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Biosorption of citric acid–cadmium complex by imprinted chitosan polymer

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ABSTRACT

Cross-linked imprinted chitosan polymer (ICP) was successfully prepared from chitosan (CS), using citric acid–cadmium complex (CA–Cd) as template, and glutaraldehyde as the cross-linker. Among different factors that influence the sorption process were studied in detail: solution pH, oscillating time, and temperature. The results showed that the most important factor affecting the effectiveness of sorption were pH and oscillating time. From the Langmuir adsorption model, the adsorption capacity of CS for CA–Cd complex was equal to 8.47 mg/g. The results indicated that the second-order kinetics model was more suitable to describe the sorption kinetics on CS than the first-order kinetics model. Furthermore, the CA–Cd–ICP could be regenerated using 0.1 M HCl solution and could be reused for seven times with 12.30% regeneration loss.

Keywords: Chitosan; Molecular imprinting; Citric acid–cadmium complex; Polymer

1. Introduction

The continued pollution of heavy metals in different biota, such as soil, water, and air, has been detected with the developed industries in countries [1]. Among heavy metals such as Cd, Hg, and Pb in the environment could accumulate to a toxic concentration level, leading to a ecological damages [2,3]. In addition to heavy metals, Cr, Co, Cu, Fe, Mg, or Zn are essential for humans. However, Cd, As, Pb, or Hg are not beneficial to humans and are toxic at certain concentration. All of them can be dispersed and accumulated in plants and animals [4], and it is suggesting that people have experienced a potential health risk due to foodstuff consume of heavy metals [5].

From the above-mentioned toxic metal elements, Cd is one of the most widely used metal element in electroplating and galvanizing, and it is a by-product of Zn, Pb mining, and smelting. Of course, the soluble cadmium salts accumulate and lead to toxicity to human health [6,7]. However, there is no chelation therapy for cadmium toxicity approved for clinical use in humans [8]. Under the above circumstances, environmental and food chemical scientists have done much works to solve the problems from the source through removing heavy metals from soil, waste water, sea product, and other materials. It is well known that the acids and metal chelating agents, like citric acid [9], EDTA [10], and dilute sulfuric acid [11] have already been reported to remove Cd from contaminated soil and sea food waste.

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Since it is necessary to remove Cd ions before discharge the leaching liquid, an economical process for removing low levels Cd ions from a large volume of organic acid leaching liquid was significant. Precipitation, oxidation, and reduction, ion exchange, filtration, reverse osmosis, electro-chemical removal, and evaporative can be used to treat industrial effluents for recovery metals [12,13]. However, these methods are all inefficient such as ion exchange and membrane separation which require high operation cost, and chemical precipitation is able to remove trace levels of heavy metal ions. Magnesia is a good precipitating agent for Cd ions which reach high pH ranges (10–11) in any other solution [14], but its precipitates are difficult to be separated because of their own characteristics [15].

Biosorbent of CS could bind heavy metal ions strongly and could be used for heavy metals absorption, and numerous articles have already researched CS and its derivatives as an adsorbent for the removal of Cd or Cd complex with polyaspartic acid from industrial waste streams [12,16–18]. CS is the major component of the shells of crustacean organisms and the second most abundant naturally occurring biopolymer next to cellulose. Furthermore, it has biological and chemical properties such as nontoxicity, biocompatibility, and high chemical reactivity, chelation and adsorption characteristics [19]. In particular, much effort of previous work has been focused on the CS resin, which was an available biosorbent for removal heavy metals from wastewater. However, nonimprinted CS resin might adsorb many heavy metals but lower specific recognition.

Recently, molecularly imprinted polymers (MIPs) have aroused rapid attention and been widely applied in many fields, such as solid-phase extraction, chemical sensors and artificial antibodies owing to their desired selectivity, physical robustness, thermal stability, as well as low cost and easy preparation [20]. As a branch of MIPs, ion-imprinted polymer has shown considerable potential as a method for ion recognition. So far, many metal ion-imprinted polymers have been prepared, including uranium [21], Cu, Zn, Ni, and Pb [22–25], as well as Cd from aqueous solution [26]. However, there are seldom investigations reported in the literatures on the removal of citric acid–cadmium complex by CA–Cd–ICP from aqueous solution.

The aim of this work was to determine the removal efficiency of less-researched CA–Cd from dilute solutions by molecular-imprinted biosorbents. Experiments were performed as a function of different pH, oscillating time, and temperature. Subsequently, the adsorption kinetics, isotherm, and selectivity were carried out to understand the mechanism of CA–Cd adsorption onto CA–Cd–ICP.

2. Experimental

2.1. Materials

CS with 92% degree of deacetylation, and molecular weight of 5.0×10^5 was purchased from Haihui Bioengineering Co., Ltd (Qingdao, China). Metal ions standard was obtained from National Steel Material Test Center (Beijing, China). Cadmium chloride, glutaraldehyde, and all the other reagents used in this study were of analytical grade and all reagents were prepared in Millipore milli-Q deionized water (DW).

2.2. Preparation of biosorbent polymer

The preparation of the new biosorbent polymer of CA–Cd–ICP was as follows: Cadmium chloride was dissolved in 50 mL 0.1 M citric acid to give a Cd(II) solution of 20 mg/L as the complex of CA–Cd. Then, the pH was adjusted to be 7.0, and 1.0 g CS (dry weight) was added into this solution, and the mixture was stirred for 12 h. The mixture was recovered by filtration through filter paper and then washed with DW until Cd(II) could not be detected. The CS composite was dried in a vacuum oven at 323 K for 4 h.

Afterwards, amount of CS composite was added in 50 mL DW, and the pH value was adjusted to 7.0 with NaOH/HCl (0.1 M), and then glutaraldehyde as a cross-linking agent was added in the above system, stirred for 4–6 h at 333 K. Then, the mixture was recovered by filtration, and the residue was rinsed with ethanol and DW for three times at least.

Finally, the template CA–Cd complex was removed from the polymer using 0.1 M HCl by monitoring with sodium sulfide, and the procedure was repeated several times until the template could not be detected. The polymer was added into 0.1 M sodium hydroxide aqueous solution for 4–8 h to active amino group and then dried in vacuum oven at 323 K for 4 h. NIMIPs was similarly synthesized in the absence of template.

2.3. Adsorption experiments

2.3.1. Effect of pH

Uptake experiments were performed at controlled pH (2–12), and 303 K by shaking 0.1 g of dry polymer with 25 mL (20 mg/L) CA–Cd solution for 12 h at 160 rpm. The solution pH was adjusted to the desired value by NaOH/M HCl (0.1 M). After equilibration, the residue concentration of CA–Cd was measured with a flaming atomic absorption spectrophotometer (FAAS) (AA-6800, Shimadzu Ins) at 228.8 nm wave number.

2.3.2. Effect of contact time

The uptake of CA–Cd at different time intervals was obtained by shaking 0.1 g of polymer in a flask containing 25 mL (20 mg/L) metal ion solution at pH 8.0 under 160 rpm and 303 K. One milliliter of sample was taken at time interval to determine the residual metal concentration in the solution.

2.3.3. Effect of temperature

The adsorption capacity of CA–Cd at different temperature was obtained by placing 0.1 g polymer in a series of flasks containing 25 mL (20 mg/L) and pH 8.0, the flasks were agitated on a shaker at 160 rpm for 12 h. After equilibration, the residual concentration of CA–Cd was determined and the uptake value was calculated.

2.3.4. Adsorption kinetics

Adsorption kinetics was performed by 0.1 g polymer in 25 mL metal solution (20 mg/L) and pH 8.0, the flasks were agitated on a shaker at 160 rpm under different time. One milliliter of samples was taken at time intervals for the analysis of residual metal concentration and the uptake value was obtained.

2.3.5. Adsorption isotherm

Complete adsorption isotherms of CA–Cd was obtained by placing 0.1 g polymer in the flasks containing 25 mL of metal ions at definite concentration (2.5–20 mg/L) and pH 8.0. The flasks were agitated on a shaker at 160 rpm for 12 h while keeping the temperature at 293, 303, 313, and 323 K. After equilibration, the residual concentration of CA–Cd was determined and the uptake value was calculated.

2.3.6. Adsorption selectivity

The adsorption selectivity behavior was measured by the uptake between CA–Cd and CA–Zn with CA–Cd–ICP, and place 0.1 g polymer with 25 mL metal ions solution (20 mg/L) in a series of flasks at pH 8.0 and 303 K for interval time.

2.3.7. Desorption and reuse after desorption

Desorption experiments were carried out using 0.1 M HCl solutions. After having adsorbed the CA–Cd, the polymer (0.1 g) was washed with DW several times and transferred into flasks. Then, 25 mL of the desorption agent (0.1 M HCl) was added and shaked at room temperature (298 K) for 1 h. Afterwards, the concentration of CA–Cd released from CA–Cd–ICP into aqueous phase. The ICP was reused in adsorption experiment, and the process was repeated for seven times.

3. Results and discussion

3.1. Influence of pH

As well known, pH is the most important parameter on adsorption studies, and affects the adsorption property of polymer for metal ions. The adsorption process of metal ions was sensitive to pH at low pH [27]. Hence, the effect of pH on the chelation between CA–Cd–ICP and CA–Cd was researched. As seen from Fig. 1, The highest uptake value was observed at pH 8.0 for CA–Cd–ICP compared with NIMIPs. At lower pH (<6.0), the active sites on polymer become protonated and their ability for interaction with CA–Cd decreases. The decrease in the adsorption capacities can be attributed to the competitive binding of H^+ and CA–Cd complex to amine groups. Hence, pH 8.0 was chosen as the optimal pH in the following experiments.

3.2. Effect of contact time

The relationship between adsorption capacity and contact time was described in Fig. 2. As can been seen

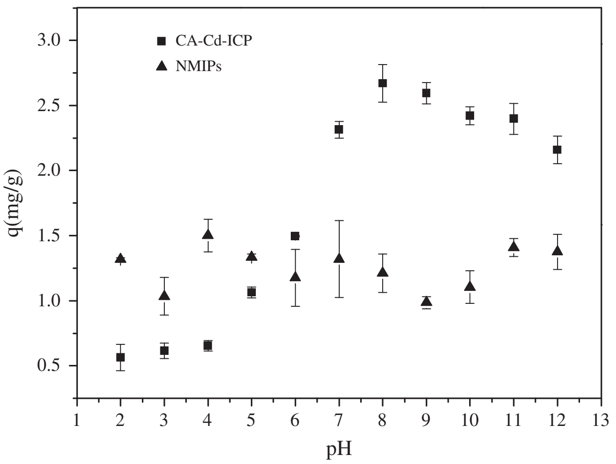

Fig. 1. Effect of pH on the uptake of CA–Cd by CA–Cd–ICP and NIMIPs (initial concentration 20 mg/L, adsorption dose 0.1 g, contact time 12 h, shaking rate 160 rpm, 303 K).

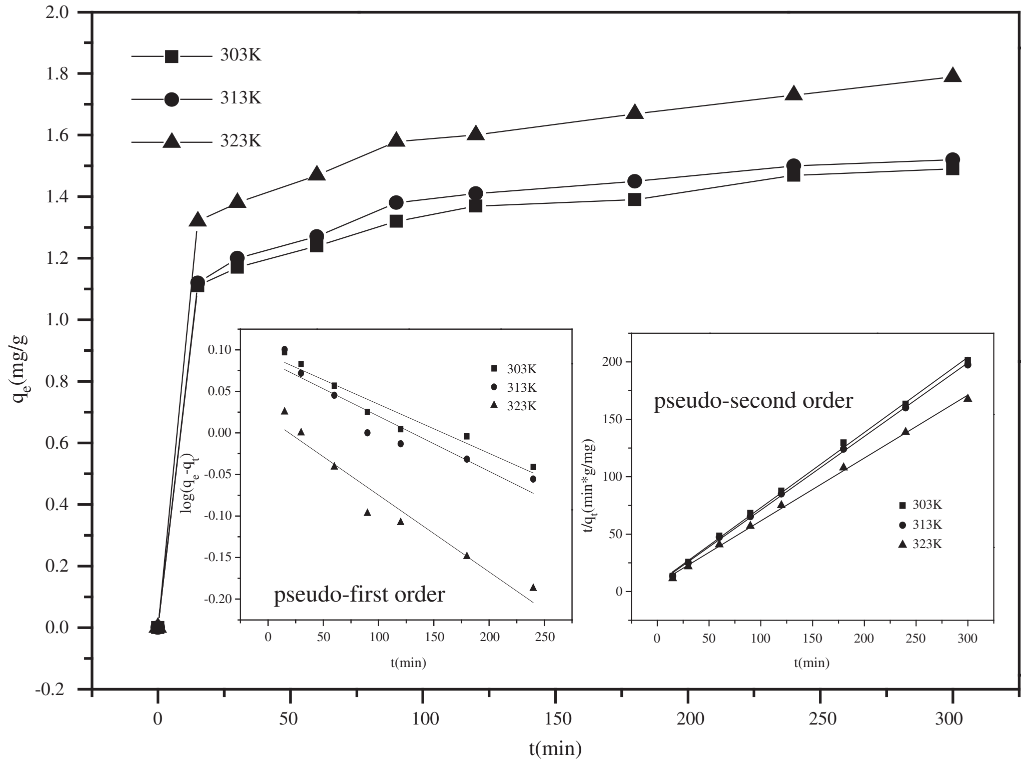

Fig. 2. Effect of adsorption time on the uptake of CA–Cd by CA–Cd–ICP (initial concentration 20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 303 K) and the first-order kinetics (the left insert figure), second-order kinetics (the right insert figure).

from Fig. 2, shows the change in the uptake of CA–Cd by the given polymer as a function of time. The kinetic curves for CA–Cd complex showed that the adsorption was initially rapid and reached equilibrium after approximately 120 min. The rapid adsorption in the beginning can be attributed to the greater concentration gradient and more available sites for adsorption. The fast adsorption equilibrium in the case of CA–Cd–ICP is probably attributed to high complexation and geometric shape affinity between CA–Cd and cavities in the CA–Cd–ICP structure. As well known when the template removed from the polymeric matrix leaving cavities of imprinting site, specific space, or chemical functionality to the template molecular [28]. The adsorption data were treated according to kinetic models of first order kinetics, Eq. (1) [29] and second-order kinetics, Eq. (2) [30].

$$\log(q_e - q_t) = \log q_e - \frac{\circ K_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where t is the contact time (h), q_t and q_e are the amount of CA–Cd complex adsorbed at an arbitrary time and at equilibrium (mg/g), and K_1 (min^{-1}) or K_2 (g/mg·min) is the rate constant, respectively (Table 1) As seen from Table 1, the Second-order model described all kinetic data very well.

3.3. Effect of temperature

Adsorption isotherms are the basic requirements for design of an adsorber by providing fundamental physic-chemical features. The adsorption isotherms of CA–Cd complex on the investigated polymer at different temperatures are shown in Fig. 3. The uptake of CA–Cd increases with the increase in the initial concentration. The most frequently used isotherms for adsorption experimental data correlations are the Langmuir and Freundlich model. The Langmuir adsorption isotherm has found successful applications in many other real sorption processes of monolayer adsorption. The Freundlich equation is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. In this work, Langmuir and Freundlich model are employed to analyze the data.

Table 1
Kinetic parameters for CA–Cd adsorption by CA–Cd–ICP

First-order model				
T (K)	Regression equation	K_1 (min^{-1})	q_e (mg/g)	R^2
303	log(q_e−q_t)=0.0878–0.0005t	0.0012	1.22	0.9322
313	log(q_e−q_t)=0.0780–0.0006t	0.0013	1.18	0.8797
323	log(q_e−q_t)=0.0122–0.0009t	0.002	1.03	0.9551
Second-order model				
T (K)	Second-order model	K_2 (g/mg·min)	q_e(mg/g)	R^2
303	$t/q = 0.6552t + 7.3783$	0.058	1.53	0.9983
313	$t/q = 0.6410t + 6.7512$	0.061	1.56	0.9992
323	$t/q = 0.5478t + 6.6337$	0.045	1.83	0.9981

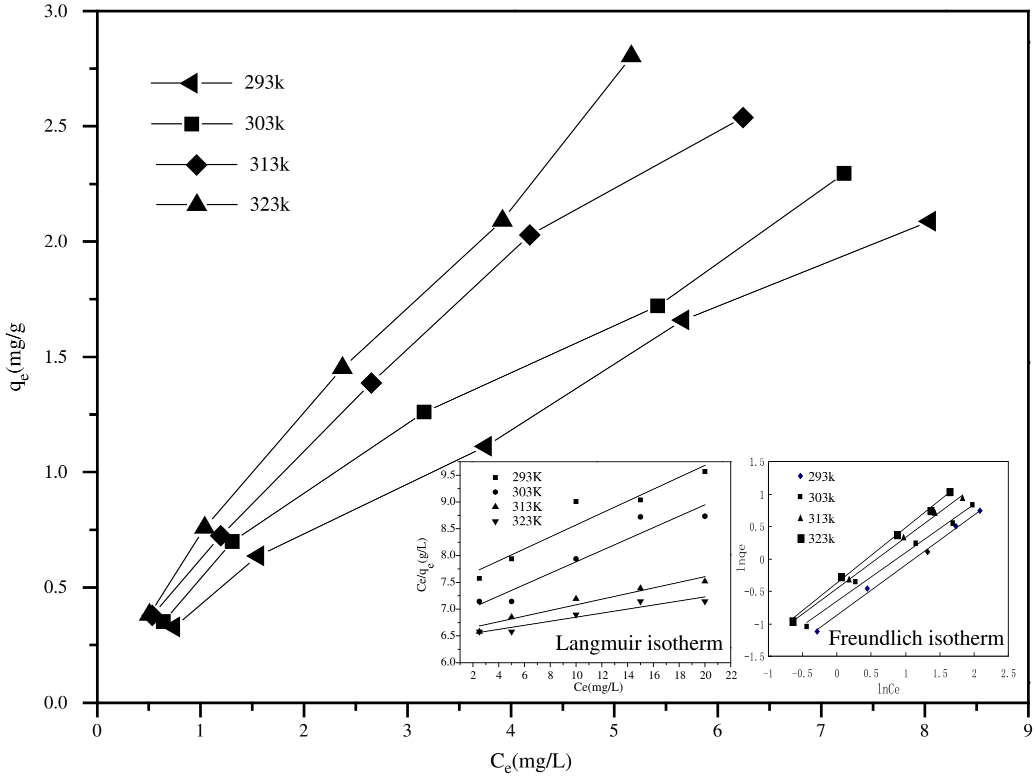

Fig. 3. Adsorption isotherms of the uptake of CA–Cd by CA–Cd–ICP (initial concentration 2.5–20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 293–323 K), the Langmuir isotherm (the left insert figure), and the Freundlich isotherm (the right insert figure).

Langmuir isotherm equation [31]:

$$\frac{C_e}{q_e} = \frac{1}{K_b q_s} + \frac{C_e}{q_s} \tag{3}$$

where q_e is the adsorption capacity of the polymer (mg/g) at equilibrium, C_e is the concentration of CA–Cd in the equilibrium solution (mg/L) and q_s is the Langmuir constant, which is equal to the monolayer adsorption capacity (mg/g). The parameter K_b is the Langmuir sorption equilibrium constant (L/mg) related to the free energy of adsorption.

The Langmuir parameter, K_b, can be used to predict the affinity between the sorbate and sorbent using the dimensionless separation factor, R_L [32].

$$R_L = \frac{1}{1 + K_b C_0} \tag{4}$$

Table 2
Langmuir isotherm constants for adsorption of CA–Cd on CA–Cd–ICP

T (K)	Langmuir isotherm equation	q_s (mg/g)	K_b (L/mg)	R^2	R_L
293	$C_e/q_e = 2.2237 + 0.2169C_e$	4.61	0.098	0.9159	0.83
303	$C_e/q_e = 1.6957 + 0.2271C_e$	4.40	0.134	0.9342	0.79
313	$C_e/q_e = 1.3828 + 0.1729C_e$	5.78	0.125	0.9760	0.79
323	$C_e/q_e = 1.3203 + 0.1181C_e$	8.47	0.089	0.9093	0.85

Table 3
Freundlich isotherm constants for adsorption of CA–Cd on CA–Cd–ICP

T (K)	Freundlich isotherm equation	K ($L^{1/n}$·mg$^{1-1/n}$/g)	R^2	n
293	$\ln q_e = -0.8633 + 0.7711 \ln C_e$	9.1367	0.9958	1.297
303	$\ln q_e = -0.6506 + 0.7425 \ln C_e$	9.3494	0.9921	1.347
313	$\ln q_e = -0.4580 + 0.7854 \ln C_e$	9.5420	0.9981	1.273
323	$\ln q_e = -0.3376 + 0.8468 \ln C_e$	9.6624	0.9975	1.180

where C_0 is the highest initial CA–Cd concentration (mg/L). The values of R_L calculated as above equation are incorporated in Table 2. As the R_L values lie between 0 and 1, the adsorption process is favorable. Further, the R_L values for the adsorption of CA–Cd complex are between 0.79 and 0.85, and therefore, its adsorption is favorable.

Freundlich isotherm equation [33]:

$$\ln q_e = \frac{1}{n} \ln c_e + \ln K \tag{5}$$

where q_e is solid phase sorbate concentration in equilibrium (mg/g), C_e is liquid phase sorbate concentration in equilibrium (mg/L). K is Freundlich constant ($L^{1/n}$·mg$^{1-1/n}$/g) and $1/n$ is the heterogeneity factor.

The Langmuir and Freundlich parameters for the adsorption of CA–Cd complex are listed in Table 2 and 3. It is evident from these data, Freundlich isotherm model is well fitted than Langmuir isotherm model, when the R^2 values are compared in Tables 2 and 3. In other words, it predicts that the CA–Cd concentrations on the adsorbent will increase so long as there is an increased in the CA–Cd concentration in the aqueous solution.

3.4. Evaluation of the selective adsorption

For the purpose of evaluating the selectivity of the polymer, the selective adsorption studies were carried out under the optimum conditions. As seen from Fig. 4, it can be seen that the adsorption capacity of CA–Cd is greater than CA–Zn complex with increasing contact time. This observation is attributed to the specific recognition cavities for CA–Cd created in CA–Cd–ICP, which are developed by ion imprinting. Based on the above results, it is evident that CA–Cd–ICP has a strong ability to selectively adsorb CA–Cd from other organic acid–metal complex present in aqueous solutions.

3.5. Desorption and regeneration studies

The regeneration of the adsorbent is likely to be considered in improving water process economic. In this work, 0.1 M HCl for desorption CA–Cd was

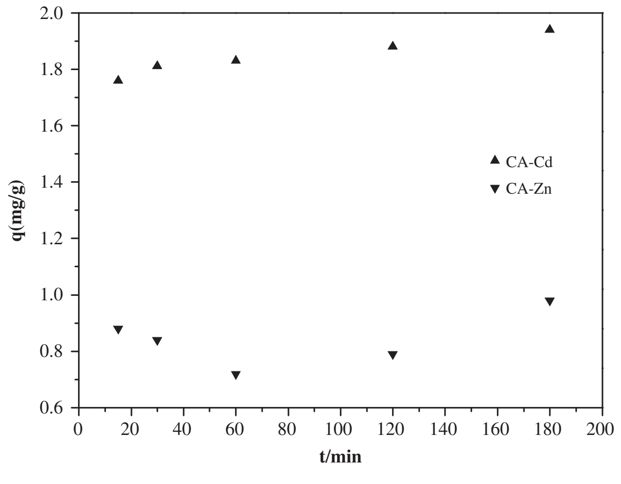

Fig. 4. Evaluation of the selective adsorption by CA–Cd–ICP (initial concentration of CA–Cd and CA–Zn are 20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 303 K).

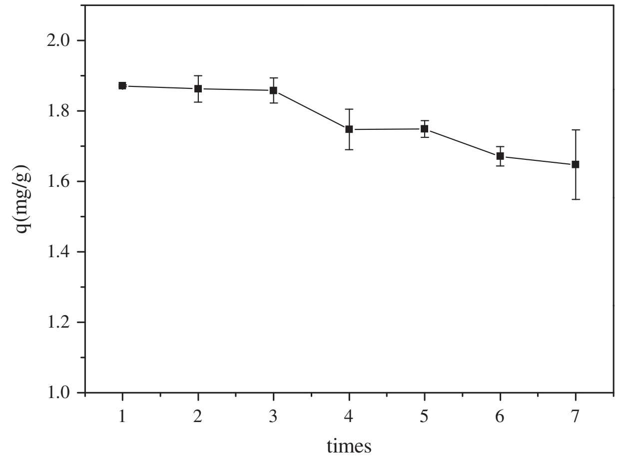

Fig. 5. Relationship between the adsorption capacity and times of reuse of CA–Cd–ICP for CA–Cd (adsorption conditions: initial CA–Cd concentration 20 mg/L, shaking for 12 h at 303 K, the concentration of regeneration solution 0.1 M HCl).

proved to be a relatively effective eluent. The reusability of CA–Cd–ICP for CA–Cd adsorption was shown in Fig. 5. It was revealed that the adsorption capacity of CA–Cd–ICP for CA–Cd decreased slightly from 1.87 to 1.64 mg/g with increasing the times of reuse. CA–Cd–ICP could be reused for seven times with 12.30% regeneration loss, which indicated that CA–Cd–ICP had a good reusability.

4. Conclusions

The new work of imprinted CA–Cd complex on chitosan polymer was prepared successfully in this work. Further, adsorption of CA–Cd onto CA–Cd–ICP fitted the Freundlich adsorption isotherms better than Langmuir. The kinetics of adsorption followed a pseudo-second-order rate equation well. An overall selectivity for CA–Cd was observed showing that CA–Cd–ICP can be used effectively to remove and recover CA–Cd from aqueous solutions. In addition, it was also revealed that CA–Cd–ICP could be reused for seven times with 12.30% regeneration loss.

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