



## Synthesis and adsorption performance of lead ion-imprinted micro-beads with combination of two functional monomers

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### Abstract

A novel ion-imprinted polymer, lead ion-imprinted micro-beads with combination of two functional monomers, was synthesized using the W/O/W polymerization method. Two functional monomers, 1,12-dodecanediol-O,O'-diphenyl-phosphonic acid (DDDPA) and 4-vinylpyridine, were used to form a suitable construction with micro-pores fitting the template and recognition sites. The effects of adsorbent dosage, solution pH and the competitive ions on the adsorption and separation efficiency of lead ions were investigated. The lead ion-imprinted micro-beads were efficient for lead ions removal from aqueous solution in a broad pH range (4–9), when the adsorbent dosage was above 0.1 g/L. The adsorption process obeyed the pseudo second-order kinetics model and it only took half an hour to reach the equilibrium. The adsorption isotherm of lead ion was described by the Langmuir model ( $R^2 > 0.99$ ) with a maximum adsorption capacity of 116.9 mg/g. In the presence of competitive ions  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$ , the lead ion-imprinted micro-beads showed a high selectivity for lead ions. The selectivity coefficient of  $\text{Pb}^{2+}/\text{Cd}^{2+}$  and  $\text{Pb}^{2+}/\text{Co}^{2+}$  are 99.3 and 114.7, respectively.

**Key words:** lead ions; adsorption; lead ion-imprinted micro-beads; selective separation; recognition

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### Introduction

Lead is one of the most harmful heavy metals, which comes from both natural sources and industrial effluents. Lead ions have strong poisoning effect on human beings, especially to children. A lot of methods have been developed to remove lead ions from water, such as chemical precipitation (Blais et al., 2008), ion exchange (Mahmoud et al., 2010; Worms et al., 2010), adsorption (Etc et al., 2010; Ozcan et al., 2010), membrane separation (Lopez-Lopez et al., 2010; Pi et al., 2010). Since the slight pollution of heavy metal ions happens more frequently nowadays, and the natural water is a complicated system containing many interfering substances, how to remove trace amount lead ions efficiently from the polluted surface and ground water has always been a challenge. An increasing number of investigations have focused on the application of novel adsorbent materials and technologies in this field. Molecular imprinting technology (MIT), as a method for tailor-made preparation of highly selective synthetic polymer receptors for given molecules, has been rapidly developed in past decades. It is regarded as a novel method to create “artificial locks” which can recognize

“molecular keys”. By using MIT, molecular imprinting polymers (MIP) are synthesized and selective recognition sites of the specific molecule (template or imprinted molecule) can be created. The preparation of MIP was first reported by Wulff and Sarhan (1972), and a worldwide upsurge in the research of molecular imprinting technology has been brought about since Group Mosbach (Vlatakis et al., 1993), which was concerning the molecular imprinting polymer of theophylline. The imprinting and recognition of metal ions in aqueous solution is an important branch in the development of molecular imprinting technology, and good progress has been made in this field in recent years. A number of metal ion imprinting polymers have been prepared through different methods. Candan et al. (2009) prepared Cd(II)-ion imprinted beads to remove the cadmium from human plasma. Singh and Mishra (2009) synthesized Cu(II)-ion imprinted polymer and used it in solid phase extraction and preconcentration. Zn(II) ion-imprinted solid-phase extraction material (Zhao et al., 2007), Ni(II) ion-imprinted polymer (Ersöz et al., 2004) and Cr(III)-imprinted polymeric beads (Birlik et al., 2007) have also been prepared and applied for the separation of trace metal ions from aqueous solution.

Recently, more attention has been paid to the

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investigation of lead ion-imprinted polymers, such as lead ion surface imprinting polymer in combination with sol-gel process (Li et al., 2009) and the synthesis of lead ion-imprinted amino-functionalized silica gel adsorbent (Zhu et al., 2009). The lead ion imprinted polymers prepared by Esen et al. (2009) showed high selectivity for lead ions, however, the maximum adsorption capacity of the polymers is only 2.01 mg/g.

The functional monomer DDDPA (1,12-dodecanediol-O,O'-diphenyl-phosphonic acid) was used in the preparation of metal ion-imprinted polymers. This functional amphiphilic monomer has a long alkyl chain with high interfacial activity, two aromatic rings that can enhance the rigidity of recognition sites, and functional groups with a high binding affinity for lead ions in solution (Yoshida et al., 1999). The monomer 4-vinylpyridine also showed a good behavior for the imprinting of metal ions (Matsui et al., 1996a, 1996b).

In this study, a novel lead ion-imprinted micro-bead was synthesized using DDDPA and 4-vinylpyridine. The adsorption and separation performances of the lead ion-imprinted micro-beads for lead ions were investigated.

## 1 Materials and methods

### 1.1 Materials

Benzenephosphonic dichloride, dodecamethylene glycol, azobisisobutyronitrile (AIBN) and trimethylolpropane trimethacrylate (TRIM) were obtained from TCI Development Co., Ltd. (China). Monomer 4-vinylpyridine and the other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). The initiator azobisisobutyronitrile was used after recrystallization, other chemicals were analytic grade, and used without further purification.

### 1.2 Synthesis of functional monomer

The functional monomer DDDPA was synthesized according to previous reported methods (Goto et al., 1987; Yoshida et al., 1998) (Fig. 1). DDDPA and 4-vinylpyridine were chosen to be co-functional monomers for lead ions imprinting. The characteristics of DDDPA obtained in the experiment was as follows: light yellow viscous liquid; MS  $m/z$  (%) (M+H) 504;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.25 (m, 16H), 1.76 (m, 4H), 4.00 (m, 4H), 7.47 (m, 6H), 7.80 (m, 4H), 8.32 (s, 2H).

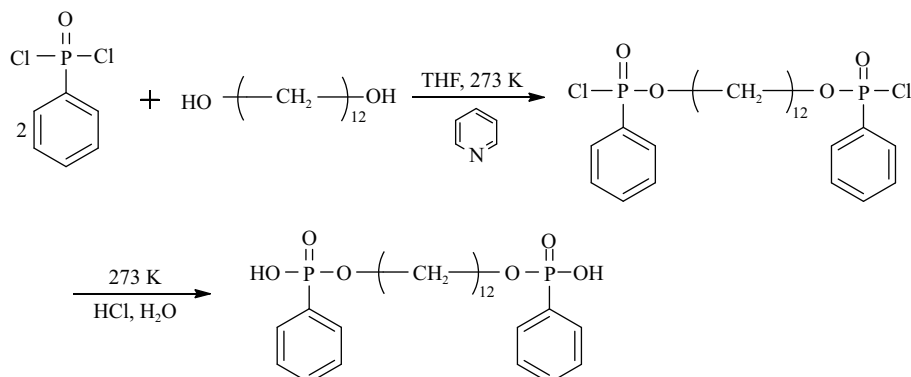


Fig. 1 Synthesis scheme of 1,12-dodecanediol-O,O'-diphenyl phosphonic acid (DDDPA).

### 1.3 Synthesis of lead ion-imprinted micro-beads

The imprinting polymer, lead ion-imprinted micro-beads, was synthesized by the emulsion polymerization method. The procedure was described as follows: 20 mmol/L DDDPA and 60 mmol/L 4-vinylpyridine were dissolved in 20 mL TRIM. Then, twenty drops of emulsifier (Span 80) and 10 mL toluene containing 5% (V/V) 2-ethylhexyl alcohol as solubility modifier were added into the solution. An aqueous solution (15 mL) of 10 mmol/L  $\text{Pb}(\text{NO}_3)_2$  buffered with acetic acid/sodium acetate at pH 3.5 was also added. After stirring over night, the mixture was sonicated for 20 min to give W/O emulsions. The emulsions were put into 250 mL aqueous solution containing 15 mmol/L dodecylsulfate (SDS) and 10 mmol/L  $\text{Mg}(\text{NO}_3)_2$  as an ionic strength controller (pH 3.5, buffered with 100 mmol/L acetic acid/sodium acetate). The mixer was then stirred at rate of 400 r/min to form the W/O/W emulsion. The oxygen in the emulsion was removed by bubbling nitrogen for 10 min. After the addition of 0.24 g of the powder initiator (AIBN), the mixture was polymerized at 323–343 K for 3 hr under a flow of nitrogen, and stirred at the rate of 400 r/min. At last, the polymer was washed with 100 mL of 2 mol/L HCl solution for several times to remove the template lead ions until no lead ions were detected in the effluent.

### 1.4 Characterization of the adsorbent

The surface appearance of the lead ion-imprinted micro-beads was analyzed by scanning electron microscope (SEM) (XL-30ESEM, Philip, Holland). The specific surface area of the particles was determined by Brunauer-Emmett-Teller (BET) model using single point analysis and a TriStar 3000 from Micromeritics Instrument Corporation (Norcross, USA). Fourier transform infrared spectra (FT-IR) of the lead ion-imprinted micro-beads were recorded in KBr media and performed on a Shimadzu FT-IR 8000 spectrophotometer (Japan).

### 1.5 Adsorption experiments

Adsorption isotherm experiments were performed using batch method. The dosage of 0.1 g/L lead ion-imprinted micro-beads was added into 100 mL solutions of initial lead ion concentrations of 1 to 30 mg/L in 250 mL conical flasks. Solutions of 0.1 mol/L HCl or 0.1 mol/L NaOH were used for pH adjustment. After shaking at

150 r/min at 298 K for 4 hr, the adsorbent particles were separated by filtration. The residual concentration of lead ions in the solution was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Optima 2100DV, PerkinElmer, USA).

Absorption kinetic experiments were carried out in a batch system. The dosage of 0.3 g/L lead ion-imprinted micro-beads were added into 100 mL solutions of 5 mg/L lead ions in 250 mL conical flasks. Solutions of 0.1 mol/L HCl or 0.1 mol/L NaOH were used for pH adjustment. The flasks were shaken at 150 r/min, 298 K. Samples were withdrawn and the adsorbent was separated by filtration at intervals of 5, 10, 30, 60, 90, 120, 150 min. The residual concentrations of lead ions were determined by ICP-AES.

All the experiments were performed in duplicates and the averaged values were recorded.

### 1.6 Separation selectivity experiments

The separation selectivity of the lead ion-imprinted micro-beads towards lead ion (MW: 207.2 g/mol, ionic radius: 120 pm) in the presence of competitive ions Cd<sup>2+</sup> (MW: 112.4 g/mol, ionic radius: 114 pm) and Co<sup>2+</sup> (MW: 58.9 g/mol, ionic radius: 74 pm) was evaluated. A 0.1 g/L lead ion-imprinted micro-beads was mixed in 250 mL conical flasks with 100 mL solutions of Cd<sup>2+</sup>, Co<sup>2+</sup> and Pb<sup>2+</sup> ions with the initial concentrations ranged from 0.5 to 30 mg/L at pH 5.0, respectively. After shaking at 150 r/min, 298 K for 4 hr, the adsorbent was separated by filtration and the residual concentrations of metal ions were determined by ICP-AES. The distribution coefficients ( $K_d$ , L/g) for Cd<sup>2+</sup>, Co<sup>2+</sup> and Pb<sup>2+</sup> were calculated by Eq. (1) (Esen et al., 2009):

$$K_d = ((C_i - C_f)/C_f) \times (V/m) \quad (1)$$

where,  $C_i$  (mg/L) and  $C_f$  (mg/L) are the initial and final concentrations of metal ions, respectively.  $V$  (L) is the volume of the aqueous solution and  $m$  (g) is the weight of the adsorbent added in the batch experiment. The selectivity coefficients ( $\alpha$ ) for the binding of lead ions in the presence of the competing species (Cd<sup>2+</sup> or Co<sup>2+</sup>) were determined by Eq. (2) (Esen et al., 2009),

$$\alpha = K_d(\text{Pb}^{2+})/K_d(X^{m+}) \quad (2)$$

where,  $X^{m+}$  is the competitive metal ion.

## 2 Results and discussion

### 2.1 Characterization of the lead ion-imprinted micro-beads

Surface appearance of lead ion-imprinted micro-beads was analyzed by SEM (Fig. 2). It is found that the obtained lead ion-imprinted polymer is well-proportioned beads with diameters ranging from 100 to 500  $\mu\text{m}$ . The surface of lead ion-imprinted micro-beads is rough with micro-pores.

The specific surface area of the particles was measured by Brunauer-Emmett-Teller (BET) model using single

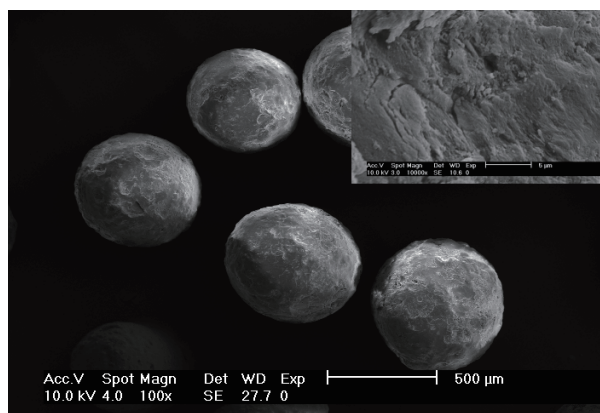


Fig. 2 Surface appearance of the lead ion-imprinted micro-beads.

point analysis. The specific surface area, total pore volume (BJH desorption cumulative pore volume of pores between 1.7 and 300 nm diameter) and average pore diameter for lead ion-imprinted micro-beads are 43.49 m<sup>2</sup>/g, 0.110 mL/g and 10.15 nm, respectively.

Figure 3 shows FT-IR spectra of lead ion-imprinted micro-beads. A pyridine ring on 4-vinylpyridine at 1470 cm<sup>-1</sup>, a para-orienting group on 4-vinylpyridine at 815 cm<sup>-1</sup>, a phosphoryl group on DDDPA at 1263 cm<sup>-1</sup>, -P-O- group on DDDPA at 1057 and 984 cm<sup>-1</sup>, and hydroxyl groups at 3428 cm<sup>-1</sup>. The result of the FT-IR is in consistent with the related references (Bourbigot et al., 1993; Cesteros et al., 1993; Keskin and Elliott, 2003).

### 2.2 Effect of adsorbent dosage and pH

The initial concentration of 1 mg/L lead ions was applied in the batch experiments. It was found that the removal efficiency reached almost 100% even at a low adsorbent dosage (0.1 g/L). Therefore, 5 mg/L solution of lead ions was selected as the initial concentration in the batch experiment to evaluate the dosage effect. As shown in Fig. 4b, when the adsorbent dosage increased from 0.1 to 1.0 g/L, the removal efficiency of lead ion by lead ion-imprinted micro-beads increased from 87% to 100%. The initial concentration of 1 mg/L lead ions was applied in the following experiments. Taking into account the removal efficiency and the relative less adsorbent consumption, 0.1 g/L was selected as the adsorbent dosage for following studies.

Batch equilibrium experiments were performed in pH range 2–9 to determine the effect of pH on the adsorption

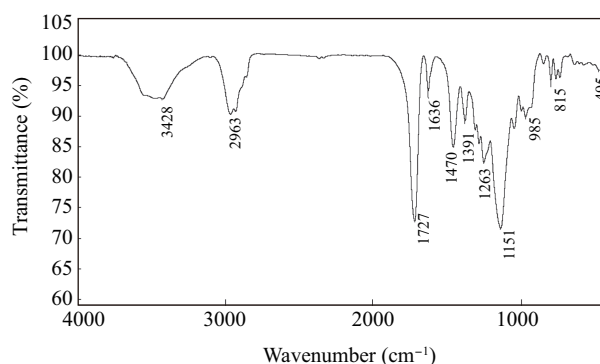
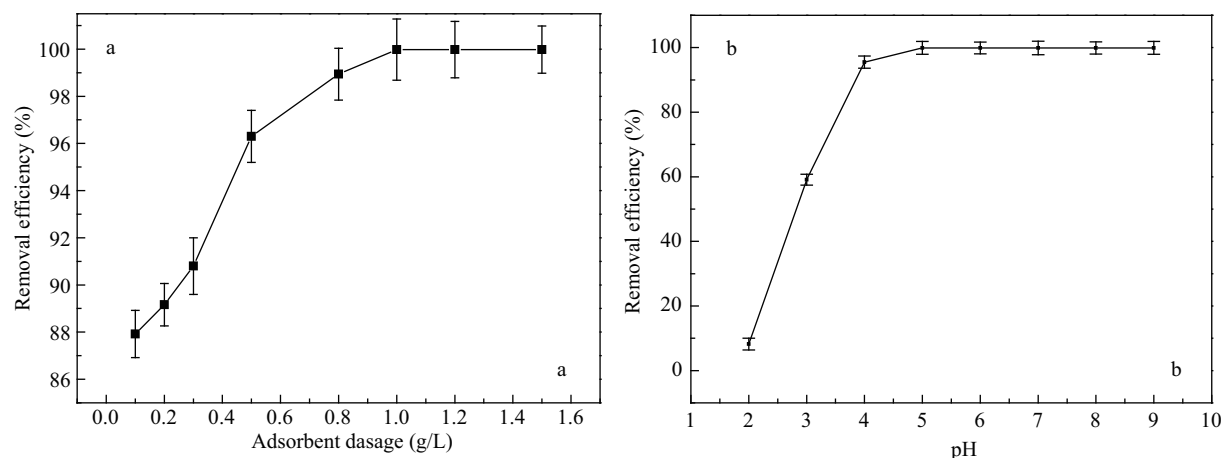


Fig. 3 FT-IR spectrum of the lead ion-imprinted micro-beads.



**Fig. 4** Effect of adsorbent dosage (a) and solution pH (b) on the removal efficiency of lead ions. Conditions: initial lead ion concentration 1 mg/L; adsorption time 2 hr; temperature 298 K; pH 6; adsorbent dosage 0.1 g/L.

efficiency of lead ions. As shown in Fig. 4b, the adsorption of lead ions on the lead ion-imprinted micro-beads was highly dependent on the solution pH. When the solution pH was below 3, the lead ion-imprinted micro-beads showed a low binding affinity to lead ions. The competition between  $H^+$  and lead ions for imprinted sites on the surface of the polymer was strong at low pH. With increasing pH, the adsorption efficiency of lead ions increased significantly. When the solution pH was higher than 4, the removal efficiency reached up to 99.9%. Precipitation reaction may contribute to the removal of lead ion at high pH ( $K_{sp-Pb(OH)_2} = 1.2 \times 10^{-15}$ ). Therefore, in adsorption studies, the solution pH should be controlled below the critical pH of hydroxide precipitation, which is 9.20 for initial concentration 1 mg/L of lead ion solution. According to the removal efficiency, the pH value range of natural water and the possible effect of hydroxide precipitation, the feasible pH range were selected at 5–6 in further experiments.

### 2.3 Adsorption kinetics

The pseudo second-order Lagergren equation (Eq.(3)) was used to describe the adsorption kinetics of lead ion-imprinted micro-beads:

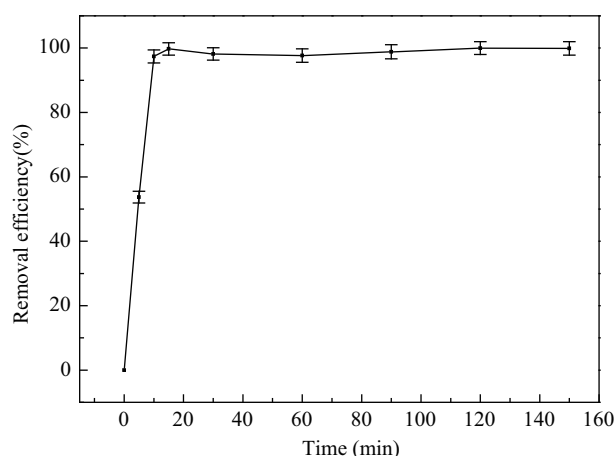
$$\frac{t}{q_t} = \left( \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \right) \quad (3)$$

where,  $k_2$  (g/(mg·min)) is the second-order Lagergren constant of adsorption;  $q_t$  (mg/g) and  $q_e$  (mg/g) are the quantities of metal ions adsorbed at time  $t$  (min) and equilibrium, respectively.

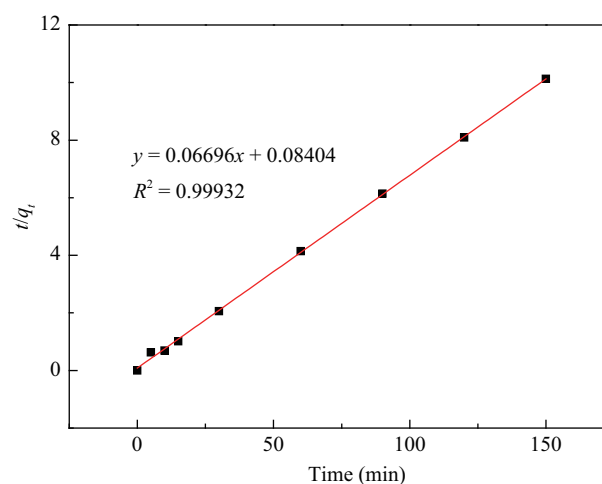
As shown in Fig. 5, the removal efficiency had reached 50% in the first 5 min and increased to 99% after 90 min. The adsorption kinetics of lead ion-imprinted micro-beads conformed to the pseudo second-order Lagergren equation with  $R^2 > 0.999$  (Fig. 6). The value of  $k_2$  calculated from the slope is  $1.1 \times 10^{-3}$  g/(mg·min).

### 2.4 Adsorption isotherms

Langmuir and Freundlich models are applied to describe the adsorption isotherms.



**Fig. 5** Effect of contact time on the removal efficiency of lead ion-imprinted micro-beads. Adsorbent dosage 0.3 g/L; pH 5–6; temperature 298 K; initial concentration of lead ion 5 mg/L.



**Fig. 6** Adsorption kinetics of lead ions on the lead ion-imprinted micro-beads. Adsorbent dosage 0.3 g/L; pH 5–6; temperature 298K; initial concentration of lead ion 5 mg/L.

Langmuir model:

$$C_e/q_e = 1/(Q_0 \cdot b) + C_e/Q_0 \quad (4)$$

where,  $C_e$  (mg/L) is the equilibrium concentration;  $q_e$  (mg/g) is the adsorption amount at equilibrium;  $Q_0$  (mg/g) is the maximum adsorption amount and  $b$  is the Langmuir

constants related to adsorption capacity and energy of adsorption.

Freundlich model:

$$\log q_e = \log K + (1/n)\log C_e \quad (5)$$

where,  $K$  is the Freundlich constant, and  $n$  is the Freundlich exponent.

By comparison of the adsorption isotherms of lead ion with Langmuir and Freundlich models (Fig. 7), it was found that the experimental data is in conformity with Langmuir isotherm better than that of Freundlich model. The maximum adsorption capacity of lead ion-imprinted micro-beads towards the lead ions was calculated as 116.9 mg/g. Compared with the previous reports, in which the lead ion surface imprinting polymer, the lead ion-imprinted amino-functionalized silica gel adsorbent and the lead ion-imprinted polymer, had the maximum adsorption capacity of 22.7, 19.66 and 2.01 mg/g, respectively (Esen et al., 2009; Li et al., 2009; Zhu et al., 2009). The lead ion-imprinted micro-beads synthesized in this study showed a much higher adsorption capacity.

## 2.5 Separation selectivity

The separation selectivity study was conducted focusing on the selective adsorption of lead ion by lead ion-imprinted micro-beads in presence of  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$  ions. These competitive ions were selected because they have the same charge and relative similar ionic radius as lead ion. In this research, we focused on the selectivity coefficient of  $\text{Pb}^{2+}/\text{Cd}^{2+}$  and  $\text{Pb}^{2+}/\text{Co}^{2+}$  ( $\text{Pb}^{2+}=120$  pm,  $\text{Cd}^{2+}=114$  pm,  $\text{Co}^{2+}=74$  pm; Shannon, 1976).

The experimental data of the selectivity study are listed in Table 1. It can be found that the lead ion-imprinted micro-beads have a high separation selectivity for lead ion in presence of  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$  ions.

The relationships between initial concentrations of three coexistent heavy metal ions and their adsorption amounts on the lead ion-imprinted micro-beads are shown in Fig. 8. The adsorption amounts of  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$  on the lead ion-imprinted micro-beads were quite low, which almost did not change with the increase in the initial  $\text{Cd}^{2+}$  and

**Table 1** Selective coefficients ( $\alpha$ ) of  $\text{Pb}^{2+}/\text{Cd}^{2+}$  and  $\text{Pb}^{2+}/\text{Co}^{2+}$

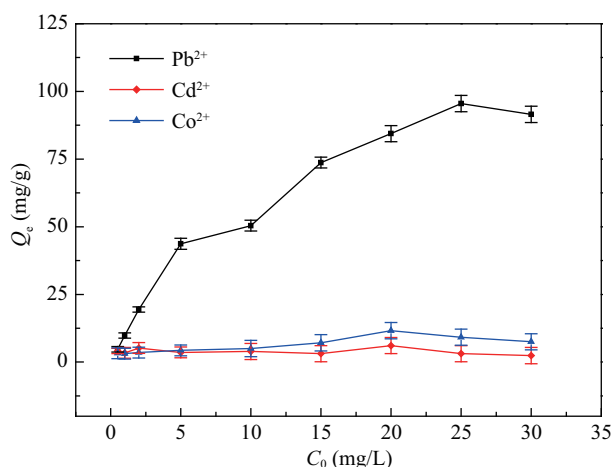
Metal ion	$C_0$ (mg/L)	$K_d$ (mL/g)	$\alpha$
$\text{Pb}^{2+}$	1	516.3	–
$\text{Cd}^{2+}$	1	5.2	99.3
$\text{Co}^{2+}$	1	4.5	114.7

$\text{Co}^{2+}$  concentrations. However, the adsorption amount of lead ion was much higher than that of  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$ . When the initial concentration of lead ions was 25 mg/L, the adsorption quantity reached the maximum level. By fitting with Langmuir isotherm model in this mixed ions solution, the maximum adsorption capacity of the lead ion-imprinted micro-beads was calculated as 93.55 mg/g, which was slightly reduced comparing with the value in single lead ion system.

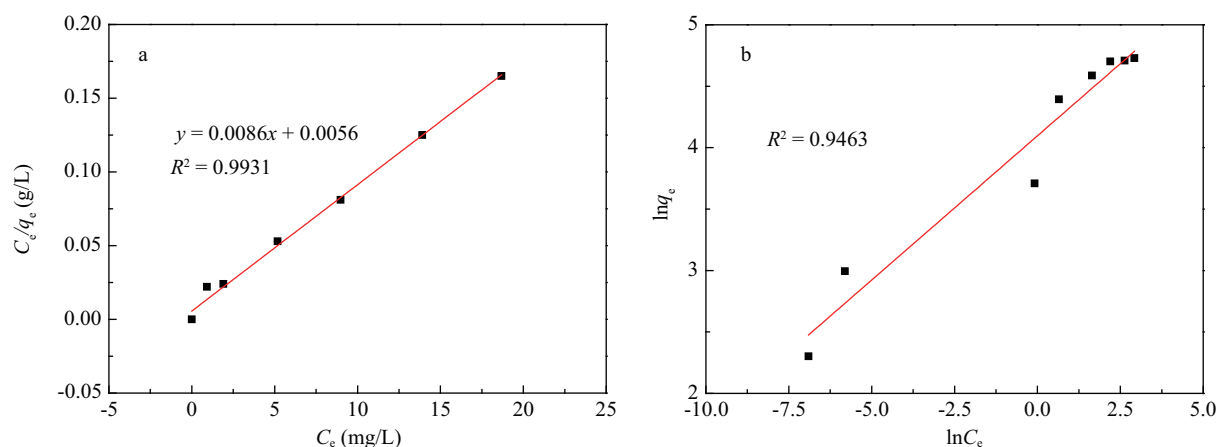
## 2.6 Desorption

Four different acids including HCl,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$  and  $\text{HCOOH}$  were used as eluants for desorption of lead ions from the lead ion-imprinted micro-beads. The desorption efficiency of acids are listed in Table 2.

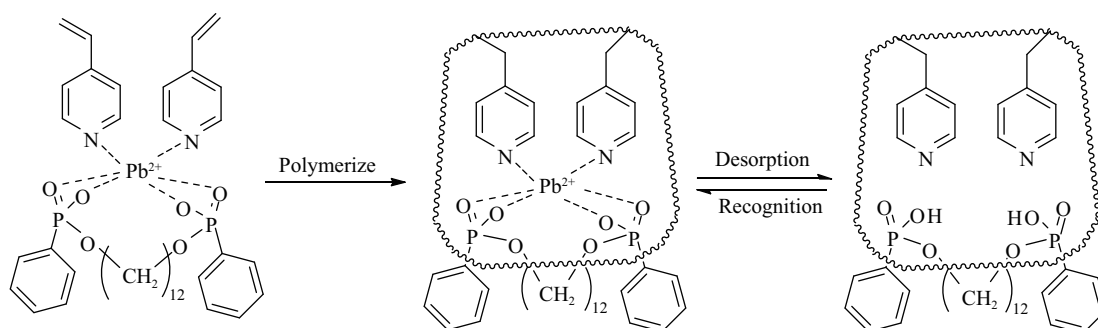
The highest desorption ratio was observed with 100 mL of 1 mol/L  $\text{CH}_3\text{COOH}$  solution. It was found that organic



**Fig. 8** Relationships between initial concentrations of three coexistent heavy metal ions and their adsorption amounts on the lead ion-imprinted micro-beads. Adsorbent dosage 0.1 g/L, pH 6, adsorption time 4 hr, temperature 298 K.



**Fig. 7** Langmuir (a) and Freundlich (b) adsorption isotherm of lead ions on the lead ion-imprinted micro-beads. Adsorbent dosage 0.1 g/L; pH 6; adsorption time 2 hr; temperature 298 K.



**Fig. 9** Scheme of preparation and recognition of the lead ion-imprinted micro-beads.

**Table 2** Desorption ratio of lead ions from lead ion-imprinted micro-beads with different acids

Acid (1 mol/L)	Desorption quantity (mg/g)	Desorption ratio (%)
HCl	8.36	83.6
HNO <sub>3</sub>	8.78	87.8
CH <sub>3</sub> COOH	9.49	94.9
HCOOH	9.09	90.9

acids had a higher desorption ratio than inorganic acids. The possible reason is that the complexing action between the carboxyl group  $\text{-COO}^-$  and lead ions is in favor of the desorption of lead ions from the lead ion-imprinted micro-beads.

The recycle experiments of adsorption-desorption have been conducted using the lead ion-imprinted polymer beads for separation of lead ions. After five recycles of adsorption-desorption experiments, the lead ion-imprinted polymer beads have kept almost 100% removal efficiency for the samples of 5 mg/L lead ion solutions.

### 2.7 Mechanism discussion

It was found that the synthesized lead ion-imprinted micro-beads showed high adsorption efficiency and selectivity for lead ions. This good performance of the lead ion-imprinted micro-beads is related with the composition and structure of the imprinting polymer with the combination of two functional monomers. The possible recognition mechanism of the lead ion-imprinted micro-beads in this research might be described by the following way (Fig. 9). Firstly, the functional monomers DDDPA and 4-vinylpyridine formed a complex with the template lead ions. Then the co-functional monomers were polymerized by emulsion polymerization mode. Finally, the target-selective cavities were produced on its surface after removing the template lead ions from the polymer. When the lead ion-imprinted polymer was used as an adsorbent to remove lead ions, the recognition sites and the proper size cavities exactly for lead ions on the surface of this polymer contributed to a high adsorption efficiency and selectivity for lead ions.

### 3 Conclusions

In the present study, using DDDPA and 4-vinylpyridine as the functional monomers, the lead ion-imprinted micro-beads were prepared by the W/O/W polymerization

method. The lead ion-imprinted micro-beads showed high adsorption ability towards lead ions in a broad pH range of 4–9 with the maximum capacity of 116.9 mg/g. The adsorption process obeys the pseudo second-order kinetics model and it only takes 90 min to reach the equilibrium. The adsorption isotherm can be well described by the Langmuir model. The lead ion-imprinted micro-beads also performed a high selectivity for lead ion when there were coexistent competitive ions of  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$ .

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