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# Synthesis and Properties of Surface Molecular Imprinting Adsorbent for Removal of $Pb^{2+}$

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**Abstract** A new chitosan imprinting adsorbent using diatomite as core material was prepared by using the surface molecular imprinting technology with the $Pb^{2+}$ as imprinted ion. The preparation process conditions of the surface molecular imprinting adsorbent were studied. The adsorbent was characterized by using Fourier transform infrared (FTIR) spectrum. FTIR spectrum indicated that it was cross-linked by epichlorohydrin. The new imprinting adsorbent could provide a higher adsorption capacity for $Pb^{2+}$, which reached 139.6 mg/g increasing 32.3% compared with cross-linking chitosan adsorbent (the initial $Pb^{2+}$ concentration of 600 mg/L). The adsorption velocity was quick and the equilibration time of the imprinting adsorbent for $Pb^{2+}$ was 3 h that shortened about 40% compared with cross-linking chitosan adsorbent. It had a more wide pH range of 5–7 than that of cross-linking chitosan adsorbent. The new imprinting adsorbent can be reused for up to ten cycles without loss of adsorption capacity. In the kinetics and isotherm study, the pseudosecond order model and Langmuir model could represent the adsorption process.

**Keywords** Surface molecular imprinting · Chitosan · Diatomite · Adsorption · Lead ion

## Introduction

The environmental pollution of heavy metals has been widely focused on recently. Wastewater containing heavy metal ions was produced mainly by traditional industry such as battery manufacturing, electroplating, mining, etc. Heavy metal like lead (Pb), cadmium (Cd), mercury (Hg), and so on could never be degradated in whatever means and enriched in biological tissue, which caused many kinds of diseases [1–4].

Chitosan is a kind of natural polysaccharide, which is structurally the partial *N*-deacetylated chitin. It is often used for metal ion concentrating and removing because of the $–NH_2$ and –OH on chitosan molecule that can chelate metal ions [5–8]. But chitosan

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easily dissolve in acidic environment and its cost is high. These cause it to be restricted in the industrial application. Therefore, the sorbent of low-cost and high adsorption capacity has attracted attention of more and more people. Diatomite is a siliceous, sedimentary rock consisting principally of the fossilized skeletal remains of the diatom, where the silica of the fossilized diatom skeleton resembles opal or hydrous, silica in composition ($SiO_2 \cdot nH_2O$). Diatomite has porous structure and high surface area to have certain adsorption capacity on metal ions [9, 10]. It is also rich in resources and lower price than chitosan.

Molecular imprinting technique was a promising affinity separation technology developed in the 1990s. Function monomers copolymerized with cross-linking agent and template molecules, then removed template molecules to form imprinting sites that could completely match the template molecules on space positions and binding sites. So the molecular imprinting polymer could selectively adsorb target molecules [11–13].

In this paper, by surface molecular imprinting technology [14–16] and using $Pb^{2+}$ as the imprinted ion, a new adsorbent, chitosan imprinting biosorbent using diatomite as core material (CIBD-Pb), was prepared. The preparation process and adsorption properties were studied in the research.

## Materials and Methods

### Chemicals

Chitosan with 85% degree of deacetylation was extracted from shrimp shells obtained in our laboratory. Diatomite was supplied by Beijing Chuangqingyuan Co. Ltd., lead sulfate ($PbSO_4$), acetic acid, sodium hydroxide (NaOH), and epichlorohydrin (ECH) were of analytical grade.

### Preparation of the Cross-linking Chitosan Adsorbent (CCTS)

Chitosan (0.6 g) were dissolved in 20 mL acetic acid (2%, *v*/*v*). The mixture was stirred for 30 min and remained for 30 min; epichlorohydrin (1 mL) was added to the mixture and allowed to react for 8 h at 25 °C. The mixture solution was dropped into 0.5 mol/L NaOH to form spheres. The formed chitosan beads were remained in the NaOH for 12 h and washed with deionized water to neutral and dried at 60 °C. The dry beads were stored in a sealed bottle for further use.

### Preparation of the Nonimprinted Chitosan Biosorbent using Diatomite as Core Material (CBD)

Chitosan (0.6 g) and diatomite (0.6 g) were dissolved in 20 mL acetic acid (2%, *v*/*v*). The mixture was stirred for 30 min and remained for 30 min; epichlorohydrin (1 mL) was added to the mixture and allowed to react for 8 h at 25 °C. The mixture solution was dropped into 0.5 mol/L NaOH to form spheres. The formed chitosan-coated diatomite beads were remained in the NaOH for 12 h and washed with deionized water to neutral and dried at 60 °C. The dry beads were stored in a sealed bottle for further use.

### Preparation of the $Pb^{2+}$ Imprinted Chitosan Biosorbent Using Diatomite as Core Material (CIBD-Pb)

Chitosan (0.6 g) and diatomite (0.6 g) were dissolved in 20 mL acetic acid (2%, *v*/*v*) and a certain concentration of lead sulfate ($PbSO_4$) solution (1 mL) was added into the above solution, respectively. The mixture was stirred for 30 min and remained for 30 min; epichlorohydrin (1 mL) was added to the mixture and allowed to react for 8 h at 25 °C. The mixture solution was dropped into 0.5 mol/L NaOH to form spheres. The formed chitosan-coated diatomite beads were remained in the NaOH for 12 h and washed with deionized water to neutral. The imprinted $Pb^{2+}$ in the sorbent was removed by treating with ethylenediaminetetraacetic acid (EDTA; 0.05%, m/m) solution, stirring at room temperature for 8 h. Regeneration was carried out by washing the adsorbent with 0.2 mol/L NaOH for 2 h. Finally, the sorbent was filtrated, washing with deionized water to neutral, and dried at 60 °C. The dry beads were stored in a sealed bottle for further use.

### Adsorption Experiments

A certain amount of adsorbent was added to a 250-mL beaker containing $Pb^{2+}$ aqueous solution and the total solution was 50 or 100 mL. The beaker rotated in constant temperature air shaker (120 rpm) at 25 °C for 12 h. The amount of $Pb^{2+}$ were determined by atomic absorption spectrometer (SpectrAA 55-B, Varian Company). The adsorption capacity was determined by mass balance calculation.

$$Q = \frac{(c_0 - c_e)V}{W} \tag{1}$$

$$\eta = \frac{(c_0 - c_e)}{c_0} \times 100\% \tag{2}$$

where $Q$ is adsorption capacity (mg/g), $\eta$ is removal rate, $c_0$ is the initial concentration of metal ion (mg/L), and $c_e$ is the equilibrated concentration of the metal ion (mg/L). $V$ (L) is volume of added solution and $W$ (g) is the weight of the adsorbent.

### Desorption and Batch Experiments

Filtrate solution after adsorption and remove the adsorbent to 250-mL beaker with 50 mL EDTA (0.05%, m/m). The beaker rotated in constant temperature air shaker (120 rpm) at 25 °C for 8 h. Then wash the adsorbent with 0.2 mol/L NaOH for 2 h. Finally, the sorbent was filtrated, washing with deionized water to neutral, and dried at 60 °C for batch experiments.

## Results and Discussions

### Influence of Imprinted $Pb^{2+}$ Concentration in Preparation on Adsorption Capacity

When the selected heavy metal ions were reversibly bound to the chitosan coating and subsequently were desorbed in the preparation of an adsorbent, the imprinting sites, or specific spaces, of the imprinted metal ion were retained on the surface coating of the adsorbent, enhancing the selectivity for the heavy metal ions. So the imprinted $Pb^{2+}$ concentration was very important in preparation. As shown in Fig. 1, when the imprinted $Pb^{2+}$ concentration increased from 0.42 to 1.67 mg in 1 g biomass, the adsorption capacity of CIBD-Pb also enhanced along with it. But the adsorption capacity improved no more when imprinting $Pb^{2+}$ concentration continued to increase to 2.5 mg in 1 g biomass. In fact,

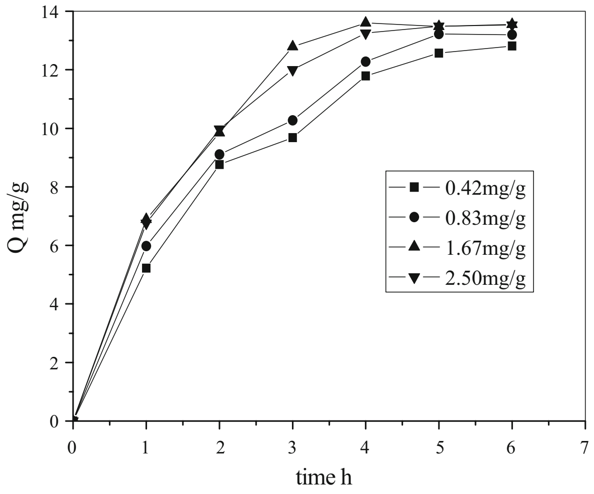


**Fig. 1** Effect of imprinted $Pb^{2+}$ concentration for the absorption of $Pb^{2+}$ on CIBD-Pb. The initial $Pb^{2+}$ concentration was 50 mg·L$^{-1}$, the volume of solution was 50 mL, 0.15 g of sorbent was used

the imprinted $Pb^{2+}$ concentration of 1.67 mg in 1 g biomass forming imprinting sites on the surface coating had saturated. More imprinting sites could not be formed even if the imprinted $Pb^{2+}$ concentration continued to increase. The adsorption capacity of CIBD-Pb for $Pb^{2+}$ did not increased anymore. So the optimum imprinted $Pb^{2+}$ concentration was selected as 1.67 mg in 1 g biomass. If the imprinted ion was $Ni^{2+}$, the concentration of imprinted $Ni^{2+}$ also had similar rule to the adsorption capacity [17].

## Influence of Cross-linking Agent Concentration in Preparation of Adsorbent

Epichlorohydrin cross-links with $–NH_2$ or –OH of chitosan and this may enhance stability of chitosan in the aqueous solution [18]. The concentrations of ECH to be investigated were 2%, 4%, 6%, 8%, respectively. As seen in Fig. 2, when concentration of ECH increased from 2% to 4%, adsorption capacity of CIBD-Pb had no obvious change. While the ECH concentration enhanced from 4% to 8%, the adsorption capacity of CIBD-Pb decreased. In fact, we all know,

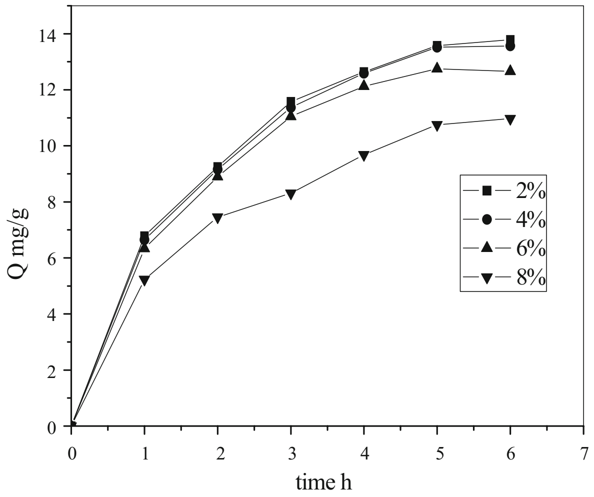


**Fig. 2** Effect of cross-linking agent ECH concentration for the absorption of $Pb^{2+}$ on CIBD-Pb. The initial $Pb^{2+}$ concentration was 50 mg·L$^{-1}$, volume of solution was 50 mL, 0.15 g of sorbent was used

the cross-linker chelates functional groups (–$NH_2$ and –OH) on chitosan, but epichlorohydrin as cross-linker also contributes a few functional –OH groups that can bind heavy metal ions. Some functional groups (–$NH_2$ and –OH) on the biosorbent could be protected through the imprinting process, so a certain amount of imprinting sites on surface coating would be formed after removing $Pb^{2+}$. This may be one reason that caused the adsorption capacity could not be decreased when ECH concentration was lower than 4%. But if it was higher than 4%, more functional groups (–$NH_2$ and –OH) on chitosan were chelated by epichlorohydrin, finally the amount of imprinting sites on biosorbent surface reduced would cause to cut down the uptake of $Pb^{2+}$. So the optimum concentration of epichlorohydrin was selected 4%.

## FTIR Results

As seen in Fig. 3, the –$NH_2$ characteristic absorption peaks of the cross-linking chitosan adsorbent (CCTS) was at 1,666 and 1,317 $cm^{-1}$. A shift of –$NH_2$ peak of CIBD-Pb was from 1,666 to 1,660 $cm^{-1}$. CCTS had first level and second level of –OH characteristic adsorption peak at 1,030 and 1,158 $cm^{-1}$, respectively. But these two peaks moved to a wide band in CIBD-Pb afterwards. It indicated that cross-linking occurred on chitosan amino and hydroxyl forming certain structure polymer with diatomite.

## Adsorption Kinetics

As shown in Fig. 4, CIBD-Pb had a rapid adsorption velocity for $Pb^{2+}$ within 1 h and only need 3 h for the adsorption equilibrium. However, it would take almost 5 h for the cross-linking chitosan adsorbent (CCTS) and the nonimprinted chitosan biosorbent using diatomite as core material (CBD). Compared with CBD and CCTS, the equilibrium time of CIBD-Pb shortened about 40%. In fact, based on the surface molecular imprinting technique, the imprinting sites for $Pb^{2+}$ was formed on the surface coating, then this made the adsorption velocity increase significantly.

So as to further understanding the essence of adsorption, the research of adsorption kinetics became important for characterizing adsorption process and exploring the

**Fig. 3** Fourier transform infrared spectra of CCTS and CIBD-Pb

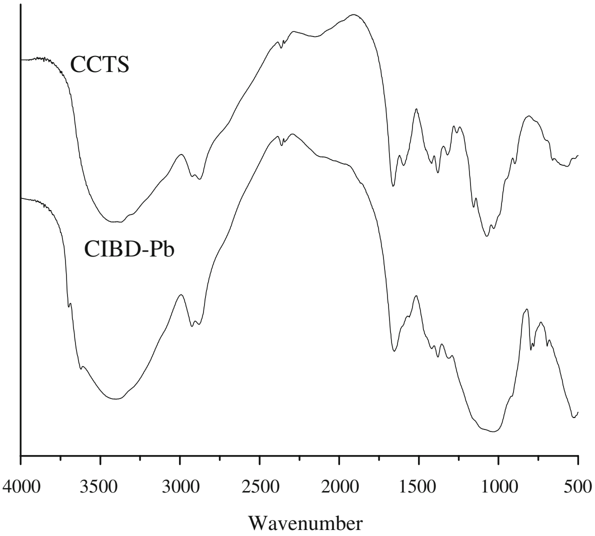
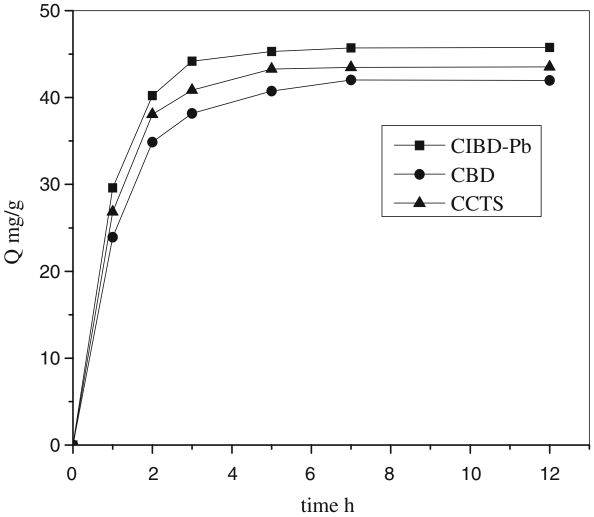


**Fig. 4** Effect of time for $Pb^{2+}$ on CIBD-Pb. The initial $Pb^{2+}$ concentration was 100 mg·$L^{-1}$, the volume of solution was 50 mL, and 0.10 g of sorbent was used



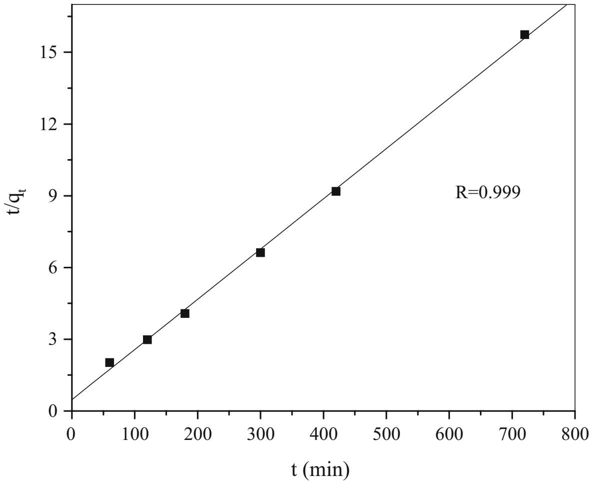
adsorption mechanism. Adsorption characteristics of CIBD-Pb for $Pb^{2+}$ could be described by pseudosecond order model. The pseudosecond order model [19] linear expression was:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where $t$ (min) is the adsorption time, $q$ (mg/g) is the adsorptive capacity of time, $q_e$ (mg/g) is balance adsorption capacity, $k_2$ [g/(mg min)] is the second-level adsorption velocity constant. The results of linear fit on $t/q$ to $t$ were shown in Fig. 5, where $q_e$=47.62 mg/g, $k_2$=9.34× $10^{-4}$ g/(mg min), and correlation coefficient $R$=0.999.

The above analysis showed that pseudosecond order model was suitable to describe adsorption characteristics of CIBD-Pb for $Pb^{2+}$. As a matter of fact, the pseudosecond order model could describe the adsorption factors, such as liquid membrane diffusion, surface adsorption, and particle inner diffusion. Thus, it contributed a more accurate understand of the mechanism of CIBD-Pb adsorption for $Pb^{2+}$.

**Fig. 5** Plots of the uptake data of $Pb^{2+}$ on CIBD-Pb according to pseudosecond order equation



### Adsorption Isotherms

As seen in Fig. 6, with the increasing of the $Pb^{2+}$ concentration in solution, the adsorption capacity of CIBD-Pb and CCTS would enhance, but uptake of CIBD-Pb increased more quickly. The maximum adsorption capacity of CIBD-Pb for $Pb^{2+}$ reached 139.6 mg $g^{-1}$ and enhanced 32.2% compared with CCTS (the initial $Pb^{2+}$ concentration of 600 mg/L). The reason was that the imprinting sites of surface layer of CIBD-Pb could completely match with $Pb^{2+}$ on space positions and binding sites, but they did not exist on CCTS surface, which greatly improved the affinity ability for $Pb^{2+}$. So the adsorption capacity of CIBD-Pb significantly enhanced.

The adsorption isotherms were described by Langmuir equation. The linear expression was as follows:

$$\frac{c_\mathrm{e}}{q_\mathrm{e}} = \frac{c_\mathrm{e}}{q_\mathrm{m}} + \frac{1}{q_\mathrm{m} b} \tag{4}$$

where $q_\mathrm{m}$ (mg/g) is maximum adsorption capacity, $q_\mathrm{e}$ (mg/g) is balance adsorption capacity, $c_\mathrm{e}$ (mg/L) is equilibrated concentration, $b$ is a constant. The experimental data were carried on the linear regression analysis by the Langmuir equation.

The results were shown in Fig. 7, which $q_\mathrm{m}$=137.93 (mg/g), $b$=0.209, and correlation coefficient $R$=0.999. It could be seen that the CIBD-Pb adsorption isotherm for $Pb^{2+}$ accorded with Langmuir equation. So adsorption of CIBD-Pb for $Pb^{2+}$ belonged to a single molecular layer adsorption (chemistry adsorption, chelated adsorption process), which all of the adsorption sites were similar to $Pb^{2+}$ adsorption. Obviously, the surface molecular imprinting technique made the surface of CIBD-Pb form the affinity sites to $Pb^{2+}$.

### Effect of pH on Adsorption Capacity

As can be seen from Fig. 8, when the pH value was 3 in aqueous solution, the adsorption capacity of CIBD-Pb for $Pb^{2+}$ was low. This showed that the lower pH went against the adsorption of $Pb^{2+}$. However, with the increasing of pH from 3 to 5, the adsorption capacity of CIBD-Pb for $Pb^{2+}$ increased rapidly and then the adsorption ability of CIBD-Pb reached

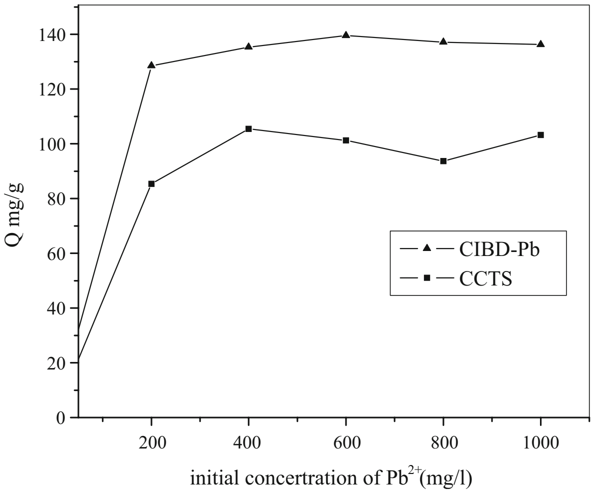


**Fig. 6** Absorption of different $Pb^{2+}$ concentration. The volume of solution was 100 mL, 0.10 g of sorbent was used, and adsorption time was 12 h

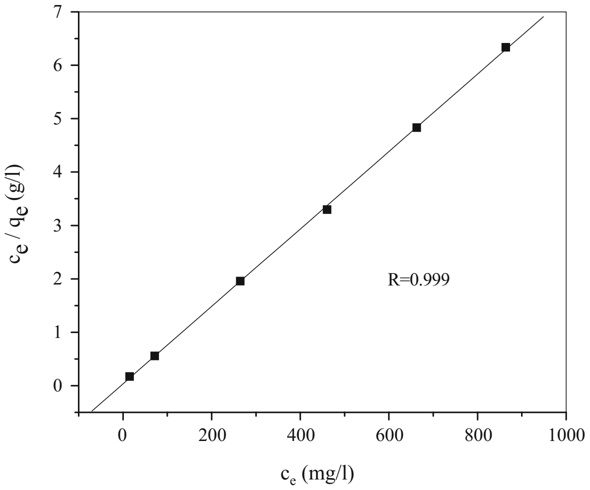


**Fig. 7** *Plots* of the uptake data of $Pb^{2+}$ on CIBD-Pb according to the Langmuir isotherm

a better effect, while adsorption capacity of CCTS for $Pb^{2+}$ was very small in pH value less than 5. This indicated the effect of pH on CCTS was stronger than that of CIBD-Pb. Obviously, CIBD-Pb could be used under neutrality or weak acid condition for $Pb^{2+}$ adsorption. The optimal pH of CIBD-Pb for $Pb^{2+}$ adsorption should be in the range of 5–7.

## Batch Experiments

The stability and adsorption batches of sorbent were often considered in practical application. As shown in Fig. 9, the surface molecular imprinting adsorbent can be reused for up to ten cycles without loss of adsorption capacity. So this showed that the new adsorbent had a higher stability in practical application.

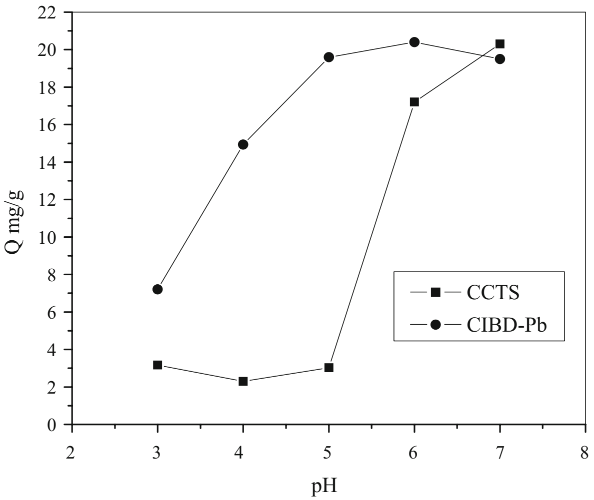


**Fig. 8** Effect of pH on adsorption of $Pb^{2+}$. The initial $Pb^{2+}$ concentration was 100 mg·L$^{-1}$, the volume of solution was 50 mL, and 0.20 g of sorbent was used

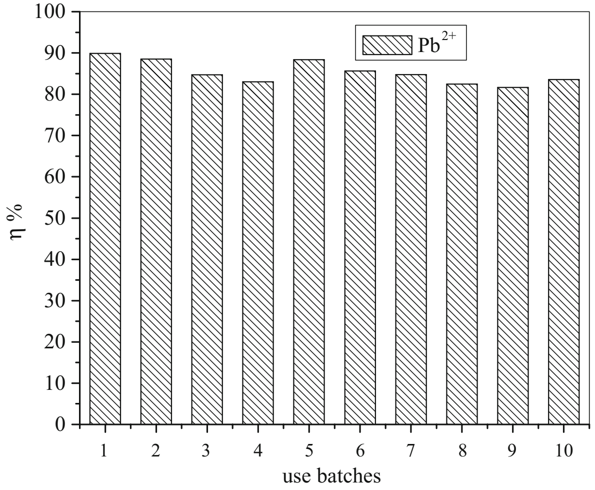


**Fig. 9** Use batches of CIBD-Pb for $Pb^{2+}$. The initial $Pb^{2+}$ concentration was 10 mg·L$^{-1}$, the volume of solution was 50 mL, and 0.15 g of sorbent was used

## Conclusions

In this work, CIBD-Pb was prepared by $Pb^{2+}$ as the imprinted ion and epichlorohydrin as the cross-linking agent. The optimum imprinted $Pb^{2+}$ ion concentration was 1.67 mg in 1 g biomass and cross-linking agent concentration of ECH was 4%. It had high adsorption ability for $Pb^{2+}$. When the initial concentration of aqueous solution was 600 mg/L, the maximum adsorption capacity reached to 139.6 mg/g, which enhanced 32.2% compared to CCTS. The adsorption velocity was quick and the equilibration time of imprinting adsorbent for $Pb^{2+}$ was 3 h that shortened about 40% compared with CBD and CCTS. The surface molecular imprinting adsorbent was easy for adsorbent desorption and regeneration. It can be reused for up to ten cycles without loss of adsorption capacity. In the kinetics study, the pseudosecond order model could represent the adsorption process. In the isotherm study, the experimental results showed that the adsorption of $Pb^{2+}$ onto CIBD-Pb could be described by Langmuir model. So the imprinting adsorbent has a good potential for the treatment of industrial wastewaters contaminated with heavy metal ions.

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## Appendix

Nomenclature

| | |
|---|---|
| $c_0$ | the initial concentration of metal ion (mg/L) |
| $\eta$ | the removal rate |
| $Q$ | the quality of the adsorbed Pb for per gram adsorbent (mg/g) |
| $c_e$ | the equilibrated concentrations of metal ion (mg/L), |
| $V$ | the volume of added solution (L) |
| $W$ | the weight of the adsorbent (g) |
| $t$ | the adsorption time (min) |
| $q$ | the adsorptive capacity of time (mg/g) |

$q_e$ the balance adsorption capacity (mg/g)
$k_2$ the second-level adsorption velocity constant [g/(mg min)]
$q_m$ the maximum adsorption capacity (mg/g)
$b$ constant

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