



Removal of lead from aqueous solution by hydroxyapatite/magnetite composite adsorbent

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ABSTRACT

A novel composite adsorbent, hydroxyapatite/magnetite (HAp/Fe₃O₄), has been prepared for the purpose of removing lead ions from aqueous solution. Varying factors that may affect the adsorption efficiency, including adsorbent dosage, solution pH and coexistent substances such as humic acid and competing cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺), have been investigated. It is remarkable that using the developed composite adsorbent, more than 99% of Pb²⁺ can be removed under desirable experimental conditions. The maximum adsorption capacity for HAp/Fe₃O₄ is 598.8 mg/g, which is much greater than that for the previously reported materials. It is found that depending on its concentrations, humic acid affects the efficiency of lead removal, but the coexisting cations, e.g., K⁺, Ca²⁺, Na⁺ and Mg²⁺, have small influence. Mechanistic studies show that the adsorption data fits the Langmuir and Freundlich isotherm models reasonably well and the adsorption processes obey the pseudo-second-order kinetics model. Based on the experiment results, it is concluded that dissolution/precipitation and the surface complexation are mutually responsible for lead adsorption on HAp/Fe₃O₄, which should be attributed to the multiple functionalities of the material.

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1. Introduction

As is well known, lead is one of the most important heavy metal pollutants in environment. Generally speaking, lead pollution, spreading over earth and ground water, comes from natural sources and industrial effluents. Lead in natural water is highly harmful to human health and aquatic animals even at low concentrations because of its bioaccumulation in the food chain. A variety of treatment techniques and processes, for example, chemical precipitation [1], ion exchange [2], nanofiltration, low energy reverse osmosis [3], have been developed to remove heavy metals from the contaminated water. However, it has been the challenge to treat the water resources that contain trace amount of heavy metals because the concentrations of Ca²⁺, Mg²⁺ and other background substances are usually higher than those of the heavy metal ions [4,5]. The adsorption technology has received increasing attention in recent years because it is simple, low-cost and effective for water purification [6]. Progress has been made for the development of efficient adsorbents to remove heavy metals from aqueous solution [7–9].

Hydroxyapatite (HAp), with the chemical formula Ca₁₀(PO₄)₆(OH)₂, is a major inorganic component of human

bones and teeth [7]. HAp has been considered as an environmental benign functional material with remarkable ability to absorb heavy metal ions, such as Pb²⁺ [8,9], Zn²⁺ [8,10], Cu²⁺ [8,11], Cd²⁺ [12,13] and Co²⁺ [14]. However, it has limited application since upon heavy metals being immobilized; isolating the suspended fine solids from aqueous solution is not an easy task. In order to improve its applicability for the purification of contaminated water, several composite materials which combine HAp with polymers have been reported. For instance, the hydroxyapatite/polyacrylamide (HAp/PAAm) composite hydrogels [15], hydroxyapatite/polyurethane (HAp/PU) composite foams [16] have been prepared and used to remove Pb²⁺ from aqueous solutions, for which the maximum adsorption capacity is 178 and 150 mg/g, respectively. It is found that composite adsorbents, hydroxyapatite/poly(vinyl alcohol) (HAp/PVA) cryogel [17], and HAp/PVA cryogel immobilized on polyurethane (PU) foam [18], are capable of removing Cd²⁺ with the maximum adsorption capacity of 53.3 and 47.7 mg/g, respectively.

Magnetic Fe₃O₄ has the advantage for the usage as support material of composite adsorbent because it can be easily manipulated by an external magnetic field [19]. Despite up to date several studies carried out on surface modification of Fe₃O₄ nanoparticles for adsorption of heavy metals [20–24], it has not been documented that HAp is combined with Fe₃O₄ to produce composite adsorbent for removal of heavy metals from aqueous solutions.

In this study, a novel hydroxyapatite/magnetite (HAp/Fe₃O₄) composite adsorbent was prepared to investigate their removal

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capability of Pb^{2+} from aqueous solutions. In order to systematically evaluate the efficiency of HAp/ Fe_3O_4 as lead adsorbent, the effects of adsorbent dosage, solution pH, coexistent humic acid and competing cations on the adsorption have been studied. The goal of this study is to develop an efficient composite adsorbent with high adsorption capacity for lead ions and facilitate its separation from the solution.

2. Materials and methods

2.1. Preparation and characterization of the composite adsorbent

Magnetite (Fe_3O_4) was prepared using a modified coprecipitation method described by Yantasee et al. [24]. Iron salts of Fe (III) and Fe (II) (in a 2:1 molar ratio) were dissolved in distilled water. A solution of NaOH (2 mol/L) was added to the ferrous solution under N_2 , producing iron oxide solids immediately. After stirring for 0.5 h, the magnetite (Fe_3O_4) particles were washed repeatedly with distilled water. HAp was combined with Fe_3O_4 by *in situ* precipitation. A suspension of Fe_3O_4 in CH_3COOH solution (2.1 wt.%) was added to the mixture solution of $\text{Ca}(\text{NO}_3)_2$ with KH_2PO_4 in a molar ratio of 5:3. The molar ratio of Fe_3O_4 to HAp was 1:1. After stirring for 0.5 h, a solution of NaOH (2 mol/L) was added to the mixture while the pH was remained at 13. The mixture was kept at 37 °C for 6 h, and then the obtained HAp/ Fe_3O_4 composite adsorbent was washed repeatedly with distilled water and dried before using. In order to compare the adsorption behaviour of the composite adsorbent HAp/ Fe_3O_4 with that of the single components, both the magnetite (Fe_3O_4) and HAp were synthesized separately using chemical precipitation method.

The adsorbent HAp/ Fe_3O_4 was characterized by X-ray diffraction (XRD) analysis on a Bruker D8ADVANCE diffractometer (D8ADVANCE, Bruker, Germany) using filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of $2\theta = 10\text{--}90^\circ$. The morphological and compositional analyses of HAp/ Fe_3O_4 were carried out using a scanning electron microscope (XL-30ESEM, Philip, Holland) equipped with an energy dispersive X-ray spectrometer (SDD, EDAX, USA). The specific surface area and average pore diameter of the adsorbent were determined from N_2 adsorption isotherm by the BET method using a Micromeritics surface analyzer model ASAP 2020. Samples for determining the contents of Ca^{2+} , Fe^{3+} , and PO_4^{3-} in the adsorbent were prepared by dissolving the particles in HNO_3 solution. Measurements were conducted on an Inductively Coupled Plasma Optical Emission Spectrometer (Optima 2100DV, PerkinElmer, USA). The pH_{ZPC} of the HAp/ Fe_3O_4 was determined by using the procedure described by Schwarz et al. [25].

2.2. Adsorption studies

Adsorption isotherm studies were conducted by mixing 0.05 g HAp/ Fe_3O_4 with 100 mL Pb^{2+} solution in a 250-mL conical flask. For the series of measurements, the initial concentration of Pb^{2+} solution was controlled in the range of 10–500 mg/L. Standard 0.1 mol/L HCl or 0.01 mol/L NaOH solutions were used for pH adjustment. To achieve saturated adsorption, the sample solution was shaken for 24 h at 150 rpm and 25 °C, and then the concentrations of the metal ions were analyzed.

Adsorption kinetic experiments were carried out by batch adsorption method at 25 °C on a shaker at 150 rpm. A series of samples were prepared by mixing Pb^{2+} solution (100 mL, 10 mg/L) with 0.05 g HAp/ Fe_3O_4 in a 250-mL conical flask. Standard HCl (0.1 mol/L) or NaOH (0.01 mol/L) solutions were used for pH adjustment. Samples were withdrawn from the shaker at different time intervals, and analyzed for the determination of metal ion concentrations. Except for the experiment of pH effect, the pH of the

original solution was controlled at 5. The initial Pb^{2+} concentration of 10 mg/L was used for the adsorption experiments considering the low concentration (0–10 mg/L) of heavy metal in natural water [4,5].

The adsorption capacity was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

The removal efficiency of lead ions was calculated by the difference of lead ion concentrations in aqueous solution using the equation expressed as follows:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where q_e (mg/g) is the amount of lead ions adsorbed onto the unit amount of the adsorbent, C_0 (mg/L) is the initial lead ion concentration, C_e (mg/L) is the final or equilibrium lead ion concentration, V (L) is the volume of the solution, and m (g) is the adsorbent weight in dry form. An Inductively Coupled Plasma Optical Emission Spectrometer (Optima 2100DV, PerkinElmer, USA) with the detection limit of 0.002–100 mg/L was used for the simultaneous determination of Pb^{2+} and Ca^{2+} ions in solution. The pH of the solution was measured using pH meter (Leici PHS-3C pH meter, Shanghai, China). An electronic temperature-controlled shaker (Taihua HZQ-F160, Taichang, China) was used for adsorption process. All the experiments were performed in duplicate and the averaged values were recorded.

2.3. Desorption studies

In order to estimate the reversibility of Pb^{2+} sorption, desorption experiments using different eluants have been carried out. Firstly, the adsorption of Pb^{2+} on HAp/ Fe_3O_4 was carried out with the adsorbent dosage of 1 g/L in a Pb^{2+} solution of 100 mg/L. After 24 h of contact at 25 °C, the adsorption equilibrium was reached and the supernatants were separated for analyses of the residual Pb^{2+} . Secondly, the filtered solid residue was thoroughly washed with distilled water and dried at 60 °C. Four different eluants, e.g., HAc, EDTA, $\text{Ca}(\text{NO}_3)_2$, NaOH solution as well as the distilled water, were used for desorption of lead from the loaded HAp/ Fe_3O_4 . Experiments started with treating 0.050 g of the Pb-loaded adsorbent with 50 mL of the selected eluants. The resultant mixture was stirred for 24 h at 25 °C before subsequent analyses were performed. The HAc solutions with pH 2.88 and 5.00 were prepared by following a published procedure [12,14].

3. Results and discussion

3.1. Characterization of HAp/ Fe_3O_4

The basic characterization results of HAp/ Fe_3O_4 samples are listed in Table 1.

Fig. 1 shows the XRD patterns for the composite adsorbents HAp/ Fe_3O_4 . All the peaks are consistent with those of JCPDS International Center for Diffraction Data (ICDD) Powder Diffraction File

Table 1
Physico-chemical properties of HAp/ Fe_3O_4 .

Properties	Values
Specific surface areas (m^2/g)	109
Adsorption average pore diameter (nm)	9.38
Ca/P ratio	1.70
HAp content (wt.%)	63.9
pH_{ZPC}	6.95

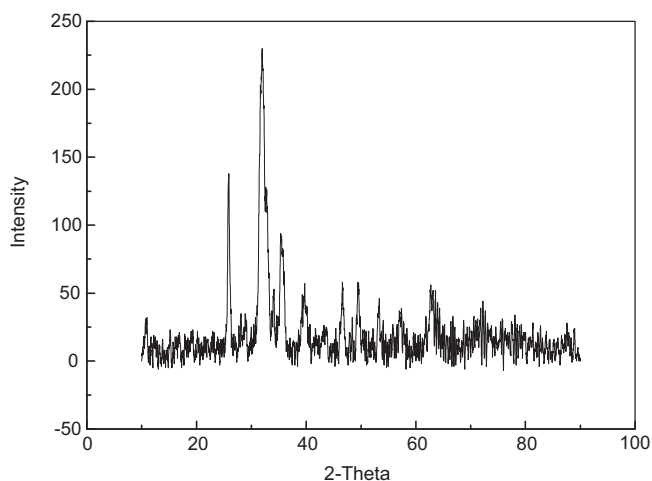


Fig. 1. The XRD pattern of composite adsorbent HAp/Fe₃O₄.

for this phase (filenumber72-1243, 75-1372). There are five characteristic peaks for HAp ($2\theta = 25.87^\circ, 31.74^\circ, 39.75^\circ, 46.61^\circ, 49.47^\circ$) and three for Fe₃O₄ ($2\theta = 35.43^\circ, 56.94^\circ, 62.53^\circ$).

3.2. Effect of the dosage

The 24-h uptake experiments were carried out at 25 °C within the HAp/Fe₃O₄ dosage range of 0.1–1.2 g/L. Measurements were based on 100 mL solution (pH 5) with initial Pb²⁺ ion concentration of 10 mg/L. The adsorption efficiency of Pb²⁺ as a function of adsorbent dosage is presented in Fig. 2. It was observed that the removal efficiency increased as the adsorbent dosage was raised. When a dosage of 0.1 g/L was used, the removal efficiency reached 99%, indicating that the composite adsorbent HAp/Fe₃O₄ showed strong affinity to Pb²⁺. The Pb²⁺ ions in the solution were essentially eliminated as the dosage was increased to 0.5 g/L. In considering the removal efficiency, an adsorption dosage of 0.5 g/L was selected for the following studies.

3.3. Effect of the pH

Batch equilibrium adsorption experiments were performed by shaking 0.05 g of HAp/Fe₃O₄ with 100 mL solution (10 mg Pb/L) for 24 h at 25 °C. Basic condition could promote hydroxide precipitation ($K_{sp}\text{Pb}(\text{OH})_2 = 1.2 \times 10^{-15}$), which introduced uncertainty into

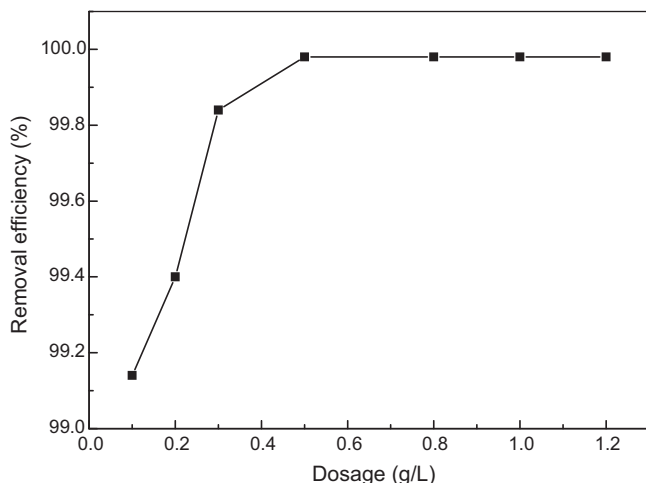


Fig. 2. Effect of the dosage on the removal of Pb²⁺ by HAp/Fe₃O₄.

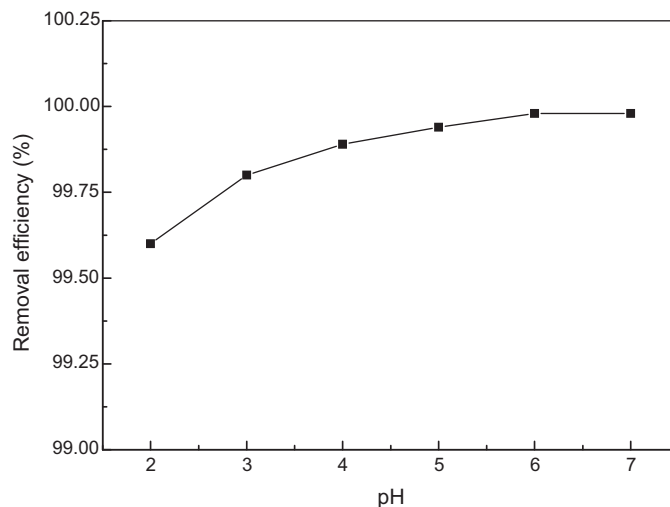


Fig. 3. Effect of pH on the removal of Pb²⁺ ions by HAp/Fe₃O₄.

the adsorption investigation; thus, the pH was controlled in the range of 2–7. As shown in Fig. 3, the influence of pH on adsorption efficiency of lead is small although relatively high pH is favourable. Removal efficiency of 99% was achieved even at pH 2. Therefore, the HAp/Fe₃O₄ showed a good adsorption performance for Pb²⁺ adsorption over a wide pH range. On the other hand, low pH condition may cause dissolution of Ca, P and Fe, which are the basic elements of the composite adsorbents. HAp/Fe₃O₄ is considered to be an efficient adsorption material to remove Pb²⁺ from natural water in that the pH of natural surface and ground water falls in the range of 5–7.

3.4. Effect of coexistent substances

3.4.1. Effect of humic acid

Humic substances (HSs) are the major components of the natural organic materials found in soil, water and geological organic deposits [26]. Because of the capability of HSs in complexation with metal ions, compounds in this catalog have recently been recognized as important materials that affect the redistribution of heavy metal ions in soil and the hydrosphere [27]. Humic acid (HA), one of the humic substances, is soluble in water at pH 4–10 [26]. It contains carboxyl (–COOH), amine (–NH₂), hydroxyl (–OH) and phenol (Ar–OH) functional groups, which is negatively charged by deprotonation in weakly acidic to basic media [28]. Therefore, the complexation of heavy metal ions with HA takes place. To evaluate the effect of HA in this system, Pb²⁺ solution (100 mL, 10 mg/L), HA with varying concentrations and 0.05 g HAp/Fe₃O₄ were mixed. The mixture was shaken for 24 h at pH 5 and 25 °C. As shown in Fig. 4, the presence of HA introduced a significant effect on the removal of Pb²⁺. It is obvious that the removal efficiency of Pb²⁺ decreased as HA increased from 1 to 20 mg/L. It is worthwhile to note that the Pb²⁺ removal efficiency increased first as the HA concentration was up to 50 mg/L, and then, kept almost constant within the HA concentration range of 50–100 mg/L. Similar phenomena were also found in some previous reports [29–33], which are attributed to the competitive adsorption of HA and heavy metals (such as Pb²⁺, Cr³⁺, Zn²⁺). In this Pb²⁺–HA–HAp/Fe₃O₄ system, the results showed that the influence of HA on the adsorption was dependent on HA concentrations. With the existence of HA at low concentrations, the reduced adsorption of Pb²⁺ could be explained by the formation of soluble HA–Pb(II) complexes in solution, which stabilizes Pb²⁺ ions in aqueous solution. While at relatively high HA concentrations, the adsorbed HA may interact with Pb²⁺ ions on the adsorbent surface,

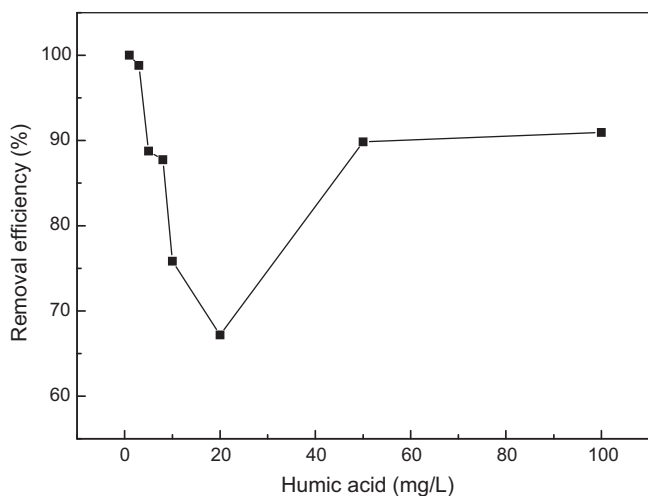


Fig. 4. Effect of HA on the removal of Pb^{2+} ions by HAP/ Fe_3O_4 .

which increases the Pb^{2+} adsorption [34,35]. This could be the reason that an increased removal efficiency of Pb^{2+} was observed at the given HA concentrations ranging from 50 to 100 mg/L.

3.4.2. Effect of competing cations

Alkali and alkali-earth metal ions such as K^+ , Na^+ and Ca^{2+} , Mg^{2+} , which exist widely in natural water sources, may compete with heavy metal ions for the available adsorptive sites. Recently, attention has been paid to the impact of coexisting metal ions on the adsorption process [36]. In this study, cations Ca^{2+} , Mg^{2+} , K^+ and Na^+ in varying concentrations were added to 100 mL Pb^{2+} solution (10 mg/L) suspended with 0.05 g HAP/ Fe_3O_4 . The mixture was shaken at pH 5 and 25 °C for 24 h. As shown in Fig. 5, under the given experimental conditions, the above competing ions do not affect significantly the removal efficiency. These results confirm that HAP/ Fe_3O_4 has the capability of selectively and efficiently removing Pb^{2+} from the solutions in the presence of the above competing cations. Similar results were reported by Smičiklas et al. [8] for Pb^{2+} sorption on HAP.

3.5. Adsorption isotherm

Sorption studies over a wide initial concentration range (1–500 mg/L) were performed in order to determine the HAP/ Fe_3O_4

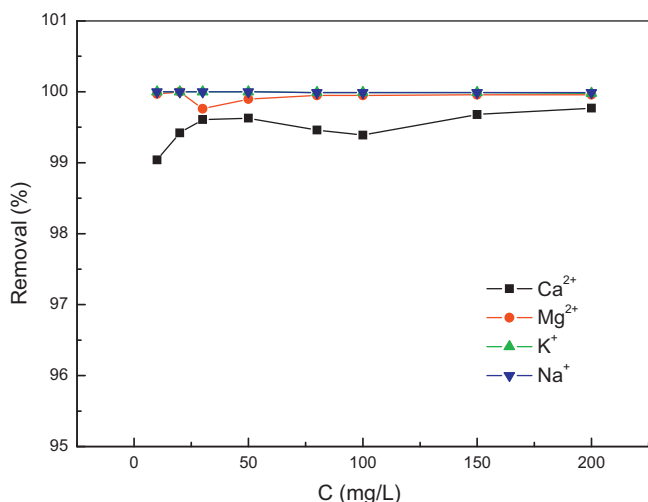


Fig. 5. Effect of competing cations on the removal of Pb^{2+} by HAP/ Fe_3O_4 .

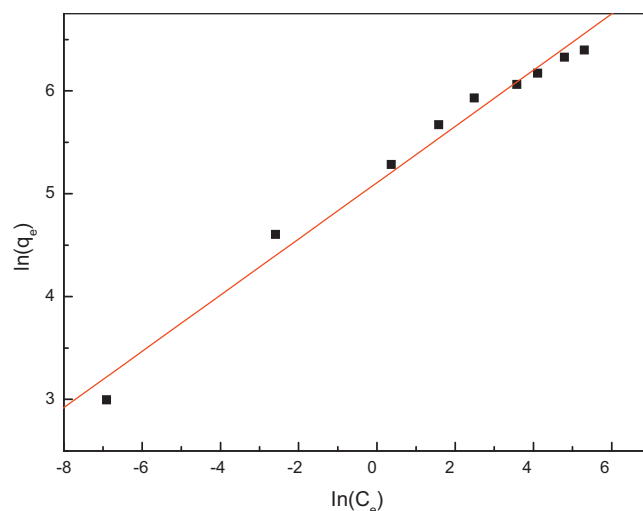


Fig. 6. The Freundlich isotherm plot for Pb^{2+} adsorption on HAP/ Fe_3O_4 .

adsorption capacity for Pb^{2+} ions. The Freundlich and Langmuir adsorption isotherm models were used to fit the experimental data of Pb^{2+} sorption onto HAP/ Fe_3O_4 . The linear form of the Freundlich equation can be expressed as follows [37]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

where q_e is the amount adsorbed at equilibrium concentration (mg/g), K_f is the empirical constant of Freundlich isotherm (L/mg) and C_e is the equilibrium concentration of heavy metal ions in solution (mg/L). The constant n is the empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the material. When $1/n$ values are in the range $0.1 < 1/n < 1$, the adsorption process is favourable [38]. The Langmuir model [39] takes the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_e q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

where q_{\max} is the maximum adsorption capacity (mg/g), and K_e is the Langmuir constant (L/g), which is related to the binding energy of the metal ions to the active site.

Fitting the data using Freundlich adsorption isotherm gives a linear relationship with $R^2 = 0.982$, $K_f = 165.3$ and $1/n = 0.273$, as shown in Fig. 6. The Langmuir adsorption isotherm for Pb^{2+} ions

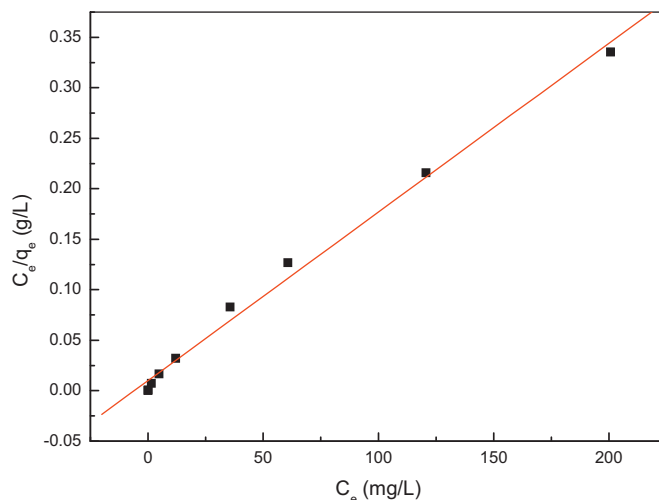


Fig. 7. The Langmuir isotherm plot for Pb^{2+} adsorption on HAP/ Fe_3O_4 .

Table 2
Comparison of adsorption capacities for Pb²⁺ between different adsorbents.

Adsorbent	q_{\max} (mg/g)	Reference
HAp/Fe ₃ O ₄	598.8	This work
Fe ₃ O ₄	111.1	This work
HAp	526.3	This work
Hydroxyapatite (70 wt.%) / polyacrylamide composite hydrogels	209	[15]
Hydroxyapatite (50 wt.%) / polyurethane composite foams	150	[16]
Hydroxyapatites	330–450	[40]
Poorly crystalline hydroxyapatites synthesized from gypsum waste	500	[41]
Synthetic HAp	91.58	[9]
Chitosan/magnetite composite beads	63.33	[42]
Sodium tetraborate-modified kaolinite clay	42.92	[43]
Quebracho tannin resin	86.2	[44]
Activated carbon prepared from Phaseolus aureus hulls	28.8	[45]

is shown in Fig. 7. The linear plot of C_e/q_e against C_e shows that the adsorption is in good agreement with the Langmuir model (correlation coefficient, $R^2 = 0.993$). The maximum adsorption capacity q_{\max} and the Langmuir constant K_e for the adsorption of Pb²⁺ were 598.8 mg/g and 0.17 L/g, respectively. Table 2 lists the adsorption capacity data for different lead adsorbents. Clearly, among the presented adsorbents, the composite adsorbent HAp/Fe₃O₄ has the highest maximum adsorption capacity.

3.6. Adsorption kinetics

The adsorption efficiency as a function of contact time is presented in Fig. 8. It shows that more than 95% of Pb²⁺ was removed within the first several minutes. And a contact time of about 1 h was required to establish the sorption equilibrium of Pb²⁺. The adsorption kinetics data were analyzed according to the pseudo-second-order kinetics [46]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_2 is the pseudo-second-order rate constant of adsorption (g/mg/min); q_e and q_t are the amount of metal ions adsorbed (mg/g) at equilibrium and at time t , respectively; t is adsorption time (min). And the following expression denotes the initial sorption rate h (mg/g/min):

$$h = k_2 q_e^2 \quad (6)$$

Linear plot of t/q_t vs. t is shown in Fig. 9. The kinetic process for the adsorption of Pb²⁺ ions by HAp/Fe₃O₄ excellently followed the

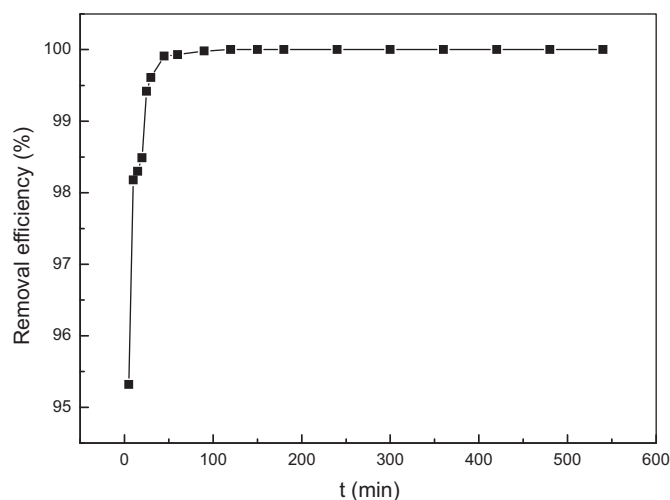


Fig. 8. Effect of the contacting time on the removal of Pb²⁺ ions by HAp/Fe₃O₄.

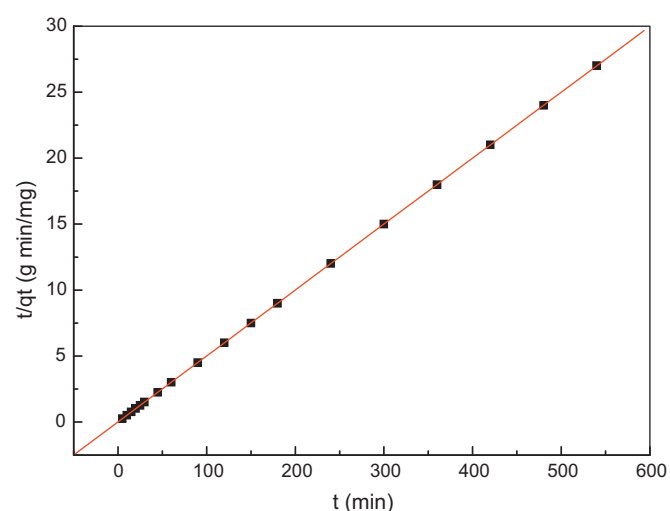


Fig. 9. The pseudo-second-order kinetics of Pb²⁺ adsorption by HAp/Fe₃O₄.

characteristics of the pseudo-second-order reaction model ($R^2 = 1$). The value of k_2 was 0.352 g/(mg min) and the initial sorption rate h was 140.8 mg/(g min), indicating that the sorption at the beginning was very fast.

3.7. SEM/EDAX analysis for lead-adsorbed HAp/Fe₃O₄

For comparison, HAp/Fe₃O₄ samples before and after the adsorption of lead ions were analyzed for their surface appearance.

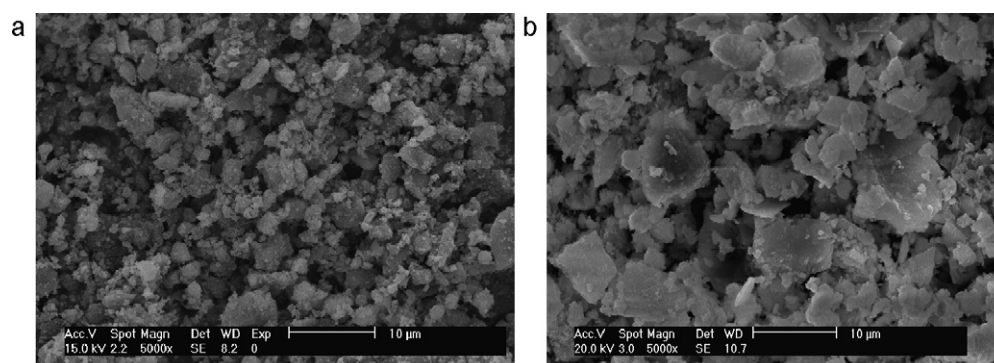


Fig. 10. SEM images of HAp/Fe₃O₄: (a) before Pb²⁺ adsorption and (b) after Pb²⁺ adsorption.

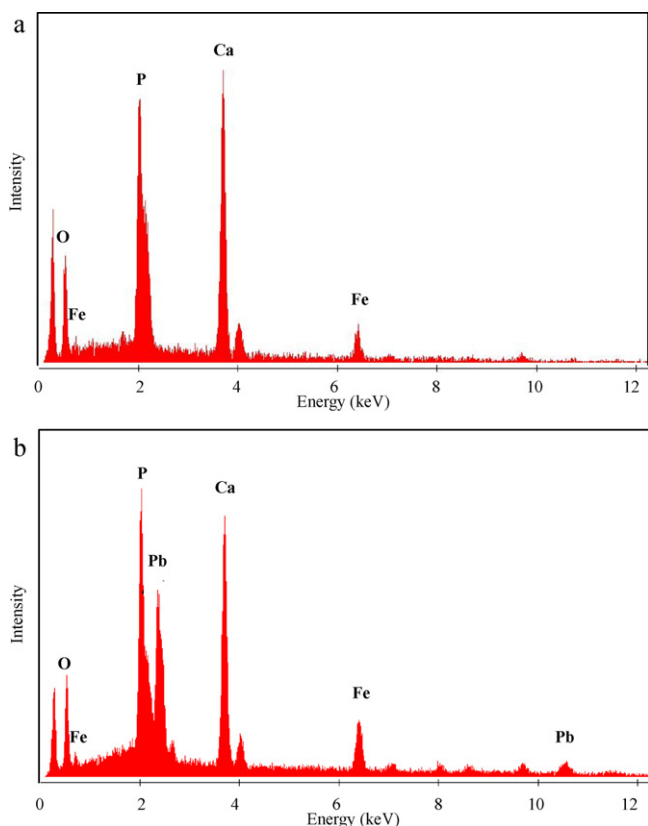


Fig. 11. EDAX spectra of HAp/Fe₃O₄: (a) before Pb²⁺ adsorption and (b) after Pb²⁺ adsorption.

The SEM micrographs are shown in Fig. 10. It is found that before adsorption, the HAp/Fe₃O₄ material was composed of irregularly shaped particles, and large flake-like species were formed on the surface of the adsorbent after the adsorption of Pb²⁺.

EDAX spectra for the HAp/Fe₃O₄ samples before and after Pb²⁺ adsorption are shown in Fig. 11a and b, respectively. The EDAX spectra of HAp/Fe₃O₄ exhibit peaks for Ca, P, Fe, O, which are the major constituents of HAp and magnetite. For the Pb²⁺ adsorbed sample, there are new peaks appearing in the EDAX spectra, which is attributed to Pb element. Therefore, the strong peaks at 2.34, 10.5 keV in the EDAX spectra provided an important evidence for Pb²⁺ adsorption on HAp/Fe₃O₄. These results confirm that Pb²⁺ was efficiently adsorbed onto the surface of HAp/Fe₃O₄.

3.8. Desorption

Desorption of Pb²⁺ from HAp/Fe₃O₄ using different eluants was investigated. The results are shown in Table 3. It is observed that the Pb²⁺ desorption efficiency from HAp/Fe₃O₄ is dependent on the extracting solution. With EDTA solution as the eluant, large amount of Pb²⁺ was desorbed due to the formation of complex between EDTA and Pb²⁺ ions. When using alkaline solution, the desorbed

Table 3
Desorption of Pb²⁺ from HAp/Fe₃O₄.

Eluants	Desorbed Pb ²⁺ (%)
EDTA (0.001 mol/L)	55.50
HAc (pH = 2.88)	1.76
HAc (pH = 5.0)	0.01
H ₂ O (pH = 7.0)	0.16
Noah (pH = 11.85)	0.005
Ca(NO ₃) ₂ (0.01 mol/L)	0.056

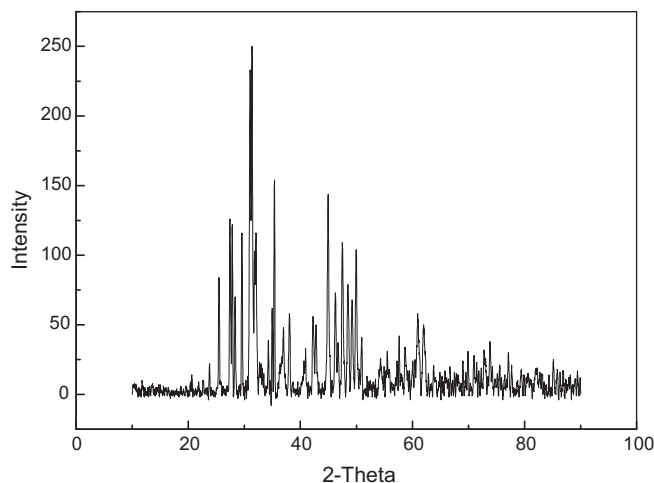


Fig. 12. The XRD pattern of Pb(II)-adsorbed HAp/Fe₃O₄.

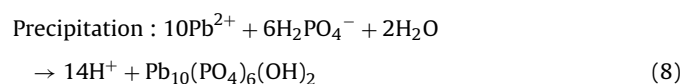
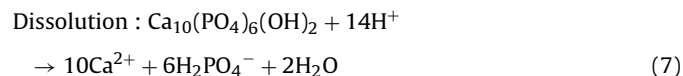
amount was decreased. The possible reason is that HAp/Fe₃O₄ is more stable in alkaline solution than in acidic solution. Formation of phosphate composition with HAp, which is highly insoluble, could be the reason for difficult desorption of Pb²⁺ from HAp/Fe₃O₄.

The low desorption efficiency of heavy metal ions from the composite HAp/Fe₃O₄ is similar to what was observed for single component HAp adsorbent in the previous studies [12,14]. In the published reports, the highest desorption was observed for the acetic acid solution as the eluant, with the efficiencies of 26.53% for Cd²⁺ and 30.36% for Co²⁺, respectively. Further work is necessary to increase the desorption efficiency and recycles of the HAp-containing adsorbents.

On the other hand, the low desorption efficiency for HAp/Fe₃O₄ reduces the transportation of lead ions in natural water. Therefore, it can be an effective adsorbent for the treatment of lead pollution, especially for slightly polluted water.

4. Mechanism discussion

For the composite adsorbent HAp/Fe₃O₄, HAp was immobilized on the surface of Fe₃O₄ during the preparation, being the major contributor for Pb²⁺ adsorption. To elucidate the adsorption of heavy metal ions on different HAp-containing adsorbents, three possible mechanisms, including ion exchange, dissolution/precipitation and surface complexation, have been proposed [47,48]. In acidic and natural aqueous solutions, HAp can dissolve partly and hydroxypyromorphite [Pb₁₀(PO₄)₆(OH)₂, HPy] may precipitate. The dissolution/precipitation mechanism is given as follows:



Calcium cation in HAp/Fe₃O₄ has stronger affinity to the HAp/Fe₃O₄ surface sites than the co-existing Mg²⁺, K⁺ and Na⁺. But the solubility product constants of Pb(II)-phosphate are much smaller than that of Ca(II)-phosphate (for K_{sp}[Pb₃(PO₄)₂] = 8.0 × 10⁻⁴³; K_{sp}[Ca₃(PO₄)₂] = 1 × 10⁻²⁵). Consequently, accompanied by dissolution of HAp, more stable Pb(II)-phosphate is formed. This explains the fact that the presence of Ca²⁺ did not influence the removal of Pb²⁺ significantly. Fig. 12

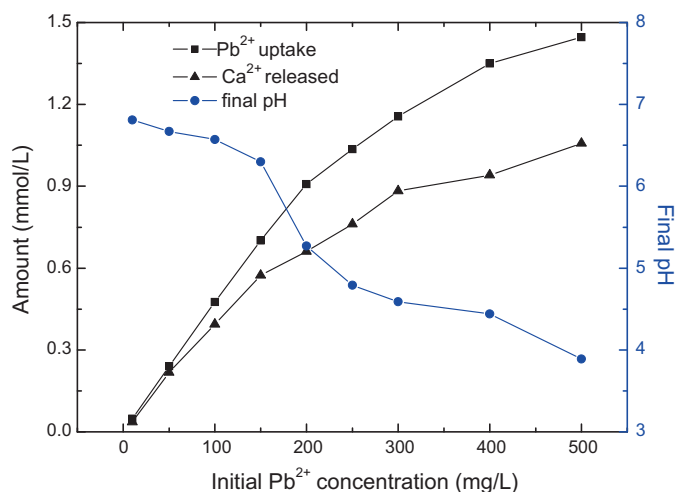


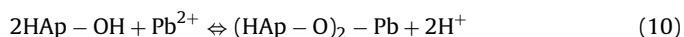
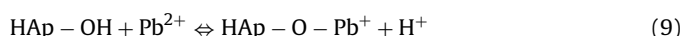
Fig. 13. The amounts of Pb²⁺ adsorbed, Ca²⁺ released and final pH of the solution at varying initial concentrations of Pb²⁺.

shows the XRD pattern for Pb(II)-adsorbed HAp/Fe₃O₄. Besides three characteristic peaks for HAp ($2\theta = 31.74^\circ, 46.61^\circ, 49.47^\circ$) and two for Fe₃O₄ ($2\theta = 35.43^\circ, 62.53^\circ$), new peaks ($2\theta = 27.68^\circ, 31.48^\circ, 40.85^\circ, 49.32^\circ, 57.53^\circ, 61.84^\circ, 69.80^\circ$) are found, which belong to Pb₁₀(PO₄)₆(OH)₂ (File number 87-2478). This result confirms that the dissolution–precipitation mechanism plays an important role for Pb²⁺ adsorption on HAp/Fe₃O₄.

To gain additional understanding for the mechanism of Pb²⁺ adsorption on HAp/Fe₃O₄, the concentrations of Pb²⁺ and Ca²⁺ ions as well as the pH variation before and after adsorption were monitored in the adsorption isotherm experiments. The amount of adsorbed Pb²⁺ and released Ca²⁺ in the solution at different initial concentrations of Pb²⁺ are presented in Fig. 13. The difference between the amounts of Pb²⁺ adsorbed and Ca²⁺ released suggests that in addition to dissolution–precipitation, other adsorption mechanisms may exist for the Pb²⁺ uptake process.

The zero point charge (pH_{ZPC}) is defined as the pH value of the suspension, at which the surface charge density $\sigma_o = 0$. The pH_{ZPC} of the HAp/Fe₃O₄ was determined to be 6.95. At pH 5, the surface of HAp/Fe₃O₄ is positively charged, which is unfavourable for the adsorption of Pb²⁺. Therefore, electrostatic attraction was inapplicable for the adsorption process of Pb²⁺ onto the adsorbent in this pH range.

The blank test was carried out by mixing the composite adsorbent and the aqueous solution at pH 5 without Pb²⁺ ions added. Because of the buffer capacity of HAp/Fe₃O₄, the final pH value was almost the same as that at the beginning and equal to the pH_{ZPC} (6.95) of the adsorbent. Fig. 13 also shows that the sorption of Pb²⁺ onto HAp/Fe₃O₄ caused a decrease of the final pH values. It is observed that the final pH value is reduced as the amount of adsorbed Pb²⁺ ions increased. The pH drop in equilibrium suggests that H⁺ ions are liberated from the solid surface into the solution as a result of exchange with Pb²⁺, which confirms that formation of surface complexes takes effect to the removal of Pb²⁺ [12,14,40].



Magnetic Fe₃O₄, as the supporting ingredient, facilitates the separation of the composite adsorbent from aqueous solution. Meanwhile, this material may also play a role in the enhancement of the adsorption ability to Pb²⁺ ions. The maximum adsorption capacity for Pb²⁺ ions on HAp/Fe₃O₄ was 598.8 mg/g, which was significantly higher than that on any of the single component mate-

rials, that is, 526.3 mg/g on HAp and 111.1 mg/g on Fe₃O₄. It is obvious that, besides facilitating the manipulation by an external magnetic field, the combination of Fe₃O₄ with HAp also significantly enhanced the lead adsorption ability of the material.

It is deduced that two mechanisms, dissolution/precipitation and the surface complexation, are mutually responsible for the adsorption of lead ions on HAp/Fe₃O₄. This may be attributed to the multiple functionalities of this material. Both the composition of HAp and Fe₃O₄ may cooperate to achieve the efficient removal of Pb²⁺ ions from the aqueous solution.

5. Conclusions

In this work, a novel composite adsorbent HAp/Fe₃O₄ has been developed and its adsorption behaviour on Pb²⁺ has been investigated. The experimental results confirm that this adsorbent has the potential application for removal of Pb²⁺ from aqueous solution. Efficient adsorption of Pb²⁺ can be realized in a wide pH range when an adsorbent dosage of more than 0.1 g/L is used. In our experiments, coexistent cations, e.g., Ca²⁺, Mg²⁺, K⁺ and Na⁺, do not interfere the elimination of Pb²⁺, while humic acid does. Both the Freundlich and Langmuir adsorption isotherms have been employed to evaluate the adsorption behaviour, indicating a maximum adsorption capacity of 598.8 mg/g. The adsorption process obeys the pseudo-second-order kinetics model very well. In concerning the mechanistic aspects, it is found that dissolution/precipitation and surface complexation mechanism work in concert for adsorption of Pb²⁺ on HAp/Fe₃O₄.

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