Adsorptive Removal of Pb(II) Ions with Magnetic Metal-Organic Frameworks from Aqueous Samples

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In this study, we report the application of magnetic metal-organic frameworks as a novel adsorbent for fast removal of Pb(II) ions from aqueous solution in view of adsorption isotherms, kinetics, thermodynamics, desorption, and adsorbent regeneration. The adsorbent was characterized by PPMS, XRD, TEM and N₂ adsorption/desorption measurement. The adsorption follows pseudo-second-order kinetics model and fits the Freundlich adsorption model with the adsorption capacity of 612 mg g⁻¹ for Pb(II) ions. It is a spontaneous and endothermic process controlled by positive entropy change. The used Fe₃O₄/HKUST-1 could be regenerated effectively and recycled at least four times without significant loss of adsorption capacity.

Keywords metal-organic frameworks, lead, magnetic separation, adsorption removal, water treatment

Introduction

Heavy metal ions are toxic pollutants existing in wastewater and their presence concerns industries and environmental organizations all over the world. Most of these pollutants are very toxic and dangerous for human health. Among these toxic heavy metals, lead is one of the most toxic and hazardous elements in human health, because it can cause detrimental effect on metabolic processes of human beings.^[1] Consequently, adsorption removal of Pb²⁺ from wastewater has great significance in environment protection and human health as well as the development of a circular economy. Up to now, various approaches have been proposed and employed for removing Pb(II) ions in wastewater such as adsorption, ion exchange, flocculation, precipitation, and membrane filtration, and so on,^[2-4] in which adsorption is highly recommended due to its simplicity, efficiency and low cost.^[5-7] Traditional adsorbents, such as activated carbon,^[8] iron oxide nanoparticles,^[9] bagasse fly ash^[10] and pristine yeast^[11] have been used for the removal of Pb(II) ions from wastewater. However, they cannot meet the growing industrial demand because of their limited adsorption capacity and tedious recovery process.^[12-16]

The inorganic-organic hybrid micro/nanoparticles have emerged as an exciting new research area owing to their highly tailorable properties.^[17] Metal-organic frameworks (MOFs), also known as porous coordination polymers, which are formed by linking inorganic and organic units through strong bonds (reticular synthesis) with permanent porosity, have attracted tremendous attention due to their diverse structures and tunable porosity. Very recently, MOFs have also been investigated for the removal of hazardous pollutants^[18] or detection of metal ions and small molecules.^[19] In general, the flexible and highly porous structure of MOFs allows guest species such as metal ions to diffuse into their bulk structure. However, systematic study in adsorptive removal of metal ions from wastewater by MOFs is still relatively deficient. For instance, Yin *et al.*^[20] synthesized

Zr-MOFs as an adsorbent for removal of Pb(II) ions, the adsorption capacity was limited, only 135 mg·g⁻¹.

HKUST-1,^[21] a well-known copper-based MOF with unsaturated metal sites and good stability, has been widely used in the field of catalysis,^[22] analytic chemistry,^[23,24] separation,^[25] gas storage,^[26] sensor,^[27] *etc.* It has a three-dimensional (3D) square-shaped channel system (9×9 Å) that contains up to 10 additional water molecules per formula unit. The coordinated water molecules in the framework as well as excess of water guests in the channels can easily be removed after vacuum treatment at 150 °C for 12 h, thus providing accessible sites for the surface functionalization. Ke *et al.*^[28] reported that the thiol-functionalized [Cu₃(BTC)₂]_n exhibited remarkably strong adsorption affinity and high adsorption capacity for Hg²⁺ ions. Zou *et al.*^[29] obtained HKUST-1-MW@H₃PW₁₂O₄₀, which presented remarkably high adsorption affinity and adsorption capacity of metal ions. Although HKUST-1 has several practical applications in pollutant removal, there are still some disadvantages for further applications, especially separating them from liquid media.

Magnetic separation based on the superparamagnetic Fe₃O₄ has received considerable attention and was widely used in wastewater treatment mainly because of its convenience, economy and efficiency. Magnetic MOF composites, inheriting the superiorities of magnetic nanoparticles and MOFs,^[30] have received increasing interest, especially due to their novel properties such as easy loading, rapid collection, a variety of external stimuli, devisable composition, high surface area, as well as controllable magnetic properties.

In the present work, we synthesized a highly porous Fe₃O₄/HKUST-1 composite by two facile steps. The application for an efficient adsorption of pollutants from aqueous solution is also discussed. The prepared Fe₃O₄/HKUST-1 composite was characterized. The adsorption isotherms, kinetics, thermodynamics and adsorption mechanism of Fe₃O₄/HKUST-1 were fully investigated using Pb(II) ion as model pollutants. The composite exhibited very excellent adsorption properties.

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Experimental

Reagents and instrument

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), lead acetate [$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$], ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), *N,N*-dimethylformamide (DMF), ethanol, sodium hydroxide (NaOH), hydrochloric acid (HCl) were obtained from Kermel (Tianjin, China). Benzene-1,3,5-tricarboxylic acid (H_3BTC), cupric acetate monohydrate [$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$], tetramethylammonium hydroxide [TMA, $(\text{CH}_3)_4\text{N}(\text{OH}) \cdot 5\text{H}_2\text{O}$], 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC), and *N*-hydroxysuccinimide (NHS) were obtained from Aladdin (Shanghai, China). A stock solution of Pb(II) ions ($2000 \text{ mg} \cdot \text{L}^{-1}$) were prepared by dissolving solid in water, and kept at 4°C in a refrigerator. High purity water was obtained from a Milli-Q water system (Millipore, Billerica, MA, USA). All other reagents were of analytical grade.

The $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ was characterized by a transmission electron microscopy (TEM, H7650, Hitachi, Japan), physical property measurement system (PPMS, Quantum Design Instrument, San Diego, CA, USA), XRD-600 diffractometer (Shimadzu, Kyoto, Japan) and Brunauer-Emmett-Teller (BET) surface area instrument (Quadrachrome SI-MP, Quantachrome, Florida, UK). The adsorption experiments were carried out at constant temperature controlled by a SHA-B shaking table (Shengtang, Tianjin, China). The TAS-990 atomic absorption spectrometer (AAS, Persee, Beijing, China) was employed for determination of Pb(II) ions.

Preparation of Fe_3O_4 magnetite

The Fe_3O_4 magnetite was prepared as follows: $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (0.01 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mol) were dissolved in 60 mL water. The mixture was stirred vigorously while the temperature increased to 80°C , and then 10 mL ammonia was added into the mixture. After 30 min, the magnetic precipitates were isolated from the solvent by a permanent magnet and washed several times with water. The Fe_3O_4 obtained was dispersed in distilled water and 1.5 mL of TMA by ultrasound for 10 min. Surface modification of Fe_3O_4 was washed and dispersed in distilled water for further use.

Preparation of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$

H_3BTC (0.5 g) was dissolved in a mixed solution of DMF/ethanol (1 : 1, 80 mL). TMA modified Fe_3O_4 (0.3 g) was added under magnetic stirring, and then the mixture was heated to 70°C . After the addition of an aqueous solution (40 mL) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.86 g, 4.31 mmol), NHS (0.2 g) and EDC (0.2 g) to the reaction mixture, the reaction was carried out at 70°C with stirring for further 4 h. The addition of NHS/EDC is to enhance the interaction between amino group of Fe_3O_4 and carboxyl group of MOF, so that the two materials can be connected together. Finally, the product was separated by a permanent magnet and washed three times with water and ethanol, respectively. Then the product was finally dried at 150°C under vacuum overnight.

Adsorption experiments

In a typical adsorption experiment, a 10 mL vial equipped received a weighed amount of adsorbent (20 mg), followed by adding 8 mL of Pb(II) ions solution ($0\text{--}2000 \text{ mg} \cdot \text{L}^{-1}$) at a controlled temperature. Finally, the test vials were placed in a magnetic field, where permanent magnet causes the particles to aggregate on the beneath of the test vials.

For a kinetics study, the adsorption was carried out at constant temperature, and the supernatant was collected at different time intervals for determination of unadsorbed Pb(II) ions. For a thermodynamic study, the adsorption proceeded for 2 h to reach apparent adsorption equilibrium at different temperatures (25 , 35 and 45°C). To determine the adsorption capacity at various pH, the pH of the Pb(II)

ions solutions was adjusted with $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl or $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH aqueous solution.

The detection of Pb(II) ions was performed by AAS. A lead hollow cathode lamp was used as the radiation source at 283.3 nm . Measurements were carried out in the integrated absorbance (peak area) mode at 5 mA, using a spectral bandwidth of 0.2 nm .

Desorption experiments

The feasibility for regenerating the exhausted $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ saturated with Pb(II) ions was evaluated using the solvent desorption technique. NaOH ($0.01 \text{ mol} \cdot \text{L}^{-1}$) was tested as eluent solution to regenerate $\text{Fe}_3\text{O}_4/\text{HKUST-1}$. The desorption solution (4 mL) was added into a 10 mL centrifugal tube containing 20.0 mg of used $\text{Fe}_3\text{O}_4/\text{HKUST-1}$. Then the mixture was shaken at 150 rpm at room temperature for 0.5 h. After separating by a permanent magnet, the desorbed $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ was washed with water twice, and dried for reuse.

Results and Discussion

Characterization of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$

PPMS analysis was employed to study the magnetic property of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$. As shown in Figure 1a, the magnetization curve showed its superparamagnetic property. The saturation magnetization of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ is $26.15 \text{ emu} \cdot \text{g}^{-1}$. This value demonstrated that the composite has strong magnetism.

To investigate the surface morphology and the microstructure of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ sample, the sample was characterized by TEM (Figure 1b). The TEM image indicates Fe_3O_4 particle uniform distribution in HKUST-1, which is a desirable feature for magnetic separation.

The XRD patterns of Fe_3O_4 , HKUST-1 and $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ are shown in Figure 1c. The crystal structure of the synthesized materials has been confirmed to be HKUST-1 because it can be readily indexed

Figure 1 Magnetization curve (a), TEM image (b), powder XRD patterns (c) and N_2 adsorption-desorption isotherm (d) of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$.

according to reported patterns of HKUST-1.^[28,31] 15.5° (222), 13.2°

(440), 16.3° (422), 17.3° (511), 20.0° (660), 25.8° (731), 29.3° (751), 35.0° (773), 38.9° (828), 46.8° (751), and the XRD patterns of the synthesized HKUST-1 match with the reported. After grafting Fe₃O₄, the characteristic peaks of HKUST-1 remained in the XRD patterns of Fe₃O₄/HKUST-1, but minor changes in the XRD peak intensities were observed. These results indicate that the crystal structure of HKUST-1 remains conspicuously intact after modification of Fe₃O₄.

The N₂ sorption-desorption isotherm of the Fe₃O₄/HKUST-1 is shown in Figure 1d. The BET surface area of the as-synthesized Fe₃O₄/HKUST-1 was 685 m²·g⁻¹. Compared with the pure HKUST-1 (1482 m²·g⁻¹),^[28] the as-prepared Fe₃O₄/HKUST-1 showed a reduced BET surface area, mainly due to the nonporous Fe₃O₄ cores and different reaction conditions.

In this work, the pore size distribution of Fe₃O₄/HKUST-1 was 5–17 nm, and the particle size of Fe₃O₄ magnetite was 6–10 nm. It is possible that some Fe₃O₄ particles can be encapsulated in the pore of MOFs.

Adsorption isotherms for Pb(II) ions removal from water

The adsorption capacity, defined as the maximum amount of metal ions adsorbed on a certain amount of the sorbent, is an important factor for evaluation of the as-synthesized Fe₃O₄/HKUST-1. In order to determine the adsorption capacity, the adsorption isotherm of Pb(II) ions adsorbing on the as-prepared Fe₃O₄/HKUST-1 was performed and shown in Figure 2a. The adsorption capacities of Pb(II) ions on the Fe₃O₄/HKUST-1 is calculated to be 612 mg/g, which is higher than that of other conventional adsorbents (Table 3).^[8–11,32–34]

The Langmuir adsorption model (Figure 2b) was employed for this study for describing the adsorption isotherm. By fitting the equilibrium adsorption data with the Langmuir adsorption model,^[35] the adsorption capacity of Pb(II) ions onto the Fe₃O₄/HKUST-1 was calculated by Eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (1)$$

where C_e is the equilibrium concentration of the remaining Pb(II) ions in the solution (mg·L⁻¹), q_e is the amount of Pb(II) ions adsorbed on the adsorbent at equilibrium (mg·g⁻¹), q_m is the mono-layer adsorption capacity (mg·g⁻¹), and K_L is the Langmuir constant (L·mg⁻¹).

The Freundlich isotherm, on the other hand, represents an empirical expression that includes the heterogeneity of the surface and an exponential distribution of the sites and their energies. This isotherm has been further extended by considering the influence of adsorption sites and the competition between different adsorbents for adsorption on available sites. The Freundlich isotherm has been observed to be applicable for a wide range of heterogeneous surfaces including activated carbon, silica, clays, and polymers. The Freundlich isotherm^[36] can be described by Eq. (2):

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where K_f (mg·g⁻¹) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. As shown in Figure 2c, these constants are determined from the intercept and slope of linear plot of $\ln Q_e$ versus $\ln C_e$, respectively.

The calculated result was found that the adsorption of Pb(II) ions on Fe₃O₄/HKUST-1 correlated well with the Freundlich equation ($R^2 = 0.999$) as compared to the Langmuir equation ($R^2 = 0.754$) under the studied concentration range. Therefore, the Freundlich model fitted Pb(II) ions sorption isotherm better than the Langmuir model.

Figure 2 Adsorption isotherm (a), Langmuir (b) and Freundlich (c) plots of the isotherm for Pb(II) ions adsorption onto Fe₃O₄/HKUST-1.

Kinetics for the adsorption of Pb(II) ions on Fe₃O₄/HKUST-1

The time-dependent adsorption of Pb(II) ions on Fe₃O₄/HKUST-1 was investigated at 2000 mg L⁻¹ initial concentration. In this work, as can be seen from Figure 3a, the adsorption equilibrium of Pb(II) ions was reached within 30 min at the concentration of 2000 mg·L⁻¹, revealing the rapid adsorption of Pb(II) ions on Fe₃O₄/HKUST-1.

To gain insight into the adsorption kinetics, two models have been studied: the pseudo-first-order kinetic model and pseudo-second order kinetic model. The linear form of the pseudo-first-order equation^[37] (Figure 3b) is given as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_t and q_e are the adsorption capacity (mg g⁻¹) at a certain time t (min) and equilibrium, respectively, and k_1 is the rate constant for the pseudo-first-order adsorption (min⁻¹).

Compared to the pseudo-first-order kinetic model, the time-dependence of the adsorption of Pb(II) ions on Fe₃O₄/HKUST-1 was much better fitted with the pseudo-second-order kinetic model^[37,38] (Figure 3c) as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_t and q_e are the adsorption capacity (mg·g⁻¹) at a certain time t (min) and equilibrium, respectively, and k_2 is the rate constant for the pseudo-second-order adsorption (g·mg⁻¹·min⁻¹). The plots of t/q_t against t show good linearity ($R^2 = 0.999$) with a slope of $1/q_e$ and an intercept of $1/(k_2 q_e^2)$.

In conclusion, the adsorption parameters for adsorption kinetics were determined at different times by the pseudo-first-order and pseudo-second-order. The values of R^2 for the pseudo-second-order model ($R^2 = 0.999$) were higher than that for pseudo-first-order ($R^2 = 0.747$). The pseudo-second-order kinetics model was feasible to describe the adsorption process of Pb(II) ions on the Fe₃O₄/HKUST-1.

Figure 3 Kinetics adsorption (a), pseudo-first-order (b) and pseudo-second-order kinetics (c) for the adsorption of Pb(II) ions on $\text{Fe}_3\text{O}_4/\text{HKUST-1}$.

Adsorption thermodynamics

To determine the effect of temperature on the Pb(II) ions adsorption, adsorption experiments were also conducted at 298, 308 and 318 K (Figure 4). The thermodynamic parameters of enthalpy change (ΔH), Gibbs free energy change (ΔG), entropy change (ΔS), and thermodynamic equilibrium constant (K_0) were computed using the following equations:^[39]

$$K_0 = \frac{q_e}{c_e} \quad (5)$$

$$\Delta G = -RT \ln K_0 \quad (6)$$

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

Figure 4 Van't Hoff plot to get the ΔH° and ΔS° of Pb(II) ions over the $\text{Fe}_3\text{O}_4/\text{HKUST-1}$.

where K_0 is the adsorption equilibrium constant, q_e the amount of Pb(II) ions adsorbed per mass of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ ($\text{mg}\cdot\text{g}^{-1}$), C_e the Pb(II) ions concentration in solution at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), R universal gas constant, and T temperature. The results are listed in Table 1. In particular, the positive values of ΔH obtained from this analysis indicate that the adsorption is endothermic, suggesting that the adsorption process is more favorable at higher temperatures. The negative ΔG values are indicative of a spontaneous adsorption. Finally, the positive values of ΔS indicate that the adsorption process is irreversible and favors sorption stability.

Table 1 The thermodynamic parameters of Pb(II) ions adsorption over the $\text{Fe}_3\text{O}_4/\text{HKUST-1}$

T/K	$\ln K_0$	$\Delta G^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S^\circ/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
298	1.2581	-3.12		
308	1.6865	-4.32	29.07	108.26
318	2.0274	-5.36		

Effect of pH on the sorption of Pb(II) ions

The solution acidity (pH) has been identified as the most important factor affecting metal adsorption onto different adsorbents because it governs the speciation of metals and also the dissociation of active functional sites on the adsorbent. An appropriate pH value can improve the adsorption efficiency and also reduce interference from the matrix. Figure 5 depicts the influence of pH on the adsorption process of Pb(II) ions on the synthesized magnetic composites in the range of pH values from 2 to 12.

Figure 5 Effect of pH on the adsorption of Pb(II) ions over $\text{Fe}_3\text{O}_4/\text{HKUST-1}$.

The adsorption of Pb(II) ions on $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ increases very quickly in the pH range 2–7, remains at a high level as the pH increases from 7–8, and then decreases steeply at pH values higher than 9. Changes in the solution pH can affect the distribution of Pb(II) ions species (Figure 6) in solution and the surface charges of the adsorbents, promoting or suppressing the adsorption of metal ions on adsorbent surfaces. The hydrolysis constants (Table 2) of Pb(II)^[40] suggest that the Pb(II) species are present as Pb^{2+} , $\text{Pb}(\text{OH})^+$, $\text{Pb}(\text{OH})_2^0$, and $\text{Pb}(\text{OH})_3^-$ at different pH values.

As shown in Figure 5, at low pH values ($\text{pH} < 7$), the main species is Pb^{2+} , the adsorption of Pb^{2+} for the adsorbent was less favorable, probably because most positively charged hydrogen ions (H^+) competed with Pb^{2+} for binding sites on the adsorbent surface.^[41,42] In the pH range 7–8, Pb(II) removal reaches a maximum and maintains a high level. The main species present in the pH range 7–8 are

Figure 6 Distribution of Pb(II) species as a function of pH.

Table 2 Equilibrium constants (log *K*) for Pb(II) ions hydrolysis reactions

Equilibrium	Log <i>K</i> (<i>T</i> =298 K)
$\text{Pb}^{2+} + \text{H}_2\text{O} = \text{Pb}(\text{OH})^+ + \text{H}^+$	6.48
$\text{Pb}^{2+} + 2\text{H}_2\text{O} = \text{Pb}(\text{OH})_2 + 2\text{H}^+$	11.16
$\text{Pb}^{2+} + 3\text{H}_2\text{O} = \text{Pb}(\text{OH})_3^- + 3\text{H}^+$	14.16

Pb^{2+} and $\text{Pb}(\text{OH})^+$. These can easily be adsorbed on the negatively charged $\text{Fe}_3\text{O}_4/\text{HKUST-1}$.

As the pH of the solution increases, the number of negative charge increases on the surface of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$. In the meantime, the main species present in the pH range 8–12 are $\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{OH})_3^-$, the dissociation level of OH groups will increase and give negative oxygen ion (O^-) resulting in electrostatic repulsion between adsorbent and metal ions. The maximum adsorption capacity for $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ was obtained at pH 8. Consequently, pH 8 is the optimum value for adsorption of Pb(II) ions on the adsorbent and all the next experiments were carried out at this optimum pH value.

Recycling and reuse of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$

To analyze the recycling and reuse properties of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ (desirable features of an excellent adsorbent), a reusability test was performed. The results are displayed in Figure 7. Desorption and regeneration of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ was successfully achieved using $0.01 \text{ mol} \cdot \text{L}^{-1}$ NaOH for Pb(II) ions. The removal efficiency at the fourth cycle decreased by about 8.23% compared to the first adsorption. This slight adsorption decrease was caused probably by the partially decomposition of as-prepared materials (Figure 8). We also investigated whether the Fe_3O_4 was leaked after recycling. The result showed that the saturation magnetization of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ has a little decrease from 26.15 to $23.37 \text{ emu} \cdot \text{g}^{-1}$ after four recycling. Our data confirmed that the magnetic composite proposed in this work can be recycled and reused several times.

Adsorption mechanism

The research about the adsorption characteristics of the $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ for Pb(II) ions is critical to explore their potential applications. From the pH study, it has been found that adsorption of Pb(II) ions is highly dependent on pH. The negatively charged surface of the $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ will favor the adsorption of Pb(II) ions due to the electrostatic attraction. At pH 7–8, a significantly high electrostatic attraction exists between the adsorbent and Pb(II) ions. In the mean

Figure 7 Reusability of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ for the adsorptive removal of Pb(II) ions.

Figure 8 Powder XRD patterns of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ after reused several times.

time, there is a physical adsorption due to textural properties for the adsorbent (surface area and total pore volume), which promotes the adsorption capacity. According to the ionic radius table and previous literature,^[43] the bare ion radius and hydrated radius of Pb(II) ions are $1.2 \text{ \AA}$ and $4.0 \text{ \AA}$, which is much smaller than square-shaped channel system ($9 \times 9 \text{ \AA}$) of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$, it is possible for Pb(II) ions to enter the inner channel of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$.

Comparison of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ with other adsorbents for the adsorption of Pb(II) ions

In order to demonstrate the applicability, $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ was used for the adsorption of Pb(II) ions. A comparison of the results in the present study with the reported systems^[8-11,30-32] for Pb(II) ions removal is summarized in Table 3. Compared with other adsorbents, the results suggest that $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ has a significant adsorption capacity. In the meanwhile, saturation has not been reached in the adsorption isotherm of Pb(II) ions on $\text{Fe}_3\text{O}_4/\text{HKUST-1}$, indicating that it has the potential for even much higher adsorption capacity. The synthesis of material is easy to control, which does not require complex processes. Moreover, because of the magnetic properties, the $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ is attractive for its rapidness, which indicated the material is superior to other adsorbents.

Conclusions

In this study, we have successfully demonstrated the use of $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ to remove Pb(II) ions from aqueous solution. The kinetic data analysis indicates that the removal of Pb(II) ions can be

Table 3 Comparison of Pb(II) ions removal with other reported systems

Adsorbents	$Q_m/$ ($\text{mg}\cdot\text{g}^{-1}$)	Conditions	Ref.
Iron oxide nanoparticles	36	Initial concentration 162 $\text{mg}\cdot\text{L}^{-1}$	[9]
		Contact time 30 min	
Bagasse fly ash	2.50	Initial concentration 20 $\text{mg}\cdot\text{L}^{-1}$	[10]
		Contact time 80 min	
Activated carbon	21.8	Initial concentration 50 $\text{mg}\cdot\text{L}^{-1}$	[8]
		Contact time 160 min	
Chitosan immobilized on bentonite	26.38	Initial concentration 25 $\text{mg}\cdot\text{L}^{-1}$	[32]
		Contact time 60 min	
Oxidized multiwall carbon nanotubes	11.2	Initial concentration 16 $\text{mg}\cdot\text{L}^{-1}$	[33]
		Contact time 24 h	
Multiwalled carbon nanotubes/polyacrylamide composites	40	Initial concentration 10.0 $\text{mg}\cdot\text{L}^{-1}$	[34]
		Contact time 240 min	
nano-ZnO/yeast composites	66.68	Initial concentration 100 $\text{mg}\cdot\text{L}^{-1}$	[11]
		Contact time 30 min	
Nano-ZnO	38.47	Initial concentration 100 $\text{mg}\cdot\text{L}^{-1}$	[11]
		Contact time 30 min	
Pristine yeast	22.48	Initial concentration 100 $\text{mg}\cdot\text{L}^{-1}$	[11]
		Contact time 30 min	
$\text{Fe}_3\text{O}_4/\text{HKUST-1}$	612	Initial concentration 2000 $\text{mg}\cdot\text{L}^{-1}$	This work
		Contact time 30 min	

modeled by the pseudo-second-order equation. On the other hand, adsorption equilibrium data is well represented by the Freundlich isotherm model. Owing to diverse structures and unique properties of MOFs, magnetic MOF composites are attractive for their efficient removal of Pb(II) ions from water samples. The addition of Fe_3O_4 nanoparticles makes the hybrid material more attractive for its rapidness compared with other adsorbents. Moreover, the $\text{Fe}_3\text{O}_4/\text{HKUST-1}$ can be reused at least four times without obvious decrease in the removal efficiency. The materials exhibited a significant adsorption capacity ($612 \text{ mg}\cdot\text{g}^{-1}$), good solvent stability and excellent reusability for Pb(II) ions, making them promising as a novel adsorbent for removal of heavy metal ions from water.

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