Adsorption Equilibrium and Kinetics of Lead Ion onto Synthetic Ferrihydrites

Shi, Zhongliang; Zou, Peichen; Guo, Man; Yao, Shuhua*+

School of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, CHINA

ABSTRACT: *Batch experiments were conducted to study the adsorption behaviors of lead ion (Pb^{2+}) onto ferrihydrites prepared using three different procedures which were characterized by textural analysis (BET). The adsorption removal of Pb^{2+} by the three ferrihydrites (called FH-1, FH-2 and FH-3, respectively) were compared, and FH-3 shows fast adsorption kinetics as well as high adsorption capacities, the adsorption properties of the three ferrihydrites for lead ion depend on the pH value and the optimal pH for Pb^{2+} adsorption of FH-3 is 6.0. The maximum adsorption capacity of lead ion on FH-3 is 13.75 mg/g and the adsorption isotherms followed Langmuir isotherm model better than the Freundlich isotherm model. The adsorption kinetic data could be described well by pseudo-second-order kinetic equation.*

KEY WORDS: *Ferrihydrite; Adsorption equilibrium; Kinetics; Lead ion.*

INTRODUCTION

Water pollution due to heavy metals is a serious environmental and public health issue. Heavy metals are generally recognized to be a threat toward humans and ecosystems because of their high potential toxicity. They could not be biologically decomposed into harmless materials and, to matters worse, were accumulated in the organisms [1]. The heavy metals such as lead, cadmium, copper and zinc, are among the most common pollutants found in industrial effluents. Drinking those that contain lead ion (Pb^{2+}) for a long term, even if in a very low concentration, could lead to a wide range of spectrum health problems, such as blood dyscrasia and kidney and nervous troubles [2, 3]. Hence, it is necessary to remove lead from wastewater before being discharged. Several methods have evolved over the years on the removal of heavy metals present in water and wastewater. These are chemical precipitations, conventional coagulation, reverse osmosis, ion exchange and adsorption. But the addition of chemicals often incurs high operational costs and may not meet strict regulatory requirements. Although reverse osmosis and ion exchange methods are effective in removing such pollutants, they are expensive in the operational procedure. These factors have limited the use of methods for the removal of lead and other heavy metals from water and wastewater especially in most of developing countries [4, 5]. One of which, adsorption method, is simple and cost-effective, thus has been widely used [6-9]. Among various absorbents, adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methodologies [10-12]. Due to its high surface area and porous structure it can efficiently adsorb gases and compounds dispersed or dissolved in liquids [13]. However, the application of activated carbon powders

in water treatment system is limited because it is difficult to separate after the treatment process and reuse the tiny particles. In addition its regeneration with refractory technique results in a 10-15% loss of the adsorbent and its uptake capacity. Thus, there has been intensive research exploring the potential of alternative low-cost, easily available materials as adsorbents for the removal of lead ion. For this purpose in recent years, various biological and industrial by-products have been investigated intensively for their ability to remove lead ion from aqueous solution as they can be obtained readily and are in great abundance, such as chitosan [14, 15], rice hull ash [16], wheat straw [17], modified clays [18], bentonite [19] and muskmelon peel [20] have the potential of being used as alternative adsorbent for the removal of dyes from aqueous solutions.

Adsorption from solution onto exposed mineral surfaces has been shown to exert a strong control on the mobility and bioavailability of trace metals in the environment [21]. Iron oxides, as an abundant component in solid phases, are considered important adsorbents for trace heavy metals [22-24]. Ferrihydrite (FH) is a poorly ordered hydrous iron oxide commonly present in low temperature geochemical processes. It is an important member of the iron oxides family, plays a substantial role in the sequestration of contaminants from groundwater and streams through adsorption and coprecipitation because of its extremely high surface area, adsorption capacity and reactivity [25]. Owing to the widespread occurrence and abundance of ferrihydrite in the environment, adsorption of lead on ferrihydrite is an important geochemical process that controls its mobility and fate in aqueous environment. The main goal of this work lies on the study of the adsorption characteristics of toxic metals in aqueous solution, specifically for Pb2+ using ferrihydrites prepared by three different procedures. In addition, the Pb^{2+} adsorption equilibrium and kinetics were determined at various concentration conditions.

EXPERIMENTAL SECTION
Preparation and characterization of ferrihydrite adsorbents

All the chemicals used in the study are of analytical grade. All the solutions were prepared using deionized water. All glassware was cleaned by rinsing with hydroxylamine hydrochloride, soaking in 10% HCl, and rinsing with deionized water.

The ferrihydrites used in this study was synthesized using a slightly modified procedure from that reported in the literature [26]. Briefly, in procedure 1 FH was prepared by the addition of $FeCl_3 \cdot 6H_2O$ to deionized water to obtain a specified iron concentration (0.5 mol/L). NaOH solution (6.0 mol/L) was added until the pH stabilized at 7.0. The suspension was centrifuged, washed with deionized water and then dried at 40 °C for 10 days. This product was called FH-1. FH-2 was prepared by reversing the mixing procedure of Fe(III) and NaOH solutions described in procedure 1. FH-3 was prepared in procedure 3: Fe(III) and NaOH solutions were simultaneously added to a certain volume of water until the Fe(III) solution was exhausted. The drip rate of the two solutions was controlled by maintaining pH 7. The surface area of all samples were calculated from nitrogen adsorption isotherms at 77 K performed in a Micromeritics ASAP 2000 surface area analyzer. Collected data were analyzed by the BET method for surface area and by the BJH method for pore volume. X-ray diffraction analysis (on a Rigaku D/max-r B X-ray diffractometer) confirmed the identity of the solid as ferrihydrite.

Adsorption amount of lead ion on three ferrihydrites

The adsorption capacities of different ferrihydrites were determined by batch adsorption experiments at 20 °C in aqueous solution. Lead ion was hardly adsorbed onto any of the FH samples in solutions having values of pH less than 3; At values of pH higher than 7, the adsorption experiments failed as a result of precipitation of lead hydroxide. Thus the solution pH values in this study ranged between 3.5 and 6.5. In several glass vials, lead ions solution (50 mg/L) was contacted with ferrihydrite suspensions (5.0 mg/L). The suspensions were adjusted to the targeted pH by adding 0.1 mol/L NaOH or HNO_3 until it remained constant (±0.10). The vials were placed in a water bath at 20 °C for approximately 6 h. Then, each solution was filtered with a polycarbonate membrane of 0.22 μm of pore diameter, and the concentration at equilibrium was determined. Initial and equilibrium concentrations were measured by an Atomic Fluorescence Spectrometer (AFS) (PS Analytical Ltd., Kent, UK). The amount of lead ion adsorbed was calculated from the difference between the quantity of metal ion added to the ferrihydrites
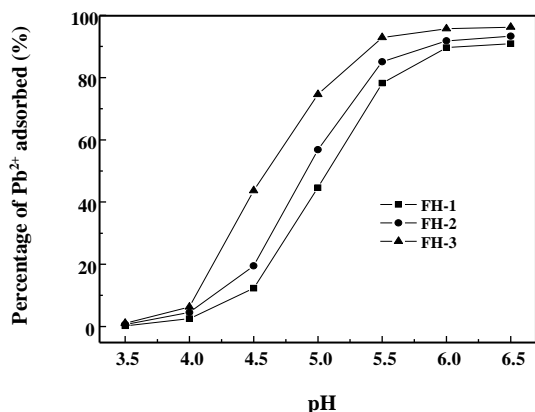
Fig. 1: Adsorption edge of Pb²⁺ on the three FHs as a function of pH (Experimental conditions employed : Pb²⁺ concentration 50 mg/L, agitation speed 180 r/min, adsorbent dosage 5.0 g/L, contact time 180 min).

and the metal ion content of the supernatant with the following equation:

$$q_e = V(C_0 - C_e)/W \qquad (1)$$

where q_e is the amount adsorbed (mg/g); C_0 and C_e are the initial and equilibrium lead concentrations in the solution (mg/L), respectively; *V* is the solution volume (L); and *W* is the mass of ferrihydrites (g).

To determine the effects of different parameters on Pb²⁺ adsorption, experiments were performed at various adsorbent dosage values ranging between 1.0 and 7.0 g/L. Initial Pb²⁺ concentration of 50 mg/L and 5.0 g/L of adsorbent were employed. The suspensions were shaken at 180 r/min for 180 min. Then the optimum adsorbent dosage was identified. The effects of initial Pb²⁺ concentration, contact time were also conducted.

Adsorption isotherms

The adsorption isotherms of lead ions on Fh-3 was conducted according to the above description, in several glass vials, 100 mL of solution containing various lead ion concentrations (50, 100, 200, 400, 600 mg/L) were contacted with 0.5 g of FH-3. The vials were placed in a water bath at 20 °C for approximately 24 h.

Kinetic study

The adsorption kinetic study was performed for lead ions in solution at pH 6.0 and room temperature (20 ± 1 °C). Several glass vials were used to hold 100mL of lead solution of known initial concentration (50, 100 mg/L)

and FH-3 suspensions (5.0 mg/L), and shaken at 180 r/min for a duration ranging from 0 to 240 min. At certain period of time, each vial was removed from the shaker, and approximately 10 mL aliquots were sampled, centrifuged for 10 min at room temperature and subsequently filtered with a polycarbonate membrane of 0.22 μm pore diameter to measure the lead concentration.

RESULTS AND DISCUSSION
Adsorption amount of lead ion on three ferrihydrites

The experimental results obtained from lead ion adsorption onto the three FHs surfaces as a function of pH are shown in Fig. 1. FH dosage (5.0 g/L), lead ion (50 mg/L) and agitation speed (180 r/min) were kept constant in all experiments. The lead ion adsorbed by the three FHs is sensitive to pH variation over the examined range of 3.5 to 6.5. The removal efficiency increases sharply with increasing pH. The results can be explained based on the competition between Pb²⁺ and H⁺ for sites on FHs. At low pH levels, excess H⁺ ions compete with lead ions for the surface of the adsorbent, which would restrict the approach of lead ions due to the repulsion [27]. Hence, the metal removal is the lower amount presumably due to the enhanced competition of proton with lead ions for ligand binding sites and complex formation. With increasing pH, adsorption of lead ion became favorable due to the deprotonation of adsorption sites, resulting in more adsorption sites available for binding with lead ion. This phenomenon favors the adsorption of lead ion due to electrostatic attraction. Our results support the observation that increasing solution pH leads to an increase in net negative surface charge on ferrihydrite where lead ion is adsorbed by a simple binding mechanism [28].

A further increase in solution pH (>6.0) did not cause significant improvement in Pb²⁺ adsorption, therefore, the pH 6.0 was chosen for the following experiments.

It can also be seen from Fig. 1 that the adsorption efficiency at the same pH is ranked in the order FH-3> FH-2>FH-1. For example, the lead adsorption efficiencies of the three FHs at pH 5.5 are 78.2, 85.1 and 92.9% for FH-1, FH-2 and FH-3, respectively. This can be explained due to the increase of the BET specific surface areas of three ferrihydrite samples. The specific surface areas are 202.61, 210.17 and 232.82 m²/g for FH-1, FH-2 and FH-3, respectively. The fact that the size of FH-3 aggregates
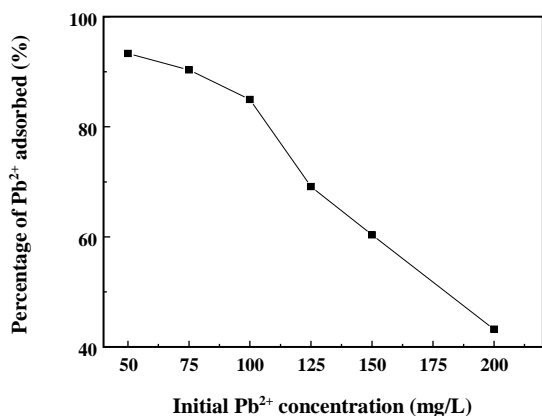
Fig. 2: Effect of initial Pb^{2+} concentration on the adsorption of Pb^{2+}. (Experiment conditions employed: adsorbent dosage 5.0 g/L, solution pH 6.0, contact time 180 min, agitation speed 180 r/min).

Fig. 3: Effect of adsorbent dosage on the adsorption of Pb^{2+}. (Experiment conditions employed: initial Pb^{2+} concentration 50 mg/L, solution pH 6.0, contact time 180 min, agitation speed 180 r/min).

is the smallest is responsible for the result of BET area [29]. The surface area is one of the key factors to control the adsorption efficiency of adsorbent. The larger surface area is, the higher adsorption efficiency is. It is noted that the surface area of FH-3 is larger than the other FHs, so the adsorption efficiency of FH-3 is higher than those of other types. Due to the higher adsorption efficiency of FH-3, it is used for all the other experimental studies.

Effect of initial Pb^{2+} concentration

Initial concentration is one of the effective factors on adsorption efficiency. Initial concentrations of Pb^{2+} solutions were changed (50, 75, 100, 150 and 200 mg/L) in order to determine proper Pb^{2+} adsorption keeping constant temperature (20 °C), solution pH (6.0), contact time (1 h) and adsorbent dosage (5.0 g/L). The experimental results were shown in Fig. 2. It can be seen that the Pb^{2+} removal rate decreased with the increase in initial Pb^{2+} concentration, the percentage adsorption of Pb^{2+} on FH-3 decreased from 93.3 to 43.2% as the initial Pb^{2+} concentration was increased from 50 to 200 mg/L. At lower Pb^{2+} concentrations, the ratio of the available adsorption sites of adsorbent to the initial number of Pb^{2+} is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher Pb^{2+} concentrations, the available sites for Pb^{2+} adsorption during the adsorption reaction become fewer, and hence the percentage removal of Pb^{2+} which depends upon the initial concentration, decreases.
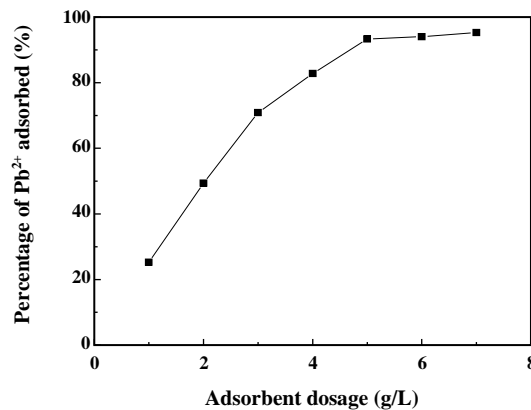
Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption of Pb^{2+} was shown in Fig. 3. The increase in adsorbent dosage from 1.0 to 7.0 g/L resulted in an increase from 25.2 to 95.3% in adsorption of Pb^{2+}. This is because of the availability of more and more adsorption sites for Pb^{2+} adsorption during the adsorption reaction. A further increase in adsorbent dosage (>5.0 g/L) did not cause significant increase in Pb^{2+} adsorption. This may be due to the adsorption of almost all Pb^{2+} to the adsorbent and the establishment of equilibrium between the Pb^{2+} adsorbed to the adsorbent and those remaining unadsorbed in the solution. The results of this study are in accordance with obtained findings by other researchers [16, 17]. Thus Thus 5.0 g/L of FH-3 was chosen for next study.

Effect of contact time

Contact time is one of the effective factors in batch adsorption process. The effect of contact time on Pb^{2+} adsorption efficiency was shown in Fig. 4. As it was shown, the adsorption was very fast and equilibrium between the aqueous solution and FH-3 was established within about 180 min. There was no significant change in Pb^{2+} removal rates after 180 min up to 240 min. Based on these results, 180 min was taken as the equilibrium time in adsorption experiments. The removal of Pb^{2+} from aqueous solutions by adsorption on FH-3 increases with contact time, till the equilibrium is attained. Similar results have been reported in literature for removal of lead ion [16, 17, 20].
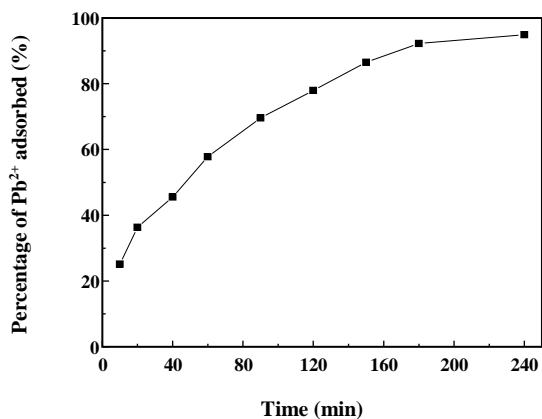
Fig. 4: Effect of contact time on the adsorption of Pb²⁺. (Experiment conditions employed: initial Pb²⁺ concentration 50 mg/L, adsorbent dosage 5.0 g/L, solution pH 6.0, agitation speed 180 r/min).
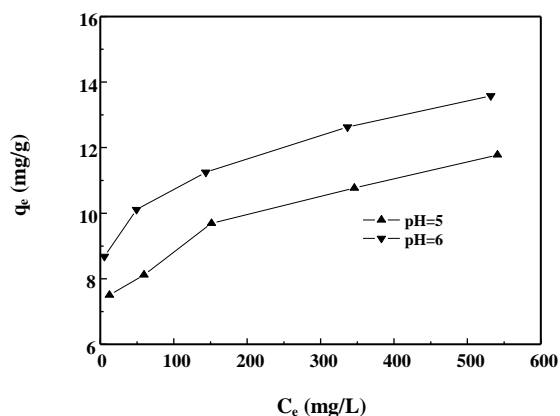

Fig. 5: Adsorption isotherms of Pb²⁺ by FH-3 (Experimental conditions employed : solution pH 6.0, agitation speed 180 r/min, adsorbent dosage 5.0 g/L, contact time 24 h).

Adsorption isotherms

For the design purpose, it is necessary to fit the isotherm data with the models. Langmuir and Freundlich isotherm equations are most widely used for the equilibrium study. Lead ion adsorption isotherms obtained for FH-3 are shown in Fig. 5. These isotherms represent the adsorption behavior of lead ion on the adsorbent as a function of increasing aqueous lead concentration for a contact time of 24 h at pH=5.0 and 6.0. These isotherms showed that the adsorption capacity increases with increasing equilibrium concentration of lead ion.

The results of lead ions adsorption on FH-3 (Fig. 5) are analyzed by using the Langmuir model to evaluate parameters associated to the adsorption behavior. The linear form of Langmuir equation at a given temperature is represented by:

$$q_e = q_m \cdot b \cdot c_e / (1 + b \cdot c_e) \tag{2}$$

where c_e is the aqueous phase ion equilibrium concentration (mg/L), q_e is the amount of lead ion sorbet onto 1 g of the considered adsorbent (mg/g), b is the adsorption constant (L/mg) related to the energy of adsorption and represents the affinity between the adsorbent and adsorbate, q_m is the maximum adsorption capacity (mg/g).

Eq. (2) can be rearranged to obtain:

$$c_e / q_e = 1 / (b \cdot q_m) + c_e / q_m \tag{3}$$

Experimental isotherm data acquired at different pH fit to the linear form of the Langmuir equation can obtained by plotting of c_e/q_e against c_e. The results are shown in Fig. 6. This linear plot is employed to obtain the values of q_m and b from the slope and intercept of the plot, the isotherm parameters related to the model obtained from the experimental data are listed in Table 1. It can be seen from Table 1 that both q_m and b increase with increasing pH from 5.0 to 6.0. High values of b are reflected in the steep initial slope of an adsorption isotherm, indicating desirable high affinity. Therefore, FH-3 performed well in lead adsorption at pH 6.0 compared to other pH values examined.

The Freundlich isotherm model is also used to analyze the results of lead ion adsorption on FH-3 adsorbent (Fig. 5). The Freundlich model can be expressed by the following equation:

$$q_e = k_f \cdot c_e^{1/n} \tag{4}$$

where k_f and n are constants related to the adsorption capacity and affinity, respectively. The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log k_f + (1/n) \log c_e \tag{5}$$

The adsorption data fit to the linear form of the Freundlich equation can be obtained by plotting of $\log q_e$ against $\log c_e$. The results are shown in Fig. 6. Experimental isotherm data acquired at different pH are fitted with the Freundlich model and the isotherm parameters related to the model obtained from the experimental data are listed in Table 1.

The data show that the k_f constant is increased

Table 1: The parameters of Langmuir and Freudlich equation for Pb²⁺ adsorption by FH-3.

Initial pH	Langmuir equation			Freundlich equation		
	q_m (mg/g)	b (L/mg)	R^2	1/n	k_f	R^2
5.0	12.04	3.98×10^{-2}	0.9977	0.1186	5.4193	0.9888
6.0	13.75	5.57×10^{-2}	0.9982	0.0963	7.1794	0.9852
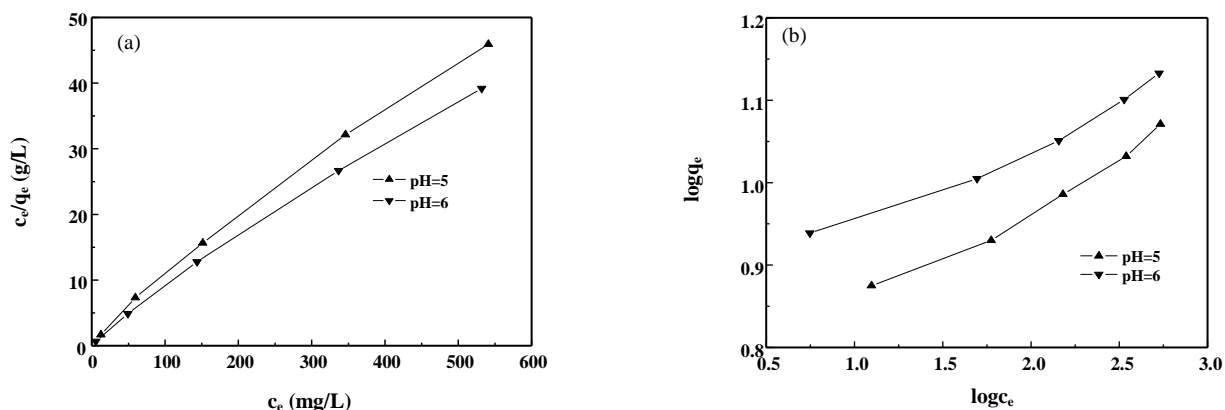
Fig. 6: Linear fitting chart of adsorption isotherms of Pb²⁺ on FH-3: (a) Langmuir; (b) Freundlich.

with the increase of pH values, at pH 6.0, k_f is larger thanthat at other pH value, and 1/n value at pH 6.0 is smaller than that at other pH value. These imply that the binding capacity reaches the higher value and the affinity between the adsorbent and lead ions is also higher than other pH value. The correlation coefficients (R^2) given in Table 1 also show that the Langmuir equation gives a better fit than Freundlich equation to the adsorption isotherms.

Kinetics study

In order to obtain the adsorption kinetic information of lead ion on FH-3 adsorbent, the change of lead ion concentration with adsorption time is recorded for an initial Pb²⁺ concentration of 50, 100 mg/L and a fixed pH solution of 6.0, adsorbent dosage 5.0 g/L (Fig. 7). It is evident from Fig. 7 that the adsorption of lead ion increases rapidly with time as well as with the increase of the initial ion concentrations. However, the time to reach the adsorption equilibrium takes longer with an increase in the concentration.

To investigate the mechanism of adsorption, the pseudo-second-order rate equation model is applied to the kinetic experimental data. The pseudo-second-order kinetic equation can be derived as [30]:

$$dq_t/dt = k_2 \cdot (q_e - q_t)^2 \tag{6}$$

Separating the variables in Eq. (6) gives

$$dq_t/(q_e - q_t)^2 = k_2 \cdot dt \tag{7}$$

Integrating both sides for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives the integrated rate law for a pseudo-second-order reaction,

$$1/(q_e - q_t) = 1/q_e + k_2 \cdot t \tag{8}$$

Equation (8) can be rearranged to obtain:

$$t/q_t = 1/(k_2 \cdot q_e^2) + t/q_e \tag{9}$$

The kinetic constant, k_2, can be determined by plotting of t/q_t against t.

The kinetic experimental data of lead ion on FH-3 adsorbent is simulated by pseudo-second-order rate Eq. (9). The results are shown in Fig. 8. The rate constants (k_2) determined by the pseudo-second-order rate equation are listed in Table 2.

Remarkably, the kinetic data can be described well by the pseudo-second-order rate equation with a minimum linear correlation coefficient of 0.9987 (see Table 2), which is based on the assumption that the rate limiting step may be chemical sorption or chemisorptions involving valency forces through sharing or exchange of

Table 2: Kinetic parameters for Pb^{2+} adsorption by FH-3

c_0 (mg/L)	q_e(mg/g)	k_2(L/mg·min)	R^2
50	10.977	1.46×10^{-3}	0.9987
100	12.832	0.877×10^{-3}	0.9998
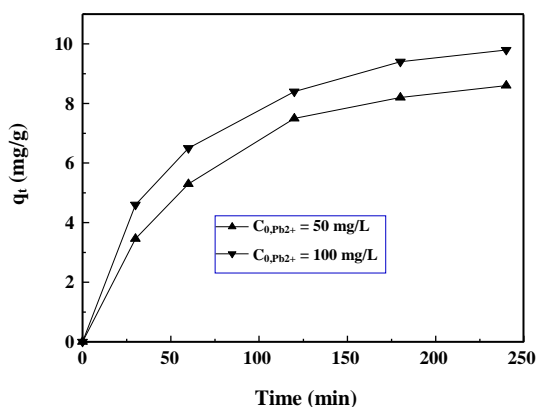
Fig. 7: *Adsorption kinetics of Pb^{2+} by FH-3 (Experimental conditions employed: pH 6.0, agitation speed 180 r/min, adsorbent dosage 5.0 g/L).*
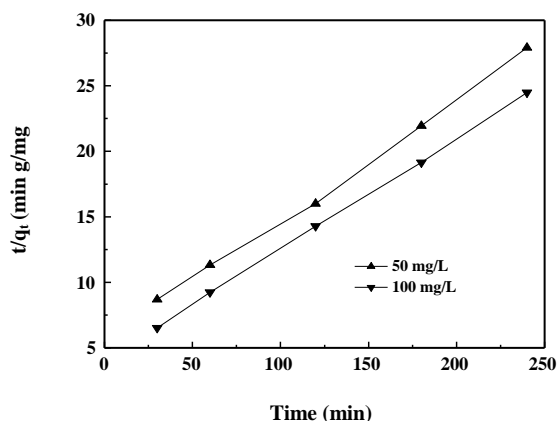
Fig. 8: *Linear fitting chart of adsorption kinetics of Pb^{2+} on FH-3.*

electron between adsorbent and adsorbate [31]. It can be seen that the values of the pseudo-second-order rate constant decrease with increasing the initial lead ion concentrations.

CONCLUSIONS

Adsorption of lead ion (Pb^{2+}) onto ferrihydrites prepared under different conditions has been studied, the results showed that the material is a suitable adsorbent to remove toxic of heavy metals such as lead in aqueous solution. The investigations on models of adsorption isotherms show that the Langmuir model describes the adsorption behaviors of Pb^{2+} better than the Freundlich model. The overall adsorption rate is illustrated well by the pseudo-second-order kinetic models. These results demonstrate that the prepared ferrihydrites could be used as an effective adsorbent for the adsorption of lead ions from aqueous solution.

REFERENCES

[1] Adewunmi C.O., Becker W., Kuehnast O., Oluwole F., Dörfler G., Accumulation of Copper, Lead and Cadmium in Freshwater Snails in Southwestern Nigeria. *Sci. Total Env.*, **193**(1)**:** 69-73 (1996).

[2] Rashed M.N., Lead removal from Contaminated Water using Mineral Adsorbent. *The Environmentalist*, **21**(3): 187-195 (2001).

[3] Li Y.H., Di Z., Ding J., Wu D., Luan Z., Zhu Y., Adsorption Thermodynamic, Kinetic and Desorption Studies of Pb^{2+} on Carbon Nanotubes, *Water Res.*, **39**(4): 605-609 (2005).

[4] Lin K.C., Chou I.N., Studies on the Mechanisms of Ni^{2+}-Induced Cell Injury: I. Effects of Ni^{2+} on Microtubules, *Toxicol. Appl. Pharmacol.*, **106**(2): 209-221 (1990).

[5] Malkoc E., Nuhoglu Y., Investigations of Nickel(II) Removal from Aqueous Solutions using Tea Factory Waste, *J. Hazard. Mater. B*, **127**(1-3): 120-128 (2005).

[6] Ghosh D., Bhattacharyyra K.G., Adsorption of Methylene Blue on Kaolinite, *Appl. Clay Sci.,* **20**(6): 295-300 (2002).

[7] Yabe M.J.S., Oliveira E., Heavy Metals Removal in Industrial Effluents by Sequential Adsorbent Treatment, *Adv. Env. Res.*, **7**(2): 263-272 (2003).

[8] Erdem M., özverdi A., Lead Adsorption from Aqueous Solution onto Siderite, *Sep. Purif. Technol.*, **42**(3): 259-264 (2005).

[9] Shukla S.R., Pai R.S., Shendarkar A.D., Adsorption of Ni(II), Zn(II) and Fe(II) on Modified Coir Fibres, *Sep. Purif. Technol.*, **47**(3): 141-147 (2006).

[10] Corapcioglu M.O., Huang C.P., The Adsorption of Heavy Metals onto Hydrous Activated Carbon, *Water Res.*, **21**: 1031-1044 (1987).

[11] Gu B., Schmitt J., Chen Z., Liang L., McCarthy J.F., Adsorption and Desorption of Nature Organic Matter on Iron Oxide: Mechanisms and Model, *Environ. Sci. Technol.*, **28**: 38-46 (1994).

[12] Akhtar S., Qadeer R., Active Carbon as an Adsorbent for Lead Ions, *Adsorp. Sci. Technol.*, **15**: 815-824 (1997).

[13] Ruthven D.M., "Principles of Adsorption and Adsorption Processes", New York: Wiley, (1984).

[14] Yan W.L., Bai R., Adsorption of Lead and Humic Acid on Chitosan Hydrogel Beads, *Water Res.*, **39**(4): 688-698 (2005).

[15] Bamgbose T.T., Adewuyl S., Bamgbose O., Adetoye A.A., Adsorption Kinetics of Cadmium and Lead by Chitosan, *African J. Biotech.*, **9**: 2560-2565 (2010).

[16] Wang L.H., Lin C.I., Adsorption of Lead(ii) Ion from Aqueous Solution using Rice Hull Ash, *Ind. Eng. Chem. Res.*, **47**(14): 4891-4897 (2008).

[17] He W.J., He Y.F., Yan D.Z., Wang Y., Wang R.M., Adsorption of Lead Ion Using Polymer-Modified Wheat Straw Carboxymethylcellulose, *J. Disper. Sci. Technol.,* **35**(10): 1378-1385 (2014).

[18] Chen H., Wang A., Kinetic and Isothermal Studies of Lead Ion Adsorption onto Palygorskite Clay, *J. Colloid Interf. Sci.*, **307**(2):309-316 (2007).

[19] Zhu S., Hou H., Xue Y., RETRACTED: Kinetic and Isothermal Studies of Lead Ion Adsorption onto Bentonite, *Appl. Clay Sci.*, **40**(1-4): 171-178 (2008).

[20] Huang K., Zhu H., Removal of Pb^{2+} from Aqueous Solution by Adsorption on Chemically Modified Muskmelon Peel, *Environ. Sci. Pollut. Res.*, **20**(7): 4424-4434 (2013).

[21] Randall S.R., Sherman D.M., Ragnarsdottir K.V., Collins C.R., The Mechanism of Cadmium Surface Complexation on Iron Oxyhydroxide Minerals, *Geochim. Cosmochim. Ac.*, **63**(19-20): 2971-2987 (1999).

[22] Mercer K.L., Tobiason J.E., Removal of Arsenic from High Ionic Strength Solutions: Effects of Ionic Strength, pH, and Preformed Versus in Situ Formed HFO, *Environ. Sci. Technol.*, **42(10):** 3797-3802 (2008).

[23] Masue Y., Loeppert R.H., Kramer T.A., Arsenate and Arsenite Adsorption and Desorption Behavior on Coprecipitated Aluminum:Iron Hydroxides, *Environ. Sci. Technol.*, **41(3):** 837-842 (2007).

[24] Arai Y., Spectroscopic Evidence for Ni(II) Surface Speciation at the Iron Oxyhydroxides−Water Interface, *Environ. Sci. Technol.*, **42(4):** 1151-1156 (2008).

[25] Filip J., Zboril R., Schneeweiss O., Zeman J., Cernik M., Kvapil P., Otyepka M., Environmental Applications of Chemically Pure Natural Ferrihydrite. *Environ. Sci. Technol.*, **41**(12): 4367-4374 (2007).

[26] Liu H., Wang Y., Ma Y., Wei Y., The Microstructure of Ferrihydrite and Its Catalytic Reactivity, *Chemosphere*, **79**(8): 802-806 (2010).

[27] Hasar H., Adsorption of Nickel(II) from Aqueous Solution onto Activated Carbon Prepared from Almond Husk, *J. Hazard. Mater. B*, **97**(1-3): 49-57 (2003).

[28] Naidu R., Kookana R.S., Sumner M.E., Harter R.D., Tiller K.G., Cadmium Sorption and Transport in Variable Charge Soils: A Review, *J. Environ. Qual.*, **26**, 602-617 (1997).

[29] Liu H., Li P., Lu L., Wei Y., Sun Y.H., Transformation of Ferrihydrite in the Presence or Absence of Trace Fe(II): The Effect of Preparation Procedures of Ferrihydrite, *J. Solid State Chem.*, **182**(7): 1767-1771 (2009).

[30] Ho Y.S., Ofomaja A.E., Pseudo-Second-Order Model for Lead Ion Sorption from Aqueous Solutions onto Palm Kernel Fiber, *J. Hazard. Mater.* B, **129**(1-3): 137–142 (2006).

[31] Ho Y.S., McKay G., The Kinetics of Sorption of Divalent Metals Ions onto Sphagnum Moss Peat, *Water Res.*, **34**(3): 735-742 (2000).