Adsorption and Recognition Properties of Ionic Imprinted Polyamine IIP-PEI/SiO_2 Towards Pb^{2+} Ion

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ABSTRACT: In this article, an ionic imprinted polyamine (IIP) grafted on the surface of silica gel was prepared through a new surface imprinting approach. The adsorption and recognition properties of IIP-PEI/SiO_2 for Pb^{2+} ion were studied in detail using batch rebinding studies. The experimental results showed that the IIP-PEI/SiO_2 had high affinity, specificity, and selectivity for the template ion. The isothermal adsorption data was fit using the Langmuir equation. The adsorption was typical of chemisorption of a monolayer. The selectivity coefficients relative to Zn^{2+} and Cr^{3+} were 32.43 and 68.36, respectively. pH and temperature were found to have a strong influence on the adsorption properties. The adsorption amount increases with rising of temperature and the value of ΔH is plus. The adsorption of Pb^{2+} by IIP-PEI/SiO_2 was spontaneous and endothermic. At pH = 7, the adsorption capacity of the polymers was the highest. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2241–2246, 2009

Key words: molecular imprinting; molecular recognition; adsorption; silicas; surfaces

INTRODUCTION

Lead ion, same as other heavy metal ions, is harmful to public health and environmental quality, and more rigorous limits on allowed amount of lead ion have been established. Especially, wastewater containing lead ion brings a series of serious environmental problem because of high toxicity and accumulation in the environment. The major sources of lead ion are its mining and recovery and its usage in a variety of products and industrial waste.

Polyethyleneimine (PEI) is a typical water-soluble polyamine, and there are 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 character of PEI has been widely applied in adsorption separation fields of heavy-metal ions.[1–4] In our previous study, the chemical structure of adsorption material for heavy-metal ions was well designed, PEI was grafted chemically onto the surface of silica gel particles via the coupling effect of γ-chloropropyl trimethoxysilane, 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 chelating adsorption material PEI/SiO_2 was prepared.[5,6] The research results showed that this material possessed excellent adsorption property for Cu^{2+} and Cd^{2+}, etc.[5–8]

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Molecular imprinting is a powerful technique for preparing polymeric materials with artificial receptor-like binding sites for various substances,[9–12] and the molecular imprinted polymers (MIPs) have been used 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.[13–16]

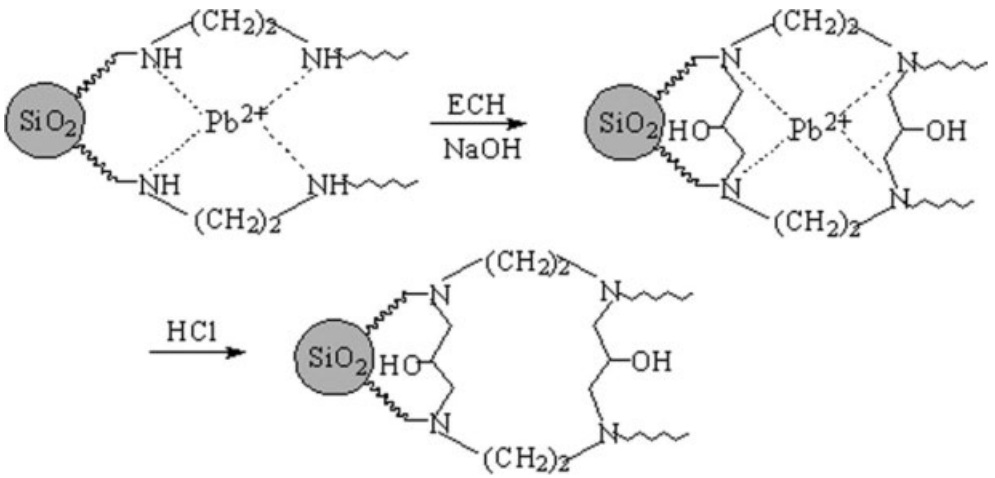
In this article, we used an advanced surface imprinting technique, prepared ionic imprinted polymer IIP-PEI/SiO_2 on the surface of silica gel particles. The adsorption and recognition properties of IIP-PEI/SiO_2 for Pb^{2+} were studied profoundly using batch rebinding method.

EXPERIMENTAL

Materials and instruments

Silica was purchased from Ocean Chemical Company (Qingdao, China). PEI was purchased Qianglong Chemical Company (Wuhan, China, AR grade).

Used instruments in this study were as follows: Unic-2602 UV spectrophotometer (Unic Company, American), Perkin–Elmer1700 infrared spectrometer (Perkin–Elmer Company, American), PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China), THZ-92C constant temperature shaker (Boxun Medical Treatment Equipment Factory of Shanghai, China), and WYX-9001 atomic absorption spectrophotometer (AAS, Analytical Instrument Factory of Shenyang, China).



Scheme 1 Schematic representation of preparing process of IIP-PEI/SiO_2.

Preparation of ionic imprinting polymer IIP-PEI/SiO_2

The preparing process of the PEI/SiO_2 was introduced in references.[5–7] A certain amount of PEI/SiO_2 particles adsorbed Pb^{2+} and epichlorohydrin (ECH)[17] were added into absolute ethanol, and the reaction was allowed to carry out for 30 min at room temperature with continuous stirring. Afterwards, sodium hydroxide was added, the reaction continued for 30 min at room temperature with continuous stirring. Finally, particles were fully washed with hydrochloric acid solution of 0.1*M* to remove the template ion, and the Pb^{2+}-imprinted polymer IIP-PEI/SiO_2 was obtained.[8]

Static adsorption of IIP-PEI/SiO_2 towards Pb^{2+} ion

Kinetic adsorption curve

About 0.2 g of IIP-PEI/SiO_2 was introduced into a conical flask directly; 100 mL of Pb^{2+} aqueous solution with concentration (C_0) of 100 mg L^{-1} and pH of 7 was then added into conical flask. This conical flask was placed in a shaker at a presettled temperature. At different time, the concentration (C_t) of Pb^{2+} solution was determined by atomic absorption spectrophotometer. The adsorption amount (Q) was calculated according to:

$$Q = V(C_0 - C_t)/m \quad (1)$$

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

Adsorption isotherm

About 0.2 g of IIP-PEI/SiO_2 was introduced into a conical flask directly; 100 mL of Pb^{2+} aqueous solution with different concentration (C_0) and same pH of 7 were then added into each conical flask. The conical flasks were placed in a shaker at a presettled temperature. After the adsorption reached equilibrium, the concentration (C_e) of Pb^{2+} solution was determined by atomic absorption spectrophotometer. The equilibrium adsorption amount (Q_e) was calculated according to eq. (1).

Selectivity experiments

The binary mixed solutions of Pb^{2+}/Zn^{2+} and Pb^{2+}/Cr^{3+} were prepared, and in these mixed solutions the concentration of Pb^{2+} was the same as other ion. The static adsorption experiments were performed for the two mixed solutions, after adsorption equilibrium were reached, the concentrations of Pb^{2+}, Zn^{2+}, and Cr^{3+} in the remaining solutions were determined by atomic absorption spectrophotometer.

Distribution coefficients (K_d) of Pb^{2+}, Zn^{2+}, and Cr^{3+} were calculated by eq. (2)[18]:

$$K_d = Q_e/C_e \quad (2)$$

Selectivity coefficient (k) of IIP-PEI/SiO_2 for Pb^{2+} ion with respect to the competitor species (B) can be obtained by eq. (3):

$$k = K_d(Pb^{2+})/K_d(B) \quad (3)$$

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

$$k' = k_{imp}/k_{non-imp} \quad (4)$$

RESULTS AND DISCUSSION

Preparing processes of IIP-PEI/SiO_2

The reaction process of preparing the PEI/SiO_2 was studied in reference.[5–7] Firstly, the ring opening

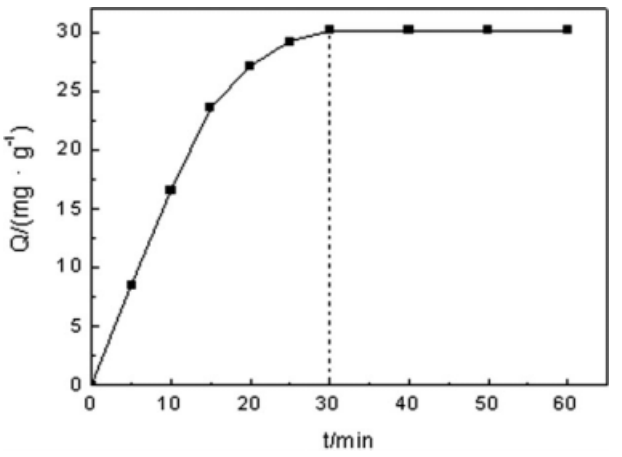


Figure 1 Adsorption kinetic curve of IIP-PEI/SiO_2 for Pb^{2+}. Temperature: 20°C; pH = 7.

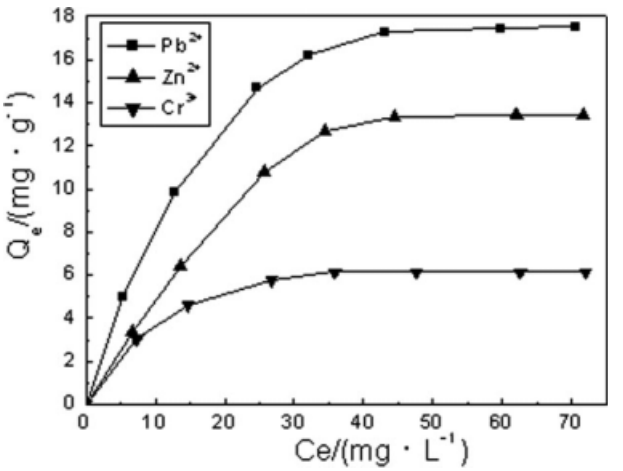


Figure 2 Adsorption isotherms of Pb^{2+}, Zn^{2+}, and Cr^{3+} on PEI/SiO_2. Temperature: 20°C; Time: 30 min; pH = 7.

reaction between ECH and amine groups of PEI chain takes place when the crosslink agent ECH is added. Then the dehydrochlorination reaction between ECH and another amine group of PEI chain occurs when NaOH is added. Finally, the template ion was removed with hydrochloric acid solution, and IIP-PEI/SiO_2 was formed. The preparing process of IIP-PEI/SiO_2 was expressed in Scheme 1.

Static adsorption characteristics of IIP-PEI/SiO_2 towards Pb^{2+} ion

Kinetic adsorption curve

The kinetic adsorption curve was shown in Figure 1. The adsorption rate of IIP-PEI/SiO_2 towards the Pb^{2+} ion was fast, and the adsorption reached to equilibrium within 30 min. It was implied that IIP-PEI/SiO_2 possesses very strong chelating adsorption ability for Pb^{2+} ion.

Adsorption isotherms

Figures 2and 3 were the adsorption isotherms of PEI/SiO_2 and IIP-PEI/SiO_2 towards Pb^{2+}, Zn^{2+}, and Cr^{3+}, respectively. It can be seen that the saturated adsorption amount of PEI/SiO_2 for Pb^{2+} is only 17.5 mg g^{-1}, but that of IIP-PEI/SiO_2 is 30.69 mg g^{-1}. Obviously, the value is enhanced nearly two times more than that of PEI/SiO_2. This fact display clearly that the affinity of IIP-PEI/SiO_2 for Pb^{2+} ion is enhanced greatly after Pb^{2+}-imprinted. The adsorption amount is increased markedly because a mass of cavities has been formed. These cavities are complementary to the template Pb^{2+} in shape and spatial arrangement of functional groups. Additional, although the adsorption amount of Zn^{2+} and Cr^{3+} on PEI/SiO_2 is smaller than that of Pb^{2+}, the differences are not too much, whereas the adsorption amount of Zn^{2+} and Cr^{3+} on IIP-PEI/SiO_2 is much smaller than that of Pb^{2+}. The above facts display fully that IIP-PEI/SiO_2 has high affinity, high recognition ability, and special selectivity for Pb^{2+}. Further data will be given in Table I.

Adsorption selectivity

Competitive adsorptions of Pb^{2+}/Zn^{2+} and Pb^{2+}/Cr^{2+} on IIP-PEI/SiO_2 from their mixtures were researched in batch systems. Table I summarized the data of the distribution coefficients K_d, selectivity coefficients k, and relative selectivity coefficients k'.

It can be seen that the selectivity coefficients and relative selectivity coefficients of IIP-PEI/SiO_2 for Pb^{2+}/Zn^{2+} and Pb^{2+}/Cr^{3+} increase after ion imprinted. This suggests that the adsorption abilities

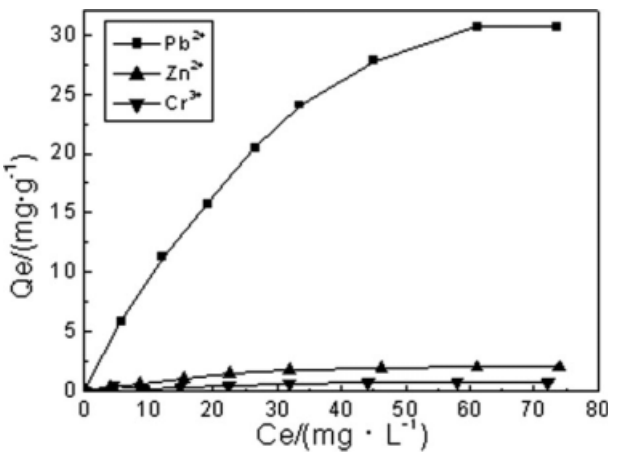


Figure 3 Adsorption isotherms of Pb^{2+}, Zn^{2+}, and Cr^{3+} on IIP-PEI/SiO_2. Temperature: 20°C; Time: 30 min; pH = 7.

TABLE I
Distribution Coefficient and Selectivity Coefficient Data of Pb^{2+}-IIP-PEI/SiO_2

Adsorbent	K_d (L g^{-1})				K_d (L g^{-1})			
	Pb^{2+}	Zn^{2+}	k	k'	Pb^{2+}	Cr^{3+}	k	k'
IIP-PEI/SiO_2	0.746	0.023	32.43	24.20	0.752	0.011	68.36	29.59
PEI/SiO_2	0.352	0.263	1.34		0.355	0.154	2.31	

of IIP-PEI/SiO_2 for Pb^{2+} are very strong, and far stronger than that for Zn^{2+} and Cr^{3+}. The reason for this is that the cavities imprinted by Pb^{2+} are non-matched to Zn^{2+} and Cr^{3+} in size, shape, and spatial arrangement of combining sites. For Zn^{2+}, the chelates of Pb^{2+} and Zn^{2+} with N atoms are all of four ligands, and the ionic radius of Zn^{2+} (74 pm) is smaller than that of Pb^{2+} (120 pm) so that it could enter into the cavity imprinted by Pb^{2+}, but the adsorption abilities of IIP-PEI/SiO_2 for Zn^{2+} are very poor. The reason is that the location of four N atoms in every cavity is stable comparatively, so the interaction between N atoms and Zn^{2+} is too weak to form stable ligands because of the long distance between Zn^{2+} and N atoms. For Cr^{3+}, although the ionic radius of Cr^{3+} (64 pm) is also smaller than that of Pb^{2+}, the adsorption amount on IIP-PEI/SiO_2 of Cr^{3+} is very poor, too. The reason is that the chelate of Cr^{3+} with PEI is six ligands, whereas the chelate of Pb^{2+} with PEI is of four ligands.[8] Cr^{3+} ion is difficult to be combined with IIP-PEI/SiO_2 because of non-matched combining sites.

Influence of pH on adsorption property

The adsorption isotherms at different pH were shown in Figure 4. It can be seen that the adsorption amount of Pb^{2+} is various at different pH. As pH < 7, the adsorption amount increases with the enhancing of pH; as pH = 7, the adsorption amount reaches to maximum. In acidic solution, most of N atoms of the amino groups in the macromolecular chains of PEI are in protonation state,[1] the protonation degree of N atoms of amino groups decreases with the decrease of acidity, and the coordination ability of N atoms of amino groups towards metal ions strengthens, so that the adsorption amount of Pb^{2+} increases with the rising of pH value. As pH > 7, the hydrolytic action of Pb^{2+} will occur, so the adsorption capacity should again decreases.

Influence of temperature on adsorption property

The adsorption isotherms of Pb^{2+} on IIP-PEI/SiO_2 at different temperatures were shown in Figure 5. It can be seen that the adsorption amount of Pb^{2+} increases with the rising of temperature, and the influence of temperature on the adsorption amount is greater. For example, the saturated adsorption amount at 35°C is 53.8 mg g^{-1}, which is far greater than 26.3 mg g^{-1} at 15°C. The fact implies that the chelation adsorbing of IIP-PEI/SiO_2 towards Pb^{2+} is an endothermic process.

The dependence of adsorption with temperature has been evaluated using the following equations:

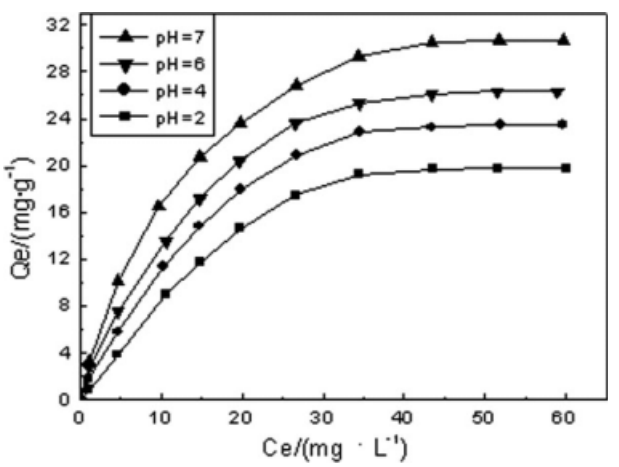


Figure 4 Adsorption isotherms of Pb^{2+} at different pH. Temperature: 20°C; Time: 30 min.

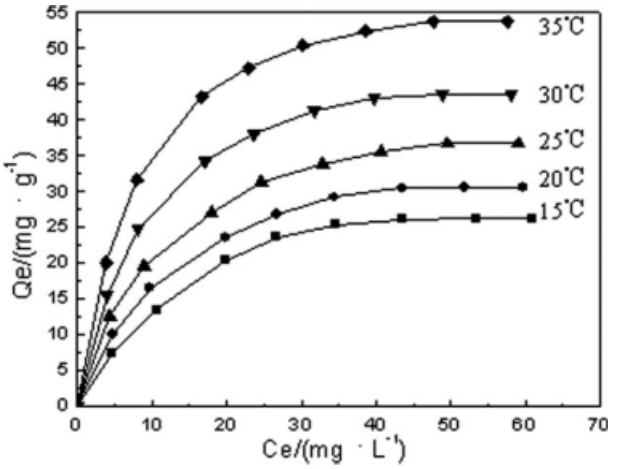


Figure 5 Adsorption isotherms of Pb^{2+} at different temperatures. Time: 30 min; pH = 7.

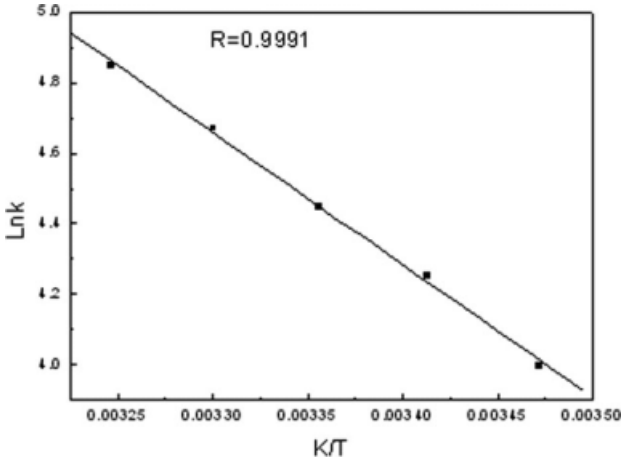


Figure 6 Plot of Lnk versus $1/T$.

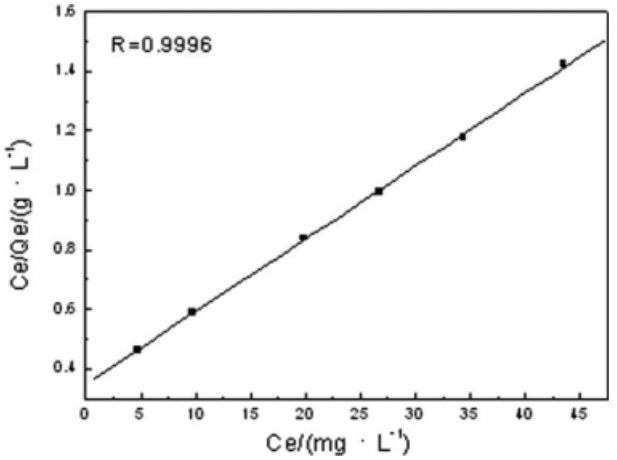


Figure 7 Plot of C_e/Q_e versus C_e.

$$\mathrm{Ln}k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

$$\Delta G = -RT\mathrm{Ln}k \tag{7}$$

where ΔH, ΔS, ΔG, and T are the enthalpy, entropy, Gibbs free energy, and temperature in Kelvin, respectively, R is the gas constant. The plot of Lnk versus $1/T$ is shown in Figure 6, it gives the numerical values of ΔH and ΔS from slope and intercept respectively, and ΔG could be calculated. The numerical values of ΔG from eq. (6) or eq. (7) and ΔH and ΔS obtained from the slope and intercept of Figure 6 are given in Table II.

The value of ΔG is negative and the value of ΔG decrease with rising of temperature may be due to spontaneous nature of adsorption and more favorable at high temperature confirming endothermic chemisorption. Similarly, the plus value of ΔH may be interpreted as the endothermic chemisorption process, whereas plus value of ΔS may be indicative of the faster adsorption of the Pb^{2+} onto active sites of the adsorbent.

TABLE II
Thermodynamic Functions of Pb^{2+} Adsorption on IIP-PEI/SiO_2

Temperature (K)	Combine constant k (L mg^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
288	54.5	−9.61	31.29	142.0
293	70.3	−10.32		
298	85.3	−11.03		
303	106.8	−11.74		
308	127.6	−12.45		

It can be seen also that as the equilibrium concentrations of Pb^{2+} ion reach to a certain values, the equilibrium adsorption amount change no longer, namely the adsorptions become saturated. These adsorption isotherms are typical unimolecular layer adsorptions of Langmuir type. Langmuir equation is as follows:

$$Q_e = Q_m \frac{kC_e}{1 + kC_e} \tag{8}$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m} \tag{9}$$

Where, C_e (mg L^{-1}) is the equilibrium concentration; Q_e (mg g^{-1}) is the equilibrium adsorption amount; Q_m (mg g^{-1})is the saturated adsorption amount; k is the combine constant. The data of 20°C in Figure 5 are regressed linearly according to eq. (9) and Figure 7 is obtained. The line in Figure 7 fits satisfactorily to the Langmuir eq. (9) obviously, and this indicates fully that the Pb^{2+} is adsorbed on the IIP-PEI/SiO_2 with monomolecular layer.

CONCLUSION

In this article, imprinting Pb^{2+} ions towards PEI on the surfaces of silica gel particles was carried out successfully, novel ionic imprinted material IIP-PEI/SiO_2 was obtained. The imprinted cavities were distributed in thin imprinted polymer layer, there was a smaller barrier for the diffusion of template ions, and so it was easy and rapid to bind with those recognition sites for the template ions. IIP-PEI/SiO_2 possessed strong affinity for template ion, and the static adsorption amount enhanced two times higher than that of PEI/SiO_2. The IIP-PEI/SiO_2 displayed special selectivity for template ion.

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