

Sorption of Pb(II) on Mg-Fe Layered Double Hydroxide

LIANG, Xuefeng^a(梁学峰) HOU, Wanguo^{*a,b}(侯万国) XU, Jie^c(徐洁)^a Environment Research Institute, Shandong University, Jinan, Shandong 250100, China^b Key Laboratory for Colloid & Interface Chemistry of Education Ministry, Shandong University, Jinan, Shandong 250100, China^c College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, Shandong 266042, China

Mg-Fe layered double hydroxide (LDH) with a Mg/Fe molar ratio of 3 : 1 was synthesized by using a coprecipitation method and the sorption removal of Pb(II) by the LDH sample from Pb(NO₃)₂ solution was investigated. It was found that Mg-Fe LDH showed a good sorption ability for Pb(II) from Pb(NO₃)₂ solution, indicating that the use of LDH as a promising inorganic sorbent for the removal of heavy metal ions is possible. The sorption kinetics and the sorption isotherm of Pb(II) on the LDH sample obeyed the pseudo-second order kinetic model and Arano-vich-Donohue equation, respectively. The sorption mechanism of Pb(II) on the LDH may be attributed to the surface-induced precipitation and the chemical binding adsorption, and the removal ability arising from the surface-induced precipitation is much higher than that from the chemical binding adsorption.

Keywords sorption, layered double hydroxide, lead, surface precipitation, surface complexation

Introduction

At present heavy metal contamination is one of the widespread environmental problems which can pose serious threats to human and ecosystem health. The remediation of heavy metal contaminated soil and the treatment of waste water have become hot topics of environmental science and engineering. The adsorption or sorption reactions of heavy metals at solid-water interface are most important behavior occurring in nature, which control the mobility, bioavailability, environmental ecological effect and geochemistry process of heavy metal.¹ The scientific knowledge of speciation, transport and fate of heavy metal at solid-liquid interface is the fundamental for remediation of polluted soil and water. A great number of studies have been focused on the adsorption of heavy metal on clay minerals, metal oxides or hydroxides and metal carbonates or phosphates.² However, the adsorbents studied are usually negatively charged materials such as kaolinite and montmorillonite, there are few studies on positively charged adsorbents, such as layered double hydroxides (LDHs in short), for the removal of heavy metal cations.³⁻⁶

Layered double hydroxides, also known as hydrotalcite-like compounds (HTlc in short) or anionic clays, are a large group of natural and synthetic layered materials and have received considerable attention in recent years due to their special structures and unique applica-

tions.^{7,8} LDHs can be represented by the empirical formula $[M_{1-x}^{2+}M_x^{3+}OH)_2]^{x+}[A_{x/n}^{n-} \cdot mH_2O]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, A^{n-} is the charge compensating anion or gallery anion, m is the number of moles of co-intercalated water per formula weight of the compound, and x is the number of moles of M^{3+} per formula weight of the compound. They are built up of brucite-like sheets and part of divalent cations (M^{2+}) are replaced by trivalent cations (M^{3+}), which is known as isomorphous substitution, to form excessive positive charges in LDH layers. The excess of the positive charges is balanced by the anions (A^{n-}) in the interlayer.⁹ The anions in the interlayer can be exchanged by other anions so that high anion exchange capability (AEC) is the most remarkable characteristic of LDHs. There has been interest in applications of LDHs to removing negatively charged species, such as $Cr_2O_4^{2-}$, PO_4^{3-} , Cl^- , F^- , humic acid and so on by adsorption or anion exchange in many researches.¹⁰ However applications of LDHs for removing metal cations are rarely reported. The studies of sorption of heavy metal cations on LDHs are of importance, which can improve the scientific knowledge for the sorption behavior on positively charged particle surface and can support instructions for remediation of polluted soils or water. In this paper, Mg-Fe LDH was prepared and the sorption of Pb(II) on the LDH was studied.

* E-mail: wghou@sdu.edu.cn

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Materials and methods

Preparation of Mg-Fe LDH

The Mg-Fe LDH sample was prepared by a coprecipitation method according to Miyata's procedure.^{11,12} MgCl₂·6H₂O and FeCl₃·6H₂O with 3 : 1 of the Mg²⁺/Fe³⁺ molar ratio and about 0.5 mol/L of total metal concentration were dissolved into deionized water to prepare a mixed solution, and an ammonia solution (ca. 6 wt%) was slowly dropped into the mixed solution under stirring until a final pH ca. 10. The reaction mixture was thoroughly stirred for 15 min and aged for 45 min in mother solution at room temperature, and then filtered, washed with distilled water to remove dissolved ions and the excess of ammonia. The filter cake was further hydrothermally treated at about 80 °C for about 24 h to improve its crystallinity, forming Mg-Fe LDH sol. The sol was dried, triturated and sieved to collect the particles of <90 μm in diameter to obtain Mg-Fe LDH sample.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a D8 advance X-ray diffractometer (Bruker AXS Inc.) using Cu Kα radiation at a scanning speed of 1.5 (°)/min over 2θ from 3° to 70° operated at 40 kV and 40 mA.

The chemical analyses of Mg and Fe in the LDH sample were carried out by dissolving the sample in 1% HNO₃ solution followed by their determination with a TAS-990 model atomic absorption spectrometer (Beijing Purkinje General Instrument Co., Ltd). The carbon content was determined by an elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH), meanwhile Cl⁻ by a chloride ion-selective electrode.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 370 model FT-IR spectrometer (Thermo Nicolet Corporation) in KBr matrix in the range of 4000—400 cm⁻¹.

Sorption experiments

Sorption kinetics experiments of Pb(II) on the LDH sample were carried out by the following steps.^{13,14} A known mass of the LDH sample was dispersed in 1000 mL of Pb(NO₃)₂ solution with a known initial Pb(II) concentration. The suspension was stirred at a constant speed and maintained at the constant temperature. At the same time, pH of the system was recorded by a PHS-3C pH meter. Aliquots (0.5 mL) of suspension were withdrawn at predetermined time intervals (*t*) and filtered through a 0.45-μm syringe filter. The remaining Pb(II) concentrations of filtrates were determined by an atomic absorption spectrometer. The sorption amount Γ_t (in mg per g of LDH sample) was calculated by the following equation:

$$\Gamma_t = (C_0 - C_t)V/m \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) are the initial and the

remaining Pb(II) concentration, respectively, V (mL) is the volume of the suspension and m (g) is the mass of Mg-Fe LDH sample.

Sorption isotherms of Pb(II) on the LDH sample were recorded by a batch equilibration technique.¹⁵⁻¹⁷ Known masses of the LDH sample were put into polyethylene centrifugal tubes, and then filled with Pb(NO₃)₂ solutions of different Pb(II) concentrations in the range of 50—450 mg/L. Since the solubility product of Pb(OH)₂ at 25 °C is 1.43×10^{-20} ,^{18,19} the initial pH must be controlled under 6 in order to avoid the precipitation of Pb(OH)₂ before sorption experiments. Then the centrifugal tubes were put into a thermostatic water bath shaker at (25 ± 0.2) °C for 24 h. Then the suspensions were centrifuged at a speed of 13000 r/min for 15 min and collected to determine the equilibrium Pb(II) concentrations. The equilibrium sorption amounts (Γ_e) were calculated from the decreases of the Pb(II) concentration in the solution phases.

The effects of electrolyte NaNO₃ on the sorption of Pb(II) on the LDH were investigated.

Sorption tests were performed in triplicate and the results were recorded as an average.

Because LDHs had a high pH-buffering capacity, the pH values of sorption systems were not controlled in the sorption processes. The initial pH of Pb(NO₃)₂ solution was adjusted using 0.1 mol/L HNO₃ and NaOH solutions.

Results and discussion

Characterizations of LDH sample and sorption products

The PXRD patterns of the LDH sample and sorption products are shown in Figure 1. The sorption products were obtained at initial pH 4.5 (without controlling pH in sorption process) and at constant pH 3.6 (controlling pH constant in sorption process), respectively. For the LDH sample (see Figure 1A), the peaks at lower 2θ values are sharp and symmetric as compared to those at higher 2θ values, which is characteristic of clay minerals having a layered structure.^{9,20,21} All the peaks are similar to magnesium iron carbonate hydroxide Mg₆Fe₂CO₃(OH)₁₆·H₂O (JCPDS card No. 25-0521) and secondary phases such as Mg(OH)₂ and Fe(OH)₃ were not observed in the PXRD patterns, indicating that the LDH sample is of pure hydrotalcite crystal structure. Using the (003) peak and Bragg equation, it is possible to calculate the interlayer space (*d*-spacing) of the LDH sample,²² then gallery height can be calculated through the interlayer space minus layer thickness (0.48 nm). For the Mg-Fe LDH sample, the *d*-spacing and the gallery height values were about 0.80 and 0.32 nm, respectively.

For sorption products (see Figures 1B and 1C), all the character peaks of the LDH sample were also observed, however, the intensities of the PXRD peaks decreased, indicating that the Pb(II) sorption did not obviously

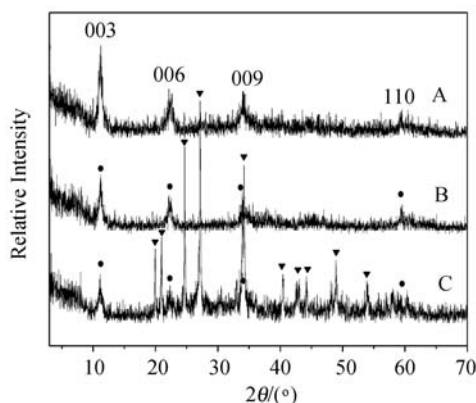


Figure 1 PXRD patterns of the pristine LDH sample and sorption products. A: pristine LDH; B: sorption product at constant pH 3.6, Pb(II) sorption amount *ca.* 15 mg/g; C: sorption product at initial pH 4.5, Pb(II) sorption amount *ca.* 350 mg/g. ●: Mg-Fe LDH; ▼: $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$.

change the layered crystal structure of the LDHs. The decrease of the PXRD peak intensities maybe arises from the slight decomposition of LDH sample, which was evidenced by analyzing the supernatant after sorption. In addition, for the sorption product obtained at initial pH 4.5 (see Figure 1C), the PXRD peaks of hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (JCPDS card No 13-0131), were observed, indicating that the Pb(II) sorption led to a significant precipitation of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; for the sorption product obtained at constant pH 3.6 (see Figure 1B), no new bulk phase or precipitation was detected by the PXRD method, which maybe arises from the low pH value. The *d*-spacing and the gallery height values of sorption products were about 0.79 and 0.31 nm, respectively, *i.e.*, obvious change of interlayer space was not observed before and after sorption.

The FT-IR spectra of the LDH sample and the sorption products are shown in Figure 2. For the pristine LDH sample (see Figure 2B), the spectrum exhibits an intense broad band at about 3440 cm^{-1} , which may be contributed to the stretching vibration of structural O—H groups hydrogen-bonded with interlamellar water or O—H groups in adjacent layers. Another broad band at about 1635 cm^{-1} is due to the bending vibration of H—O—H ($\delta_{\text{H-O-H}}$) and it should be assigned to the adsorbed water molecules in the interlayer. An intense absorption band at about 1384.15 cm^{-1} was assigned to the ν_3 mode asymmetric stretching of CO_3^{2-} in the interlayer,²³ indicating that some CO_3^{2-} ions existed in the gallery of the LDH. However, the content of carbonate in the sample was so little that there is no carbon detected in elemental analyses. The strong absorption at 573.08 cm^{-1} may be related to the lattice vibration, such as O—Mg—O or Mg—O—Fe vibration.²⁴

For the sorption products (see Figures 2A and 2C), the FT-IR spectra exhibit all the characteristic adsorption bands of the pristine LDH. It is worthy to note that

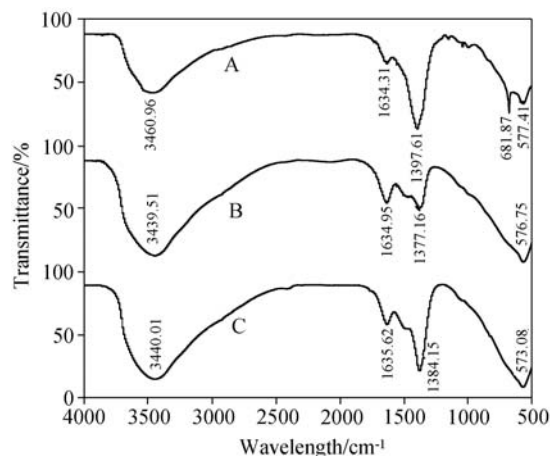


Figure 2 FT-IR spectra of the pristine LDH and sorption products. A: sorption product at initial pH 4.5, Pb(II) sorption amount *ca.* 350 mg/g; B: pristine LDH; C: sorption product at constant pH 3.6, Pb(II) sorption amount *ca.* 15 mg/g.

some adsorption bands of the pristine LDH were shifted after the Pb(II) sorption. For the sorption product obtained at initial pH 4.5 (see Figure 1A), the peak at 1377.16 cm^{-1} corresponding to the ν_3 mode asymmetric stretching of CO_3^{2-} of the pristine LDH was shifted to 1397.61 cm^{-1} , and a new peak at about 681.87 cm^{-1} corresponding to the ν_4 stretching mode of CO_3^{2-} appeared,²⁵ which may be attributed to the formation of precipitation $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; in addition, the peak at 3439.51 cm^{-1} corresponding to the stretching vibration of structural O—H groups of the pristine LDH was shifted to 3460.96 cm^{-1} , which maybe arises from the effect of the coating layer or OH^- ions of precipitation $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. For the sorption product obtained at constant pH 3.6 (see Figure 2C), the peak at 1377.16 cm^{-1} corresponding to the ν_3 mode asymmetric stretching of CO_3^{2-} of the pristine LDH was shifted to 1384.15 cm^{-1} , which maybe arises from the interaction between CO_3^{2-} and Pb(II) ions. In addition, it can be seen from Figure 2 that the intense of the peak corresponding to the ν_3 mode asymmetric stretching of CO_3^{2-} increased after the Pb(II) sorption, indicating that the suspension may sorb CO_2 from atmosphere to form CO_3^{2-} in the Pb(II) sorption process, which was verified by the carbon content analysis for the sorption products. The carbon content of the pristine LDH sample was not detected in elemental analyses, however those of the sorption products obtained at initial pH 4.5 and at constant pH 3.6 were about 1.371% and 0.009%, respectively.

The chemical composition of the pristine LDH sample determined by chemical analysis is $[\text{Mg}_{0.72}\text{Fe}_{0.28}(\text{OH})_2]\text{Cl}_{0.06}(\text{OH})_{0.22}$. The compensating ions of the LDH sample are Cl^- and OH^- ions. The presence of OH^- as the balancing anions is because the LDH sample was washed with distilled water in the synthesis process.

Sorption kinetics

In the sorption kinetic research, a proper mathematical model which not only may fit the experimental data but also complies for a reasonable mechanism must be chosen. Sorption kinetic studies are significant because the kinetic data can be used to determine the time required for sorption equilibrium and the rate of sorption can be used to develop predictive models. Three different kinetic models usually used to fit the experimental data are summarized as follows.

(i) First-order kinetic model Lagergren's first order rate equation^{26,27} is the earliest known one to describe the adsorption rate based on the sorption amount, which can be expressed as follows:

$$d\Gamma_t/dt = k_1(\Gamma_e - \Gamma_t) \quad (2)$$

where k_1 (min^{-1}) is the rate constant of first order adsorption. The linear form of the first-order kinetic equation with the initial conditions $\Gamma_0 = 0$ at $t = 0$ is

$$\Gamma_t = \Gamma_e(1 - e^{-k_1 t}) \quad (3)$$

(ii) Pseudo-second order kinetic model The pseudo-second order kinetic model^{27,28} is expressed as

$$d\Gamma_t/dt = k_2(\Gamma_e - \Gamma_t)^2 \quad (4)$$

where k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant of pseudo-second order adsorption. The linear form of the pseudo-second order kinetic equation is,

$$t/\Gamma_t = 1/(\Gamma_e^2 k_2) + t/\Gamma_e \quad (5)$$

The plot of t/Γ_t versus t should be a straight line.

(iii) Double-exponential function model Wilczak and Keinath²⁹ used a double-exponential function model to correlate the two-step kinetics of the sorptions of Pb(II) and Cu(II) ions onto activated carbon. The following equation is a mathematical description of the two-step contribution to the sorption amount,

$$\Gamma_t = \Gamma_0 + \Gamma_1(1 - e^{-k_1' t}) + \Gamma_2(1 - e^{-k_2' t}) \quad (6)$$

where Γ_1 and Γ_2 are sorption amounts of the rapid and the slow steps, respectively, Γ_0 is sorption amount at $t = 0$ and $\Gamma_0 = 0$ may be reasonably assumed when $t = 0$, k_1' and k_2' are rate parameters (min^{-1}).

Figure 3 shows the kinetic data of Pb(II) sorption on the LDH. It is evident that the kinetic profiles in all cases exhibit a relative rapid initial rate of sorption followed by a slow approach to equilibrium. For all systems studied, Pb(II) ions may be completely removed within 600 min. So, a sorption time of 24 h was selected to determine the equilibrium sorption amount in order to reach enough sorption equilibrium.

With the simulation of above three kinetic models for the sorption data, it was found that the pseudo-second order model and double-exponential function model can describe the Pb(II) sorption kinetics on the LDH, as shown in Figures 3 and 4. The parameters of pseudo-second order model and double-exponen-

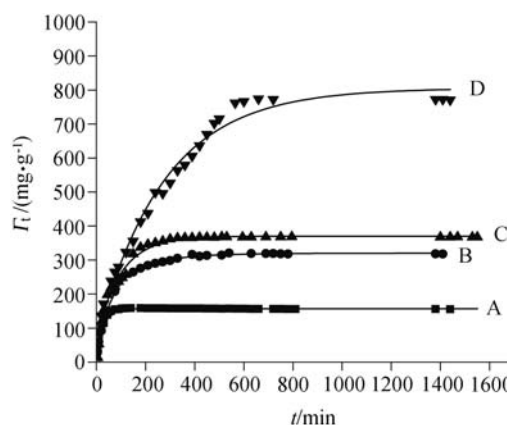


Figure 3 Sorption kinetics of Pb(II) on LDH at various initial Pb(II) concentrations and LDH concentrations. A: 1.01 g/L LDH, 159.57 mg/L Pb(II); B: 0.50 g/L LDH, 167.76 mg/L Pb(II); C: 1.00 g/L LDH, 375.20 mg/L Pb(II); D: 0.49 g/L LDH, 395.42 mg/L Pb(II). The dots represent the experimental data and the lines represent the double-exponential function model fits.

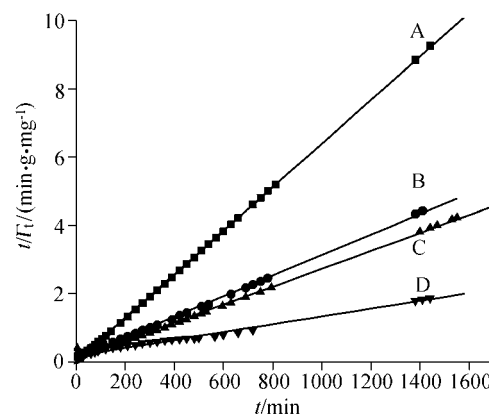


Figure 4 Pseudo-second order model fits for sorption kinetics. A: 1.01 g/L LDH, 159.57 mg/L Pb(II); B: 0.50 g/L LDH, 167.76 mg/L Pb(II); C: 1.00 g/L LDH, 375.20 mg/L Pb(II); D: 0.49 g/L LDH, 395.42 mg/L Pb(II). The dots represent the experimental data and the lines represent the model fits.

tial function model are listed in Tables 1 and 2, respectively.

Sorption isotherms

A sorption isotherm is a measure of the relationship between the equilibrium concentrations (C_e) and equilibrium sorption amounts (Γ_e) over a certain concentration range. Equilibrium isotherm studies were carried out in order to determine the optimum conditions for maximum Pb(II) sorption on the LDH. The commonly used isotherms^{30,31} for quantitative description of sorption data are (i) Langmuir isotherm, (ii) Freundlich isotherm, (iii) Langmuir-Freundlich isotherm and (iv) Aranovich-Donohue isotherm.³²

(i) Langmuir isotherm The linear form of the Langmuir isotherm can be expressed as

$$C_e/\Gamma_e = 1/(K_L \Gamma_m) + C_e/\Gamma_m \quad (7)$$

Table 1 Parameters of pseudo-second order model fits for Pb(II) sorption kinetics^a

Run No.	LDH conc./($\text{g}\cdot\text{L}^{-1}$)	$C_0/(\text{m}\cdot\text{L}^{-1})$	$\Gamma_{e,\text{exp}}/(\text{m}\cdot\text{L}^{-1})$	$\Gamma_{e,\text{cal}}/(\text{mg}\cdot\text{g}^{-1})$	$k_2/(\text{g}\cdot\text{min}^{-1}\cdot\text{g}^{-1})$	R^2
A	1.01	159.57	158.07	156.74	$3.03\text{E}-3$	0.99972
B	0.50	167.76	320.95	332.23	$7.85\text{E}-5$	0.99876
C	1.00	375.20	365.58	380.23	$7.13\text{E}-5$	0.99736
D	0.49	395.42	773.63	869.57	$7.61\text{E}-6$	0.98736

^a $\Gamma_{e,\text{exp}}$ and $\Gamma_{e,\text{cal}}$ represent the experimental and the model fitting results, respectively.

Table 2 Parameters of double-exponential function model fits for Pb(II) sorption kinetics

Run No.	LDH conc./($\text{g}\cdot\text{L}^{-1}$)	$C_0/(\text{m}\cdot\text{L}^{-1})$	$\Gamma_1/(\text{m}\cdot\text{L}^{-1})$	$k_1'/(\text{min}^{-1})$	$\Gamma_2/(\text{mg}\cdot\text{g}^{-1})$	$k_2'/(\text{min}^{-1})$	R^2
A	1.01	159.57	78.73	0.046	78.73	0.046	0.99769
B	0.50	167.76	260.77	0.011	55.92	0.081	0.98950
C	1.00	375.20	292.33	0.010	77.71	0.063	0.98966
D	0.49	395.42	725.75	0.004	82.73	0.148	0.99223

where Γ_m is the maximum sorption amount and K_L is Langmuir constant. The Γ_m and K_L values can be obtained from a linear plot of C_0/Γ_e versus C_e .

(ii) Freundlich isotherm

$$\Gamma_e = K_F C_e^n \quad (8)$$

where K_F and n are Freundlich constants. Unlike the Langmuir isotherm, Freundlich isotherm does not predict a maximum sorption amount on the sorbent surface. The linear form of Freundlich isotherm is

$$\lg \Gamma_e = \lg K_F + n \lg C_e \quad (9)$$

(iii) Langmuir-Freundlich isotherm

$$\Gamma_e = \Gamma_m K_L C_e^n / (1 + K_L C_e^n) \quad (10)$$

Langmuir-Freundlich isotherm is a composite of Langmuir and Freundlich isotherms and can reduce to either one at its limits. When $n = 1$, Langmuir-Freundlich isotherm reduces to Langmuir isotherm; as either K_L or C_e approaches 0, Langmuir-Freundlich isotherm reduces to Freundlich isotherm. The Langmuir-Freundlich isotherm has been successful in modeling the sorption behavior of many heterogeneous systems, including gas adsorption onto surfaces, adsorption of metal ions to environmental samples.³³

(iv) Aronovich-Donohue isotherm³²

$$\Gamma_e = [K_1 C_e / (1 + K_2 C_e)] \cdot [1 / (1 - K_3 C_e)]^n \quad (11)$$

where K_1 , K_2 and K_3 are constants. This isotherm is the improvement of BET equation and derived for the multilayer adsorption at gas-solid interface. There are many successful applications such as those to correlate adsorption equilibrium data of water vapor on alumina and a zeolite/activated carbon composite³⁴ and to describe the sorption behavior of benzene on Kettleman soil.³²

The sorption isotherm of Pb(II) on the LDH sample is shown in Figure 5, where it can be seen that the LDH has a good sorption ability for Pb(II) from $\text{Pb}(\text{NO}_3)_2$ solution,³⁵ indicating that the use of LDHs as a promising inorganic sorbent for the removal of heavy metal

ions is possible. It is a Type-II isotherm in the IUPAC classification scheme.³⁶ The Type-II isotherm represents unrestricted monolayer-multilayer adsorption. The point where the second order derivation of the data curve is zero is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin. Hence, the mathematical function used to describe the isotherm curve must have a singularity. With the simulation of above four isotherms for the sorption data (see Figure 5), it was found that Aronovich-Donohue isotherm gave a better fit to the experimental data than other three isotherms on the basis of regression coefficients R^2 . The parameters of the isotherms obtained by non-linear fits are listed in Table 3.

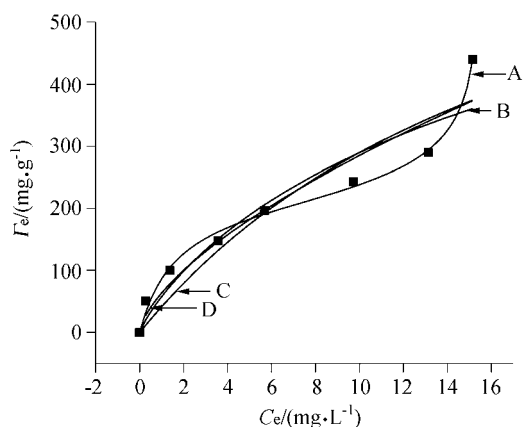


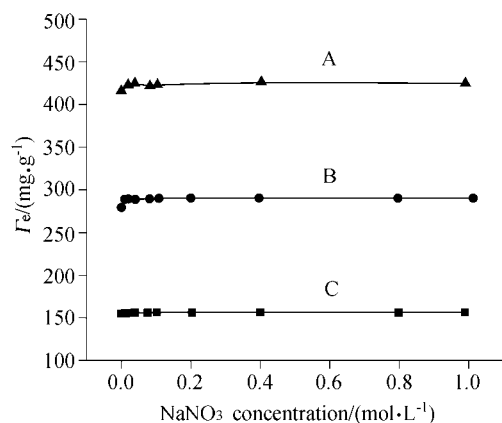
Figure 5 Sorption isotherm and non-linear model fits. The dots represent the experimental data and the lines represent the model fits. A: Aronovich-Donohue; B: Langmuir-Freundlich; C: Langmuir; D: Freundlich.

Effect of NaNO_3 on sorption

The effects of NaNO_3 on the Pb(II) sorption at different initial Pb(II) concentrations are shown in Figure 6. It can be seen that the presence of NaNO_3 did not almost influence the Pb(II) sorption, only initial slight increase of the Pb(II) sorption was observed with the

Table 3 Parameters of non-linear fits for Pb(II) sorption isotherm

Model	$\Gamma_m/(\text{mg}\cdot\text{g}^{-1})$	K_1 or K_L or $K_F/(\text{L}\cdot\text{mg}^{-1})$	$K_2/(\text{L}\cdot\text{mg}^{-1})$	$K_3/(\text{L}\cdot\text{mg}^{-1})$	n	R^2
Langmuir	865.36	0.050	—	—	—	0.90991
Freundlich	—	63.69	—	—	0.65	0.90905
Langmuir-Freundlich	865	0.072	—	—	0.85	0.91632
Aranovich-Donohue	—	138.2	0.623	0.064	0.215	0.99531

**Figure 6** Effects of NaNO_3 on Pb(II) sorption at various initial Pb(II) concentrations. A: 434.4 mg/L Pb(II); B: 296.4 mg/L Pb(II); C: 160.1 mg/L Pb(II).

increase of NaNO_3 concentration. The initial slight increase of the Pb(II) sorption amount maybe arises from the co-ion effect.

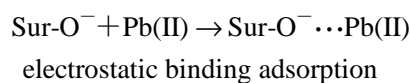
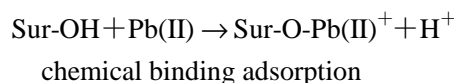
Sorption mechanism

Sorption, which involves the loss of a metal ion from an aqueous to a contiguous solid phase, may be broadly defined as the transfer of ions from the solution phase to the solid phase via various mechanisms, such as physical and chemical adsorption, surface precipitation, and fixation (or solid state diffusion).^{2,37-39}

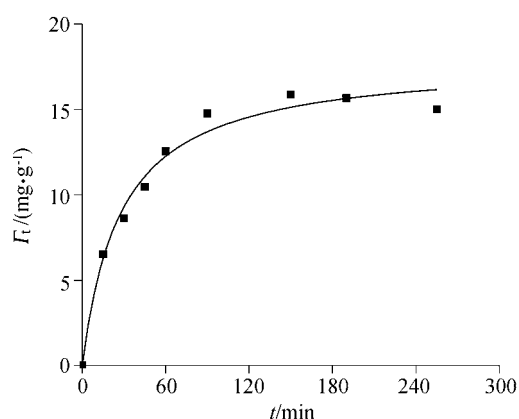
Adsorption, the accumulation of matter at the solid-liquid interface, is the basis of most surface processes.⁴⁰ Adsorption reactions are discussed primarily in terms of intermolecular interactions between solute and solid phases, and the interactions may be described as surface complexation. These complexation interactions may be comprised of two surface reactions: first, a chemical binding reaction between the metal ions and the respective surface functional groups, forming inner-sphere surface complexes; second, an electrostatic binding reaction between the metal ions and the oppositely structurally charged sites or the oppositely charged surface functional groups, forming outer-sphere complexes at a certain distance from the surface. The former may be described as specific adsorption, which is characterized by more selective and less reversible reactions; the latter may be described as nonspecific adsorption, which is characterized by less selective and rather weak and reversible reactions.

LDH surface has some deprotonated hydroxyl groups (Sur-O^-) which may form outer-sphere com-

plexes with Pb(II) through electrostatic binding reactions. The complexation adsorption of Pb(II) on LDH can be described as follows:⁴¹⁻⁴³



where, the “Sur” represents the surface of LDH, and the “ \cdots ” means electrostatic binding effect. The result that the presence of NaNO_3 did not almost influence the Pb(II) sorption (see Figure 6) shows that the electrostatic binding adsorption of Pb(II) should not exist. In order to identify if the chemical binding adsorption does exist, a sorption experiment under a constant pH 3.6 was carried out at 150 mg/L of initial Pb(II) concentration (see Figure 7), and it was found that a part of Pb(II) was adsorbed. However, the PXRD patterns of the sorption product obtained at constant pH 3.6 have no significant difference from those of the pristine LDH sample (see Figure 1), that is to say, no new bulk phase is detected by the PXRD method. These results may be the evidence for the chemical binding adsorption existing.

**Figure 7** Sorption kinetics at constant pH 3.6 and initial Pb(II) concentration of 150 mg/L, with LDH concentration of 0.5 g/L.

The fixation involves the diffusion of an aqueous metal species into the solid phase. Heavy metals may diffuse into the pore space and the lattice structure of the solid (solid-state diffusion). We believed that the diffusion of Pb(II) into the lattice structure of the LDH was not basically possible, which was identified by the results that there was almost no change of the lattice

parameters between the pristine LDH and Pb(II) sorption products (see Figure 1). The ionic diameter of Pb(II) is about 0.24 nm, which is smaller than the mean pore diameter of the LDH. The diffusion of Pb(II) into the pore space of the LDH should be possible, however the sorption amount of Pb(II) arising from this mechanism may be evaluated to be very low according to the mean pore volume of the LDH.

Surface precipitation^{44,45} involves the growth of a new bulk solid phase exhibiting a primitive molecular unit that repeats itself in a 3-D order. The surface precipitation model postulates a multilayer sorption process along a newly formed hydroxide surface which is caused by the metal adsorption at the surface and includes the formation of a surface phase that is called solid solution. Sparks *et al.*⁴⁴ divided the mechanism into two categories: (1) those to be driven by changes in sorbate properties induced by the sorbent surface and (2) those driven by modification of the solution composition near the interface. It has been reported that surface precipitation of hydrous oxide-type soil constituents occurs at pH values lower than those required for metal hydroxide precipitation in pure aqueous solutions without soil suspension.⁴⁰ The surface phase of positively structurally charged LDHs is of higher pH value, which is favourable to the form of precipitation of heavy metal hydroxides. According to the PXRD results (Figure 1), it can be concluded that one of removal mechanisms of Pb(II) is the surface-induced precipitation of Pb(II) carbonate hydroxides, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. The presence of CO_3^{2-} may be the result of dissolved CO_2 from atmosphere.

On the whole, the removal of Pb(II) cations by the LDH sample may be attributed to the surface-induced precipitation of Pb(II) carbonate hydroxides and the chemical binding adsorption. Contrasting the results of Figure 3 and Figure 7, it can be concluded that the removal ability arising from the surface-induced precipitation is much higher than that from the chemical binding adsorption.

Conclusion

Mg-Fe LDH showed a good sorption ability for Pb(II) from $\text{Pb}(\text{NO}_3)_2$ solution, indicating that the use of LDHs as a promising inorganic sorbent for the removal of heavy metal ions is possible. The sorption kinetics and the sorption isotherm of Pb(II) on the LDH sample obeyed the pseudo-second order kinetic model and Aranovich-Donohue equation, respectively. The sorption mechanism of Pb(II) on the LDH may be attributed to the surface-induced precipitation and the chemical binding adsorption, and the removal ability arising from the surface-induced precipitation is much higher than that from the chemical binding adsorption.

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