperature. The values of Arrhenius equation parameters were shown in Table 2. The R^2 values are all above 0.99. The A values of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions are temperature independent and are 1.23, 1.39, 3.02, and 2.13 g/(mg min), respectively. The E_a values of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions, respectively, are 2.96, 4.10, 7.76, and 8.76 kJ/mol. Kinetic

Table 1
Values of kinetic parameters for the adsorption of thiacalix[4]arene-modified resin

			Pseudo-first-order parameters			Pseudo-second-order parameters		
Metal ions	Temperature (K)	q_e (mg/g)	q_1 (mg/g)	k_1 (min^{-1})	R^2	q_2 (mg/g)	k_2 (g/(mg min))	R^2
Cu^{2+}	288	2.49	0.274	0.0407	0.9939	2.51	0.357	1.0000
	298	2.49	0.411	0.0570	0.9692	2.51	0.377	1.0000
	308	2.49	0.203	0.0290	0.9796	2.51	0.386	1.0000
Zn^{2+}	288	2.46	0.367	0.0393	0.9911	2.489	0.252	0.9999
	298	2.46	0.313	0.0340	0.9843	2.50	0.265	0.9999
	308	2.47	0.278	0.0304	0.9788	2.50	0.282	1.0000
Cd^{2+}	288	2.41	0.801	0.0469	0.9672	2.48	0.119	0.9998
	298	2.41	0.647	0.0408	0.9663	2.48	0.131	0.9998
	308	2.42	0.582	0.0401	0.9624	2.48	0.146	0.9999
Pb^{2+}	288	2.33	1.65	0.0551	0.9623	2.49	0.0550	0.9991
	298	2.35	1.61	0.0562	0.9702	2.49	0.0618	0.9993
	308	2.37	1.47	0.0552	0.9670	2.49	0.0697	0.9994

Table 2
Values of Arrhenius equation parameters

Metal ions	A (g/(mg min))	E_a (kJ/mol)	R^2
Cu^{2+}	1.23	2.96	0.9901
Zn^{2+}	1.39	4.10	0.9942
Cd^{2+}	3.02	7.76	0.9958
Pb^{2+}	2.13	8.76	0.9993

sorption processes usually have energies greater than 25–30 kJ/mol and diffusion sorption processes have energies usually less than 25–30 kJ/mol [38]. The E_a values were all less than 25 kJ/mol, indicating that diffusion mechanisms are involved in the adsorption process.

The heavy metal ions are most likely transported from the solutions onto the adsorption sites of thiacalix[4]arenetetrasulfonate-modified resin through an intraparticle diffusion process. The effect of the intraparticle diffusion was investigated from the adsorption data of the contact time according to the following equation:

$$q_t = k_i t^{1/2} + C \tag{5}$$

where q_t is the adsorption capacity (mg/g) at time t (min), k_i is the intraparticle diffusion rate constant (mg/(g min$^{1/2}$)), and C is the straight line intercept, which reflects the boundary layer thickness [39]. The plotting of q_t vs. $t^{1/2}$ was shown in Fig. 8 for the four heavy metal ions. All of the plots have the same features, where an initial linear portion is followed by a curved portion and a plateau. This phenomenon could be attributed to the fact that heavy metal ions are adsorbed from the solution diffusion of the linear portion to the intraparticle diffusion of the curved portion, and then to the equilibrium adsorption sites of the plateau. This indicates that heavy metal ions are transported from solutions through the particle interface into the pores of the particle, and then reach the adsorption sites of thiacalix[4]arenetetrasulfonate-modified resin.

The k_i values of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions are 0.0220, 0.0291, 0.0573, and 0.104 mg/(g min$^{1/2}$) at 288 K, are 0.0210, 0.0278, 0.0534, and 0.0950 mg/(g min$^{1/2}$) at 298 K, and are 0.0203, 0.0265, and 0.0868 mg/(g min$^{1/2}$) at 308 K, respectively (Table 3). Extrapolation of the linear portions of the plots back to the Y-axis provides the boundary layer thickness. The larger the intercept is, the greater the boundary layer effect is. The deviation of the curves from the origin indicates that intraparticle transport is not the only rate-limiting step.

3.2.3. Adsorption isotherms and thermodynamic analysis

The equilibrium adsorption isotherm is of importance in the adsorption systems. The adsorption isotherms of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions by thiacalix[4]arenetetrasulfonate-modified resin at the temperatures of 288, 298, and 308 K were shown in Fig. 9. For all four metal ions, the adsorption capacities increased linearly with temperature. The adsorption data of heavy metal ions at different temperatures were correlated with the isotherm models of Langmuir and Freundlich.

The Langmuir model is based on the assumptions that the adsorption energy is constant, that a

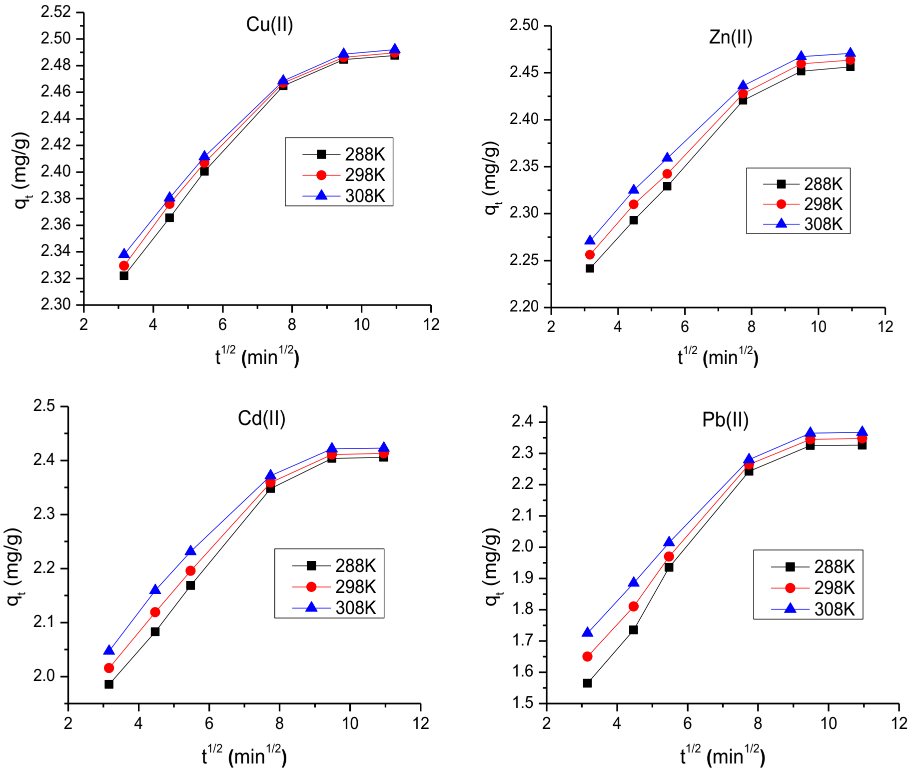

Fig. 8. Plots of particle internal diffusion.

Table 3
Values of intraparticle diffusion parameters

Metal ions	Temperature (K)	k_i (mg/(g $min^{1/2}$))	C
Cu^{2+}	288	0.0220	2.27
	298	0.0210	2.28
	308	0.0203	2.29
Zn^{2+}	288	0.0291	2.17
	298	0.0278	2.19
	308	0.0265	2.21
Cd^{2+}	288	0.0573	1.84
	298	0.0534	1.88
	308	0.0493	1.94
Pb^{2+}	288	0.1035	1.31
	298	0.0950	1.41
	308	0.0868	1.51

maximum adsorption capacity is obtained from the saturated monolayer of adsorbate molecules on the adsorbent surface, and that there is no movement of the adsorbate on the adsorbent surface [40], which is expressed as follows:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max}} \cdot c_e + \frac{1}{q_{\max} k_L} \tag{6}$$

where c_e is the equilibrium concentration of metal ion (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), $q_{\max}$ is the maximum adsorption capacity (mg/g), and k_L is the Langmuir adsorption constant (L/mg). The values of $q_{\max}$ and k_L are obtained from the slope and intercept of the straight lines by plotting of c_e/q_e vs. c_e.

The Freundlich model has been widely used for adsorption isotherms [41]. The Freundlich equation has the general form:

$$\ln q_e = \frac{1}{n} \ln c_e + \ln k_F \tag{7}$$

where q_e is the adsorption capacity at equilibrium (mg/g), c_e is the equilibrium concentration of the metal ion (mg/L), k_F is the Freundlich adsorption isotherm constant related to adsorption capacity ((mg/g) $(L/g)^n$), and $1/n$ reflects the adsorption intensity.

The constants of the two equations at different temperatures were obtained from fitting the adsorption equilibrium data to the two isotherm models and are given in Table 4. It is apparent that the adsorption of heavy metal ions onto thiacalix[4]arenetetrasulfonate-modified resin fits better to the Langmuir

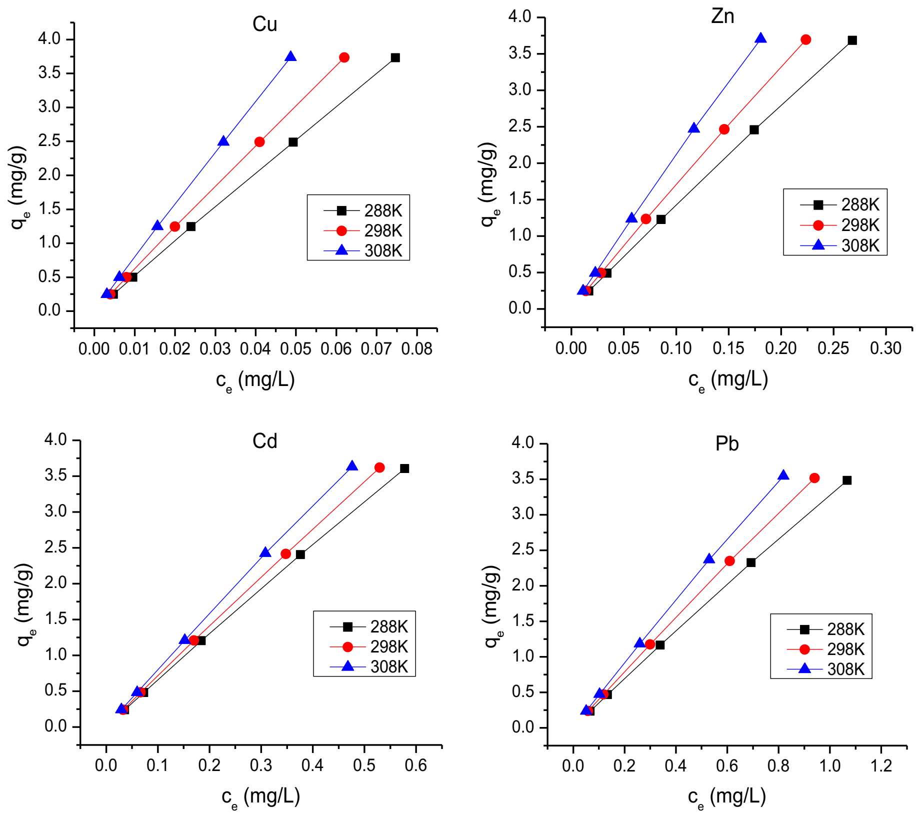

Fig. 9. Adsorption isotherms of metal ions by the thiacalix[4]arenetetrasulfonate-modified resin.

Table 4
Values of isotherm parameters for the adsorption of thiacalix[4]arene-modified resin

		Langmuir parameters			Freundlich parameters		
Metal ions	Temperature (K)	$q_{\max}$ (mg/g)	K_L (L/g)	R^2	$1/n$	K_F (mg/g)(L/g)^n	R^2
Cu^{2+}	288	75.8	0.691	0.9999	0.984	48.2	0.9623
	298	77.5	0.811	1.0000	0.984	57.8	0.9619
	308	78.1	1.03	1.0000	0.984	73.8	0.9904
Zn^{2+}	288	56.8	0.258	1.0000	0.977	13.5	0.9572
	298	58.5	0.301	1.0000	0.979	16.1	0.9884
	308	65.8	0.332	0.9999	0.981	20.1	0.9491
Cd^{2+}	288	51.3	0.131	0.9999	0.976	6.22	0.9961
	298	52.9	0.138	1.0000	0.976	6.76	0.9705
	308	54.3	0.151	0.9999	0.977	7.59	0.9711
Pb^{2+}	288	46.3	0.076	0.9999	0.974	2.83	0.9974
	298	47.8	0.0843	1.0000	0.975	3.13	0.9840
	308	49.8	0.0939	0.9999	0.976	3.57	0.9939

isotherm than to the Freundlich isotherm, as indicated by the numerical values of the determination coefficients (R^2). In the Langmuir isotherm, the maximum adsorption capacity demonstrated monolayer coverage of heavy metal ions at the outer surface of the modified resin. As can be observed, the maximum adsorption capacities $q_{\max}$ of four metal ions all increased with temperature, and the highest values of $q_{\max}$ obtained at 308 K were 78.1 mg/g for Cu^{2+}, 65.8 mg/g for Zn^{2+}, 54.3 mg/g for Cd^{2+}, and 49.8 mg/g for Pb^{2+}, which are substantially higher than that values of previous thiacalix[4]arene-loaded resin with 717 resin as the carrier [32]. The reasons for this is that the adsorption capacities of thiacalix[4]arenetetrasulfonate-modified resin for heavy metal ions were ascribed primarily to the complex of the loaded thiacalix[4] arenetetrasulfonate with heavy metal ions, and the loading capability of D201 resin for thiacalix[4]arenetetrasulfonate was substantially stronger than that of 717 resin. Table 5 also showed the comparison of adsorption capacities of the thiacalix[4]arenetetrasulfonate-modified D201 resin with other adsorbents.

The thermodynamic parameters for the adsorption process were calculated by plotting $\ln K_0$ against $1/T$ according to the van't Hoff equation [52]:

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{8}$$

where R is the universal gas constant (8.314 J/(mol K)), T is the absolute temperature (K), and k_0 is the thermodynamic equilibrium constant. As the concentration of metal ions in the solution decreases and approaches zero, the value of k_0 is obtained by plotting a straight line of $\ln(q_e/c_e)$ vs. q_e and extrapolating the line to zero, and then the intercept of the vertical axis gives the k_0 value. ΔH^0 (J/mol) and ΔS^0 (J/(mol K)) are the enthalpy and entropy changes of the adsorption process. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the regression line after plotting $\ln k_0$ against the reciprocal of absolute temperature, $1/T$.

The free energy change (ΔG^0) for the adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions are calculated from the Gibbs free energy equation:

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \tag{9}$$

The thermodynamic parameter values of ΔH^0, ΔS^0, and ΔG^0 were given in Table 6. The positive values of ΔH^0 indicate an endothermic nature of the adsorption process, which is consistent with the situations in Figs. 6 and 8 where the adsorption capacities increased with the increase in temperature. The observed positive values of ΔS^0 reflect a state of increased randomness at the solid/solution interface due to the liberation of water molecules during the chelating process. The higher values of $|T\Delta S^0|$ relative to $|\Delta H^0|$ indicate that the adsorption process is entropically driven.

3.2.4. *Adsorption selectivity and competition among metal ions*

Usually there are several metal ions occurring in a wastewater, and some are relatively harmless for human health, such as K^+, Na^+, and Ca^{2+}. These harmless metal ions would compete with harmful metal ions for the adsorption sites of the adsorbent, leading to the consumption of more adsorbent material. Therefore, the adsorption selectivity of an absorbent is an important factor for the removal of harmful metal ions from wastewater. However, unmodified adsorbents, such as resin, bentonite, and activated carbon do not

Table 5
Comparison of adsorption capacities (q_{max}, mg/g) for heavy metal ions of different adsorbents (298 K)

	q_{max}, mg/g				
	Heavy metal ion				
Adsorbent	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	References
CG.Dh cryogel	40.7	7.5	19.3	–	[6]
RRresin impregnated with C-(4-carboxyphenyl) resorcin[4]arene	–	60.9	49.0	322.6	[24]
Thiacalix[4]arene-loaded resin with 717 resin as the carrier	21.4	–	47.9	44.9	[32]
Lignite	–	15.2	5.2	39.0	[42]
ECH-cross-linked metal-imprinted chitosan	21.1	14.3	–	74.5	[43]
Fe_3O_4–glycidyl methacrylate–iminodiacetic acid–St–DVB resin	56.3	–	87.4	167.7	[44]
Fe(III)-modified zeolites	–	14.5	12.2	176.4	[45]
Aminated Epoxy-Lignin	72.5	–	–	55.4	[46]
Fe_3O_4-P(Cys/HEA) hydrogel	15.7	–	27.6	39.1	[47]
Xanthate-modified magnetic chitosan	34.5	20.8	–	76.9	[48]
Carboxymethylated chitosan-bound Fe_3O_4 nanoparticles	21.5	–	–	–	[49]
Root powder of Eichhornia crassipes	32.5	–	–	–	[50]
EDTA-modified chitosan/SiO_2/Fe_3O_4	42.8	–	63.1	123.4	[51]
Thiacalix[4]arenetetrasulfonate-modified D201 resin	78.1	65.8	54.3	49.8	This study

Table 6
Values of thermodynamic parameters for the adsorption of thiacalix[4]arene-modified resin

Metal ions	Temperature (K)	k_0	ΔH° (kJ/mol)	ΔS° (J/(mol K))	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
Cu^{2+}	288	3.96	3.79	24.6	−3.29	7.08
	298	4.14	3.79	24.6	−3.54	7.33
	308	4.39	3.79	24.6	−3.78	7.58
Zn^{2+}	288	2.69	5.05	25.7	−2.36	7.41
	298	2.87	5.05	25.7	−2.62	7.67
	308	3.08	5.05	25.7	−2.88	7.93
Cd^{2+}	288	1.90	3.67	18.1	−1.54	5.21
	298	1.99	3.67	18.1	−1.72	5.39
	308	2.10	3.67	18.1	−1.90	5.57
Pb^{2+}	288	1.26	7.39	27.6	−0.555	7.95
	298	1.40	7.39	27.6	−0.831	8.22
	308	1.54	7.39	27.6	−1.11	8.50

have improved adsorption selectivity. Fig. 10 shows the adsorption removal efficiencies of different metal ions by thiacalix[4]arenetetrasulfonate-modified resins under the coexistence of several metal ions. It is evident that the adsorption removal efficiencies of heavy metal ions (such as Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}) all exceed 95% and those of alkali metal and alkaline earth metal ions (such as K^+, Na^+, Ca^{2+}, and Mg^{2+}) are all less than 20%, which indicates that the prepared modified resin has high adsorption selectivity for heavy metal ions under the co-occurrence of alkali metal and alkaline earth metal ions. These could be reasonably explained by the rule of hard and soft acids and bases. The bridging sulfur atoms of the loaded thiacalix[4]arenetetrasulfonate, categorized as a soft base, almost have no ligation to hard metal ions, leading to poor adsorption ability of thiacalix[4]arenetetrasulfonate-modified resin for hard metal ions, such as Ca^{2+}, Mg^{2+}, and Na^+ [32].

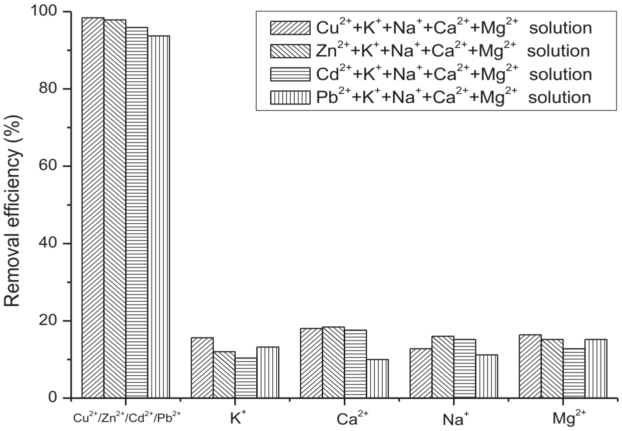

Fig. 10. Adsorption removal efficiencies of different metal ions.

The adsorption competition among the four heavy metal ions were also investigated and the results were shown in Table 7. When Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} coexist, four metal ions could be removed simultaneously, the adsorption priority sequence is $Cu^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$, and Cu^{2+} has the highest adsorption priority. However, the adsorption removal efficiencies of Cu^{2+} exhibited various values at different systems where two metal ions coexist, and the value order is $Cu^{2+}/Zn^{2+} < Cu^{2+}/Cd^{2+} < Cu^{2+}/Pb^{2+}$, which is in accordance with the adsorption priority sequence. The removal efficiencies of the other three metal ions (Zn^{2+}, Cd^{2+}, and Pb^{2+}) in two-metal ion systems exhibit similar patterns.

3.3. Regeneration and recycling studies

The recycling of the used absorbent should be considered in an integrated water adsorption treatment

Table 7
Adsorption removal efficiencies of heavy metal ions in coexisting system

	Adsorption removal efficiency (%)			
Coexisting metal ion	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
Cu^{2+}/Zn^{2+}	95.2	94.8	–	–
Cu^{2+}/Cd^{2+}	96.4	–	89.6	–
Cu^{2+}/Pb^{2+}	96.8	–	–	83.2
Zn^{2+}/Cd^{2+}	–	95.1	89.4	–
Zn^{2+}/Pb^{2+}	–	95.9	–	83.6
Cd^{2+}/Pb^{2+}	–	–	91.2	84.4
$Cu^{2+}/Zn^{2+}/Cd^{2+}/Pb^{2+}$	93.8	92.8	87.9	81.6

The initial concentrations of metal ions used are 10 mg/L.

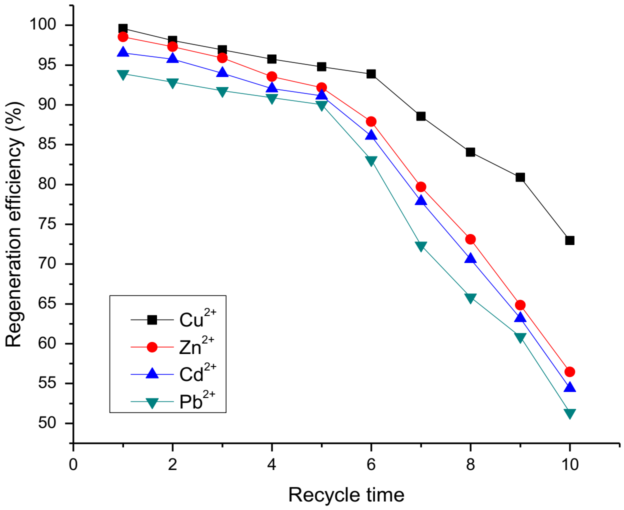

Fig. 11. Regeneration efficiency of the modified resin with different cycles.

process. In this work, thiacalix[4]arenetetrasulfonate-modified resin was regenerated by washing with nitric acid solution. The acid condition is disadvantageous for the complex of thiacalix[4]arenetetrasulfonate with heavy metal ions, leading to the release of the adsorbed heavy metal ions from the surface of the modified resins and the restoration of the thiacalix[4]arenetetrasulfonate-modified resin. The regenerated resins were used to adsorb heavy metal ions for several cycles. The regeneration efficiency was calculated by the following equation:

$$\text{Regeneration efficiency } (\%) = \frac{\text{Adsorption capacity in the following run}}{\text{Adsorption capacity in the first run}} \times 100\% \tag{10}$$

Fig. 11 shows the regeneration efficiencies of thiacalix[4]arenetetrasulfonate-modified resins with different recycle times. Although the regeneration efficiencies of thiacalix[4]arenetetrasulfonate-modified resin slowly decreased with the increase in recycle time, the regeneration efficiencies were still more than 90% after five cycles for all four heavy metal ions, which indicated that the prepared thiacalix[4]arenetetrasulfonate-modified resin could be favorably recycled.

4. Conclusions

In this work, a modified resin was prepared by loading thiacalix[4]arenetetrasulfonate onto the D201 resin and was then characterized. The thiacalix[4]arenetetrasulfonate-modified resin has excellent selective adsorption capacities for heavy metal ions coexisting with alkali metal and alkaline earth metal ions, which are most likely attributed to the complexation of the loaded thiacalix[4]arenetetrasulfonate to heavy metal ions that can be categorized as Lewis soft acids by the SHAB rule. The kinetic behavior for the adsorption of four heavy metal ions onto thiacalix[4]arenetetrasulfonate-modified resin fits very well with the pseudo-second-order kinetic model over a range of temperatures. The Langmuir isotherm model provides a better match than the Freundlich isotherm model for the adsorption behavior of thiacalix[4]arenetetrasulfonate-modified resin. Regeneration experiments indicated that the thiacalix[4]arenetetrasulfonate-modified resin could be favorably recycled.

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