

Adsorption and recognizing ability of molecular imprinted polymer MIP-PEI/SiO₂ towards phenol

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Abstract

Firstly, functional macromolecule polyethyleneimine (PEI) was grafted onto the surfaces of silica gel particles via the coupling grafting method, the adsorption material PEI/SiO₂ was formed. Secondly, the molecular imprinting was carried out towards the macromolecule PEI grafted on the surface of silica particles using phenol as a template and diepoxyalkyl (669) as a crosslinking agent. Finally, imprinted polymer MIP-PEI/SiO₂ with high affinity, specific recognition ability and excellent selectivity for phenol was prepared. The adsorption and recognition ability of MIP-PEI/SiO₂ for phenol were researched by static methods. The experimental results show that MIP-PEI/SiO₂ possesses very strong adsorption and recognition ability for phenol. The saturated adsorption capacity could reach to 46.6 mg g⁻¹. The selectivity coefficients relative to resorcin and *p*-nitrophenol are 35.41 and 37.40, respectively. The empirical Freundlich isotherm was found to describe well the equilibrium adsorption data. pH and temperature have great influence on the adsorption capacity. Diluted hydrochloric acid solution is used as eluent, and the adsorbed phenol is eluted easily from MIP-PEI/SiO₂.

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1. Introduction

Phenol has great harmful effects for public health and environmental quality because of its high toxicity and accumulation of phenol in the environment. The separation and determination processes of low levels of phenol are mainly based on a suitable utilization of available separation/preconcentration material and techniques. The preconcentration procedure is an essential step for the accurate measurement and analysis of the analytes in trace level.

Molecular imprinting technique is a new method for preparation of highly selective polymer receptors for given molecules [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 and catalysts,

etc. [5–11]. The conventional method to prepare molecular imprinted polymers (MIPs) is an entrapment way. The molecular imprinted polymers prepared with conventional 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 several technologies, and among them, grafting polymerization method on the surfaces of silica gel particle has received some attention. Sulitzky et al. [18] grafted thin films of molecularly imprinted poly-

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mers on silica gel particle surfaces by utilizing “grafting from” method.

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and there are a great number of nitrogen atoms of amino groups on its macromolecular chains, very strong hydrogen bond interaction can be produced between PEI and phenol [19]. In this study, functional macromolecule polyethyleneimine was grafted onto the surfaces of silica gel particles, and then the molecular imprinting was carried out towards the macromolecule PEI grafted on the surface of silica particles using phenol as a template, diepoxyalkyl (669) as a crosslinking agent. Finally, imprinted polymer MIP-PEI/SiO₂ with high affinity, specific recognition ability and excellent selectivity for phenol was prepared, and the adsorption and recognition ability of MIP-PEI/SiO₂ for phenol were researched by static methods.

2. Experimental

2.1. Materials and instruments

Silica was purchased from Ocean Chemical Limited Company (about 150 μm in diameter, pore size: 5 nm, pore volume: 0.8 mL g⁻¹, surface area: 310 m²/g, Qingdao, China). PEI was purchased from Qianglong Chemical Limited Company (molecular mass, 10,000, Wuhan, China, AR grade). γ-Chloropropyl trimethoxysilane was purchased from Yongchang Chemical Limited Company (Naking, China, AR grade). Phenol and other chemicals were purchased from Beijing Chemical Plant (AR grade).

Used instruments in this study were as follows: Unic-2602 UV spectrophotometer (Unic Company, American), PerkinElmer1700 infrared spectrometer (PerkinElmer 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).

2.2. Preparation and characterization of MIP-PEI/SiO₂

The material PEI/SiO₂ was prepared and characterized according to the process described in previous study [20,21]. For preparation of MIP-PEI/SiO₂, a certain amount of PEI/SiO₂ particles adsorbed phenol and diepoxyalkyl (669) were added into absolute ethanol, and the reaction was allowed to carry out for 6 h at room temperature with continuous stirring. Finally, particles were fully washed with hydrochloric acid solution of 0.1 M to remove the template, and the phenol-imprinting polymer MIP-PEI/SiO₂ was obtained.

The infrared spectrums of PEI/SiO₂ and MIP-PEI/SiO₂ were determined in order to confirm the chemical structure change of PEI/SiO₂ after molecular imprinting.

For researching the imprinting effect, crosslinking polymer CP-PEI/SiO₂ was prepared with absence of phenol when crosslinking reaction was carried out.

2.3. Measurement of kinetic adsorption curve

About 0.2 g of MIP-PEI/SiO₂ was introduced into a conical flask directly. 50 mL of aqueous phenol solution with a initial concentration (C₀) of 4000 mg L⁻¹ was then added into conical flasks. This conical flask was placed in a shaker at a presettled temperature and pH and shaken. At different times, the concentration (C_t) of phenol solution was determined. The adsorption capacity (Q) was calculated according to Eq. (1).

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

where Q (mg g⁻¹) is the adsorption capacity; V (L) is the volume of the phenol solution; m (g) is the weight of the adsorbent MIP-PEI/SiO₂.

2.4. Measurement of adsorption isotherm

About 0.2 g of MIP-PEI/SiO₂ was introduced into a conical flask directly. 50 mL aqueous solution of phenol with concentration (C₀) of 1000, 2000, until 8000 mg L⁻¹ were then added into each conical flask. The conical flasks were placed in a shaker at a presettled temperature and pH and shaken. After the adsorption reached equilibrium, the concentration (C_e) of phenol solution was determined. The equilibrium adsorption capacity (Q_e) was calculated according to Eq. (2).

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

2.5. Influences of various factors on adsorption property of MIP-PEI/SiO₂

Varying the pH of each sample solution by buffer solutions (NH₄NO₃-NH₃·H₂O and NaAc-HAc), the influence of pH on the adsorption property of MIP-PEI/SiO₂ was examined. Varying the temperature of each sample solution, the influence of temperature on the adsorption property of MIP-PEI/SiO₂ was examined.

2.6. Selectivity studies

In order to show the selectivity of MIP-PEI/SiO₂ for phenol, competitive adsorptions of resorcin and *p*-nitrophenol with respect to phenol were also studied. The binary mixed solutions of resorcin/phenol and *p*-nitrophenol/phenol were prepared. In these mixed solutions, the concentration of phenol was 5000 mg L⁻¹ and same as other two components. The static adsorption experiments were performed for the two mixed solutions. After adsorption equilibrium was reached, the concentrations of phenol, resorcin and *p*-nitrophenol in the remaining solutions were determined with spectrophotometry, respectively.

Distribution coefficients of phenol, resorcin and *p*-nitrophenol were calculated by Eq. (3).

$$K_d = \frac{Q_e}{C_e} \quad (3)$$

where K_d represents the distribution coefficient ($L g^{-1}$); Q_e ($mg g^{-1}$) is the equilibrium adsorption capacity; C_e ($mg L^{-1}$) is the equilibrium concentration.

The selectivity coefficient of MIP-PEI/SiO₂ for phenol with respect to the competitor species (assigned as B) can be obtained from the equilibrium binding data according to Eq. (4)

$$k = \frac{K_d(\text{phenol})}{K_d(B)} \quad (4)$$

where k is the selectivity coefficient and B represents the resorcin or *p*-nitrophenol. The value of k allows an estimation of selectivity of MIP-PEI/SiO₂ for phenol. A relative selectivity coefficient k' can be defined as expressed in Eq. (5), and the value of k' can indicate the enhanced extent of adsorption affinity and selectivity of imprinting material MIP-PEI/SiO₂ for the template with respect to CP-PEI/SiO₂.

$$k' = \frac{k_{MIP}}{k_{CP}} \quad (5)$$

2.7. Desorption and repeated use

The repeated usability, i.e., regenerability, is an important factor for the absorption material. Desorption of the adsorbed phenol from the MIP-PEI/SiO₂ also studied in by static experimental. Adsorbed phenol was desorbed by treatment with 0.1 M of hydrochloric acid solution. The phenol adsorbed by MIP-PEI/SiO₂ was placed in the eluent and stirred continuously at room temperature for 2 h. The final phenol concentration in aqueous phase was determined. Desorption ratio was calculated from the amount of phenol adsorbed on the MIP-PEI/SiO₂ and final phenol concentration in the eluent. In order to test the reusability of MIP-PEI/SiO₂, phenol adsorption–desorption procedure was repeated ten times by using the same imprinted polymer.

3. Results and discussion

3.1. Preparing process and structure characterizing of MIP-PEI/SiO₂

Firstly, the ring opening reaction between diepoxyalkyl (669) and amine groups of PEI chain takes place when the crosslinking agent diepoxyalkyl (669) is added. Then the template was removed with hydrochloric acid solution. Finally, molecular imprinted polymer MIP-PEI/SiO₂ was formed. The preparing process of MIP-PEI/SiO₂ is expressed in Scheme 1.

The FTIR spectra of PEI/SiO₂ before and after imprinting were measured and are shown in Fig. 1. After imprinting, the absorption band at 1191 cm^{-1} is strengthened distinctly, which is the characteristic absorption of C–N bond of tertiary amine groups. Whereas all the absorption bands at 3584, 1660 and 802 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 alkyl, namely, all of primary and secondary amine groups in PEI chains have changed

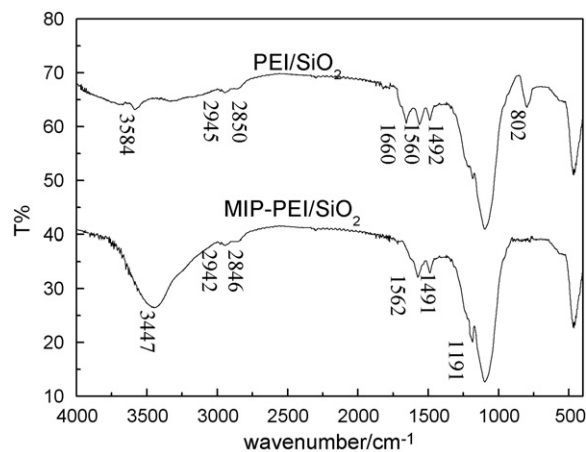


Fig. 1. FTIR spectrum of PEI/SiO₂ and MIP-PEI/SiO₂.

into tertiary groups. At the same time, the vibration absorption of O–H groups has been appeared at 3447 cm^{-1} , and it indicates further that the ring opening reaction has been occurred. The above observations show fully that the crosslinking between macromolecules of PEI has been produced by the effect of the crosslinking agent 669, and a layer of molecular imprinted polymer has been formed on the surfaces of silica gel particle, i.e., the surface molecular imprinted polymer MIP-PEI/SiO₂ has been obtained.

3.2. Kinetic adsorption curve of MIP-PEI/SiO₂ for phenol

The kinetic adsorption curve is shown in Fig. 2. The adsorption of MIP-PEI/SiO₂ towards phenol reaches to equilibrium in 8 h. It was implied that MIP-PEI/SiO₂ possesses high affinity for phenol. The high affinity attributes to the hydrogen bond interaction (main) and electrostatic interaction between them.

3.3. Adsorption isotherm of MIP-PEI/SiO₂ for phenol

The adsorption isotherms at different pH values are shown in Fig. 3. The effect of pH value on the adsorption property of MIP-PEI/SiO₂ can be seen clearly from Fig. 4, which comes

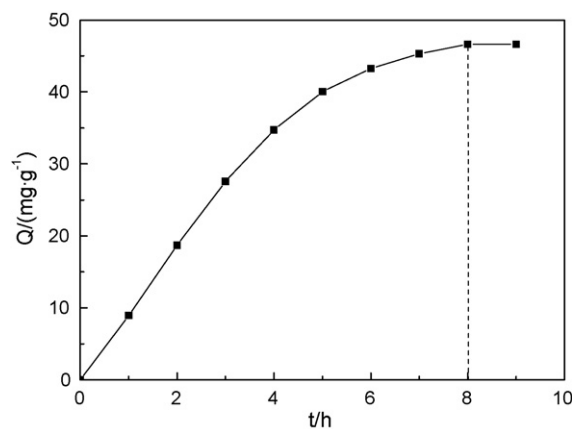
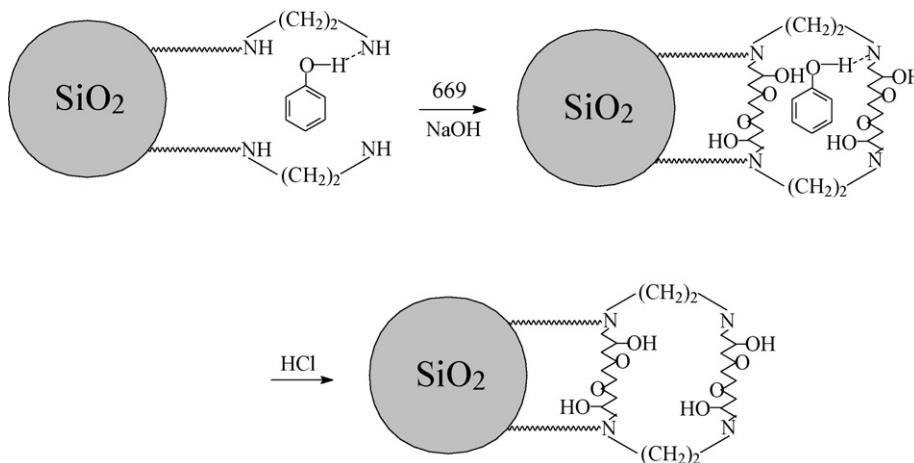


Fig. 2. Kinetic adsorption curve of MIP-PEI/SiO₂ for phenol. Temperature: 20 °C; pH 7; initial concentration of phenol: 4000 $mg L^{-1}$.



Scheme 1. Synthesis process of MIP-PEI/SiO₂.

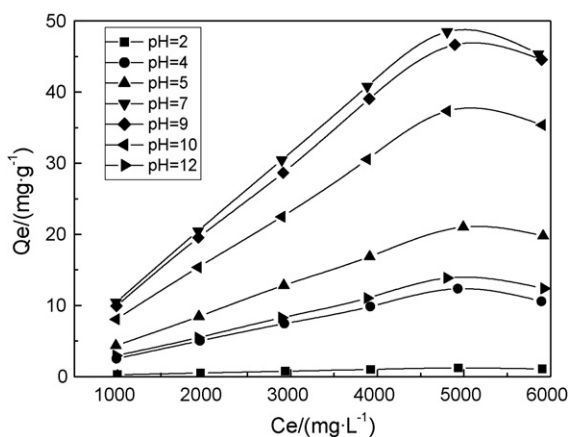


Fig. 3. Adsorption isotherms of MIP-PEI/SiO₂ for phenol at different pH. Temperature: 20 °C; adsorption time: 8 h.

from the data of Fig. 3. Obviously, the value of pH has a great influence on the adsorption property of MIP-PEI/SiO₂ for phenol, in acidic and basic solutions, the adsorption capacities are all lower, and in neutral solution there is the greatest adsorption capacity. Different molecule forms of PEI and phenol and different acting forces between them causes the adsorption capacity

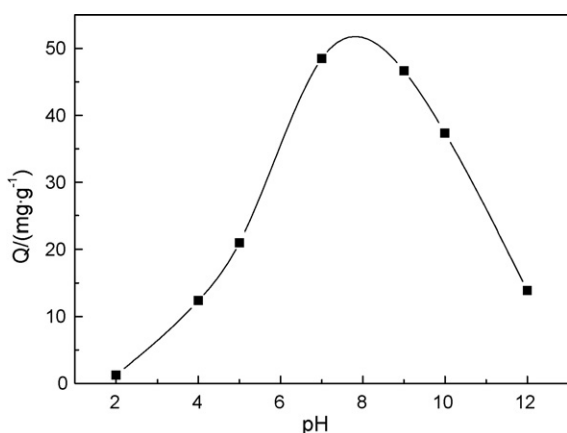


Fig. 4. Adsorption capacity of MIP-PEI/SiO₂ at different pH.

Table 1

The linear regression coefficient, parameter *n* and *k* in Freundlich equation at different pH

pH	2	4	5	7	9	10	12
<i>n</i>	0.9726	0.9844	0.9728	0.9745	0.9726	0.9674	0.9801
10 ⁴ <i>k</i>	3.18	28.72	53.71	127.90	122.86	102.13	33.64
<i>R</i>	0.9998	0.9999	0.9999	0.9997	0.9996	0.9999	0.9997

differences at different pH values. The reasons for this have been analyzed in detail in the previous study [19].

Freundlich adsorption equation and its logarithms form are follows:

$$Q_e = kC_e^n \tag{6}$$

$$\ln Q_e = \ln k + n \ln C_e \tag{7}$$

The data in Fig. 3 are treated using Freundlich adsorption equation, and the straight line is displayed in Fig. 5. Linear regression is performed according to the logarithmic form, and the curve of the $\ln Q_e$ vs. $\ln C_e$ fit satisfactorily to Freundlich equation. The linear regression coefficient, parameter *n* and *k* are listed in Table 1.

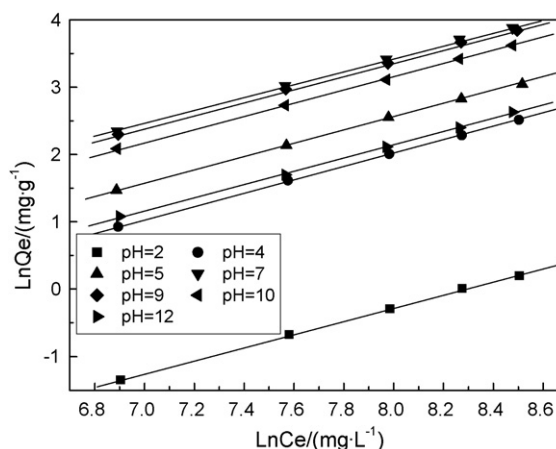


Fig. 5. Plot of $\ln Q_e$ vs. $\ln C_e$ at different pH.

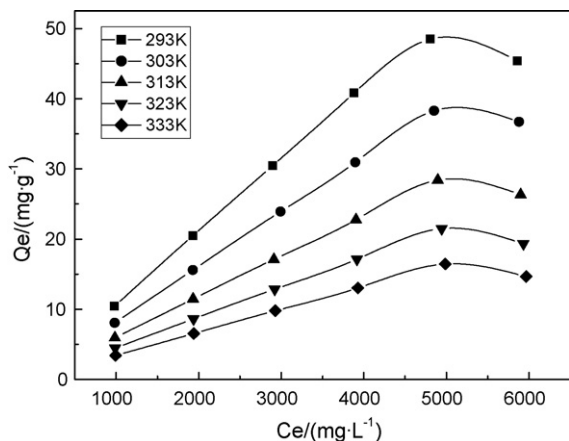


Fig. 6. Adsorption isotherms of MIP-PEI/SiO₂ for phenol at different temperature. pH 7; adsorption time: 8 h.

Table 2

The linear regression coefficient, parameter n and k in Freundlich equation at different temperature

T/K	293	303	313	323	333
n	0.9745	0.9743	0.9746	0.9745	0.97269
$10^4 k$	127.90	98.14	71.97	54.03	40.86
R	0.9997	0.9998	0.9999	0.9995	0.9998

The adsorption isotherms at different temperatures are shown in Fig. 6. The linear regression coefficient, parameter n and k are listed in Table 2. It can be seen that the influence of temperature on the adsorption capacity is greater, and the adsorption capacity decreases with the rising of temperature. This implies that the adsorption of MIP-PEI/SiO₂ towards phenol is an exothermic process.

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

$$\ln k = -\frac{\Delta H}{RT} + C \quad (8)$$

where ΔH and T are the change of enthalpy and temperature in Kelvin, respectively, R is the gas constant. The plot of $\ln k$ vs. $1/T$ is shown in Fig. 7; it gives the numerical values of ΔH from slope. The numerical values of ΔH is $-23.33 \text{ kJ mol}^{-1}$. The negative value of ΔH also indicates the adsorption of MIP-PEI/SiO₂ towards phenol is an exothermic process.

3.4. Adsorption selectivity

Figs. 8 and 9 are the adsorption isotherms of CP-PEI/SiO₂ and MIP-PEI/SiO₂ towards phenol, resorcin and *p*-nitrophenol, respectively. It can be seen that the saturated adsorption capacity of phenol on CP-PEI/SiO₂ is lower than that of resorcin and *p*-nitrophenol. The reason is that there are two functional groups in resorcin and *p*-nitrophenol, and the two functional groups could produce hydrogen bond interaction with PEI, but phenol has only one functional group could produce hydrogen bond interaction with PEI. After imprinted with phenol, the adsorption capacity of phenol on MIP-PEI/SiO₂ does not change, but the adsorption

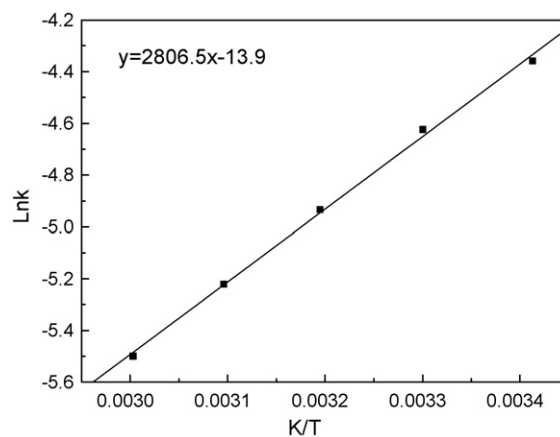


Fig. 7. Plot of $\ln k$ vs. K/T .

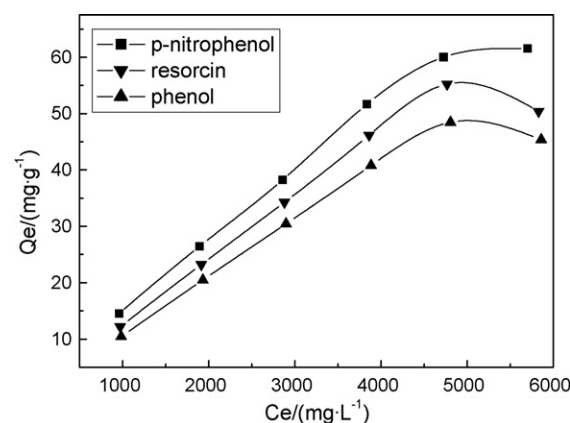


Fig. 8. Adsorption isotherms of phenol, resorcin and *p*-nitrophenol on CP-PEI/SiO₂. Temperature: 20 °C; time: 8 h; pH 7.

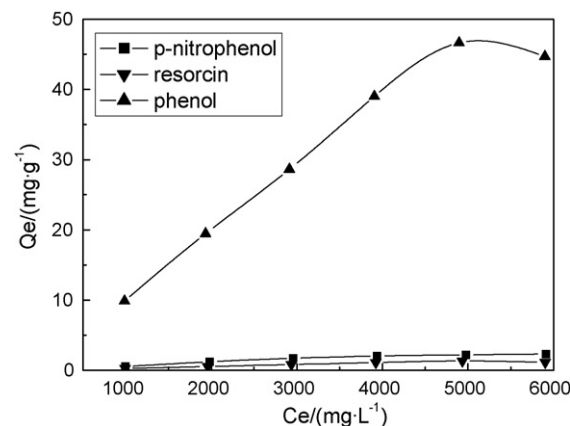


Fig. 9. Adsorption isotherms of phenol, resorcin and *p*-nitrophenol on MIP-PEI/SiO₂. Temperature: 20 °C; time: 8 h; pH 7.

capacity of resorcin and *p*-nitrophenol on MIP-PEI/SiO₂ is much lower than that of phenol. The above facts display fully that MIP-PEI/SiO₂ has high affinity, high recognition ability and special selectivity for phenol. Further data will be given in Table 3.

Competitive adsorptions of phenol/resorcin and phenol/*p*-nitrophenol on MIP-PEI/SiO₂ from their mixtures were

Table 3
Distribution coefficient and selectivity coefficient data of MIP-PEI/SiO₂

Adsorbent	K_d (L g ⁻¹)		k	k'	K_d (L g ⁻¹)		k	k'
	Phenol	Resorcin			Phenol	p-Nitrophenol		
MIP-PEI/SiO ₂	9.56	0.27	35.41	40.70	9.35	0.25	37.40	38.96
CP-PEI/SiO ₂	10.09	11.59	0.87		9.84	10.25	0.96	

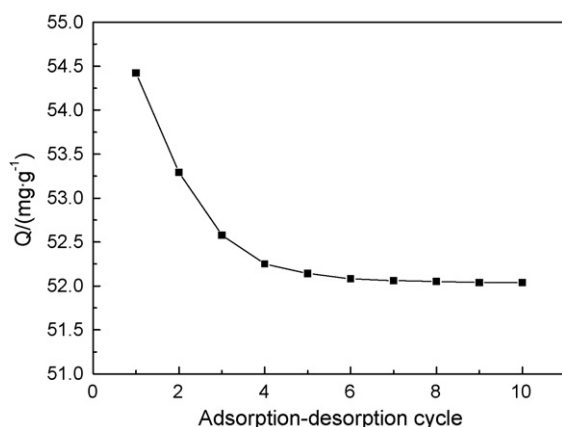


Fig. 10. Curve of reusability.

researched in static systems. Table 3 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 of MIP-PEI/SiO₂ for phenol/resorcin and phenol/*p*-nitrophenol increase after imprinted. This suggests that the adsorption abilities of MIP-PEI/SiO₂ for phenol are very strong, and far stronger than that for resorcin and *p*-nitrophenol. The reason for this is that the cavities imprinted by phenol are nonmatched to resorcin and *p*-nitrophenol in size, shape and spatial arrangement of combining sites. Resorcin and *p*-nitrophenol are bigger than phenol in size, so they could not enter into the cavity imprinted by phenol, and difficult to produce hydrogen bond interaction with PEI. This results in the adsorption capacity of resorcin and *p*-nitrophenol on MIP-PEI/SiO₂ is very poor. The relative selectivity coefficients relative to resorcin and *p*-nitrophenol are 40.70 and 38.96, respectively

3.5. Desorption and reusability

Desorption ratios are very high (97.9%). When hydrochloric acid is used as an eluent, the hydrogen bond interaction between phenol and PEI is disrupted and subsequently phenol are released into desorption medium. In order to show the reusability of the MIP-PEI/SiO₂, sorption–desorption cycle was repeated 10 times by using same imprinted material.

Adsorption–desorption cycle of phenol-imprinted polymer MIP-PEI/SiO₂ was shown in Fig. 10. The results clearly showed that the phenol-imprinted polymer MIP-PEI/SiO₂ could be used repeatedly without losing significantly their adsorption capacities.

4. Conclusions

In this paper, imprinting towards polyethyleneimine on the surfaces of silica gel particles was carried out successfully, and novel molecular imprinted material MIP-PEI/SiO₂ was obtained. The imprinted cavities are distributed in thin imprinted polymer layer, there is a smaller barrier for the diffusion of template, and so it is easy and rapid to bind with those recognition sites for the template. MIP-PEI/SiO₂ possesses high affinity, specific recognition ability and excellent selectivity for phenol. The selectivity coefficients relative to resorcin and *p*-nitrophenol are 35.41 and 37.40, respectively. Additional, MIP-PEI/SiO₂ has excellent reusability.

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