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Synthesis and Evaluation of an Ion-Imprinted Functionalized Sorbent for Selective Separation of Cadmium Ion

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Abstract: An ion-imprinted functionalized sorbent for selective separation of Cd^{2+} from aqueous solution was prepared by molecular imprinting technique in combination with the sol-gel process. The procedures involved the synthesis of mesoporous silica through hydrolysis of tetraethoxysilicate with cetyltrimethylammonium bromide as the structure director, the complex formation between Cd^{2+} and 3-mercaptopropyltrimethoxysilane, and subsequent co-hydrolysis and co-condensation of the complex with the mesoporous silica. After template Cd^{2+} was removed with hydrochloric acid, specific cavity for selective recognition of Cd^{2+} was left. The selectivity of the sorbent was investigated by a batch competitive ion-binding experiment using an aqueous Cd^{2+} and Pb^{2+} mixture. The largest selectivity coefficient for Cd^{2+} in the presence of Pb^{2+} was found to be over 67, the largest relative selectivity coefficient between Cd^{2+} and Pb^{2+} over 18. The uptake capacity and selectivity coefficient of the imprinted functionalized sorbent are higher than those of the nonimprinted sorbent. The sorbent offered a fast kinetics for the extraction/stripping of Cd^{2+} and good recyclability.

Keywords: Cadmium, separation, ion imprinting, mesoporous sorbent

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INTRODUCTION

Environmental pollution as a result of rapid technological development is a serious concern for ecology. Heavy metal ion contamination represents a significant threat to the ecosystem and especially to humans due to the severe toxicological effects on living organisms (1, 2). Cadmium is one of the most toxic heavy metal elements for animals and humans. In mammals cadmium is known to accumulate exclusively in the kidneys. It has a long biological half-life in the human body, ranging from 10–33 years (3). Removal and separation of Cd^{2+} are of great interest in current research.

Selective removal of toxic metal ions from aqueous solutions is usually achieved by solvent extraction and solid-phase extraction. For metal extractions from dilute solutions, the adsorption technique has greater applicability than traditional solvent extraction processes (4). Various adsorbents such as activated carbon (5), metal oxides (6), ion exchangers (7), metal-chelation resins (8), and surface functionalized ceramic adsorbents (9) have been studied for this purpose. Surface functionalized ceramic adsorbents are an important type because of the rigid pore structures, high surface areas, good physical-chemical stabilities of the supports, and the affinity of ligand grafted for metals, which enhance the capacity and selectivity. Feng et al. (10, 11) have developed effective mesoporous sorbents based on mesoporous materials as supports for the removal of toxic metal ions. The selectivity of these sorbents relies solely on the affinity of the surface-coated functional ligand for a specific metal ion, with no consideration of the stereochemical arrangement interactions between the ligand and metal ion. However, the stereochemistry of the ligand with respect to the targeted metal ion plays a key role in molecular recognition (12) and dative bond formation between the toxic metal ion and coordinating ligands (10). A novel method for imprint-coated, functionalized ordered mesoporous sorbents through surface molecular imprinting was proposed by Dai et al. (13). The essence of this methodology is that the functional groups are introduced onto the pore surface of mesoporous silica through imprint coating (coating the mesopore surface with complexes of ligands and target metal ions rather than just the free ligands). After removal of the metal ions, the ligand imprints of the template metal ions are created on the mesopore surfaces. This organization reflects both the size and stereochemical signature of the template ion and ultimately should lead to future ion recognition and selective rebinding of the target ion from ion mixture.

Herein we apply this concept to prepare a new imprint-coated, functionalized sorbent with the selectivity of the cavities and the affinity of the functional ligand [3-mercaptopropyltrimethoxysilane (MPS)] for selective separation of Cd^{2+} from aqueous solutions.

EXPERIMENTAL

Instrumentation

A model SOLAAR S2 atomic absorption spectrometer equipped with quadline deuterium arc background correction, a universal air-cooled titanium burner, and a PTFE spray chamber with impact bead and baffle Pt/Ir PTFE nebulizer (Thermo Elemental Co., U.S.A.) was used to measure the concentration of metal ions in aqueous solution for the study of the uptake and removal of Cd^{2+} and selectivity of the prepared new sorbent. FT-IR spectra ($4000-400\,cm^{-1}$) in KBr were recorded using a Magna-560 spectrometer (Nicolet, U.S.A.). Average pore diameter and surface area of the sorbents were measured by nitrogen sorption with a Model CHEMBET-3000 Sorptometer (Quantachrome, U.S.A.).

Reagents

All reagents used were of analytical grade. Doubly deionized water (DDW, $18\,M\Omega\,cm^{-1}$) was obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO) was used throughout. Tetraethoxysilicate (TEOS), 3-mercaptopropyltrimethoxysilane (MPS, Wuhan University Chemical Factory, Wuhan, China), cetyltrimethylammonium bromide (CTAB), and $CdCl_2 \cdot 2.5H_2O$, Pb (Tianjin Chemical Co., Tianjin, China) were used for the preparation of the new sorbent without further purification. The pH of the solutions was adjusted using the following solutions: hydrochloric acid for $pH = 1$, sodium acetate/hydrochloric acid for $pH = 2-3$, and sodium acetate/acetic acid for $pH = 4-7$.

Preparation of Ordered Mesoporous Silica

1.92 g of NaOH and 3 g of CTAB were dissolved in 160 g of DDW. The solution was stirred and heated at 30°C for 0.5 h. To the solution, 16 mL of TEOS was added. After the mixture was stirred and refluxed for 24 h, the solid product was recovered by filtration, washed with DDW, and dried under vacuum at 80°C for 12 h. The dried material was then refluxed in ethanol for 72 h to extract the surfactants and dried under vacuum at 80°C for 12 h. Ordered mesoporous silica was thus obtained. Such ordered mesoporous material synthesized by using cationic surfactant CTAB has surface area of $244\,m^2/g$ with an average pore size of 3.4 nm.

Preparation of Cd^{2+} Imprinted Thiol Functionalized Sorbent

Two g of $CdCl_2 \cdot 2.5H_2O$ was dissolved in 80 mL methanol under stirring and heating. To the solution, 4 mL of MPS was added. After stirring and refluxing the mixture for 1 h, 2 g of prepared mesoporous silica was added. The mixture was subject to additional 20 h stirring and refluxing, then the product was recovered by filtration, washed with ethanol, and stirred in 50 mL of 6 M hydrochloric acid for 6 h. The final product was recovered by filtration, washed with DDW up to the eluant $pH = 4–5$, and dried under vacuum at 80°C for 12 h. The Cd^{2+}–imprinted thiol functionalized sorbent prepared has an average pore size of 3.2 nm with the surface area of 290 m^2/g. For comparison, the control blank sorbent was also prepared using an identical procedure, but without the addition of $CdCl_2 \cdot 2.5H_2O$. The surface area and average pore size of the control blank sorbent were determined to be 313 m^2/g and 3.0 nm, respectively. The loss of the functionality of the prepared sorbents is possible due to the oxidation of thiol to disulfide in the presence of air and moisture from the laboratory, so care should be taken to prevent the contact of sorbents with air and moisture during storage.

Adsorption Test

To test the effect of pH, 100 mg of Cd^{2+}-imprinted sorbents was equilibrated with 10 mL of the buffered solutions containing 100 $mg\,L^{-1}$ of Cd^{2+} with different pH.

To measure adsorption capacity, 100 mg of Cd^{2+}-imprinted or control blank sorbents was equilibrated with 10 mL of various concentrations of Cd^{2+} solutions buffered with sodium acetate/acetic acid solution at $pH = 5.5$.

Competitive loading of Cd^{2+} and Pb^{2+} by Cd^{2+}-imprinted or control blank sorbents was measured at $pH = 5.5$ buffered with sodium acetate/acetic acid solution. Hundred mg of Cd^{2+}-imprinted or control blank sorbent was equilibrated with 10 mL of the buffered solutions containing 1.8 $mmol\,L^{-1}$ of Cd^{2+} and 1.8 $mmol\,L^{-1}$/3.6 $mmol\,L^{-1}$ of Pb^{2+}, respectively.

In all the above batch experiments, the mixtures were mechanically shaken for 2 h at room temperature, then centrifugally separated. The supernatants were measured for the unextracted Cd^{2+} by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Synthesis of the Ion-Imprinted Functionalized Sorbent

Schematic representation of the synthesis route is shown in Fig. 1. The ordered mesoporous silica hosts were prepared by a surfactant assembly pathway that

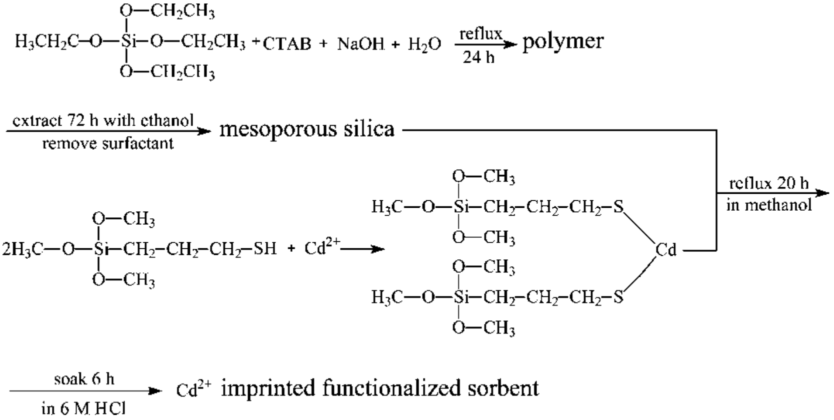

Figure 1. Schematic representation of the synthesis process.

involves charge matching between surfactant and inorganic silica precursors (10, 13). The typical procedure involves mixing CTAB, water, and NaOH. The molar ratio of CTAB : H_2O : NaOH is 0.12 : 130 : 0.7. To this solution, TEOS was added at 30°C. The mixture was refluxed for 24 h. The solid product was recovered by filtration. The cationic surfactant ions are organized in the form of a cylindrical micellar structure with hydrophilic positive ends coulombically interacting with silica pore surfaces. Such ordered mesoporous material synthesized by using cationic surfactant CTAB has the same structural feature as ionic intercalate materials (13). The complex formed between Cd^{2+} and MPS was then co-hydrolyzed and co-condensed with the mesoporous material. Thus, the mesoporous surfaces were coated with the complex of Cd^{2+} and MPS rather than just the free MPS. After removal of the Cd^{2+} from the mesoporous material, the MPS imprints of the template Cd^{2+} were created on the mesoporous surfaces, reflecting the size and sterochemical signature of the template Cd^{2+}.

Characterization of the FTIR Spectra

To ascertain the presence of MPS in the silica material, FTIR spectra were obtained from the mesoporous silica, imprinted sorbent, and nonimprinted sorbent. As shown in Fig. 2, the features around 1081.6 and 947.7 cm^{-1} indicate Si-O-Si and Si-O-H stretching vibrations, respectively. The presence of adsorption water was reflected by ν_{OH} vibration at 3442.0 and 1634.8 cm^{-1}. The bands around 803.2 and 461.2 cm^{-1} resulted from Si-O vibrations. A characteristic feature of the imprinted sorbent and nonimprinted sorbent when compared with the mesoporous silica is a S-H bond around 2559.7 cm^{-1}, indicating that –SH was grafted onto the mesoporous silica

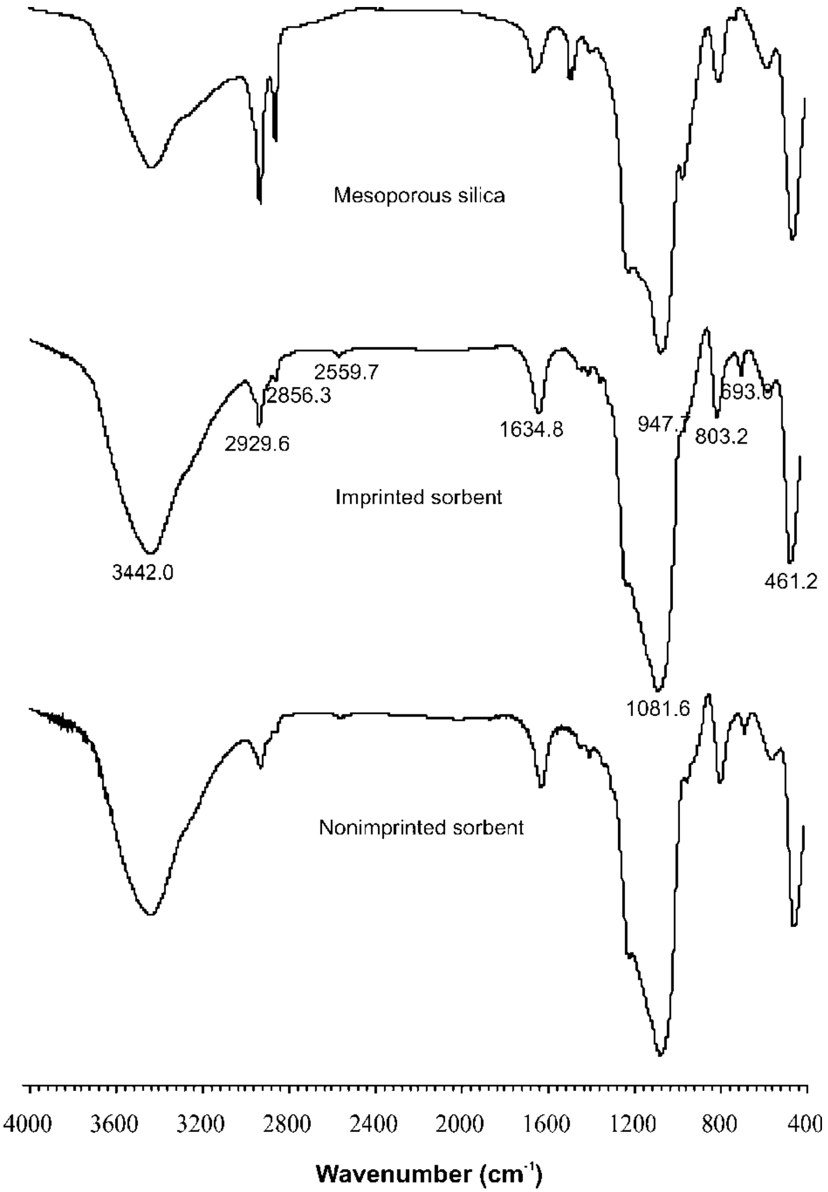

Figure 2. FTIR spectra of the mesoporous silica, the imprinted sorbent, and the nonimprinted sorbent.

after surface imprinting. Both imprinted and nonimprinted sorbents showed very similar location and appearance of the major bands. The result indicates that –SH was recovered after removal of Cd^{2+} from the imprinted sorbent.

Adsorption Capacity

Figure 3 describes the adsorption capacity of the imprinted and nonimprinted sorbents for Cd^{2+} as a function of the initial concentration of Cd^{2+}. Obviously, the imprinted sorbent exhibited larger adsorption capacity than the nonimprinted sorbent. The largest capacity of the Cd^{2+}-imprinted and the nonimprinted sorbents were 550 μmol g^{-1} and 429 μmol g^{-1}, respectively.

Effect of pH on the Adsorption of Cd^{2+}

The pH dependence of the percentage of the Cd^{2+} extracted is shown in Fig. 4. The percentage of the Cd^{2+} extracted increased as the pH of the aqueous solution increased from 3 to 5, then remained constant with further increase in pH. Below pH = 3, no Cd^{2+} was extracted onto the imprinted sorbent due to the protonation of the thiol moiety. The optimum pH for the extraction of Cd^{2+} from aqueous solution ranged from 5 to 7. In this pH range, neither precipitation of the metal hydroxide nor the protonation of the thiol group is expected.

Uptake Kinetics of Cd^{2+} by the Imprinted Functionalized Sorbent

In a typical uptake kinetics test, 100 mg of the sorbent was added to 10 mL of 100 mg L^{-1} of Cd^{2+} aqueous solution buffered to pH = 5.5. The mixture was

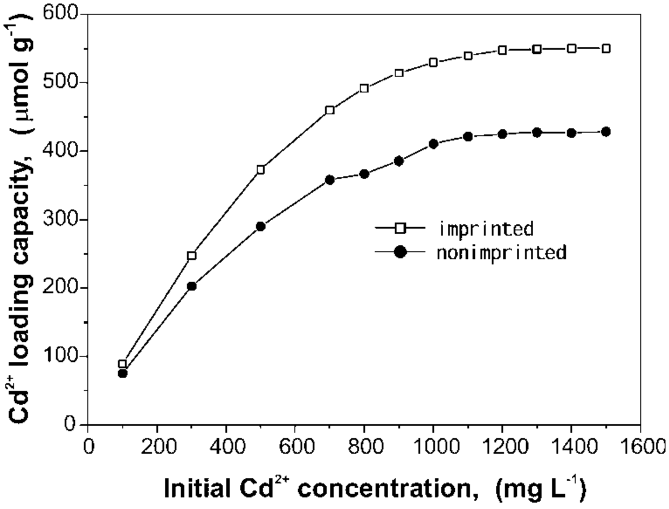

Figure 3. Loading capacity of Cd^{2+} by the Cd^{2+}-imprinted and nonimprinted sorbents at pH = 5.5.

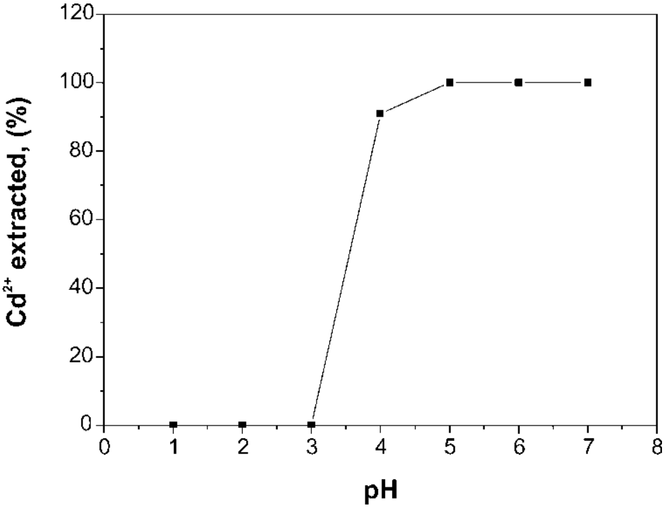

Figure 4. Effect of pH on the uptake of 100 mg L^{-1} Cd^{2+} onto 100 mg of the imprinted functionalized sorbent.

mechanically shaken for 10, 20, 30, 60, 120, 180 min at room temperature, respectively, and then centrifugally separated. The excessive unextracted Cd^{2+} in the supernatant was determined by atomic absorption spectrometry. Figure 5 shows the uptake kinetics of Cd^{2+}. It is clear that the solid phase extraction process of the sorbent is fairly rapid; the 93% uptake of Cd^{2+} was achieved within 10 min.

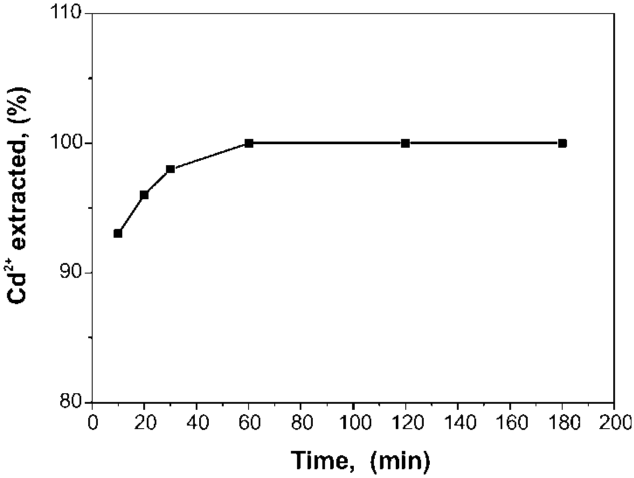

Figure 5. Uptake kinetics for 100 mg L^{-1} Cd^{2+} onto 100 mg of the imprinted functionalized sorbent at pH = 5.5.

Selectivity for Cd^{2+} in Competitive Adsorption on the Imprinted Functionalized Sorbent

Adsorption and competitive ion recognition studies were performed with Cd^{2+} and Pb^{2+} in order to measure the selectivity of the imprinted materials. The Pb^{2+} was chosen as the competitive species because it has the same charge, similar ionic radius, and also binds well with the thiol ligand. The distribution of ion between the solution and sorbent is represented as distribution coefficient, K_d(13)

$$K_d = \{(C_i - C_f)/C_f\} \times \{\text{volume of solution [mL]}\}/\{\text{mass of gel [g]}\}$$

where C_i and C_f represent the initial and final solution concentrations, respectively.

The equilibrium of the target ion and competitive ion between the solution and sorbent can be shown as follows (13):

$$M_1(\text{solution}) + M_2(\text{sorbent}) \rightleftharpoons M_2(\text{solution}) + M_1(\text{sorbent})$$

and the selectivity of the sorbent can be represented by k and k' (13):

$$k = \{[M_2]_{\text{solution}}[M_1]_{\text{sorbent}}\}/\{[M_1]_{\text{solution}}[M_2]_{\text{sorbent}}\} = K_d(\text{Cd})/K_d(\text{Pb})$$
$$k' = k_{\text{imprinted}}/k_{\text{nonimprinted}}$$

Table 1 summarizes the data for the percentage metal ion adsorbed, uptake capacity, distribution coefficient (K_d), selectivity coefficient of the sorbent toward Cd^{2+} (k), and the relative selectivity coefficient $(k)'$ obtained in these competitive ion-binding experiments between Pb^{2+} and Cd^{2+}. Comparison of the K_d values for the Cd^{2+}-imprinted sorbent with the

Table 1. Competitive loading of Cd^{2+} and Pb^{2+} by Cd^{2+}-imprinted and nonimprinted sorbents at pH = 5.5

	Initial solution (mmol L^{-1})		% Uptake		Capacity μmol g^{-1}		K_d (mL g^{-1})			
Sorbent	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	k	k'
Imprinted	1.8	1.8	93.6	22.1	170	39	1452	41	35.4	8.1
	1.8	3.6	92.3	15.0	165	51	1208	18	67.1	18.6
Non imprinted	1.8	1.8	77.3	43.7	138	78	341	78	4.4	
	1.8	3.6	77.0	25.2	131	90	320	89	3.6	

Note: K_d, distribution coefficient, the ratio of mole of Cd^{2+} absorbed per gram of sorbent to the molar concentration of Cd^{2+} in final solution; k, selectivity coefficient, $K_d(\text{Cd})/K_d(\text{Pb})$; k', relative selectivity coefficient, $k' = k_{\text{imprinted}}/k_{\text{nonimprinted}}$.

corresponding nonimprinted sorbent reveals a significant increase in K_d for Cd^{2+} through imprinting. In addition, the uptake capacity of the imprinted functionalized sorbent is higher than the nonimprinted sorbent. In the Cd^{2+}-imprinted sorbent, the presence of Cd^{2+} makes the ligands arrange orderly. After the removal of Cd^{2+}, the imprinted cavities and specific binding sites of the functional groups in a predetermined orientation were formed. In contrast, in nonimprinted sorbent the flexibility of -CH_2-CH_2-CH_2-, which was joined to the $-SH$ group, resulted in no such specificity.

Comparison of the selectivity coefficients of the imprinted and nonimprinted sorbents for the adsorption of Cd^{2+} and Pb^{2+} shows that a great improvement in the selectivity for Cd^{2+} over Pb^{2+} was achieved through imprinting. The largest selectivity coefficient of the imprinted sorbent for Cd^{2+} in the presence of Pb^{2+} is over 67 and the largest relative selectivity coefficient between Cd^{2+} and Pb^{2+} is over 18.

Desorption of Cd^{2+} from the Imprinted Sorbent

The desorption of Cd^{2+} from the sorbent was investigated by mechanically shaking the mixture of 100 mg of the loading Cd^{2+}-imprinted functionalized sorbent and 10 mL various concentrations of HCl for 2 h at room temperature. The mixture was centrifugally separated, and the desorbed Cd^{2+} in the supernatant was measured by atomic absorption spectrometry. As is shown in Fig. 6, over 1 M of HCl can effectively remove the absorbed Cd^{2+} from the sorbent. With a single wash of 1 M HCl, 94% of Cd^{2+} of the absorbed Cd^{2+} was removed.

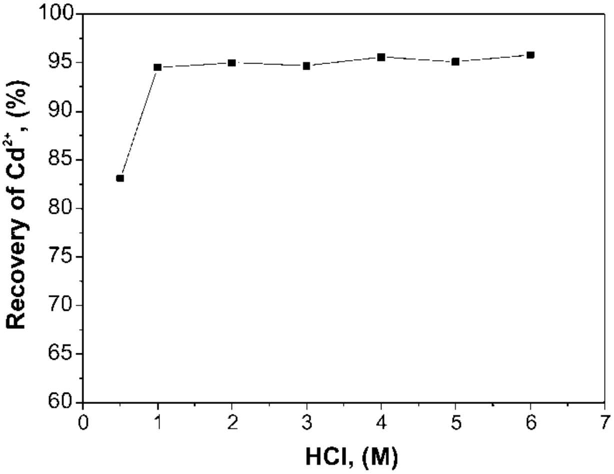

Figure 6. Effect of HCl concentration on the desorption of Cd^{2+} from 100 mg imprinted functionalized sorbent.

Table 2. Extraction recyclability through five extraction/stripping cycles with 100 mg of the ion-imprinted functionalized sorbent in 10 mL of 200 mg L^{-1} Cd^{2+} solutions at pH = 5.5

Extraction cycle	% Uptake	K_d (mL g^{-1})	Capacity (μmol g^{-1})
1	98.1	5163	175
2	97.2	3471	174
3	96.4	2678	173
4	95.8	2281	172
5	94.6	1752	169

Recycling of the Imprinted Functionalized Sorbent

In a test of sorbent recyclability, the imprinted functionalized sorbent was used to extract Cd^{2+} through five extraction/stripping cycles. Two M of HCl was used to strip the adsorbed Cd^{2+}. The results are shown in Table 2. The same sample of the sorbent was found to remove 96 ± 1% of the Cd^{2+} from solution through five extraction cycles. The capacity of the sorbent in these four recycles was 98 ± 1% of the fresh sorbent. The results indicate that the prepared sorbent is promising for many separation applications that require recyclable solid phases.

CONCLUSIONS

This work demonstrated the feasibility of the preparation of the ion-imprinted functionalized mesoporous sorbent for selective separation of Cd^{2+} from aqueous solution. The loading capacity and selectivity for Cd^{2+} of the imprinted sorbent is obviously larger than that of the nonimprinted sorbent. The sorbent possesses a fast kinetics for the extraction/stripping of Cd^{2+} and exhibits good recyclability.

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