Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 2288–2297

polymer

www.elsevier.com/locate/polymer

Novel surface ionic imprinting materials prepared via couple grafting of polymer and ionic imprinting on surfaces of silica gel particles

Baojiao Gao*, Fuqiang An, Yong Zhu

Department of Chemical Engineering, North University of China, Taiyuan, Shanxi 030051, People's Republic of China

Received 3 September 2006; received in revised form 15 December 2006; accepted 22 December 2006

Available online 4 January 2007

Abstract

In this paper, a new surface molecular imprinting technique is put forward, and a kind of novel ion-imprinted polymers (IIPs) were prepared through a new approach: firstly functional macromolecule polyethyleneimine (PEI) was grafted onto the surfaces of silica gel particles via the coupling grafting method ("grafting to" method) and the composite material PEI/SiO_2 with chemical linking was formed; secondly the ionic imprinting was carried out towards the macromolecule PEI grafted on the surface of silica particles using Cu^{2+} or Cd^{2+} ion as a template, epichlorohydrin (ECH) as a crosslinking agent and by coordination linkage actions, and Cu^{2+} ion (or Cd^{2+} ion)-imprinted material IIP-PEI/SiO_2 was prepared. The binding characteristics of IIP-PEI/SiO_2 for Cu^{2+} ion (or Cd^{2+} ion) were studied in detail by adopting both static and dynamic methods. The experimental results show that the ion-imprinting material IIP-PEI/SiO_2 has specific recognition ability for the template ions, and this character displays mainly in two aspects: (1) it has high affinity for the template ions, its binding amounts for the template ions are much greater than that of the non-imprinted composite material PEI/SiO_2, and the adsorption capacity enhances nearly two times compared to PEI/SiO_2; (2) it has excellent selectivity for the template ions, for the IIP-PEI/SiO_2 by using Cu^{2+} as template ion, its selectivity coefficients relative to Zn^{2+} and Ni^{2+} are 80.21 and 86.08, respectively, and for the IIP-PEI/SiO_2 by using Cd^{2+} as template ion, its selectivity coefficients relative to Cr^{3+} and Pb^{2+} are 77.05 and 88.22, respectively. Besides, the imprinting material IIP-PEI/SiO_2 has a fine elution property using HCl solution as eluent. The obtained imprinting material by using the new surface molecular imprinting techniques possesses superexcellent binding property for template molecules or ions because of the distribution of imprinted cavities in a thin polymer layer and smaller diffusion barrier.

Keywords: Polyethyleneimine; Silica gel; Surface imprinting technique

1. Introduction

Molecular imprinting is a powerful technique for preparing polymeric materials with artificial receptor-like binding sites for various substances [1–4], and the polymers prepared with this technique, molecular imprinted polymers (MIPs), have been utilized as materials of molecular recognition in many scientific and technical fields, such as solid-phase extraction, chromatograph separation, membrane separations, sensors, drug releases, catalysts, etc. [5–11]. The conventional method to prepare molecular imprinted polymers (MIPs) is a entrapment way, and the process is generally as follows. In the first step, the functional monomers are assembled around the template through either non-covalent or covalent interactions. Following this pre-assembly step, the monomer–template complex and crosslinker are copolymerized (with bulk or solution polymerization method). After polymerization is complete, the template molecules are removed, molecular cavities remain in the polymer, which are complementary to the template in size, shape and spatial arrangement of functional groups. Finally, the obtained monoliths are ground and sieved to the required particle dimensions. The preparing process of ion-imprinted polymers (IIPs) is similar to that of molecular imprinted polymers, only by using ion as template. The molecular imprinted polymers prepared with conventional

---

* Corresponding author. Tel.: +86 351 3921414; fax: +86 351 3922118. *E-mail address:* gaobaojiao@sohu.com (B. Gao).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.12.041

methods have some disadvantages: (1) the imprinted polymer matrices are usually thick, and the number of recognition sites per unit volume of the polymer is relatively low [12]; (2) the template molecules are embedded in the matrices too deeply, so that not only the elution is difficult, but also the diffusion barrier for the template molecules is introduced [12,13], the rate of mass transfer is lower, and the template molecules are not easy to bind with recognition sites. In order to overcome these drawbacks effectively, the surface molecular printing technique has been developed in recent years [13–17]. The surface printing technique can be divided basically into two kinds: (1) the surface printing technique based on the emulsion and precipitation polymerization [13–15]; (2) the surface printing technique based on the surface modification of silica gel particles [16,17]. For the latter method, there are also several technologies, and among them, grafting polymerization method on the surfaces of silica gel particle is received some attention. Sulitzky et al. [18] grafted thin films of molecularly imprinted polymers on silica gel particle surfaces by utilizing ‘‘grafting from’’ method. The distribution of the imprinted cavities in the thin polymer layer on silica gel particles is of great advantage to the fast binding of the template molecules with the recognition sites.

In this paper, we developed an advanced surface molecular imprinting technique on the surface of silica gel particles: firstly functional macromolecule polyethyleneimine (PEI) was grafted on the silica gel particle surfaces via coupling grafting method; secondly ion printing was preformed using heavy-metal ion, Cd^{2+} or Cu^{2+}, as a template, which has been coordinated with PEI, and epichlorohydrin as crosslinking agent; finally ion-imprinted composite material IIP-PEI/SiO_2 was formed. The binding characteristics of IIP-PEI/SiO_2 for Cd^{2+} or Cu^{2+} were studied profoundly with both static and dynamic methods.

Polyethyleneimine (PEI) is a typical water-soluble polyamine, and there is a large quantity of nitrogen atoms of amino groups on the macromolecular chains, so it can produce very strong chelation towards heavy-metal ions [19–21], and the character of PEI has been widely applied in adsorption separation fields of heavy-metal ions. For example, some researchers coat PEI on the surfaces of ion exchange resins or silica gel particles to remove heavy-metal ions from water medium [21–23]. In our previous study, the chemical structure of adsorption material for heavy-metal ions was well designed, PEI was grafted onto the surface of silica gel particles via the coupling effect of γ-chloropropyl trimethoxysilane (CP), the strong chelation of PEI towards heavy-metal ions was combined with the high specific area and fine mechanical property of silica gel, and the novel composite chelating adsorption material PEI/SiO_2 was prepared [24]. The research result showed that this composite material possessed excellent adsorption property for Cd^{2+}, Cu^{2+}, Cr^{3+}, etc. Thereby, it is a promising route for preparing functional particles of composite type to graft functional polymer on the surface of inorganic particles. Based on the previous study, in the present work, the route to prepare functional composite materials is developed further. Many heavy-metal ions are toxic and are hazardous to human health, so for their removal from wastewater much attention needs to be paid. In this paper, heavy-metal ion imprinting of PEI was carried out on the surface of silica gel surfaces, and ion-imprinted polyethyleneimine was prepared using Cu^{2+}–PEI/SiO_2 and Cd^{2+}–PEI/SiO_2 as model systems. To our knowledge, this is the first report on the new surface molecular imprinting technique.

2. Experimental section

2.1. Material and equipment

Silica (120–160 mesh, about 125 μm in diameter, Ocean Chemical Limited Company, Qingdao, China) was received; γ-chloropropyl trimethoxysilane (Yongchang Chemical Limited Company, Naking, China) was of analytical grade, and polyethyleneimine ($M_w = 2 \times 10^4$–5×10^4, Qianglong Chemical Limited Company, Wuhan, China) was of chemical grade. Epichlorohydrin (ECH, Beijing Chemical Plant) was received. Analytical grade of several kinds of heavy-metal salts were received, and were purchased from Chinese companies.

The instruments used in this study were as follows: Unic-2602 UV spectrophotometer (Unic Company, Shanghai), Perkin–Elmer 1700 infrared spectrometer (Perkin–Elmer Company, USA), DDS-11Ar digit conductivity meter (Leici Instrument Limited Company, Shanghai), PHS-2 acidimeter (The Second Analytical Instrument Factory, Shanghai), TG16-WS high-speed centrifuge with desk type (Changsha Xiangyi Centrifuge Factory, China), and THZ-92C constant temperature shaker equipped with gas bath (Boxun Medical Treatment Equipment Factory, Shanghai).

2.2. Measuring coordination action between PEI and heavy-metal ions and determining structures of chelates

2.2.1. Conductometric titration

A certain amount of PEI dried to constant weight was weighed, dissolved in water, the solution was transferred into a measuring flask, diluted to index mark with distilled water, and PEI solution with a molarity (monomeric unit molarity) of 15.74 mM was obtained. Six kinds of heavy-metal ion solutions, Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+} and Pb^{2+} solutions, with a molarity of 15.74 mM were prepared with the corresponding inorganic salts. Five milliliters of these solutions were taken in conical flasks using pipettes, respectively, and the pH values of these solutions were adjusted to 6 with buffer solution. These ionic solutions were titrated with PEI solution, respectively, the conductivity changes of these solutions during titration were recorded with a digit conductivity meter, and at the same time, the volumes of consumed PEI solution were noted.

2.2.2. Absorption spectroscopy

For PEI–Cu^{2+} system, 10 mL of PEI solution of 15.74 mM was taken in several measuring flasks, different volumes of Cu^{2+} solution of 15.74 mM were added into these flasks, respectively, and these mixed solutions were diluted to index mark with distilled water. The absorption spectra of these solutions in the wavelength region of 550−650 nm were determined with a spectrophotometer.

For PEI−Cr^{3+} system, 5 mL of Cr^{3+} solution of 15.74 mM was taken in several measuring flasks (aquated ion Cr^{3+} appears brown), different volumes of PEI solution of 15.74 mM were added into these flasks, respectively, and damask water-insoluble substance was produced, and these mixtures were diluted to index mark with distilled water. These mixtures were centrifuged, and the absorption spectra of supernatants (actually they are the absorption spectra of the residuary aquated ion Cr^{3+}) in the wavelength region of 490−660 nm were determined.

2.3. Synthesizing and characterizing composite material PEI/SiO_2

The composite material PEI/SiO_2 was prepared according to the steps described in Ref. [24], and a typical preparing process is as follows. Firstly silica gel particles were treated for activating by using aqueous solution of methane sulfonic acid as an activation reagent. Secondly activated silica gel was reacted with γ-chloropropyl trimethoxysilane (CP) at 80 °C by using xylene as a solvent into which a little water was added, and chloropropylation silica (CP-SiO_2) was prepared. Finally CP-SiO_2 was added into PEI aqueous solution with a certain concentration, reaction was carried out at 90 °C for 6 h, PEI was grafted onto silica gel surface in a coupling manner, and the composite adsorption particles of PEI/SiO_2 were prepared. The chemical structure of PEI/SiO_2 was characterized by infrared spectrum. The amount of amino groups on PEI/SiO_2 was determined with conductivity titration method by using hydrochloric acid as titrant, and PEI amount (g/100 g) of grafting was calculated further.

2.4. Preparing and characterizing ion-imprinted material IIP-PEI/SiO_2

In this work, two kinds of ion-imprinted material IIP-PEI/SiO_2 were prepared using Cu^{2+} and Cd^{2+} as template ions, respectively, and the preparing procedure will be mainly described using Cu^{2+} system as an example.

Five grams of PEI/SiO_2 composite particles with a PEI-grafting amount of 3.21 g/100 g was mixed with a certain amount of Cu^{2+} solution with a concentration of 100 mg L^{-1}, the pH value of the medium was adjusted to 6 with NaAc−HAc buffer solution, and the mixture was shaken on a constant temperature shaker for a certain period of time until the PEI grafted on silica gel particles was fully swelled and the chelation adsorption reached equilibrium. After filtrating, the PEI/SiO_2 particles, which had adsorbed Cu^{2+} in a saturation state, were washed repeatedly with water until Cu^{2+} could not be detected in the filtrate, and dried in a vacuum oven. A certain amount of PEI/SiO_2 particles adsorbing Cu^{2+} was added into absolute ethanol, a certain amount of ECH was also added, this solution was stirred magnetically, and the reaction was allowed to carry out for 30 min at room temperature. Afterward, sodium hydroxide was added, the reaction continued for 30 min at room temperature with continuous stirring. Final particles were fully washed with hydrochloric acid solution of 0.1 M to remove the template ions (i.e., Cu^{2+}), and after filtrating the Cu^{2+}-imprinted material IIP-PEI/SiO_2 (denoted as (Cu^{2+}) IIP-PEI/SiO_2) was obtained. The infrared spectrum of IIP-PEI/SiO_2 was determined in order to confirm the chemical structure change of PEI/SiO_2 after ion imprinting.

Cd^{2+}-imprinted material IIP-PEI/SiO_2 (denoted as (Cd^{2+}) IIP-PEI/SiO_2) was prepared with the same procedures as above described, and only difference was that the pH of the mixture of PEI/SiO_2 and Cd^{2+} solution was adjusted to 7 with NaAc−HAc buffer solution.

2.5. Measuring the binding property of IIP-PEI/SiO_2 towards template ions with static method

2.5.1. Measuring binding kinetic curve of adsorption

One hundred milliliters of Cu^{2+} solution of 100 mg L^{-1} was taken and transferred into conical flasks with a plug, 0.1328 g of (Cu^{2+}) IIP-PEI/SiO_2 particles was added, and the content was shaken on a constant temperature shaker. After an interval of time, the mixture was taken out and centrifuged, and the Cu^{2+} concentration in the supernatant was determined with spectrophotometry. The binding amount of (Cu^{2+}) IIP-PEI/SiO_2 towards Cu^{2+} ions was calculated by Eq. (1), the curve of the binding amount vs. time was plotted, the binding rate of (Cu^{2+}) IIP-PEI/SiO_2 towards Cu^{2+} was examined, and the time in which the adsorption reached to equilibrium was determined.

$$Q = \frac{V(C_0 - C_t)}{m} \tag{1}$$

where C_0 (mg L^{-1}) is the initial concentration of Cu^{2+} (without absorbent) and C_t is the concentration of Cu^{2+} at the time of t; V (L) is the volume of the Cu^{2+} solution; m is the mass of the absorbent IIP-PEI/SiO_2; Q (mg g^{-1}) is the binding amount of Cu^{2+} ions on IIP-PEI/SiO_2.

Similarly, the adsorption kinetic curve of (Cd^{2+}) IIP-PEI/SiO_2 towards Cd^{2+} was measured.

2.5.2. Measuring binding isotherm

Cu^{2+} solutions with same volume but different concentrations were taken and transferred into conical flasks; the pH value of each solution was adjusted to 6 and (Cu^{2+}) IIP-PEI/SiO_2 particles with same mass were added into these solutions. These mixtures were shaken on a shaker, centrifuged after reaching equilibrium, and these equilibrium concentrations of Cu^{2+} in the supernatants were determined with spectrophotometry. The equilibrium binding amounts of (Cu^{2+}) IIP-PEI/SiO_2 towards Cu^{2+} ions were calculated according to Eq. (2), and the binding isotherm was plotted.

$$Q_e = \frac{V(C_0 - C_e)}{m} \tag{2}$$

where C_0 (mg L^{-1}) is the initial concentration of Cu^{2+} (without absorbent) and C_e is the equilibrium concentration of Cu^{2+};

V (L) is the volume of the Cu^{2+} solution; m is the mass of the absorbent (Cu^{2+}) IIP-PEI/SiO_2; Q_e (mg g^{-1}) is the equilibrium binding quantity of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+} ions.

Similarly, binding isotherm of (Cd^{2+}) IIP-PEI/SiO_2 for Cd^{2+} ion was measured using the similar procedures of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+}, except that the pH value of absorption medium was adjusted to 6.

2.5.3. Selectivity experiments

In order to show the specificity of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+}, competitive adsorptions of Zn^{2+} and Ni^{2+} with respect to Cu^{2+} were also studied. The binary mixed solutions of Zn^{2+}/Cu^{2+} and Ni^{2+}/Cu^{2+} were prepared, and in these mixed solutions the concentration of Cu^{2+} was the same as other two ions. The static adsorption experiments were performed for the two mixed solutions, after adsorption equilibrium was reached and the concentrations of Cu^{2+}, Zn^{2+} and Ni^{2+} in the remaining solutions were determined with spectrophotometry.

Distribution coefficients of Cu^{2+}, Zn^{2+} and Ni^{2+} were calculated by Eq. (3), and this equation was derived from the equation of Ref. [25].

$$K_d = \frac{Q_e}{C_e} \tag{3}$$

where K_d represents the distribution coefficient (L/g); Q_e (mg g^{-1}) is the equilibrium binding quantity; C_e (mg L^{-1}) is the equilibrium concentration.

The selectivity coefficient of (Cu^{2+}) IIP-PEI/SiO_2 for the binding of Cu^{2+} ion with respect to the competitor species (assigned as B) can be obtained from the equilibrium binding data according to Eq. (4).

$$k = \frac{K_d(Cu^{2+})}{K_d(B)} \tag{4}$$

where k is the selectivity coefficient and B represents the Zn^{2+}or Ni^{2+}. The value of k allows an estimation of selectivity of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+} ions. A relative selectivity coefficient k' can be defined as expressed in Eq. (5) [25], and the value of k' can indicate the enhanced extent of adsorption affinity and selectivity of imprinting material for the template with respect to non-imprinting material.

$$k' = \frac{k_{\text{impr}}}{k_{\text{non-impr}}} \tag{5}$$

Similarly, in order to show Cd^{2+} specificity of (Cd^{2+}) IIP-PEI/SiO_2 for Cd^{2+}, the binary mixed solutions of Cr^{3+}/Cd^{2+} and Pb^{2+}/Cd^{2+} were prepared, the competitive adsorptions of Cr^{3+} and Pb^{2+} with respect to Cd^{2+} were also studied, and various data were also obtained.

2.6. Measuring the binding property of IIP-PEI/SiO_2 towards template ions with dynamic method

1.3376 g of (Cu^{2+}) IIP-PEI/SiO_2 was packed in a piece of glass pipe with an internal diameter of 0.8 cm, and the bed volume (BV) of the packed column was 2 mL. At room temperature, Cu^{2+} solution with a concentration of 1000 mg L^{-1} was allowed to flow gradually through the column at a rate of five bed volumes per hour (5 BV/h) in a countercurrent manner. The effluent with a certain volume (BV) interval was collected, the concentration of Cu^{2+} ion was determined with spectrophotometry, the dynamics binding curve was measured, and the leaking adsorption amount and the saturated adsorption amount of (Cu^{2+}) IIP-PEI/SiO_2 towards Cu^{2+} ions were also calculated.

3. Results and discussion

3.1. Coordination process between PEI and heavy-metal ions and structures of chelates

According to the steps described in Section 2.2.1, 5 mL of the solutions of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+} and Cr^{3+} with the same concentrations with PEI solution were titrated by using PEI solution, respectively, and the conductivities as a function of the consumed volumes of PEI solution during titration process are shown in Fig. 1. The following facts can be seen clearly: (1) during the titration process the conductivity decreases with the consuming of PEI solution in each system because of chelation of PEI towards metal ions; (2) for those solutions of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+}, clear-cut breaks appear on various curves as the consumed volume of PEI solution reaches to 20 mL; (3) for the solution of Cr^{3+}, a clear inflection point appears as the consumed volume of PEI solution reaches to 30 mL. These facts reveal that the coordination of PEI with these heavy-metal ions has occurred, the stoichiometric amounts of the reaction between PEI and Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} are all in the ratio of 4:1, and the chelates with four ligands have been formed; whereas for the reaction between PEI and Cr^{3+}, the stoichiometric amounts ratio is equal to 6:1, and the chelates with six ligands have been formed.

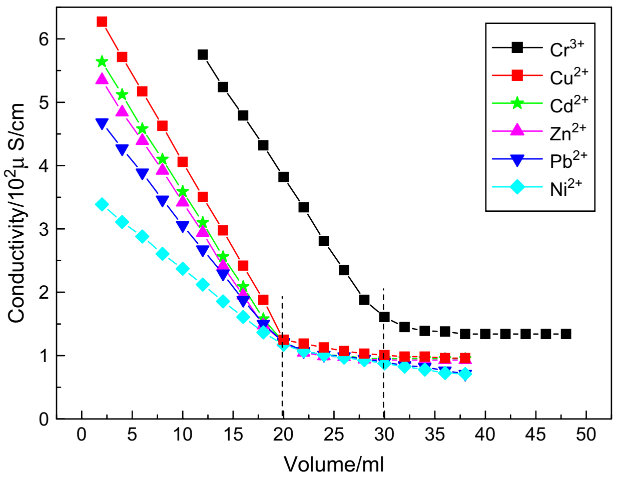

Fig. 1. Curves of conductometric titration of PEI solution towards various heavy-metal ion solutions.

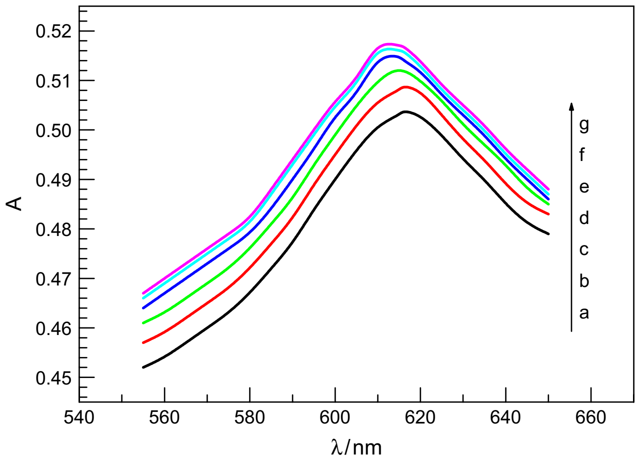

Fig. 2. Absorption spectrum variation of PEI–Cu^{2+} chelate system with reaction ratio. Volume of PEI solution: 10 mL. Volume of Cu^{2+} solution: (a) 2.02 mL; (b) 2.30 mL; (c) 2.40 mL; (d) 2.44 mL; (e) 2.48 mL; (f) 2.50 mL; (g) 2.54 mL.

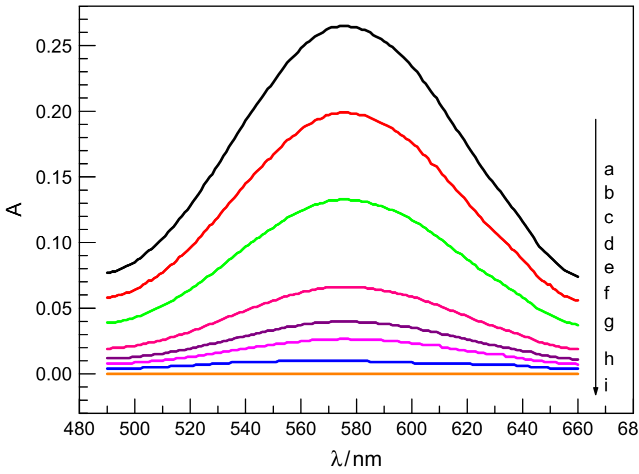

Fig. 3. Absorption spectrum variation of PEI–Cr^{3+} chelate system with reaction ratio. Volume of Cr^{3+} solution: 5 mL. Volume of PEI solution: (a) 27.0 mL; (b) 28.0 mL; (c) 29.0 mL; (d) 29.2 mL; (e) 29.4 mL; (f) 29.6 mL; (g) 29.8mL; (h) 30.0 mL.

In Fig. 1 the initial conductivities of five titration curves of the first groups are different due to dissimilar conductance properties of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+}, which can be reflected from their infinite dilution molar conductivity (Λ_m^∞), and Λ_m^∞ of Cu^{2+} is the greatest [26] among the five kinds of ions.

During titration experiments it was still discovered that the chelates between PEI and Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} are all water soluble, except for different colors. The chelate of PEI–Cu^{2+} is deeply blue, the chelate of PEI–Ni^{2+} is absinthe-green, and all the chelates of PEI–Cd^{2+}, PEI–Zn^{2+} and PEI–Pb^{2+} in aqueous solution are colorless, and this is attributed to the different types of d-orbitals of the outermost electronic shell. The chelate between PEI and Cr^{3+} is light red water-insoluble substance in spite of brown aquated ion Cr^{3+}.

According to the method described in Section 2.2.2, the reactions between 10 mL of PEI solution and Cu^{2+} solutions with different volumes but with the same concentration as PEI solution were carried out, and the absorption spectra of these water-soluble product systems are shown in Fig. 2. It can be seen from Fig. 2 that the absorbance of these systems is boosted up gradually with the increase of added amount of Cu^{2+} solution; as the volume of Cu^{2+} solution reaches to 2.5 mL (curve f), that is as the molar ratio of added Cu^{2+} to N atom of PEI raises to1:4, the absorbance of the system reaches to maximum value; afterward continually adding Cu^{2+} solution, the absorbance of the system changes no longer, and the curve g and curve f superimpose each other. The above results again show clearly that the coordination between amino group N atoms on PEI macromolecules and Cu^{2+} is carried out quantificationally, the stoichiometric ratio is equal to 4:1, and the coordination number of the chelate is 4.

The reactions of 5 mL of Cr^{3+} solution with PEI solutions with different volumes but with the same concentration as Cr^{3+} solution were performed, the absorption spectra of these supernatants are shown in Fig. 3. It can be found from Fig. 3 that the absorbance of these systems (actually they are the absorbance of the residual aquated Cr^{3+} ions) decreases gradually with the increase of added amount of PEI solutions; as the volume of PEI solution reaches 30 mL (curve h), that is as the molar ratio of added PEI to Cr^{3+} raises to 6:1, the absorbance of the system reaches to a minimum value, $A = 0$, indicating the exhausting of Cr^{3+} ions; afterward, continually adding PEI solution, the absorbance of the system still is zero, and curve i and curve h superimpose each other. The results again show clearly that the coordination between amino group N atoms on PEI macromolecules and Cr^{3+} is carried out quantificationally, the stoichiometric ratio is equal to 6:1, and the coordination number of the chelate is 6.

3.2. Preparing processes of two kinds of composite materials

The molecules of commercial PEI often have branch chains (branched PEI), and it contains primary, secondary and ternary amino groups in a ratio of approximately1:2:1 [27] (its chemical structure can be seen from Fig. 4). γ-Chloropropyl trimethoxysilane (CP) was chosen as a coupling agent to link silica gel and PEI. After silica gel is activated, a great deal of silanol groups are produced on silica gel particle surfaces, and then γ-chloropropyl trimethoxysilane reacts with these silanol groups to form modified silica gel (it can be called chloropropylation silica gel, CP-SiO_2). The chloropropyl groups on CP-SiO_2 react further with amine groups on PEI, macromolecule PEI is grafted onto silica surface in a coupling manner, and the composite particles of PEI/SiO_2 are formed finally. The coupling grafting reactions occur possibly on the active sites of the primary amine groups or the active sites of secondary amine groups of PEI, so there are two types of coupling grafting reactions. The reaction processes to prepare the composite material PEI/SiO_2 can be expressed schematically in Fig. 4.

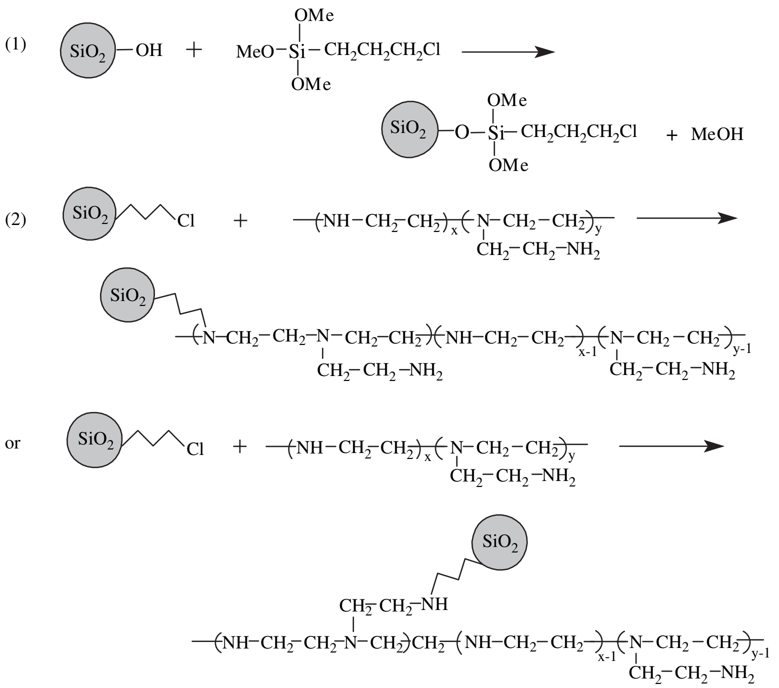

Fig. 4. Synthesis route of composite material PEI/SiO_2.

After PEI macromolecules grafted on silica gel surfaces are swelled fully in water medium and they will produce strong chelation towards Cu^{2+} or Cd^{2+} ions. When the crosslink agent ECH is added, the ring opening reaction of ECH takes place firstly, in which an amine group on a PEI chain acts as attacking group, then the dehydrochlorination reaction occurs as NaOH added between ECH and an amine group of another PEI chain, so the crosslinking is produced between PEI chains. Finally the template ions (Cu^{2+} or Cd^{2+}) are removed with hydrochloric acid solution, then the cavities of Cu^{2+} or Cd^{2+} leave behind in the polymer layer, and two ion-imprinted materials of (Cu^{2+}) IIP-PEI/SiO_2 and (Cd^{2+}) IIP-PEI/SiO_2 formed. The preparing process of IIP-PEI/SiO_2 is expressed schematically in Fig. 5.

3.3. Infrared spectra of PEI/SiO_2 and IIP-PEI/SiO_2

The FTIR spectra of PEI/SiO_2 before and after ion imprinting were measured and are shown in Fig. 6. It is found that after ion imprinting the absorption band at 1201 cm^{-1} is strengthened distinctly, which is the characteristic absorption of C–N bond of tertiary amine groups . Whereas all the absorption bands at 3641 cm^{-1}, 1701 cm^{-1} and 807 cm^{-1}, which are vibration absorption of N–H bond, disappear, and the disappearance of these bands reveals that the H atoms of the primary and secondary amine groups in PEI chains have been substituted completely by methylene of ECH (via ring-opening reaction and dehydrochlorination reaction), namely, all of primary and secondary amine groups in PEI chains have changed into tertiary groups. At the same time, the vibration absorption of O–H groups has been appeared at 3312 cm^{-1}, and it indicates further that the ring-opening

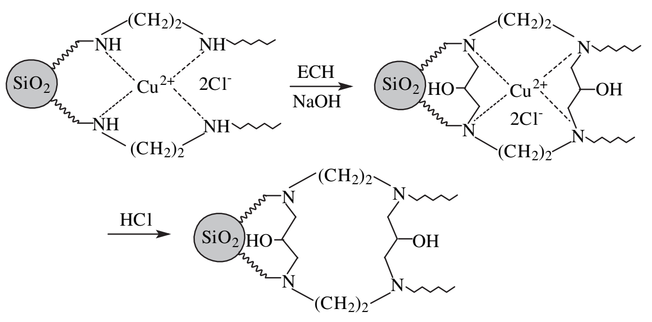

Fig. 5. Schematic representation of preparing process of IIP-PEI/SiO_2.

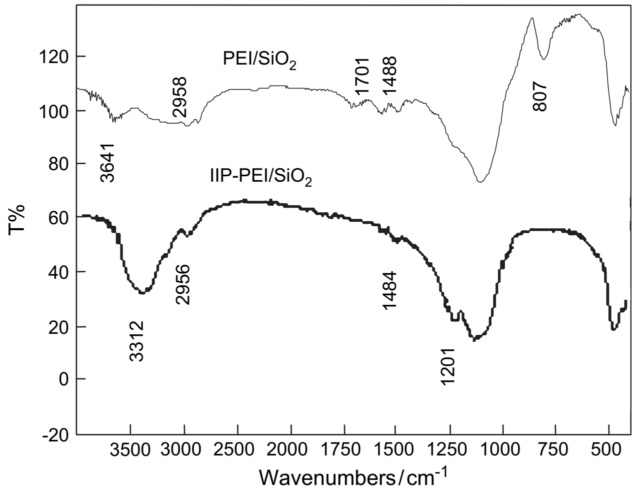

Fig. 6. FTIR spectrum of PEI/SiO_2 and IIP-PEI/SiO_2 on PEI/SiO_2.

reaction of ECH has been occurred. Besides, after ion imprinting the vibration absorption bands of C—H bond at 2958 cm^{-1} and 1488 cm^{-1} have shifted slightly towards low wavenumbers, perhaps it is caused owing to the change of the chemical surroundings around C—H bond after crosslinking reaction. The above observations show fully that the crosslinking between macromolecules of PEI has been produced by the effect of the crosslinker ECH, and a layer of ion-imprinted polymer has been formed on the surfaces of silica gel particle, i.e., the surface imprinting material IIP-PEI/SiO_2 has been obtained.

3.4. Static binding characteristics of IIP-PEI/SiO_2 towards template ions

3.4.1. Kinetic curve of binding

Fig. 7 shows the time dependence of the binding amounts of Cu^{2+} and Cd^{2+} ions on IIP-PEI/SiO_2. As seen here, both the adsorption amounts of Cu^{2+} and Cd^{2+} increase with the time during the first 30 min and then level off as equilibriums are reached. It is reasonable to assume that this fast adsorption equilibrium is not only due to strong chelation and good affinity of imprinted cavities of IIP-PEI/SiO_2 towards Cu^{2+} and Cd^{2+}, but also owing to the smaller diffusion barrier in the thin imprinted polymer layer for Cu^{2+} and Cd^{2+}. The smaller diffusion resistance leads to that Cu^{2+} and Cd^{2+} ions are easy to enter into the cavities and easy to bind with the recognition sites. The kinetic experiment result proves that this surface molecular imprinting technique on silica gel surfaces possesses obvious advantage indeed.

3.4.2. Binding isotherms

Figs. 8 and 9 give the binding isotherms of PEI/SiO_2 and (Cu^{2+}) IIP-PEI/SiO_2 towards Cu^{2+}, Zn^{2+} and Ni^{2+}. From the two figures the following facts can be found: (1) when the equilibrium concentrations of these metal ions reach to a certain value, the equilibrium binding amounts are change no longer, the adsorption reach saturation, and these adsorptions are typical Langmuir model with monolayer owing to chemical adsorptions resulted from chelation; (2) before ion imprinting, the saturated adsorption amount of PEI/SiO_2 for Cu^{2+} is 20.25 mg/g, however after ion imprinting, the saturated adsorption amount of IIP-PEI/SiO_2 is 40.69 mg/g, obviously, the value is enhanced two times more than that of PEI/SiO_2, and this fact displays clearly that after Cu^{2+} ion-imprinted, the affinity of IIP-PEI/SiO_2 for Cu^{2+} ions is enhanced greatly, the adsorption capacity is increased markedly because a mass of cavities whose shape and spatial arrangement of functional groups are complementary to the template Cu^{2+} have been formed; (3) although the adsorption amounts of Zn^{2+} and Ni^{2+} onto PEI/SiO_2 are smaller than that of Cu^{2+}, their differences are not too notable, whereas the adsorption amounts of Zn^{2+} and Ni^{2+} onto IIP-PEI/SiO_2 are much smaller than that of Cu^{2+}, and the adsorption amounts of Zn^{2+} and Ni^{2+} with respect to Cu^{2+} are nearly equal to

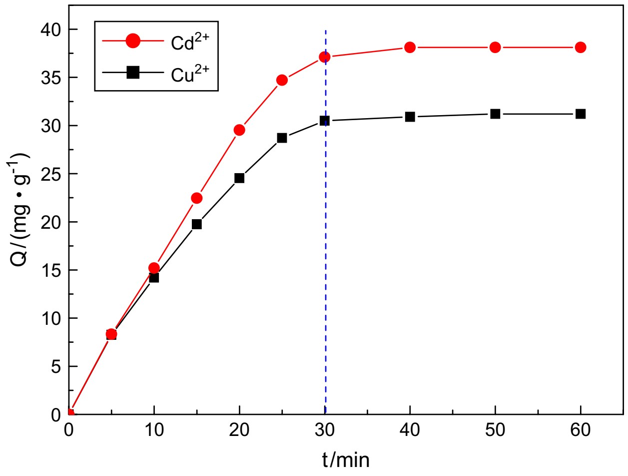

Fig. 7. Adsorption kinetic curve of IIP-PEI/SiO_2 for Cu^{2+} and Cd^{2+}. Temperature: 20 °C; for Cu^{2+} pH = 6; for Cd^{2+} pH = 7.

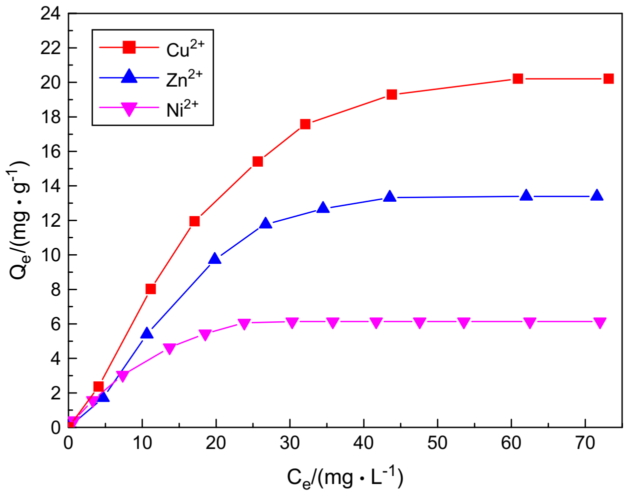

Fig. 8. Combining isotherms of Cu^{2+}, Zn^{2+} and Ni^{2+} on PEI/SiO_2. Grafting amount of PEI on SiO_2: 3.21 g/100 g; temperature: 20 °C; time: 30 min; pH = 6.

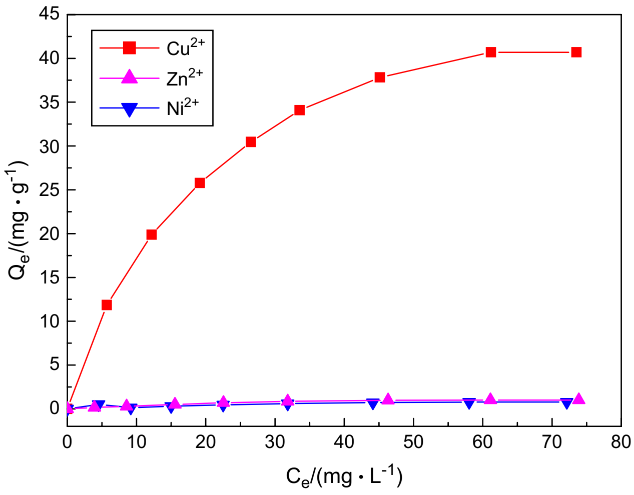

Fig. 9. Combining isotherms of Cu^{2+}, Zn^{2+} and Ni^{2+} on (Cu^{2+}) IIP-PEI/SiO_2. Grafting amount of PEI on SiO_2: 3.21 g/100 g; temperature: 20 °C; time: 30 min; pH = 6.

Table 1
Distribution coefficient and selectivity coefficient data for (Cu^{2+}) IIP-PEI/SiO_2

Adsorption material	K_d ($L\,g^{-1}$)		k	k'[a]	K_d ($L\,g^{-1}$)		k	k'[a]
	Cu^{2+}	Zn^{3+}			Cu^{2+}	Ni^{2+}		
MIP-PEI/SiO_2	2.246	0.028	80.21	20.57	2.152	0.025	86.08	31.65
PEI/SiO_2	0.441	0.113	3.90		0.425	0.156	2.72	

[a] k' is the ratio of the upper k to the lower k, and its meaning has been defined in Eq. (5).

zero. The above facts display fully that (Cu^{2+}) IIP-PEI/SiO_2 has high affinity and high recognition ability for Cu^{2+}. About the special selectivity of (Cu^{2+}) IIP-PEI/SiO_2, further data are given in Table 1.

Figs. 10 and 11 give the binding isotherms of PEI/SiO_2 and (Cd^{2+}) IIP-PEI/SiO_2 towards Cd^{2+}, Cr^{3+} and Pb^{2+}. By comparing the two types of isotherms, the following facts can be found: (1) before ion imprinting the saturated adsorption amount of PEI/SiO_2 for Cd^{2+} is 18.71 mg/g, however after ion imprinting, the saturated adsorption amount of IIP-PEI/SiO_2 is 38.12 mg/g, so obviously, the value is enhanced two times more than that of PEI/SiO_2; (2) although the adsorption amounts of Cr^{3+} and Pb^{2+} onto PEI/SiO_2 are smaller than that of Cd^{2+}, their differences are not too notable, whereas the adsorption amounts of Cr^{3+} and Pb^{2+} onto IIP-PEI/SiO_2 are much smaller than that of Cd^{2+}, and the adsorption amounts of Cr^{3+} and Pb^{2+} with respect to Cd^{2+} nearly are equal to zero. The results display fully that (Cd^{2+}) IIP-PEI/SiO_2 has high affinity and high recognition ability for Cd^{2+}. About the special selectivity of (Cd^{2+}) IIP-PEI/SiO_2, further data are given in Table 2.

3.4.3. Adsorption selectivity

Competitive adsorptions of Cu^{2+}/Zn^{2+} and Cu^{2+}/Ni^{2+} on (Cu^{2+}) IIP-PEI/SiO_2 from their mixtures were researched in batch systems. Table 1 summarizes the data of the distribution coefficient K_d, selectivity coefficient k and relative selectivity coefficient k'.

From the data in Table 1 the following facts can be found: (1) the selectivity coefficients of PEI/SiO_2 without imprinting for Cu^{2+} with respect to Zn^{2+} and Ni^{2+} are lower, and they are 3.90 and 2.72, respectively. The adsorption ability differences of PEI/SiO_2 for the three ions only are caused by different chelation forces of N atoms of PEI for them due to their different structures of bonding orbital. (2) The selectivity coefficients of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+} with respect to Zn^{2+} and Ni^{2+} are very high, and they are 80.21 and 86.08, respectively. (3) The relative selectivity coefficients of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+}/Zn^{2+} and Cu^{2+}/Ni^{2+} are 20.27 and 31.65, respectively. The above facts suggest that the binding abilities of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+} is far stronger than that for Zn^{2+} and Ni^{2+}. Although all the chelates of the three ions with PEI are of four ligands, the binding abilities of (Cu^{2+}) IIP-PEI/SiO_2 for Zn^{2+} and Ni^{2+} are very poor. The reason for this is that the cavities imprinted by Cu^{2+} are not suited to Zn^{2+} and Ni^{2+} in size, shape and spatial arrangement of action sites. The ionic radius of both Zn^{2+} (74 pm) and Ni^{2+} (72 pm) are larger than that of Cu^{2+} (69 pm), so obviously, it is difficult for Zn^{2+} and Ni^{2+} to enter into the cavity imprinted by Cu^{2+}, resulting in high recognition ability and high selectivity of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+}.

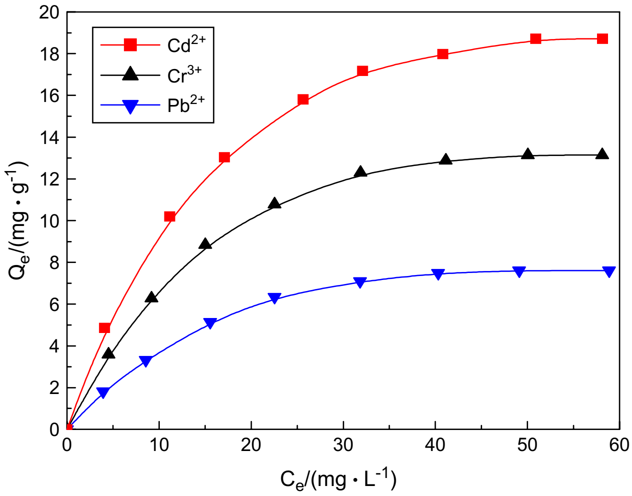

Fig. 10. Combining isotherms of Cd^{2+}, Cr^{3+} and Pb^{2+} on PEI/SiO_2. Grafting amount of PEI on SiO_2: 3.21 g/100 g; temperature: 20 °C; time: 30 min; pH = 7.

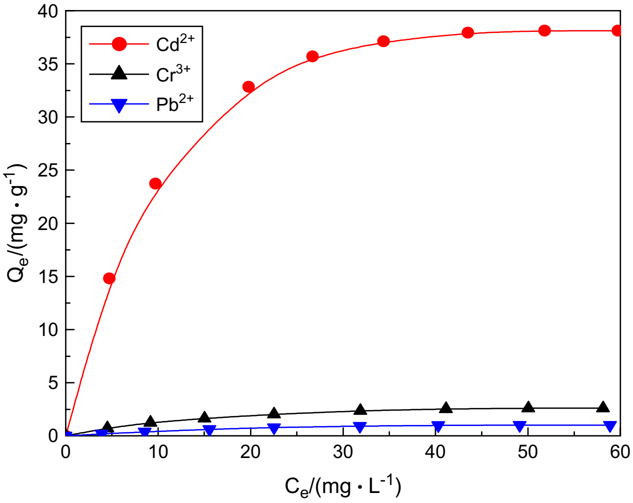

Fig. 11. Combining isotherms of Cd^{2+}, Cr^{3+} and Pb^{2+} on (Cd^{2+}) IIP-PEI/SiO_2. Grafting amount of PEI on SiO_2: 3.21 g/100 g; temperature: 20 °C; time: 30 min; pH = 7.

Table 2
Distribution coefficient and selectivity coefficient data for (Cd^{2+}) IIP-PEI/SiO_2

Adsorption material	K_d (L g^{-1})		k	k'	K_d (L g^{-1})		k	k'
	Cd^{2+}	Cr^{3+}			Cd^{2+}	Pb^{2+}		
MIP-PEI/SiO_2	2.913	0.041	71.05	28.88	2.823	0.032	88.22	32.67
PEI/SiO_2	0.425	0.173	2.46		0.478	0.177	2.70	

Competitive adsorptions of Cd^{2+}/Cr^{3+} and Cd^{2+}/Pb^{2+} on (Cd^{2+}) IIP-PEI/SiO_2 from their mixtures were researched. Table 2 summarizes the data of the distribution coefficient K_d, selectivity coefficient k and relative selectivity coefficient k'.

From the data in Table 2 it can be found that the binding ability of (Cd^{2+}) IIP-PEI/SiO_2 for Cd^{2+} is far stronger than that for Cr^{3+} and Pb^{2+}, and the binding abilities of (Cd^{2+}) IIP-PEI/SiO_2 for Cr^{3+} and Pb^{2+} are very poor. The reason for this is that the cavities imprinted by Cd^{2+} are non-matched to Cr^{3+} and Pb^{2+} in size, shape and spatial arrangement of action sites. Although the chelates of Cd^{2+} and Pb^{2+} with PEI are all of four ligands, the binding abilities of (Cd^{2+}) IIP-PEI/SiO_2 for Pb^{2+} are very poor. The ionic radius of Pb^{2+} (120 pm) is larger than that of Cd^{2+} (97 pm), so obviously, it is difficult for Pb^{2+} to enter into the cavity imprinted by Cd^{2+}. It has been known that the chelate of Cr^{3+} with PEI is of six ligands, whereas the chelate of Cd^{2+} with PEI is of four ligands. Although the ionic radius of Cr^{3+} (64 pm) is smaller than that of Cd^{2+} (97 pm), Cr^{3+} ions are difficult to be combined by IIP-PEI/SiO_2 because of non-matched combining sites.

3.5. Dynamic binding characteristics of IIP-PEI/SiO_2 towards template ions

Fig. 12 shows the dynamic binding curves of PEI/SiO_2 and IIP-PEI/SiO_2 towards Cu^{2+} ion. It can be found that when Cu^{2+} solution passes through the column packed with PEI/SiO_2 at a flow rate of 5 bed volumes per hour (5 BV/h) upstream, the leaking appears at 24 BV, the leaking adsorption amount calculated is 5.57 mg/g, and the saturated adsorption amount calculated is 20.47 mg/g. Whereas when Cu^{2+} solution passes through the column packed with IIP-PEI/SiO_2, the leaking appears at 58 BV, the leaking adsorption amount calculated is 22.43 mg/g, and the saturated adsorption amount calculated is 34.68 mg/g. Obviously, after ion imprinting for PEI/SiO_2, the affinity of IIP-PEI/SiO_2 for Cu^{2+} is increased remarkably, and its dynamic binding amount for Cu^{2+} is enhanced outstandingly similar to the static binding amount.

Fig. 13 shows the dynamic binding curves of IIP-PEI/SiO_2 towards Cd^{2+} ion. It can be found that when Cd^{2+} solution passes through the column packed with PEI/SiO_2, the leaking appears at 5 BV, the leaking adsorption amount calculated is 4.88 mg/g, and the saturated adsorption amount calculated is 18.06 mg/g. Whereas when Cd^{2+} solution passes through the column packed with IIP-PEI/SiO_2, the leaking appears at 18 BV, the leaking adsorption amount calculated is 23.67 mg/g, and the saturated adsorption amount calculated is 37.80 mg/g. Obviously, after imprinting for PEI/SiO_2, the affinity of IIP-PEI/SiO_2 for Cd^{2+} is increased remarkably, and its dynamic binding amount for Cd^{2+} is enhanced outstandingly similar to the static binding amount.

Besides, the elution experiment results show that IIP-PEI/SiO_2 has a fine elution property by using HCl solution as an eluting agent, and has excellent reusability.

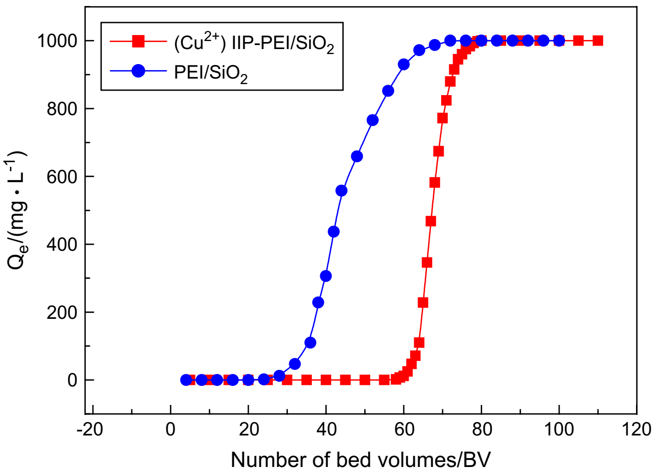

Fig. 12. Breakthrough curves of Cu^{2+} ion on PEI/SiO_2 and IIP-PEI/SiO_2 column. BV of IIP-PEI/SiO_2: 2 mL; at room temperature; initial concentration of ion: 1 g/L; flow rate: 5 BV/h.

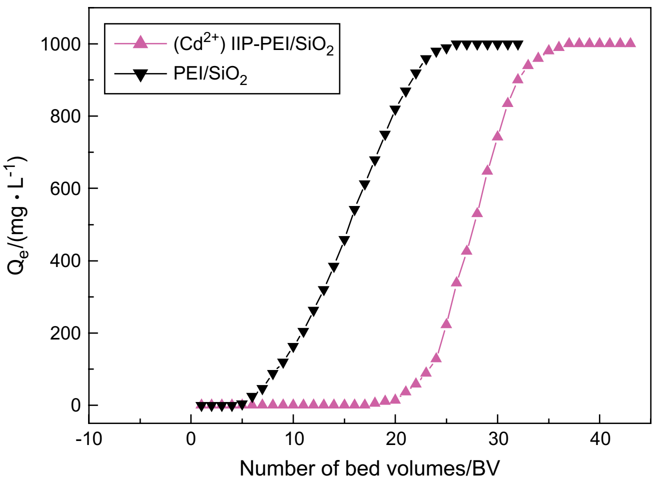

Fig. 13. Breakthrough curves of Cd^{2+} ion on PEI/SiO_2 and IIP-PEI/SiO_2 column. BV of IIP-PEI/SiO_2: 2 mL; at room temperature; initial concentration of ion: 1 g/L; flow rate: 5 BV/h.

4. Conclusions

In this paper, imprinting heavy-metal ions towards polyethyleneimine on the surfaces of silica gel particles was carried out successfully using Cu^{2+} or Cd^{2+} as the template and epichlorohydrin as the crosslinker, novel ionic imprinted material IIP-PEI/SiO_2 with composite type was obtained, and an advanced surface molecular imprinting technique was developed. The imprinted cavities are distributed in thin imprinted polymer layer, there is a smaller barrier for the diffusion of template ions, so it is easy to bind with those recognition sites for the template ions, and a rapid binding rate of IIP-PEI/SiO_2 towards the template ions is resulted in. IIP-PEI/SiO_2 possesses strong affinity for template ions, and both the static and dynamic binding amount enhanced two times higher than that of PEI/SiO_2 without imprinting. The IIP-PEI/SiO_2 displays special selectivity for template ions. The selectivity coefficients of (Cu^{2+}) IIP-PEI/SiO_2 for Cu^{2+} with respect to Zn^{2+} and Ni^{2+} are very high, and they are 80.21 and 86.08, respectively. The selectivity coefficients of (Cd^{2+}) IIP-PEI/SiO_2 for Cd^{2+} with respect to Cr^{2+} and Pb^{2+} are also very high, and they are 71.05 and 88.22, respectively. Besides, the ions adsorbed on IIP-PEI/SiO_2 are easy to be eluted using HCl solution as eluent, and it is very advantageous to the regeneration and reuse of IIP-PEI/SiO_2. In this new surface molecular imprinting technique put forward in this work, not only the treatment process is simple, but also the well combining of high affinity of MIPs for template and high mechanical property and specific area of inorganic support particles has been realized. This new surface molecular imprinting technique is a new route to prepare adsorption and separation materials with high property.

References

[1] Shiomia T, Matsuia M, Mizukamib F, Sakaguchi K. Biomaterials 2005; 5564–71.

[2] Baggiani C, Giraudi G, Giovannoli C, Tozzi C, Anfossi L. Analytica Chimica Acta 2004;504:43–52.

[3] Kubo T, Hosoya K, Watabe Y, Ikegami T, Tanaka N, Sano T, et al. Journal of Chromatography A 2004;1029:37–41.

[4] Castro B, Whitcombe MJ, Vulfson EN, Vazquez-Duhalt R, Bárzana E. Analytica Chimica Acta 2001;435:83–90.

[5] Brüggemann O, Visnjevski A, Burch R, Patel P. Analytica Chimica Acta 2004;504:81–8.

[6] Vallano PT, Remcho VT. Journal of Chromatography A 2000;887: 125–35.

[7] Araki K, Maruyama T, Kamiya N, Goto M. Journal of Chromatography B 2005;818:141–5.

[8] Yano K, Karube I. Trends in Analytical Chemistry 1999;18(3):199–204.

[9] Brüggemann O. Biomolecular Engineering 2001;18:1–7.

[10] Tada M, Iwasawa Y. Journal of Molecular Catalysis A: Chemical 2003; 199:115–37.

[11] Alvarez-Lorenzo C, Concheiro A. Journal of Chromatography B 2004; 804:231–45.

[12] Zayats M, Lshav M, Kharitonov AB, Willner I. Tetrahedron 2002;58: 815–24.

[13] Yoshida M, Hatate Y, Uezu K, Goto M. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2000;169:259–69.

[14] Araki K, Goto M, Furusaki S. Analytica Chimica Acta 2002;469: 173–81.

[15] Ye L, Mosbach K. Reactive and Functional Polymers 2001;48:149–57.

[16] Markowitz MA, Kust PR, Klaehn J, Deng G, Gaber BP. Analytica Chimica Acta 2001;435:177–85.

[17] Hunnius M, Rufińska A, Maier WF. Microporous and Mesoporous Materials 1999;29:389–403.

[18] Sulitzky C, Ruckert B, Hall AJ, Lanza F, Unger K, Sellergren B. Macromolecules 2002;35(1):79–91.

[19] Bisset W, Jacobs H, Koshti N, Stark P, Gopalan A. Reactive and Functional Polymer 2003;55:109–19.

[20] Radi S, Ramdani A, Lekchiri Y, Morcellet M, Crini G, Janus L, et al. Journal of Applied Polymer Science 2000;78:2495–9.

[21] Chanda M, Rempel GL. Reactive Polymer 1995;25:25–36.

[22] Amara M, Kerdjoudj H. Desalination 2004;168:195–200.

[23] Amara M, Kerdjoudj H. Hydrometallurgy 2002;65:59–68.

[24] Gao BJ, An FQ, Liu KK. Applied Surface Science 2006;253: 1946–52.

[25] Ersöz A, Say R, Denizli A. Analytica Chimica Acta 2004;502:91–7.

[26] Robert C. Handbook of chemistry and physics. 58th ed. USA: CRC Press; 1977–1978. p. C-726–32.

[27] Amara M, Kerdjoudj H. Talanta 2003;60:991–1001.