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Selective adsorption of lead(II) from aqueous solution by ion-imprinted PEI-functionalized silica sorbent: studies on equilibrium isotherm, kinetics, and thermodynamics

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ABSTRACT

A new ion-imprinted poly(ethyleneimine)(PEI)-functionalized silica sorbents were synthesized by a hydrothermal-assisted surface grafting technique with Pb(II) as the template, PEI as the functional molecular, and epichlorohydrin as the cross-linking agent for the selective adsorption of Pb(II) from aqueous solution, and was characterized by FTIR, SEM, TGA-DTA, nitrogen adsorption, and the static batch experiment. Static adsorption experiment results showed that Pb(II)-imprinted PEI-functionalized silica sorbents had high static adsorption capacity of 60.4 mg g^{-1}, reached an equilibrium state within 20 min, displayed stable adsorption ability for Pb(II) ions in the range of pH 4–8, had satisfactory selectivity toward Pb(II) and could be used repeatedly. Compared with Freundlich and Dubinin–Radushkevich isotherms, equilibrium data fitted to Langmuir adsorption model. The kinetic process of adsorption followed a pseudo-second-order model compared to pseudo-first-order, Elovich and intraparticle diffusion models. Negative values of ΔG° indicated spontaneous adsorption and the degree of spontaneity of the reaction increased with increasing temperature. Positive values of ΔH° showed that the adsorption process was endothermic in the experimental temperature range. The results indicated that Pb(II)-imprinted PEI-functionalized silica sorbents could be employed as an effective material for the selective adsorption of Pb(II) ions from aqueous solutions.

Keywords: Pb(II); Poly(ethyleneimine); Ion-imprinted polymer; Hydrothermal-assisted; Adsorption

1. Introduction

Industrial wastewater contaminated with heavy metals is commonly produced from various industrial activities. The removal of toxic heavy metal ions from wastewater has been desired for the prevention of possible hazards in our environment. Lead (Pb) is one of the most common environmental pollutants listed among the priority pollutants regulated by US EPA due to its toxicity to human health [1,2]. Strict environmental protection legislation on the disposal of Pb(II) ions and increasing demands for water cleaning with fairly low level of Pb(II) ions make it

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greatly significant to exploit various effective methods for the removal of Pb(II) ions [3]. Adsorption is considered to be a particularly competitive and effective process for the removal of trace quantities of heavy metals [4]. Numerous adsorbents, such as activated carbon [5], zeolite [6] diatomite [7], lignite [8], clayey soil [9], multi-walled carbon nanotubes [10], polymeric adsorbent [11], industrial byproducts [12], agricultural waste biomass [13], and biosorbents [14], have been tested for their potential application to remove Pb(II) ions from wastewater. Recent studies mainly focus on the exploration of novel adsorbents with fast adsorption rate, large adsorption capacity, and high adsorption selectivity for heavy metal ions [3].

Ion-imprinted polymer (IIPs) based on the use of imprinting technology has widely been exploited as the new sorbents for the selective adsorption or removal of heavy metal ions [15,16]. IIPs can create the selective recognition sites in which complexing ligands are arranged so as to match the charge, coordination number, coordination geometry, and size of the target ion [15,16]. The surface imprinting technique is the most important method of the IIPs synthesis with outstanding advantages, such as simple, good selectivity, and high adsorption capacity [16,17]. Some IIPs have been prepared by the surface imprinting technique making the functional group immobilized on the surface of the silica gel for selective removal or separation of heavy metals from aqueous solution [18–27]. According to the theory of Hard and Soft, Acids and Bases [28], Pb(II) is classified as borderline acids and prefers to bind to ligands containing N-donor atoms which is classified as borderline bases. Poly(ethyleneimine) (PEI) is a typical alkaline water-soluble functional macromolecular which contains a large quantity of N-donor atoms with primary, secondary and ternary amino groups in a ratio of approximately1:2:1 [29]. Gao et al. reported an PEI-functionalized IIPs as a sorbent for Cu(II) and Cd(II) ions [30]. However, Pb(II)-imprinted PEI-functionalized silica sorbents have not been reported.

In this study, a simple procedure was developed to synthesize a new Pb(II)-imprinted PEI-functionalized silica sorbents by the surface imprinting technique for the selective removal of Pb(II) ions from aqueous solutions. The structural characteristics, adsorption and desorption properties of the imprinted silica sorbents for Pb(II) ions in aqueous solution were investigated. The kinetic and thermodynamic behaviors of the adsorption of Pb(II) ions onto the imprinted silica sorbents were also studied.

2. Experimental

2.1. Chemicals and materials

3-Chloropropyltriethoxsilane was purchased from Jingzhou Jianghan Fine Chemical Co., Ltd. Hubei, China. Branched PEI (molecular weight of 25,000) was obtained from Sigma-Aldrich. Silica gel (60–80 mesh) was purchased from Qingdao Ocean Chemical Co., Ltd., Shandong, China. Epichlorohydrin, ethanol, ammonia, $CuSO_4{\cdot}5H_2O$, $ZnCl_2$, $Pb(NO_3)_2$, $CdCl_2{\cdot}2.5H_2O$, hydrochloric acid, nitric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The stock solutions of metal ions (1,000 $mg\,L^{-1}$) were purchased from the National Research Center for Standard Materials (NRCSM, Beijing, China). The working solutions were prepared by series dilution of the stock solutions immediately prior to their use. The solutions were prepared weekly and stored in a refrigerator. All reagents used were of the highest available purity and of at least analytical grade. Deionized water (18.2 $M\Omega\,cm^{-1}$) was obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO) and was used throughout this work.

2.2. Apparatus

Analysis by Fourier transmission infrared (FT-IR) spectroscopy was carried out by Nicolet 6700 FT-IR spectrometer in the range from 400 to 4,000 cm^{-1} with a resolution of 1 cm^{-1} using KBr window. The scanning electron microscope (SEM) characterization was obtained using a microscope (Shimadzu Corporation, Japan) to obtain information of the surface with resolution in the micrometer range. The thermogravimetric curves of the materials were obtained in a HCT-2 thermoanalyzer equipment (Beijing Scientific Instrument Factory, China) warming the samples with a speed of 10 C min^{-1} up to a temperature of 1,000℃ under 30 mL min^{-1} of nitrogen gas. The surface area, pore volume, and pore diameter of the sample particles synthesized were determined using a porosimetry analyzer (ASAP 2010C, Micromertics, USA) in a Brunauer–Emmett–Teller (BET) nitrogen adsorption and desorption modes. The samples were degassed and dried before this measurement. The concentrations of metals in aqueous solutions was determined by an AA-6300c flame atomic absorption spectrometer (FAAS, Shimadzu Corporation, Japan) with Pb, Cu, Cd, Zn, and Ni hollow cathode lamps and air-acetylene flame. The pH of solution was measured by a PB-10 digital pH-meter (Sartorius, German) equipped with a combined glass electrode.

2.3. Preparation of the imprinted PEI-functionalized silica sorbents

The imprinted PEI-functionalized silica sorbents were prepared as follows: Firstly, 10 g of silica gel (60–80 mesh) for activating was mixed with 100 mL of 33% methanesulfonic acid. The activated silica gel was recovered by filtration, washed with doubly deionized water to neutral, and dried under vacuum at 60℃ overnight. Secondly, 8 g of activated silica gel reacted with γ-chlopropyltriethoxysilane using xylene as solvent and refluxed under stirring at 80℃ for 24 h. The modified silica gel was recovered by filtration, washed with ethanol, and dried under vacuum at 60℃ overnight. Six gram of modified silica gel reacted with 20 mL of 10% PEI aqueous solution in a Teflon-lined stainless steel autoclave at 120℃ for 24 h. Thirdly, 4 g of $Pb(NO_3)_2$ was dissolved in 10 mL of water under stirring and heating, and then mixed and added into above solution with stirring in a Teflon-lined stainless steel autoclave at 120℃ for 24 h. Finally, 4 mL of epichlorohydrin as the cross-linking agent was added at 60℃ for 2 h and the product was recovered by filtration, washed with ethanol, and stirred in 50 mL of 1 mol L^{-1} HCl for 4 h. The final product was recovered by filtration, washed with doubly deionized water up to the fluent pH 5–6, and dried under vacuum at 60℃ overnight. For comparison, the non-imprinted polymer sorbent (NIP) was also prepared using an identical procedure, but without the addition of $Pb(NO_3)_2$. The Pb(II) concentration in the gel before and after released was analyzed by FAAS. The chemical structure of the solid prepared after grafting was characterized by infrared spectrum in order to confirm that PEI had been grafted onto the surface of silica gel particle. The SEM, TGA-DTA, and surface areas of the imprinted and non-imprinted silica sorbents were characterized.

2.4. Adsorption experiments

The adsorption studies were carried out by the batch method to obtain rate and equilibrium data, which consisted in suspending a series of flasks containing near 100 mg of the sorbents in 20.0 mL of an aqueous solutions of Pb(II) ions with different concentrations for desired time interval. The suspensions were magnetically stirred at 400 rpm at room temperature and then were centrifugally separated at 3,000 rpm for 10 min. The effects of contact time (5–60 min), temperature (25, 35, and 45℃), initial concentration of Pb(II) ions (100–800 mg L^{-1}), and pH (2–10) were studied. The suspensions were brought to the desired pH by adding sodium hydroxide and hydrochloric acids. The Pb(II) ion concentrations in the solutions were determined by FAAS. The uptake of metal ions in solution was calculated by the difference in their initial and final concentrations according to the following equation:

$$q = (C_i - C_f)V/1000\ \mathrm{m} \tag{1}$$

where q represents the adsorption capacity (mg·g^{-1}); C_i and C_f are the initial and final concentrations of metals (mg L^{-1}), respectively. V is the volume of the solution (mL) and m is the mass used of the sorbents (g).

In order to determine the competitive adsorption of Pb(II) with respect to Cu(II), Cd(II), Zn(II), and Ni (II), 0.1 g of the imprinted or non-imprinted sorbents were added into binary mixture solutions of Pb(II)/Cu (II), Pb(II)/Cd(II), Pb(II)/Zn(II), and Pb(II)/Ni(II) at pH 5 for 30 min by batch process. The distribution coefficient (K_d), the selectivity coefficient (k) of Pb(II) with respect to Cd(II), Cu(II), Zn(II), and Ni(II), and the relative selectivity coefficient (k') were calculated as the following equations [31]:

$$K_d = q/C_e \tag{2}$$

$$k = K_d(\mathrm{Pb(II)})/K_d(\mathrm{X(II)}) \tag{3}$$

$$k' = k_{\mathrm{imprinted}}/k_{\mathrm{non-imprinted}} \tag{4}$$

where C_e is the equilibrium concentrations of metal ions (mg L^{-1}). X(II) represents Cd(II), Cu(II), Zn(II), and Ni(II) ions, respectively, $k_{\mathrm{imprinted}}$ and $k_{\mathrm{non\text{-}imprinted}}$ represent the selectivity factor of the imprinted and non-imprinted silica sorbents.

2.5. Desorption and regeneration experiments

In order to study the reusability of the sorbents, the consecutive adsorption–desorption cycles were realized as follows: the dried sorbents were suspended in 100 mg L^{-1} of Pb(II) solution at pH 5 for 30 min with the ratio of solid-to-solution at 5 g L^{-1}. Pb(II)-loaded imprinted PEI-functionalized silica sorbents were filtered and washed with deionized water to remove any unadsorbed Pb(II). The desorption experiments were performed using 1 mol L^{-1} HCl solution in batch method. After 2 h stirring, the solution mixture was filtered and the sorbent washed several times with distilled water in order to remove excess acid. The regenerated beads were introduced again in the above solution. This adsorption–desorption cycle was repeated five times and the concentrations of Pb(II) in the filtrates were analyzed by FAAS.

2.6. Removal of Pb(II) ion from aqueous solution

The selective removal of Pb(II) was performed at pH 5 at room temperature in the flasks stirred magnetically by added 100 mg the imprinted sorbents from a multi-metal mixture solution (25 mL) containing 20 mg L^{-1} heavy metal ions (Cd(II), Ni(II), Cu(II), and Pb(II) individually), spiked with 10, 20, and 40 mg L^{-1} Pb(II) ions. After adsorption equilibrium, the concentration of heavy metal ions in the remaining solution was measured.

Unless stated all laboratory measurements were performed in triplicate. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin error. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. All statistical analysis was done using Microsoft Excel 2003, Version office XP.

3. Results and discussion

3.1. Synthesis of the imprinted PEI-functionalized silica sorbents

The imprinted PEI-functionalized silica sorbents were prepared by grafting method on the surface of silica. As known, silica gel is an amorphous inorganic polymer. After silica gel was activated by 33% of methanesulfonic acid solution, a great deal of silanol groups (Si-OH) was produced on the surface of silica gel, and then 3-chlopropyltriethoxysilane as a coupling agent to link silica gel and PEI reacted with Cl atoms to form modified silica gel. The PEI-modified silica gel was obtained by the reaction between chloropropyl groups on modified silica gel and amine groups of PEI. The complex was formed between Pb(II) and amine groups on PEI-modified silica gel. The epichlorohydrin as the cross-link agent was added, the ring-opening reaction of epichlorohydrin took place firstly, in which an amine group on a PEI chain acted as the attacking group, and then the dehydrochlorination reaction occurred between epichlorohydrin and an amine group of another PEI chain. Finally the Pb(II) ions are removed with hydrochloric acid solution, the Pb(II)-imprinted PEI-functionalized silica sorbents which contained a tailor-made cavity for Pb(II) ion were formed on the surface of silica. The preparing process of Pb(II)-imprinted PEI-functionalized silica sorbents is expressed schematically in Fig. 1.

3.2. Characteristics of sorbents

FT-IR spectra of the imprinted PEI-functionalized silica sorbents and silica gel are shown in Fig. 2. The absorption band at 3,450 and 1,652 cm^{-1} is attributed to

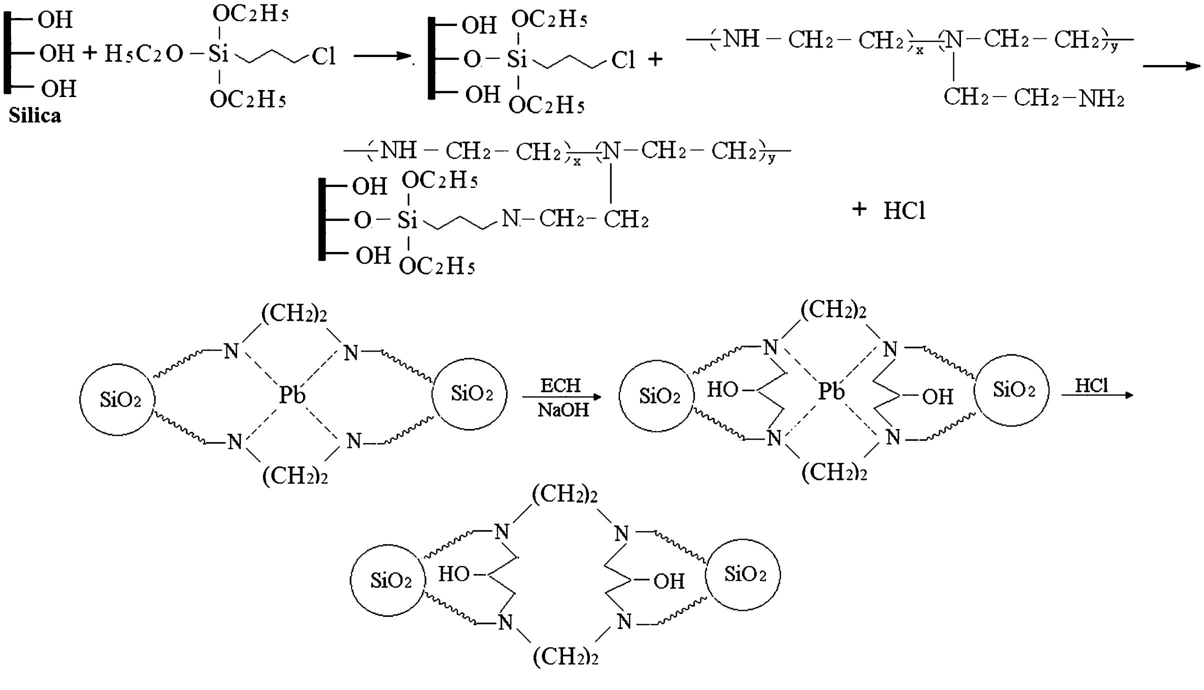

Fig. 1. Preparation procedure of Pb(II)-imprinted PEI-functionalized silica sorbent.

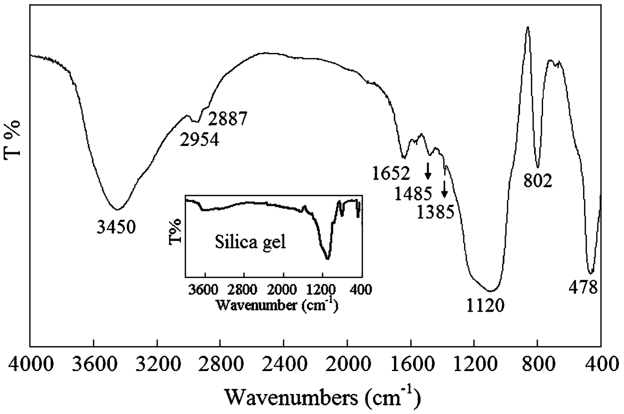

Fig. 2. IR spectra of Pb(II)-imprinted PEI-functionalized silica sorbent and silica gel.

the stretching vibration and deformation vibration of O–H groups due to the remaining adsorbed water molecules. The absorption bands at 2,954 and 2,887 cm^{-1} are ascribed to the asymmetric stretching vibrations of –CH_2– groups, while the absorption peaks at 1,485 is related to the bending vibrations of –CH_2–groups. The absorption band at 1,385 cm^{-1} is the bending vibration of N–H bond. The absorption bands at 1,120 and 802 cm^{-1} are due to the Si–O–Si and Si–O stretching vibrations, respectively. The absorption peak at 478 cm^{-1} is assigned to the bending vibrations of Si–O–Si groups. The contents of amino groups on the imprinted PEI-functionalized silica sorbents were 5.8% by acid–base titration analysis [32]. These indicated that PEI had been grafted on the surface of silica. Similar result was reported previously [33].

The imprinted and non-imprinted PEI-functionalized silica sorbents were characterized using SEM in order to know the surface morphological image. The SEM images of sorbents are showed in Fig. 3. Compared with the non-imprinted silica sorbents, the morphology of the imprinted silica sorbents displayed the irregular particles in shape. The rough surfaces and smaller particle size of beads should be considered a factor providing an increase in the surface area. These results were in agreement with specific surface area data, where the imprinted PEI-functionalized silica sorbents presented a value of 126.8 $m^2 g^{-1}$, much higher than the non-imprinted one with 90.7 $m^2 g^{-1}$. The effect of Pb(II) ions, as the templates in the synthesis process, was fundamental and significant for the morphological features of the imprinted sorbent.

Thermogravimetric analyses of the extracted organosilicas were performed from 20 to 1,000℃ to test the thermal stability of the samples. The differential thermal analysis (DTA) and thermo gravimetric analyzer (TGA) curves of the imprinted PEI-functionalized silica sorbents are shown in Fig. 4. A small weight loss (4 wt.%) occurred below 150℃, associated with the water physically adsorbed on surface with a small endothermic peak at 135℃ in DTA curve. Between 150 and 800℃ the samples had a large weight loss of 16 wt%, due to the decomposition of organic groups with a broad exothermic peak at 308℃ in DTA curve. A continuous and small weight loss was observed above 800℃, which was attributed to the combustion of residual organic material and/or to the desorption of water resulting from silanol condensation. The total weight loss was 20%. The results indicated that the imprinted PEI-functionalized silica sorbents were stable at temperature below 150℃.

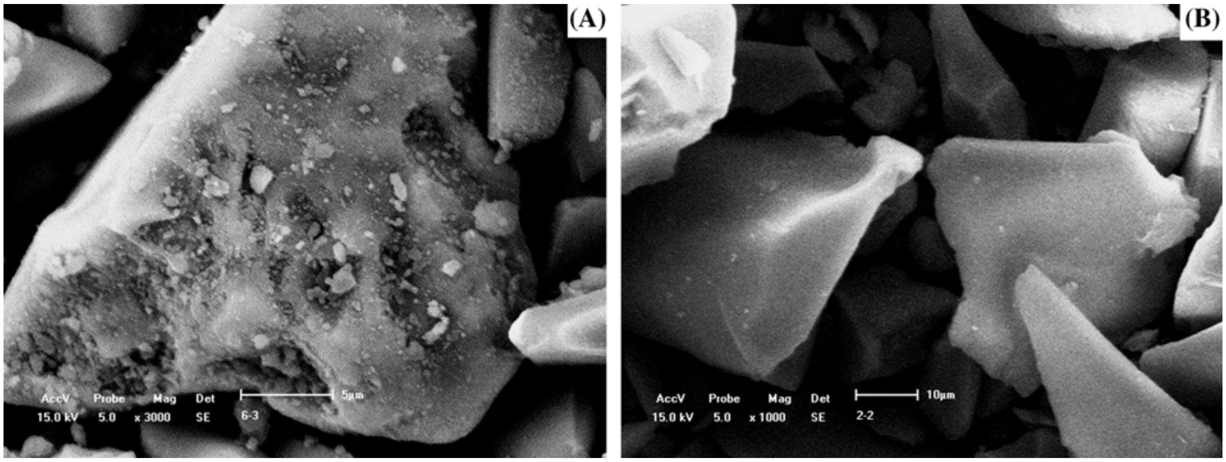

Fig. 3. SEM images of Pb(II)-imprinted PEI-functionalized silica (A) and non-imprinted silica (B) sorbents.

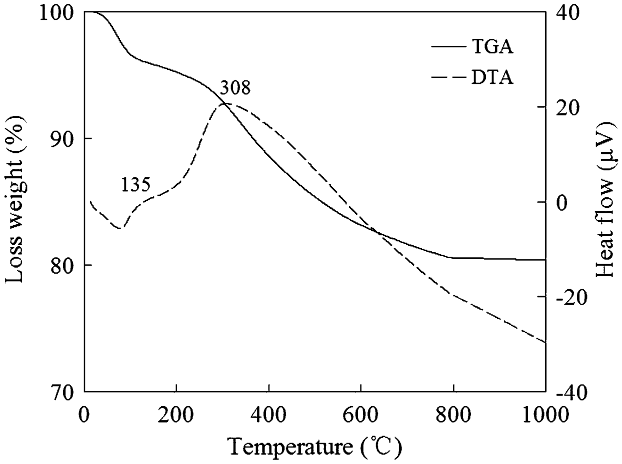

Fig. 4. TGA -DTA of Pb(II)-imprinted PEI-functionalized silica sorbent.

3.3. Effect of pH

The species of Pb(II) is mainly Pb(II) at $pH < 7$ and follows by a sharp reduction in Pb(II) at pH above 7, while the precipitation of $Pb(OH)_2$ is formed at $pH > 7$ and reaches its peak at pH 11. Thus, the study on the effect of pH was limited to pH values less than 7. The effect of solution pH on the adsorption of Pb(II) ion is shown in Fig. 5. The imprinted PEI-functionalized silica sorbent exhibited a low affinity in acidic ($pH < 4$) solutions. At $pH < 4$, the concentration of hydrogen ions caused the protonation of amino group which minimizes the extent of Pb(II) ion adsorption. At the pH in range of pH 4–6, the adsorption quantity remained relatively constant. The removal acidity for subsequent experiments was selected at pH 5.

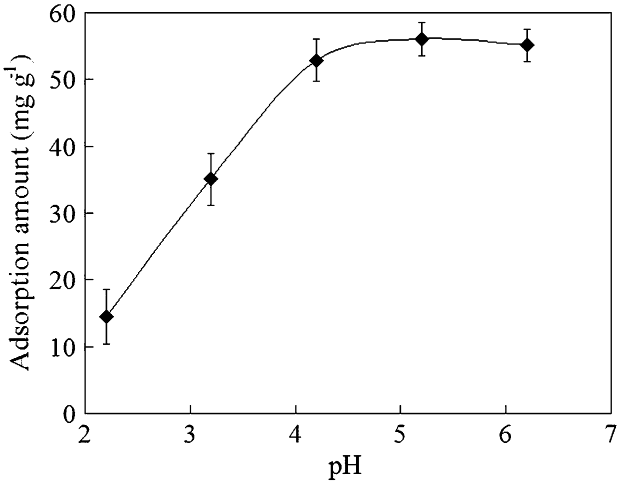

Fig. 5. Effect of pH on the adsorption capacity of Pb(II)-imprinted PEI-functionalized silica sorbent for Pb(II) ions.

3.4. Kinetic curve of adsorption rate

The effect of equilibration time on the adsorption of Pb(II) ion was analyzed kinetically over a range of 5–60 min. Fig. 6 shows the time dependence of the adsorption capacity of the imprinted PEI-functionalized silica sorbents for Pb(II) ions. During the first 20 min, the adsorption capacity of Pb(II) increased with time and more than 95% of the total adsorption capacity was obtained. After 20 min, the adsorption capacity further increased with a much slower rate, and then an equilibrium value was reached. The shorter time indicated Pb(II) ions were easy to enter into the cavities and bind with the recognition sites at the surface of the imprinted PEI-functionalized silica sorbents owing to the smaller diffusion barrier of the imprinted cavities on the surface. Based on the kinetic results, an equilibration time of 30 min was selected for the further experiment.

To investigate the adsorption kinetic of Pb(II) ions onto the imprinted PEI-functionalized silica sorbents, four different kinetic models, such as pseudo-first-order model [34], pseudo-second-order model [35], Elovich model, [36] and intraparticle diffusion model [37], were used to fit the experimental data.

The linear form of pseudo-first-order model can be expressed as:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \tag{5}$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption. q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t (min), respectively. The rate constants k_1, q_e, and correlation coefficients r^2 were calculated using the slope and intercept of plots of log (q_e–q_t) vs. t (as shown in Fig. 7(a)).

The pseudo-second-order rate expression is linearly expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{6}$$

where q_e and q_t are the adsorption capacity at equilibrium and time t (mg g^{-1}), k_2 ($\text{g mg}^{-1}\,\text{min}^{-1}$) is the rate constant of the pseudo-second-order adsorption. The rate constants k_2, q_e, and correlation coefficients r^2 were calculated from the linear plots of t/q_t vs. t (as shown in Fig. 7(b)).

The Elovich equation is another rate equation in which the absorbing surface is heterogeneous. It is generally expressed as:

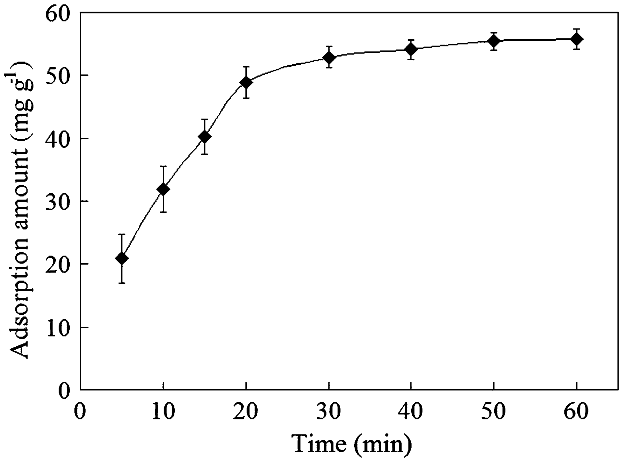

Fig. 6. Effect of contact time on the adsorption equilibrium for Pb(II) ions.

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{7}$$

where α is the initial adsorption rate of Elovich equation ($\text{mg g}^{-1}\text{min}^{-1}$) and β is related to the extent of surface coverage and activation energy for chemisorption. Integrating this equation for the boundary conditions, Eq. (7) becomes

$$q_t = (1/\beta)\ \ln(\alpha\beta) + (1/\beta)\ \ln t \tag{8}$$

A plot of q_t vs. ln t gives a linear trace with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ ln($\alpha\beta$) (as shown in Fig. 7(c)).

Another simplified model, the intraparticle diffusion model, has been tested to better identify the diffusion mechanism involved. The intraparticle diffusion model is expressed as:

$$q_t = k_p t^{0.5} + C_p \tag{9}$$

where k_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1}\text{min}^{-0.5}$) and is calculated by the slope of straight-line portion of plotting q_t vs. $t^{0.5}$ (as shown in Fig. 7(d)). C_p, the intercept of stage i, gives an idea about the thickness of boundary layer, i.e. the larger the intercept, the greater the boundary layer effect [38].

The parameters of four kinetic models are given in Table 1. The coefficient of correlation (r^2) of pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models for Pb(II) ions were 0.8364, 0.9942, 0.9413, and 0.8477, respectively. The r^2 of pseudo-second-order kinetic model at 298.15 K was almost equal to 1, much higher than the correlation coefficients derived from pseudo-first-order, Elovich and intraparticle diffusion fits. The estimated values of q_e derived from Eq. (6) also agreed with the experimental values. Both factors suggested that the adsorption of metal ions followed the pseudo-second-order kinetic

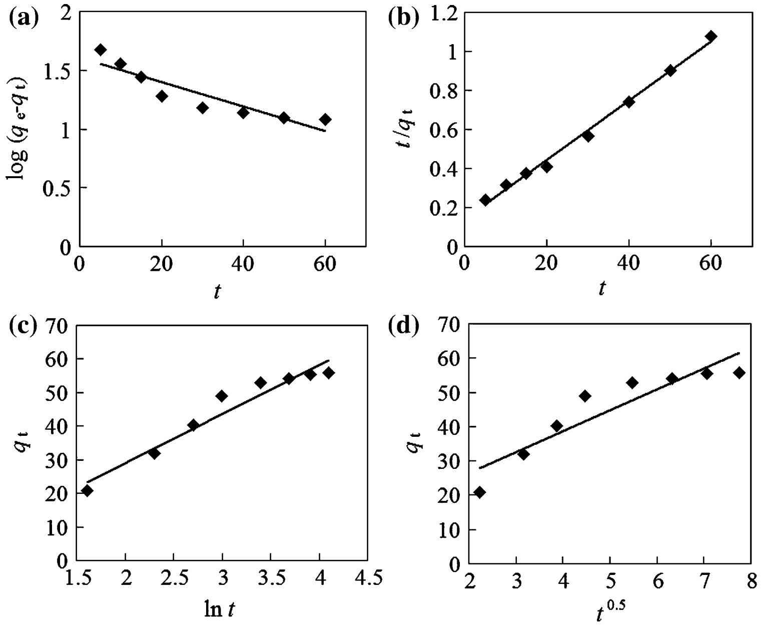

Fig. 7. The plots of pseudo-first-order (a), pseudo-second-order (b), Elovich (c) intra-particle diffusion, and (d) models for the adsorption of Pb(II) ions onto Pb(II)-imprinted PEI-functionalized silica sorbent.

Table 1
Calculated kinetic parameters for the adsorption of Pb(II) onto Pb(II)-imprinted PEI-functionalized silica sorbents

Pseudo-first-order model	Pseudo-second-order model	Elovich model	Intraparticle diffusion model
$k_1 = 0.024$ min^{-1}	$k_2 = 1.64 \times 10^{-3}$ g mg^{-1} min^{-1}	$\alpha = 14.24$ mg g^{-1} min^{-1}	$k_p = 6.11$ mg g^{-1} min$^{-0.5}$
q_{eq} (cal) = 40.3 mg g^{-1}	q_{eq} (cal) = 65.8 mg g^{-1}	$\beta = 0.0692$ g^{-1} mg	
$r^2 = 0.8364$	$r^2 = 0.9942$	$r^2 = 0.9431$	$r^2 = 0.8477$

model, indicating that the rate-limiting step was a chemical adsorption process between Pb(II) ions and the imprinted PEI-functionalized silica sorbents.

3.5. Adsorption capacity and adsorption isotherms

The adsorption capacity is an important factor to evaluate the imprinted PEI-functionalized silica sorbent. Fig. 8 shows the initial concentrations of the Pb(II) ions dependence of the adsorption amounts of Pb(II) ions onto the imprinted PEI-functionalized silica and non-imprinted PEI-functionalized silica sorbents. The values of adsorption amount firstly increased with increasing the initial concentrations of Pb(II) ions in the range from 100 to 500 mg L^{-1}, and then the adsorption amount reached a plateau at the initial Pb(II) ions ion concentration in the range from 500 to 800 mg L^{-1}. The experimental values of maximum static adsorption capacities of the imprinted PEI-functionalized silica and non-imprinted PEI-functionalized silica sorbents were 60.4 and 45.2 mg g^{-1}, respectively. The maximum static adsorption capacity of the imprinted PEI-functionalized silica sorbent for Pb(II) was as much as 1.34 times that of non-imprinted one. It indicated that ion-imprinting technique played an important role in the adsorption behavior. During the preparation of the imprinted sorbent, the presence of Pb(II) made the ligands arrangement ordered. After the removal of Pb(II), the imprinted cavity and specific binding sites of functional groups in a predetermined orientation were formed, whereas the non-imprinted sorbent do not exhibit such specificity. Although the direct comparison of the imprinted sorbent obtained with the other sorbents was difficult, owing to the different experimental conditions, it had been seen that the imprinted PEI-functionalized silica sorbent had a relatively high adsorption capacity for Pb(II) in comparison with the other Pb(II)-imprinted sorbents previously reported in the literatures (shown in Table 2) [11,22,39–45], except for Pb(II)-imprinted silica functionalized with amino groups [43]. The adsorption rate of Pb(II) ions on the Pb(II)-imprinted PEI-functionalized silica sorbent obtained was faster with many other sorbents listed in Table 2, except for magnetic imprinted sorbent functionalized with thiol groups [45].

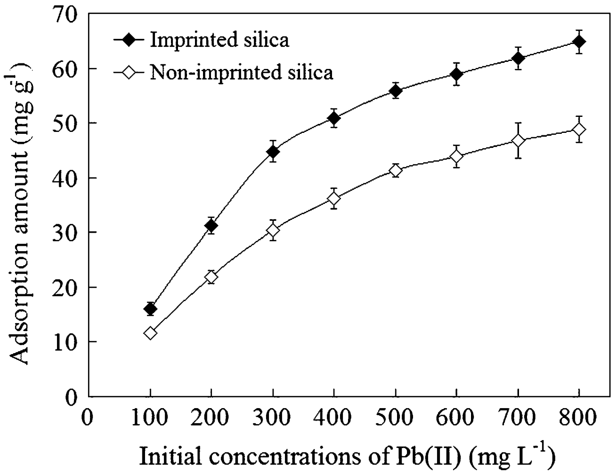

Fig. 8. Adsorption capacities of Pb(II)-imprinted PEI-functionalized and non-imprinted silica sorbent for Pb(II) ions.

Different models of adsorption, such as Langmuir [46], Freundlich [47] and Dubinin–Radushkevich [48] isotherms, were used to describe the adsorption data, to calculate the corresponding constants and to predict the theoretical capacities of Pb(II) on the surface of the imprinted PEI-functionalized silica sorbents.

The Langmuir adsorption isotherm is the best known of all isotherms describing adsorption, is often used to describe adsorption of a solute from a liquid solution, and can be described in a linear expression as the Eq.(10) [46].

$$C_e/q_e = 1/(q_{\max}\, b) + C_e/q_{\max} \tag{10}$$

where q_e is the equilibrium amount of adsorbed metals in the sorbent (mg g^{-1}), C_e is the equilibrium ion concentration in solution (mg L^{-1}), b is the Langmuir isotherm constant related to the free energy of adsorption (L mg^{-1}), and $q_{\max}$ is the calculated values of maximum adsorption capacity for a monolayer coverage (mg g^{-1}).

The Freundlich expression is an exponential equation that describes reversible adsorption and is not restricted to the formation of the monolayer [47]. The

Table 2
Adsorption results of Pb(II) ions from the literature by various imprinted sorbents

Sorbents	Imprinted methods	Contact time (min)	Capacity (mg/g)	Ref.
IIPs with dual functional monomers	Suspension polymerization	80	8.4	[11]
Magnetic IIPs functionalized with amino groups	Surface imprinting	25	19.6	[22]
IIPs functionalized with 3-(trimethoxysilyl) propylmethacrylate	Bulk polymerization	60	3.5	[39]
Metal-imprinted chitosan	Precipitation polymerization	180	30.5	[40]
Ion-imprinted mesoporous sorbent	Surface imprinting	50	36.6	[41]
IIPs functionalized with N-methacryloyl-(L)-cysteine	Bulk polymerization	30	2.0	[42]
Pb(II)-imprinted silica functionalized with amino groups	Surface imprinting	30	61.9	[43]
Ion-imprinted crown ether	Free-radical polymerization	60	28.0	[44]
Magnetic IIPs functionalized with thiol groups	Surface imprinting	10	32.6	[45]
Pb(II)-imprinted silica functionalized with PEI	Surface imprinting	20	60.4	This study

linear form equation of Freundlich adsorption isotherm can be represented by Eq. (11)

$$\log\ q_e = \log K_F + (1/n)\ \log\ C_e \tag{11}$$

where K_F and n are the Freundlich constants.

The Dubinin–Radushkevich isotherm is more general because it does not assume a homogenous surface or constant adsorption potential [48]. The linear form can be represented as:

$$\ln\ q_e = \ln\ q_s - k_{ad}\varepsilon^2 \tag{12}$$

where k_{ad} is the Dubinin–Radushkevich isotherm constant ($\text{mol}^2\,\text{kJ}^{-2}$); q_s is the theoretical isotherm saturation capacity (mg g^{-1}); ε is the Polanyi potential and calculated as follows:

$$\varepsilon = RT\ \ln\ (1 + 1/C_{eq}) \tag{13}$$

where R is universal gas constant ($8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$); T is temperature (K). C_{eq} is the concentration of Pb(II) in equilibrium solution (mol L^{-1}). The experimental isotherm data of Langmuir, Freundlich and Dubinin–Radushkevich isotherms equations had been analyzed separately by linear methods from the plots of C_e/q_e vs. C_e, log q_e vs. log C_e, and ln q_e vs. ε^2, respectively. The values of the Langmuir, Freundlich and Dubinin–Radushkevich constants are presented in Table 3.

Among the available models for adsorption data analysis, it was concluded that the Langmuir isotherm model was slight better than Fruendlich and Dubinin–Radushkevich isotherms to fit Pb(II) adsorption data well according to the values of correlation coefficients (r^2). There was no significant difference between the calculated ($74.1\ \text{mg g}^{-1}$) and experimental values ($60.4\ \text{mg g}^{-1}$) of saturation adsorption capacity. The results indicated that Fruendlich and Dubinin–Radushkevich isotherms could not be used for explaining the equilibrium relationship of Pb(II) with the imprinted PEI-functionalized silica sorbents, and the experimental equilibrium data were found to be fitted well with the Langmuir isotherm model which showed the monomolecular adsorption of Pb(II) onto the imprinted PEI-functionalized silica sorbents.

Table 3
Isotherms parameters for the adsorption of Pb(II) on Pb(II)-imprinted PEI-functionalized silica sorbents

Langmuir adsorption isotherm	Freundlich adsorption isotherm	Dubinin–Radushkevich isotherm
$q_{max} = 74.1\ \text{mg g}^{-1}$	$K_F = 6.16$	$k_{ad} = 0.0043\ \text{mol}^2\,\text{kJ}^{-2}$
$b = 0.016\ \text{L mg}^{-1}$	$n = 2.47$	$q_s = 187.8\ \text{mg g}^{-1}$
$r^2 = 0.9980$	$r^2 = 0.9049$	$r^2 = 0.9267$

3.6. Selectivity

Competitive adsorption of the imprinted PEI-functionalized silica sorbents for Pb(II) was investigated in the double mixture system of Pb(II)/Cd(II), Pb(II)/Cu (II), Pb(II)/Ni(II), and Pb(II)/Zn(II) under the optimal conditions. The distribution ratios (K_d), selectivity coefficients (k), and relative selectivity coefficients (k') of Pb(II) with respect to Cd(II), Cu(III), Zn(II), and Ni(II) using the imprinted and non-imprinted sorbents are shown in Table 4. It could be observed that the distribution ratio of the imprinted PEI-functionalized silica sorbents for Pb(II) was two times greater than that of non-imprinted silica sorbents because there were more specific cavities on the imprinted sorbent than that of non-imprinted silica sorbents, indicating that the imprinted PEI-functionalized silica sorbents were more suitable for Pb(II) ions. The relative selectivity coefficient values for Pb(II)/Cd(II), Pb(II)/Ni(II), Pb (II)/Cu(II), and Pb(II)/Zn(II) systems are 8.1, 7.8, 6.6, and 9.7, respectively. Therefore, the competitive adsorption of the imprinted PEI-functionalized silica sorbents for Pb(II) ions was apparent from the mixture solutions of Pb(II)/Cd(II), Pb(II)/Cu(II), Pb(II)/Ni(II), and Pb(II)/Zn(II). The results indicated that the imprinted PEI-functionalized silica sorbents had higher selectivity for Pb(II) even in the presence of Cd (II), Cu(II), Ni(II), and Zn(II) interferences in the same medium due to the coordination-geometry selectivity of the imprinted PEI-functionalized silica sorbents which could provide the ligand groups arranged in a suitable way required for coordination of Pb(II) ion [49].

3.7. Thermodynamic study

Based on fundamental thermodynamics concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The thermodynamic parameters can be determined from the thermodynamic equilibrium constant, K_0. The standard Gibbs free energy ΔG° (kJ mol^{-1}), standard enthalpy change ΔH° (kJ mol^{-1}), and standard entropy change ΔS° (J mol^{-1} K^{-1}) are calculated using the following equations:

Table 4
The selectivity parameters of Pb(II)-imprinted PEI-functionalized silica sorbents for Pb(II)

Metals	Sorbent	K_d (Pb)	K_d (X)	k	k'
Pb(II)/Cd (II)	IIP	7,680	1,830	4.197	8.1
	NIP	3,205	6,180	0.519	
Pb(II)/Ni(II)	IIP	7,490	1,680	4.458	7.8
	NIP	3,470	6,050	0.574	
Pb(II)/Cu(II)	IIP	7,890	2,480	3.181	6.6
	NIP	3,290	6,790	0.485	
Pb(II)/Zn(II)	IIP	7,350	1,870	3.930	9.7
	NIP	2,650	6,530	0.406	

$$\Delta G^\circ = -RT \ln K_0 \tag{14}$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{15}$$

R, the universal gas constant, 8.314 J mol^{-1} K^{-1}, and T is the solute temperature (K). K_0 can be defined as [50]:

$$K_0 = \frac{a_s}{a_e} = \frac{\gamma_s}{\gamma_e}\frac{C_s}{C_e} \tag{16}$$

where a_s is the activity of adsorbed metals, a_e is the activity of metals in solution at equilibrium, γ_s is the activity coefficient of adsorbed metals, γ_e is the activity coefficient of metals in equilibrium solution, C_s is the metals adsorbed on the imprinted PEI-functionalized silica sorbents (mol g^{-1}), and C_e is the metals concentration in equilibrium solution (mol L^{-1}). The expression of K_0 can be simplified by assuming that the concentration in the solution approaches zero resulting in $C_s \rightarrow 0$ and $C_e \rightarrow 0$ and the activity coefficients approach unity at the every low concentration [51]. Eq. (16) can be written as:

$$C_s \overset{\lim}{\longrightarrow} 0 \frac{C_s}{C_e} = \frac{a_s}{a_e} = K_0 \tag{17}$$

K_0 at different temperatures was determined by plotting ln (C_s/C_e) vs. C_s and extrapolating C_s to zero. The straight line obtained was fitted to the points by least-squares analysis. Based on Eqs. (14) and (15), the values of ΔH° and ΔS° were calculated from the slope and intercept of linear plot of ln K_0 vs. $1/T$, respectively.

Table 5 presents the thermodynamic parameters. ΔH° and ΔS° were found to be 18.26 kJ mol^{-1} and 82.09 J mol^{-1} K^{-1}, respectively. The Gibbs free energy was calculated from Eq. (14), setting the temperature at 298.15, 308.15, and 318.15 K, and corresponded to the value of −6.20, −7.09, and −7.84 kJ mol^{-1}, respectively. The negative ΔG° value indicated that adsorption of Pb(II) ions onto imprinted PEI-functionalized

Table 5
Values of various thermodynamic parameters for adsorption of Pb(II) on Pb(II)-imprinted PEI-functionalized silica sorbents

	Temperature (K)		
Thermodynamic constants	298.15	308.15	318.15
K_0	26.98	29.71	33.55
ΔG° (kJ mol^{-1})	−6.20	−7.09	−7.84
ΔH° (kJ mol^{-1})	18.26		
ΔS° (J mol^{-1} K^{-1})	82.09		

silica sorbents was a thermodynamically feasible and spontaneous process. The increase in values of ΔG° with an increase in temperature showed an increased feasibility of adsorption at higher temperature. In our study, the positive values of ΔH° confirmed the endothermic nature of the process. A positive ΔS° value indicated the increase of randomness due to the release of water molecules in the absorption reaction between the Pb(II) ions and the functional groups on the surfaces of the imprinted PEI-functionalized silica sorbents [52].

3.8. Desorption and regeneration

Regeneration allows for the repeated use of the sorbent and is one of key factors for decreasing costs [52]. In our work, the same sample of the sorbent was used for the five cycles of adsorption–desorption were tried in order to regenerate the sorbent. 1 mol L^{-1} HCl solution was used to be a relatively effective fluent for desorption of Pb(II) ions from the imprinted PEI-functionalized silica sorbents with 98% of desorption ratio. After the fifth adsorption/desorption cycle, the adsorption capacity of Pb(II) ions decreased slightly from 52.8 to 43.2 mg g^{-1} with increasing the reuse cycles and were found to about 80% of the fresh sorbent. The result indicated that the imprinted PEI-functionalized silica sorbents owned good regeneration ability.

3.9. Application

The removal rates of imprinted sorbent for Pb(II) ions from mutli-competitive synthetic wastewater spiked with 10, 20, and 40 mg L^{-1} Pb(II) ions were 72.3, 68.9, and 70.8%, respectively. The average removal rate of the imprinted PEI-functionalized silica sorbent for As(V) was about 70%. Compared with the removal rates of Pb(II), the removal rates of other heavy metal ions by the imprinted sorbent were very low (Fig. 9). The results indicated that the imprinted sorbent could effectively and selectively remove Pb(II) ions from aqueous solution.

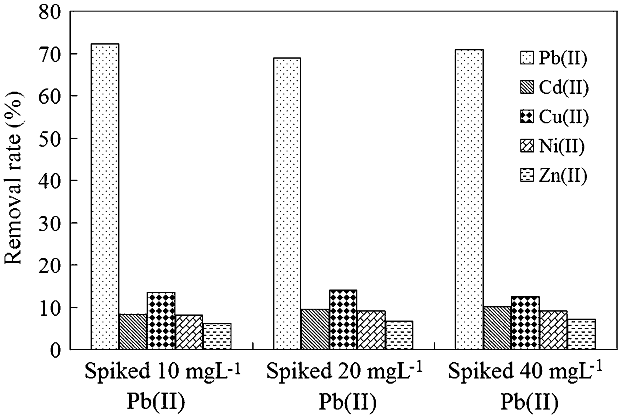

Fig. 9. Selective removal of Pb(II) ions by Pb(II)-imprinted PEI-functionalized silica sorbent from aqueous solution.

4. Conclusion

A novel Pb(II)-imprinted PEI-functionalized silica sorbent was successfully prepared with hydrothermal-assisted surface imprinting. The prepared Pb(II)-imprinted PEI-functionalized silica sorbent exhibits good characteristics, such as fast adsorption kinetics, high adsorption capacity, satisfactory selectivity toward Pb(II) and obvious regenerative capacity. The adsorption of Pb(II) ions onto Pb(II)-imprinted PEI-functionalized silica sorbent fitted well with the Langmuir isotherm model and the adsorption kinetics followed the pseudo-second-order model. The thermodynamic results showed that the adsorption of Pb(II) ions onto Pb(II)-imprinted PEI-functionalized silica sorbent took place as a spontaneous and endothermic nature, accompanied by increase of the degree of freedom the solid–solution interface. Pb(II)-imprinted PEI-functionalized silica sorbent can be used as one of the effective sorbents for the selective adsorption of Pb(II) ions from aqueous media.

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