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Removal of Fe(II) from Ce(III) and Pr(III) rare earth solution using surface imprinted polymer

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ABSTRACT

Rare earth solution is a very important strategic resource. But, impurities, such as Fe^{2+}, have great influence on the optical properties of rare earth material. In this study, a novel Fe^{2+}-ionic imprinted polyamine functionalized silica gel adsorbent was prepared by a surface imprinting technique for selective adsorption of Fe^{2+} from rare earth solution. The adsorption and recognition properties of IIP-PEI/SiO_2 for Fe^{2+} were studied in detail. The experimental results showed that the IIP-PEI/SiO_2 possessed strong adsorption affinity, specific recognition ability and excellent selectivity for Fe^{2+}. The adsorption isotherm data greatly obey the Langmuir model, and the adsorption was typical monolayer. The adsorption capacity could reach up to 0.334 mmol g^{-1}, and relative selectivity coefficients relative to Pr^{3+} and Ce^{3+} are 23.25 and 18.42, respectively. Besides, the IIP-PEI/SiO_2 was regenerated easily using diluted hydrochloric acid solution, as eluent and IIP-PEI/SiO_2 possess better reusability.

Keywords: Surface ionic imprinting; Selectivity; Removal; Fe(II); Rare earth; Polyethyleneimine

1. Introduction

The rare earth elements (REEs) have excellent physical and chemical properties and have been used widely in optical, electrical and magnetic field. For high technology and new materials, not only high relative purity was required, but also content of non-rare earth impurity was limited strictly. For example, heavy-metal impurities have great quenching effect on the luminescence properties of fluorescent powder. For lanthanum oxide that is used in optical glass, a small amount of Fe, Cr, Ni, Co will seriously affect the optical properties of glass. For La_2O_2S cathode material, its relative brightness is reduced by 59% because of doping 600 ppm of Fe. For LnF_3 (Ln: La, Gd or Y) used in ultra low-loss infrared optical fibre, the content of transition metal impurities (Fe, Co, Ni, and Cu) is required to be at ppm level or lower. Removal of impurities, especially of trace non-rare earth impurities, attracts more and more the attention of manufacturer and user. Therefore, efficient and easy removal of non-rare earth impurities from high-purity rare earth solution was extremely important. Researchers have done some impurity removal studies in the last century [1,2]. Solvent extraction and extraction–elution resin (solvent-impregnated resins) method is mainly used. However, a large amount of

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organic phase was consumed in solvent extraction method, and secondary pollution for the environment is inevitable. The adsorption capacity of extraction–elution resin is small, and separating efficiency is low. So, researching a new extraction and separation system is important for economic and social benefit. Lamentably, relative research has not been reported over the past decades.

Molecular imprinting is a powerful technique for preparing polymeric materials with artificial receptor-like binding sites for various substances. The 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 and catalysts, etc. [3–7].

Polyethyleneimine (PEI) possesses large quantities of nitrogen atoms of amino groups on the macromolecular chains. So, it can produce very strong chelation towards heavy-metal ions, and this property of PEI has been widely applied in adsorption separation fields of heavy-metal ions [8,9]. In our previous study, chelating adsorption material PEI/SiO_2 was prepared, and its adsorption ability was researched. The research results showed that this material possesses excellent adsorption property for metal ion [10,11]. Based on our recent study, the route to prepare PEI/SiO_2 was developed further.

In this study, an advanced surface imprinting technique was used, and ionic imprinted polymer IIP-PEI/SiO_2 was prepared. The adsorption and recognition properties of IIP-PEI/SiO_2 for Fe^{2+} were studied deeply using batch and column method.

2. Experimental

2.1. Materials and instruments

Silica gel was purchased from Ocean Chemical Co., Ltd. (120–160 mesh, about 125 μm in diameter, pore size: 6 nm, pore volume: 1.0 ml g^{-1}, surface area: 350 $m^2 g^{-1}$. Qingdao, China). PEI was purchased from Qianglong Chemical Co., Ltd. ($M_w = 1 \times 104–2 \times 10^4$, Wuhan, China, AR grade). γ-Chloropropyl trimethoxysilane was purchased from Yongchang Chemical Co., Ltd. (Naking, China, AR grade). Ethylene glycol diglycidyl ether (EGDE, 669) was purchased from Wuxi Wanrong Material Co., Ltd. (Jiangsu, China, CR grade). Other chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

Instruments used in this study were as follows: THZ-92C constant temperature shaker (Boxun Medical Treatment Equipment Factory of Shanghai, China), Perkin-Elmer1700 infrared spectrometer (Perkin-Elmer Company, American), WYX-9001 atomic absorption spectrophotometer (AAS, Analytical Instrument Factory of Shenyang, China).

2.2. Preparation of ionic imprinting polymer IIP-PEI/SiO_2

The preparing process of PEI/SiO_2 was similar but different to references [10,11]. Firstly, 5 g of silica gel particles were activated using 30 ml of hydrochloric acid aqueous solution of 5%; secondly, 5 g of activated silica gel reacted with 100 ml of γ-chlopropyl trimethoxysilane (CP) at 80℃ into which 1 ml of water was added intermittently, and chloropropylation silica (CP-SiO_2) was prepared; finally, 1 g of CP-SiO_2 was added into 50 ml of PEI aqueous solution (50%), the reaction was carried out at 90℃ for 6 h, and the adsorption material PEI/SiO_2 were prepared.

For preparation of IIP-PEI/SiO_2, 1 g of PEI/SiO_2 particles adsorbed Fe^{2+} and 0.25 g of EGDE (669) were added into 50 ml of absolute ethanol, and the reaction was allowed to carry out for 4 h at 25℃ with continuous stirring. Finally, particles were fully washed with 0.1 mol L^{-1} of hydrochloric acid solution to remove the template ion and the cross-linking agent. After being filtrated and dried, the ionic imprinted polymer IIP-PEI/SiO_2 was obtained.

For researching the imprinted effect, the non-imprinted polymer (NIP-PEI/SiO_2) was prepared using the same method in the absence of the template Fe^{2+}.

2.3. Batch adsorption of IIP-PEI/SiO_2 towards Fe^{2+} ion

2.3.1. Kinetic adsorption curve

About 0.2 g of IIP-PEI/SiO_2 was introduced into a conical flask directly. 100 ml of Fe^{2+} aqueous solution with concentration (C_0) of 10 mmol L^{-1} and pH of 5 was then added into the conical flask. This conical flask was placed in a shaker at a presettled temperature (25℃). At different time, the concentration (C_t) of Fe^{2+} solution was determined by atomic absorption spectrophotometer. The adsorption capacity (Q) was calculated according to Eq. (1) [12].

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

where V is the volume of the solution (L); m is the weight of absorbent IIP-PEI/SiO_2 (g).

2.3.2. Adsorption isotherm

About 0.05 g of IIP-PEI/SiO_2 was introduced into conical flask directly. An amount of 25 ml of Fe^{2+} aqueous solution with different concentration (C_0) and same pH of 5 were then added into each conical flask. The conical flasks were placed in a shaker at a presettled temperature (25°C). After the adsorption reached equilibrium, the equilibrium concentration (C_e) of Fe^{2+} solution was determined by atomic absorption spectrophotometer. The equilibrium adsorption capacity (Q_e) was calculated according to Eq. (1).

2.3.3. Selectivity experiments

The binary mixed solutions of Fe^{2+}/Ce^{3+} and Fe^{2+}/Pr^{3+} were prepared, and the molarity of Fe^{2+} was the same as Ce^{3+} and Pr^{3+}. The batch adsorption experiments were performed for the two mixed solutions using the same condition as foregoing experiment; after adsorption equilibrium were reached, the concentrations of Fe^{2+}, Ce^{3+} and Pr^{3+} in the remaining solutions were determined by atomic absorption spectrophotometer.

Distribution coefficients (K_d) of Fe^{2+}, Ce^{3+} and Pr^{3+} were calculated by Eq. (2) [12]

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

Selectivity coefficient (k) of IIP-PEI/SiO_2 for Fe^{2+} with respect to the competitor species (B) can be obtained by Eq. (3) [12]

$$k = K_d(\mathrm{Fe}^{2+})/K_d(\mathrm{B}) \tag{3}$$

The value of k allows an estimation of selectivity of IIP-PEI/SiO_2 for Fe^{2+}. A relative selectivity coefficient k' can be defined by Eq. (4) [12], and the value of k' can indicate the enhanced extent of adsorption affinity and selectivity of imprinted material IIP-PEI/SiO_2 for Fe^{2+} with respect to non-imprinted material NIP-PEI/SiO_2.

$$k' = k_{\mathrm{IIP}}/k_{\mathrm{NIP}} \tag{4}$$

2.4. Repeated use experiment

The repeated usability, such as regenerability, is an important factor for the absorption material. Desorption of the adsorbed Fe^{2+} from the IIP-PEI/SiO_2 also studied by batch experimental [12]. Adsorbed Fe^{2+} was desorbed with 0.01 mol L^{-1} of hydrochloric acid solution. The IIP-PEI/SiO_2 adsorbed Fe^{2+} was placed in the eluent and stirred continuously at room temperature for 2 h. The final Fe^{2+} concentration in aqueous phase was determined by atomic absorption spectrophotometer. Desorption ratio was calculated from the amount of Fe^{2+} adsorbed on the IIP-PEI/SiO_2 and final Fe^{2+} concentration in the eluent. In order to test the reusability of IIP-PEI/SiO_2, Fe^{2+} adsorption-desorption procedure was repeated 10 times using the same imprinted polymer.

2.5. Dynamics adsorption and elution experiment

An amount of 1.4824 g of IIP-PEI/SiO_2 was filled in a glass column with 8 mm of diameter and 2 mL of the bed volume. The Fe^{2+} aqueous solution with concentration of 10 mmol L^{-1} and pH of 5 was allowed to flow gradually through the column at a rate of five bed volumes per hour (5 BV h^{-1}). The effluent with one bed volume was collected, and the concentration was determined by atomic absorption spectrophotometer. Then, the dynamics adsorption curve was plotted. The leaking adsorption amount and the saturated adsorption amount were also calculated [12].

Elution experiment was performed using hydrochloric acid solution with concentration of 0.01 mol L^{-1} as eluting agent, and the flow rate of the eluting agent was controlled at 1 BV h^{-1}. The eluent with one bed volume was collected, the concentration was determined by atomic absorption spectrophotometer, and the elution curve was plotted [12].

According to the same method, the dynamics adsorption curve and elution curve of PEI/SiO_2 and IIP-PEI/SiO_2 towards Pr^{3+} was plotted.

3. Results and discussion

3.1. Preparing process and structure characterizing of IIP-PEI/SiO_2

Firstly, the ring opening reaction between EGDE (669) and amine groups of PEI chain takes place when the cross-linking agent EGDE (669) is added. Then, the template was removed with hydrochloric acid solution. Finally, ionic imprinted polymer IIP-PEI/SiO_2 was formed. The preparing process of IIP-PEI/SiO_2 is expressed in Fig. 1.

The FTIR spectra of PEI/SiO_2 and IIP-PEI/SiO_2 were measured and shown in Fig. 2.

After imprinting, the absorption band at 1195 cm^{-1} is strengthened distinctly, which is the characteristic absorption of C–N bond of tertiary amine groups,

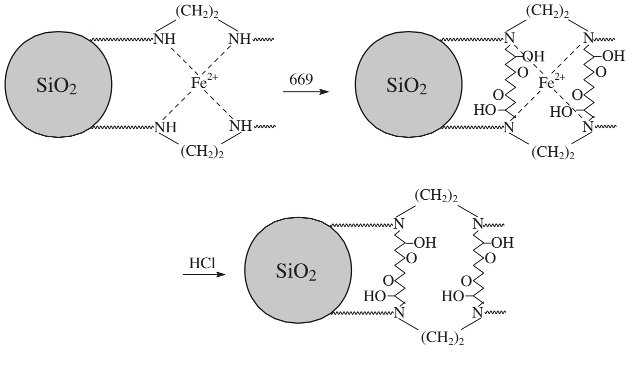

Fig. 1. Synthesis process of IIP-PEI/SiO_2.

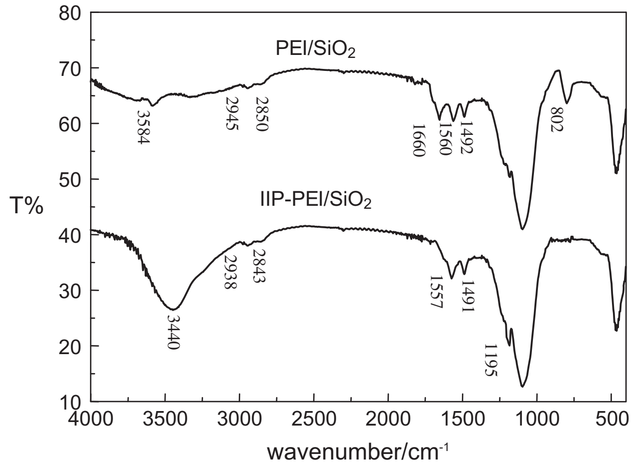

Fig. 2. FTIR spectrum of PEI/SiO_2 and IIP-PEI/SiO_2.

whereas all the absorption bands at 3584, 1660 and 802 cm^{-1}, which are vibration absorption of N–H bond, disappear. The disappearance of these bands reveal that the H atoms of the primary and secondary amine groups in PEI chains have been substituted completely by alkyl, 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 appeared at 3440 cm^{-1}, and it indicates further that the ring opening reaction has occurred. The above observations show fully that the cross-linking between macromolecules of PEI has been produced by the effect of the cross-linking agent EGDE (669), and the ionic imprinted polymer IIP-PEI/SiO_2 has been obtained.

3.2. *Batch adsorption characteristics of IIP-PEI/SiO_2 towards Fe^{2+} ion*

3.2.1. *Kinetic adsorption curve*

The kinetic adsorption curve was shown in Fig. 3. The adsorption rate of IIP-PEI/SiO_2 towards the Fe^{2+} ion was fast, and the adsorption reached equilibrium within 30 min. It was implied that IIP-PEI/SiO_2 possesses very strong chelating adsorption ability for Fe^{2+} ion.

3.2.2. *Adsorption isotherms*

Figs. 4 and 5 were the adsorption isotherms of PEI/SiO_2 and IIP-PEI/SiO_2 towards Fe^{2+}, Ce^{3+} and Pr^{3+}, respectively. It can be seen that the saturated adsorption capacity of IIP-PEI/SiO_2 for Fe^{2+} is 0.334 mmol g^{-1}, consistent with that of PEI/SiO_2 is 0.333 mmol g^{-1}. But, the adsorption capacity of IIP-PEI/SiO_2 for Ce^{3+} and Pr^{3+} decline significantly, much lower than that of PEI/SiO_2. The above facts display fully that IIP-PEI/SiO_2 has high affinity, high recognition ability and special selectivity for Fe^{2+}. Further data are given in Table 1.

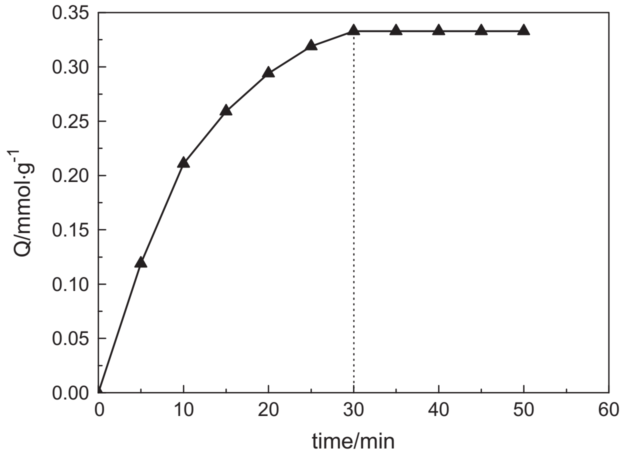

Fig. 3. Kinetic adsorption curve of IIP-PEI/SiO_2 for Fe^{2+}. Temperature: 25℃; pH = 5.

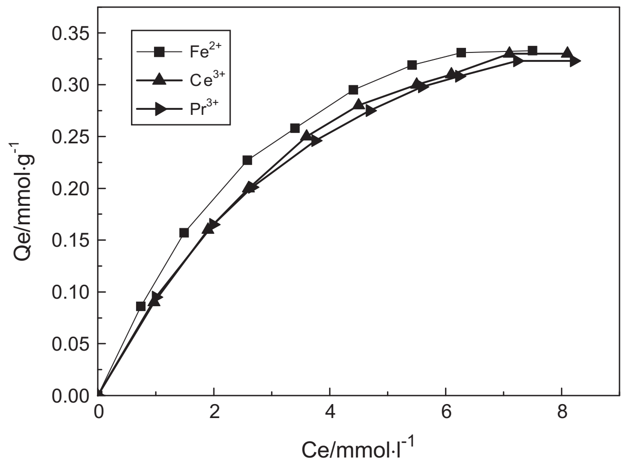

Fig. 4. Adsorption isotherm of PEI/SiO_2 for Fe^{2+}, Ce^{3+} and Pr^{3+}. Temperature: 25℃; pH = 5.

Langmuir equation is as follows [10]:

$$Q_e = Q_m \frac{bC_e}{1 + bC_e} \tag{5}$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \tag{6}$$

where C_e (mol L^{-1}) is equilibrium concentration, Q_e (mmol g^{-1}) is the equilibrium adsorption capacity, Q_m (mmol g^{-1}) is the saturated adsorption capacity, b is the combine constant.

The data of Fe^{2+} in Fig. 5 are regressed linearly according to Eq. (6), and Fig. 6 is obtained. The line in Fig. 6 fits satisfactorily to the Langmuir equation

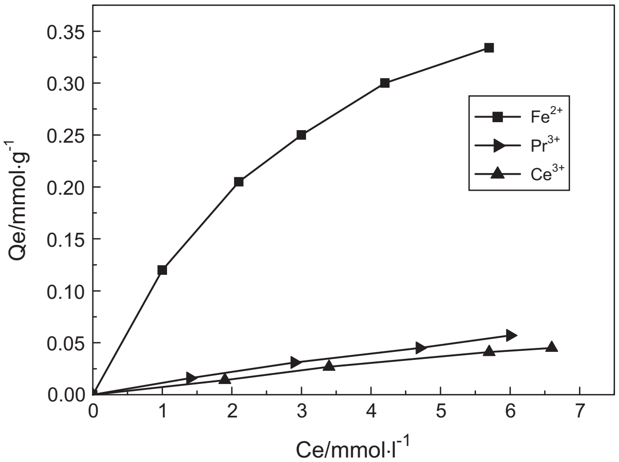

Fig. 5. Adsorption isotherm of IIP-PEI/SiO_2 for Fe^{2+}, Ce^{3+} and Pr^{3+}. Temperature: 25℃; pH = 5.

obviously, and this indicates fully that the Fe^{2+} is adsorbed on the IIP-PEI/SiO_2 with monomolecular layer [10].

3.2.3. Adsorption selectivity

Competitive adsorptions of IIP-PEI/SiO_2 and NIP-PEI/SiO_2 for Fe^{2+} from Ce^{3+}/Fe^{2+} and Pr^{3+}/Fe^{2+} mixtures were researched in batch systems. Table 1 summarizes the data of the distribution coefficients K_d, selectivity coefficients k and relative selectivity coefficients k'.

It can be seen that the selectivity coefficients (k) of IIP-PEI/SiO_2 for Fe^{2+} increase significantly after ion is imprinted. This suggests that the adsorption recognition of IIP-PEI/SiO_2 for Fe^{2+} is very strong, and far stronger than that for Ce^{3+} and Pr^{3+}. The reason is that the imprinted cavities by Fe^{2+} are non-matched to Ce^{3+} and Pr^{3+} in size, shape and spatial arrangement of combining sites. The ionic radii of Ce^{3+} (103 pm) and Pr^{3+} (101 pm) are bigger than that of Fe^{2+} (74 pm) [14]; as a result, Ce^{3+} and Pr^{3+} could not enter into the caviies imprinted by Fe^{2+}. So, the adsorption ability of IIP-PEI/SiO_2 for Ce^{3+} and Pr^{3+} is very poor, and the selectivity coefficient of IIP-PEI/SiO_2 for Fe^{2+} is very high. This confirms again that IIP-PEI/SiO_2 has high selectivity for Fe^{2+}.

3.2.4. Desorption and reusability

The desorption ratio was calculated as follow [13]:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ion desorbed to the elution medium}}{\text{Amount of metal ion adsorbed on IIP} - \text{PEI/SiO}_2} \times 100\%$$

Desorption ratio is very high (98.1%). When hydrochloric acid was used as an eluent, the interaction between Fe^{2+} and PEI is disrupted, and subsequently, Fe^{2+} are released into desorption medium. In order to show the reusability of the IIP-PEI/SiO_2, adsorption-desorption cycle was repeated 10 times using same imprinted polymer.

Adsorption-desorption cycle of Fe^{2+} imprinted polymer IIP-PEI/SiO_2 was shown in Fig. 7. The result clearly shows that the IIP-PEI/SiO_2 could be used repeatedly without losing significantly the binding amount.

3.3. Column adsorption characteristics of IIP-PEI/SiO_2 towards Al^{3+} ion

3.3.1. Dynamic adsorption curve

Figs. 8 and 9 show the dynamic adsorption curves of PEI/SiO_2 and IIP-PEI/SiO_2 for Fe^{2+} and Pr^{3+}.

In dynamic adsorption curves of PEI/SiO_2 for Fe^{2+} and Pr^{3+}, the leaking bed volume for Fe^{2+} is 17 BV and for Pr^{3+} is 16 BV. But in the dynamic adsorption curves of IIP-PEI/SiO_2 for Fe^{2+} and Pr^{3+}, the leaking bed volume for Fe^{2+} is 17 BV, which is similar to that the leaking bed volume of PEI/SiO_2 for Fe^{2+} and the leaking bed volume for Pr^{3+} is 1 BV, which is significantly less than that of PEI/SiO_2 for Pr^{3+} and Fe^{2+}. Similarly, the leaking adsorption capacity of IIP-PEI/SiO_2 for Fe^{2+} is 0.224 mmol g^{-1}, which is similar to that the leaking adsorption capacity of PEI/SiO_2 for Fe^{2+} (0.224 mmol g^{-1}). But the leaking adsorption capacity of IIP-PEI/SiO_2 for Pr^{3+} is 0 mmol g^{-1}, and significantly less than that of PEI/SiO_2 for Pr^{3+} (0.22 mmol g^{-1}). The above facts confirm obviously again that IIP-PEI/SiO_2 has high affinity, high recognition ability and special selectivity for Fe^{2+}.

3.3.2. Elution curve

Good desorption performance of an adsorbent is important for its potential practical applications. Fig. 10 gives the elution curve of Fe^{2+} from IIP-PEI/SiO_2.

Hydrochloric acid solution with a concentration of 0.01 mol L^{-1} is used as the eluent, and the eluent at a rate of 1 BV h^{-1} flows upstream through the column of IIP-PEI/SiO_2 particles on which the adsorption of

Table 1
Distribution coefficient, selectivity coefficient data and relative selectivity coefficient

Adsorbent	$K_d/(\mathrm{mL\,g^{-1}})$		k	k'	$K_d/(\mathrm{mL\,g^{-1}})$		k	k'
	Fe^{2+}	Ce^{3+}			Fe^{2+}	Pr^{3+}		
IIP-PEI/SiO_2	49.87	1.95	25.57	24.35	48.28	2.34	20.63	19.46
NIP-PEI/SiO_2	45.32	43.24	1.05		44.87	42.16	1.06	

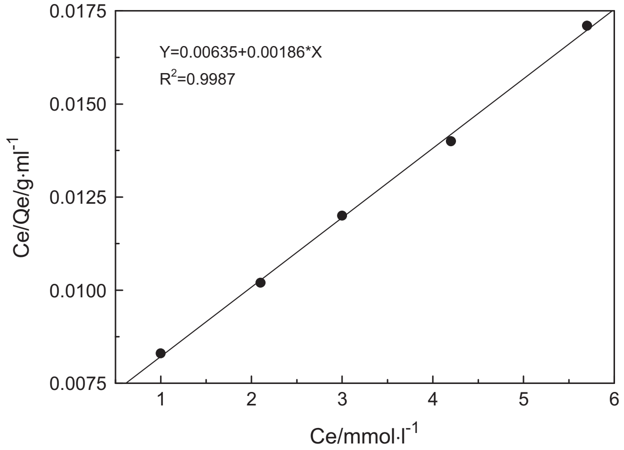

Fig. 6. Plot of C_e/Q_e vs. C_e.

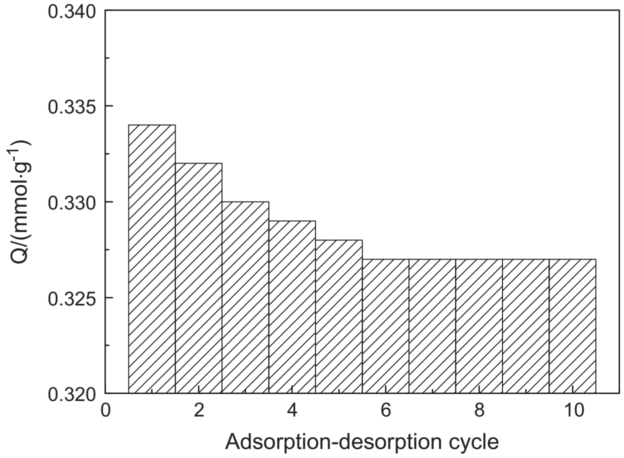

Fig. 7. Adsorption–desorption cycle of IIP-PEI/SiO_2.

Fe^{2+} has reached to saturation. It can be seen that the shape of desorption curve is cuspate and without tailing, and it shows the fine elution result. The calculation results show that within 23 bed volumes, Fe^{2+} is eluted from IIP-PEI/SiO_2 column with a desorption ratio of 99.71%. The fact reveals fully that IIP-PEI/SiO_2 has outstanding elution property, and this novel adsorbent IIP-PEI/SiO_2 has excellent reusing property.

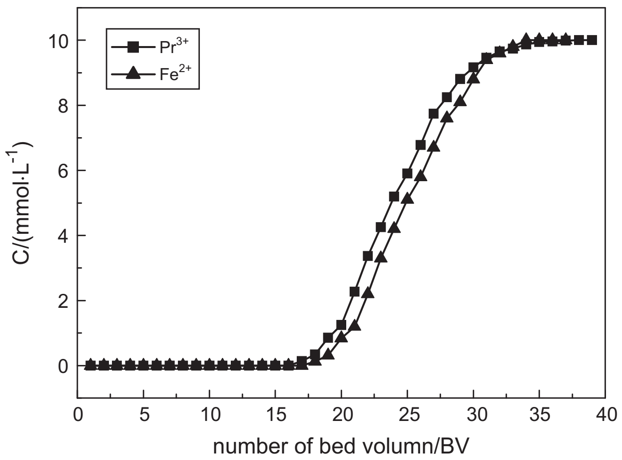

Fig. 8. Dynamic adsorption curve of PEI/SiO_2 for Fe^{2+} and Pr^{3+}. Temperature: 25℃; initial concentration: 0.01 mol L^{-1}; pH = 5.

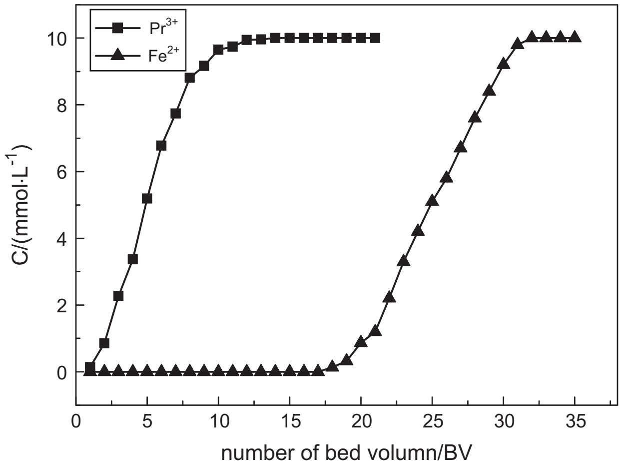

Fig. 9. Dynamic adsorption curve of IIP-PEI/SiO_2 for Fe^{2+} and Pr^{3+}. Temperature: 25℃; initial concentration: 0.01 mol L^{-1}; pH = 5.

3.4. Practical application

In order to demonstrate its practical application value, the mixture of Pr^{3+} and Fe^{2+} were treated using IIP-PEI/SiO_2 column with upstream flows. The

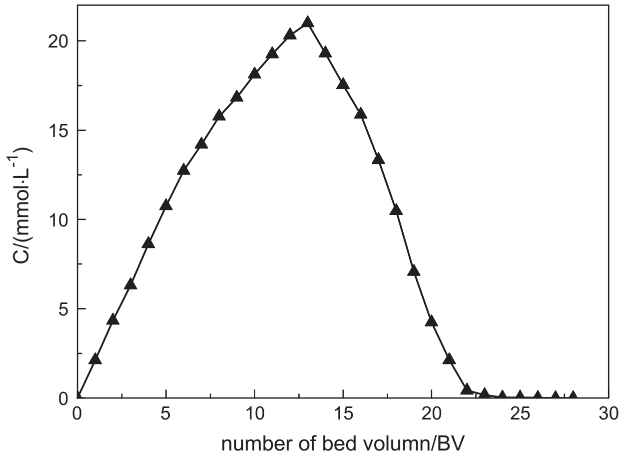

Fig. 10. Elution curve of Fe^{2+} from IIP-PEI/SiO_2. Temperature: 25℃.

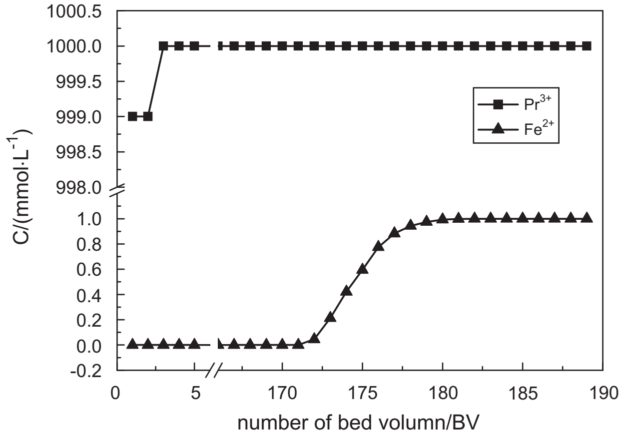

Fig. 11. Practical dynamic adsorption curve of IIP-PEI/SiO_2 for mixture of Fe^{2+} and Pr^{3+}.

concentration of Pr^{3+} and Fe^{2+} is 1000 and 1 mmol L^{-1}, respectively. The dynamic adsorption curve was shown in Fig. 11.

It can be seen that the adsorption behaviour of IIP-PEI/SiO_2 for Fe^{2+} is still very strong. The Fe^{2+} could not be detected in the outflow liquid in front of the over 171 BV. However, the concentration of Pr^{3+} in the outflow liquid is always equal to the initial concentration except the first 2 BV. This means that when 342 ml (171 BV) of Pr^{3+} and Fe^{2+} mixture were treated using IIP-PEI/SiO_2 column with upstream flows, the impurity Fe^{2+} could be adsorbed absolutely and pure Pr^{3+} solution could be obtained. This result clearly shows that IIP-PEI/SiO_2 could be used for selective adsorption and enrichment of trace amount of Fe^{2+} from Pr^{3+} rare earth solution.

4. Conclusion

In this study, Fe^{2+}-ionic imprinted material IIP-PEI/SiO_2 was prepared. IIP-PEI/SiO_2 possessed strong adsorption affinity, specific recognition ability and excellent selectivity for Fe^{2+}. The adsorption isotherm data greatly obey the Langmuir model, and the adsorption was typical monolayer. The adsorption capacity could reach up to 0.334 mmol g^{-1}, and relative selectivity coefficients relative to Ce^{3+} and Pr^{3+} are 23.25 and 18.42, respectively. Additionally, IIP-PEI/SiO_2 has excellent reusability. On the basis of the results obtained in this study, we believe that the synthetic imprinted sorbent IIP-PEI/SiO_2 can be used for selective adsorption and enrichment of trace amount of Fe^{2+} from rare earth solution and other aqueous solutions.

Acknowledgements

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