

Adsorption of Pb^{2+} from aqueous solution using spinel ferrite prepared from steel pickling sludge

Binbin Fang, Yubo Yan, Yang Yang, Fenglian Wang, Zhen Chu, Xiuyun Sun, Jiansheng Li and Lianjun Wang

ABSTRACT

In this paper, spinel ferrite with high crystallinity and high saturation magnetization was successfully prepared from steel pickling sludge by adding iron source and precipitator in the hydrothermal condition. The obtained spinel ferrite was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), vibrating sample magnetometer (VSM), and Zeta potential methods and investigated as an adsorbent for removal of Pb^{2+} from aqueous solution. Batch experiments were performed by varying the pH values, contact time, temperature and initial metal concentration. The result of pH impact showed that the adsorption of Pb^{2+} was a pH dependent process, and the pH 5.8 ± 0.2 was found to be the optimum condition. The achieved experimental data were analyzed with various kinetic and isotherm models. The kinetic studies revealed that Pb^{2+} adsorption onto spinel ferrite followed a pseudo-second order model, and the Langmuir isotherm model provided the perfect fit to the equilibrium experimental data. At different temperatures, the maximum Pb^{2+} adsorption capacities calculated from the Langmuir equation were in the range of 126.5–175.4 mg/g, which can be in competition with other adsorbents. The thermodynamic results showed that the spinel ferrite could spontaneously and endothermically adsorb Pb^{2+} from aqueous solution. The regeneration studies showed that spinel ferrite could be used five times (removal efficiency (%) >90%) by desorption with HNO_3 reagent.

Key words | adsorption, desorption, Pb^{2+} , spinel ferrite, steel pickling sludge

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INTRODUCTION

With the rapid development of the lead-acid rechargeable battery industry, water pollution caused by lead ion has become a major environmental problem. As a highly toxic heavy metal ion, lead cannot be biodegraded and easily accumulates in the human body to induce lead poisoning. Removal of lead ions in the water is an important and highly significant need. During the past decades, various techniques have been developed to reduce the pollution of lead ions, including leaching-solvent extraction (Silva *et al.* 2005), electrolysis (Vegliò *et al.* 2003), ion exchange (De Villiers *et al.* 1995; Parkpian *et al.* 2002), membrane separation (Chaudry *et al.* 1998) and microbiological methods (Chen & Lin 2001; Ryu *et al.* 2003; Shanableh & Omar 2003). Many of

them, however, may be essentially limited by economic feasibility, technical difficulty and relatively low recovery. Adsorption, compared with the above approaches, is considered as a most promising technique for removal of heavy metals from wastewater because of its high removal efficiency, easy operation and less residue production.

Spinel ferrites have the general formula $MeFe_2O_4$ (AB_2O_4), where Me^{2+} (A) can be any divalent ion such as Pb^{2+} , Cd^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , etc. or their combination, and Fe^{3+} (B) can be substituted by trivalent Al^{3+} , Cr^{3+} , etc. (Goldma 2006). If multi-ions simultaneously occupy the position Me^{2+} (A) or the position Fe^{3+} (B), complex ferrite will be formed; on the other hand, the ions will be removed from

solution. During the past decades, the use of spinel ferrites to immobilize heavy metal ions from wastewater has attracted particular attention on the basis of the above theory (Tamura *et al.* 1991; Demirel *et al.* 1999; Perales-Perez & Umetsu 2002). As we know, the practical application of spinel ferrites is a cost decision, so finding an interesting potential market to get the low-cost spinel ferrites is the core problem. Steel pickling sludge, a common waste from the steel process of pickling and polishing, is mainly composed of iron compounds. At present, the main treatment for such waste is landfill, but unidentified components of sludge may pose a potential risk to the soil and groundwater (Flyhammar 1997). Therefore, exploring a viable and environment friendly technology to efficiently reuse and recycle steel pickling sludge is becoming an increasing topic.

As a potentially valuable resource, the steel pickling sludge can be mineralized into ferrite with various methods, including sonochemical process (Yang *et al.* 2007), citrate precursor techniques (Shafi *et al.* 1997), coprecipitation (Prasad & Gajbhiye 1998), mechanical alloying (Yang *et al.* 1999), sol-gel (George *et al.* 2006), shock wave (Dhara & Bhargava 2003), reverse micelle (Liu *et al.* 2001), hydrothermal (Kale *et al.* 2004) and ultrasonically assisted hydrothermal processes (Zhou *et al.* 2005). Because the ferrite preparation process belongs to the solid-liquid reactions with the uneven complicated multi-phase system, the traditional methods cannot achieve high conversion efficiency. The hydrothermal reaction is able to produce highly crystallized and weakly agglomerated powder. Moreover, its main process factors are easy to control (Meskin *et al.* 2006).

Up to now, no report has ever been published regarding conversion of steel pickling sludge to spinel ferrite and then application for adsorbing lead ion. Therefore, the objectives of this work were: (1) to assess the feasibility of preparing spinel ferrite using steel pickling sludge by adding iron source and precipitator in the hydrothermal condition, (2) to thoroughly characterize the spinel ferrite by X-ray diffraction (XRD), vibrating sample magnetometer (VSM), field emission scanning electron microscopy (FE-SEM), and Zeta meter methods, and (3) to evaluate the spinel ferrite's adsorption properties (pH effects, adsorption kinetics, isotherms, thermodynamics) and reusability toward Pb^{2+} .

MATERIALS AND METHODS

Materials

The steel pickling sludge used in this experiment was provided by Nanjing Hazardous Waste Management Centre, China.

Before use, the sample was subjected to conventional pretreatment processes. Briefly, it was washed thoroughly with deionized water to remove any solute salt and dirt, dried at 80 °C for a week to a constant weight and ground with a mechanical grinder to obtain the fine powder. Simulated wastewater (1,000 mg Pb^{2+} /L) was prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ in deionized water. The required concentrations in experiments were obtained by appropriately diluting the stock solution. All chemical reagents used in this work are analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Spinel ferrite synthesis and characterization

The spinel ferrite powder (SFP) was synthesized by the following procedures: (1) 1.0 g steel pickling sludge powder was mixed with a certain amount of $FeCl_3 \cdot 6H_2O$ in 20 mL deionized water under ultrasound for 5 min; (2) the mixture was maintained at a pH value of 9.0–10.0 by adding $NH_3 \cdot H_2O$ and then the mixture was transferred to 50 mL Teflon-lined stainless steel autoclave and kept in an oven at 200 °C for 8 h; and (3) the black product obtained from the cooled autoclave was rinsed several times with ethanol and dried at 60 °C for 12 h.

The crystalline phase of SFP was analyzed by XRD (D8 Advance, Bruker, Germany) with $Cu K\alpha$ radiation. Its morphology and micro-structure were investigated by FE-SEM (Quanta 250FEG, FEI, USA). The magnetic property of material was measured at room temperature by VSM (HH-15, NanDa Instrument, China). The zeta potential was measured by a Zeta meter (ZetaPALS, Brookhaven Instruments, USA), using 0.01 M KCl solution as a background electrolyte.

Adsorption tests

Batch experiments were performed by mixing a certain amount of SFP with wastewater in 250 mL conical flasks, and the mixtures were agitated in an air bath oscillator at a speed of 200 rpm. After adsorption, samples were withdrawn and separated by a strong magnet, and the residual Pb^{2+} concentration was determined by inductively coupled plasma spectrometer (ICP-AES, Optima 7000DV, PerkinElmer, USA). The removal efficiency (R , %) and the adsorption capacity (q_e , mg/g) were calculated from the following equations (Boudrahem *et al.* 2011):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e (mg/L) are the initial and final concentrations of Pb^{2+} in conical flasks, respectively, V (L) is the volume of the wastewater, and m (g) is dosage of SPF.

To determine the pH effect on adsorption, 0.1 g SFP was left in contact with 100 mL wastewater (50 mg Pb^{2+} /L) at 25 °C for 3 h with continuous shaking. 0.1M HCl or NaOH was used to adjust the initial solution to pH values of 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0.

For kinetic studies, 0.04, 0.08 and 0.1 g SFP was respectively loaded in 250 mL conical flasks containing 100 mL wastewater (50 mg Pb^{2+} /L). Then the flasks were capped and agitated on a thermostatic shaker at 25 °C. Samples were withdrawn at predetermined time intervals (0, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 270, 300 and 330 min) for the analysis of residual Pb^{2+} concentration in solution.

For adsorption isotherm studies, 0.1 g SFP was separately added to 100 mL wastewater with various concentrations of 10, 20, 40, 50, 60, 80 and 100 mg Pb^{2+} /L. The mixtures were shaken at 25 °C for 3 h.

For adsorption thermodynamics studies, 0.1 g SFP was equilibrated with 100 mL wastewater containing 50 mg Pb^{2+} /L at 298, 308 and 318 K for 3 h.

For investigating the effect of competing ions, Ca^{2+} , Mg^{2+} , K^+ and Na^+ in varying concentrations were added to 100 mL Pb^{2+} solution (50 mg/L) suspended with 0.1 g SFP. The mixture was shaken at 25 °C for 3 h.

Theories

Kinetic models

To investigate the controlling mechanism of the adsorption process such as mass transfer, diffusion control and chemical reaction, the well-known kinetic models pseudo-first order model (Lagergren 1898) and pseudo-second order model (Ho 2006) were used to test experimental data. Their linear forms are expressed as:

Pseudo-first order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

Pseudo-second order equation:

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

where q_e and q_t (mg/g) represent the amount of metals adsorbed at equilibrium and at time t (min), and k_1 (min^{-1}) and k_2 ($\text{g}/(\text{mg min})$) are the rate constants for the pseudo-first order and pseudo-second order, respectively.

Isotherm models

The Langmuir isotherm model (Langmuir 1918) assumes that a single molecular layer is adsorbed on the adsorbent uniform coverage of the surface, and each molecule on the surface has equal activation energy. Its linear form can be written by:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}} \quad (5)$$

where C_e (mg/L) is the equilibrium concentration of Pb^{2+} , q_e (mg/g) is the amount of Pb^{2+} adsorbed under equilibrium, q_{\max} (mg/g) is the maximum adsorption capacity, and b (L/g) is a Langmuir constant related to the affinity of the binding sites and energy of adsorption.

The Freundlich isotherm model (Freundlich 1906) is usually used to describe the adsorption characteristics of a heterogeneous surface. The linear form of the isotherm equation is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F and n are Freundlich constants, with n giving an indication of how favorable the adsorption process is and K_F (mg/g) related to the bonding energy.

The Dubinin-Radushkevich (D-R) model (Dubinin 1960) can evaluate in depth the mechanism of Pb^{2+} adsorption on SFP, as well as distinguish between physisorption and chemisorption. Its linear equations can be represented by:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

where q_m (mg/g) is the theoretical saturation adsorption capacity, β ($\text{mol}^2 \text{J}^{-2}$) is a constant correlated with the mean free energy of adsorption, ε is the Polanyi potential,

R (8.3145 J/(mol K)) is the universal gas constant, T (K) is the absolute temperature in Kelvin, and E (mol²/kJ²) is the mean free energy of adsorption per molecule of the adsorbate when transferred to the surface of the solid from infinity in the solution.

Thermodynamics

Thermodynamic parameters, including the Gibbs free energy change (ΔG° , kJ/mol), the enthalpy change (ΔH° , kJ/mol) and the entropy change (ΔS° , kJ/(mol K)) are critical for determining if the process is endothermic or exothermic, and the spontaneity of the adsorption process, which can be calculated by (Aydın & Aksoy 2009):

$$K = \frac{C_s}{C_e} \quad (10)$$

$$\Delta G^\circ = -RT \ln K \quad (11)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where K is the adsorption equilibrium constant, C_s (mg/g) is the amount of Pb²⁺ adsorbed per weight unit of SFP after equilibrium, C_e (mg/L) is the phosphate concentration in solution at equilibrium, R (8.3145 J/(mol K)) is the universal gas constant, and T (K) is the temperature. ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln K$ versus $1/T$.

RESULTS AND DISCUSSION

Characterizations

The structure of SFP prepared from steel pickling sludge was analyzed by XRD and the result is shown in Figure 1(a). The wide-angle XRD pattern exhibited seven characteristic peaks that appeared at $2\theta = 30^\circ$, 36° , 43° , 54° , 57° and

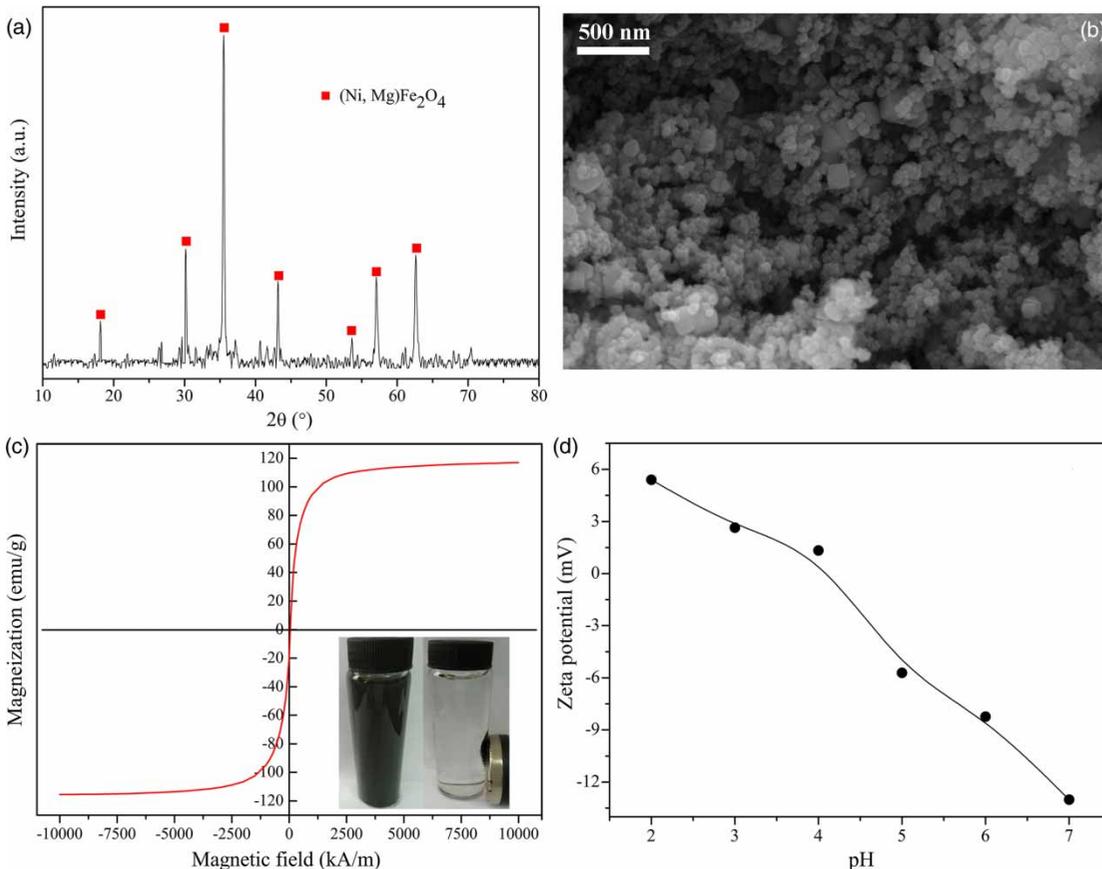


Figure 1 | Characterizations of SFP prepared from steel pickling sludge: (a) XRD, (b) VSM, (c) FE-SEM, (d) Zeta potential.

63°. It has been assigned to the typical crystal planes of (Ni, Mg)Fe₂O₄, demonstrating the feasibility of producing spinel ferrite from steel pickling sludge. Figure 1(b) shows the FE-SEM image of SFP. The SFP particles presented a relatively uniform spherical shape 50–110 nm in diameter. From Figure 1(c), the saturation magnetization of SFP was measured as 116.4 emu/g, which was greater than the ferrite material derived from electroplating sludge (Chen *et al.* 2010). The complete separation between SFP and solution only needed 2 min (insert image). Figure 1(d) exhibits the change of surface charge of SFP. With pH increasing from 2.0 to 7.0, zeta potential of SFP decreased from 5.40 to –13.01 mV. The point of zero charge (pH_{pzc}) was obtained at pH 4.35.

Toxicity evaluation

Evaluation of the hazardous nature of adsorbent is an essential step for its use. In this work, the toxicity characteristic leaching procedure (TCLP) method was selected for assessing the leachability of toxic metals from steel pickling sludge and SFP. Figure 2(a) shows that the Pb, Cd and Cr were leached from the raw sludge, and the concentrations of metals were all below the USEPA regulatory levels, indicating that raw sludge had little environmental impact. From Figure 2(b), it is obvious that only Cr was detected, and its TCLP concentration in leachate (pH 4.93 ± 0.05) was considerably lower than the level of raw sludge, deducing that the SFP could immobilize the Pb, Cd and Cr properly.

Effect of pH

The solution pH is one of the important factors for sorption of heavy metal ions, which not only significantly influences the hydrolytic species of metal ions but also affects the surface charge of adsorbents (Azouaou *et al.* 2010; Boudrahem *et al.* 2011). To study the effect of this parameter on the Pb²⁺ adsorption on SFP, the solution initial pH was controlled within the range of 2.0 to 7.0 to avoid lead hydroxide precipitation. Figure 3 shows the effect of wastewater initial pH on the uptake of Pb²⁺. At low pH values, there was excessive protonation on the SFP's surface, resulting in a decrease in the sorption of Pb²⁺, which was consistent with the literature (Kobyas *et al.* 2005). On increasing the pH of Pb²⁺ solution from 2.0 to 6.0, the removal percentage increased from 12.07 to 75.53%. This can be attributed to the fact that the negative charge on the SFP surface (Figure 1(d)) obviously increases and thus attracts the positively charged Pb²⁺ more strongly. When pH > 6.5, the lead hydroxide

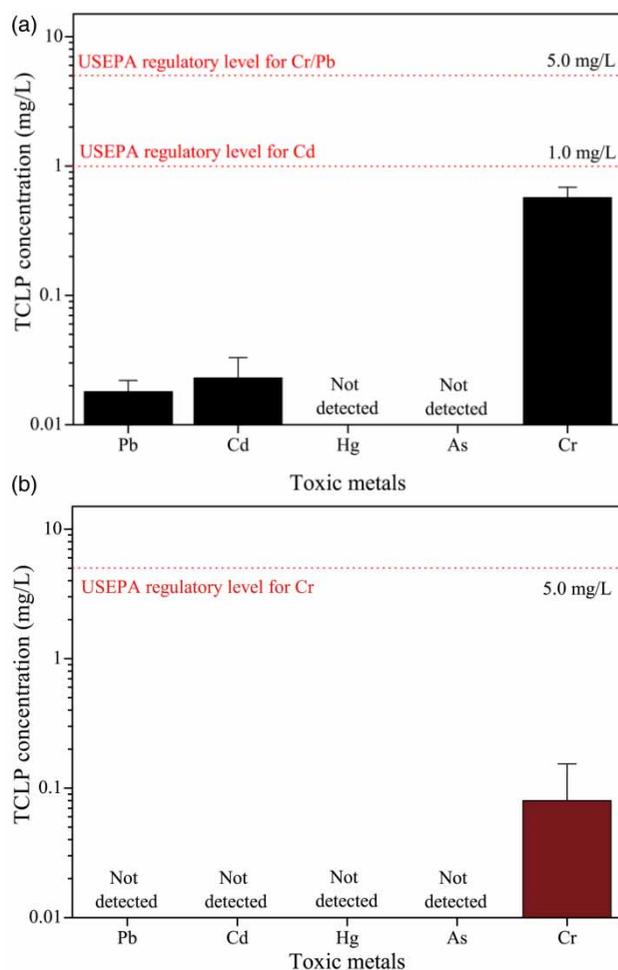


Figure 2 | Toxicity characteristics leaching procedure (TCLP) extracted various metals in (a) raw steel pickling sludge and (b) spinel ferrite powder (SFP).

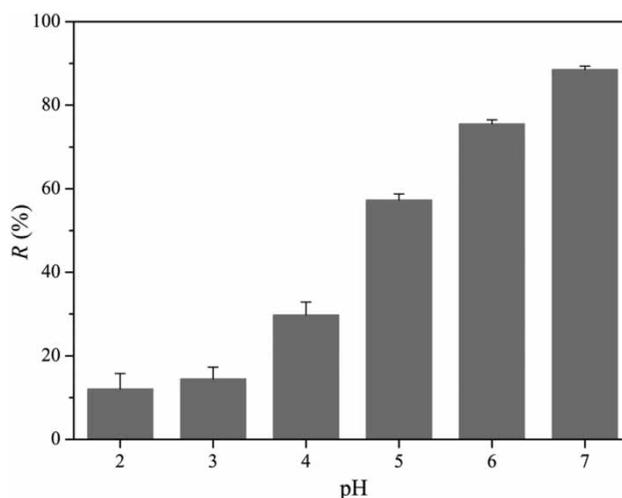


Figure 3 | Effect of pH on the removal of Pb²⁺ by SFP from aqueous solution.

precipitation was partly formed, leading to the higher removal efficiency of Pb^{2+} . Subsequent studies were conducted at $\text{pH } 5.8 \pm 0.2$.

Kinetics studies

The effects of dosage and contact time on the removal of Pb^{2+} by SFP are shown in Figure 4(a). From the figure, it can be seen that Pb^{2+} sorption occurred rapidly. The removal efficiency of Pb^{2+} increased gradually with increasing contact times and reached a plateau afterward. On increasing the SFP dose from 0.04 to 0.1 g, the removal efficiency of Pb^{2+} increased from 52.68 to 96.20%. This may be ascribed to an increased contact surface and available active sites resulting from the increased dosage of the adsorbent. At an amount of adsorbent higher than 0.1 g, the incremental Pb^{2+} removal became very low (only 3.0%); therefore, dosage of 0.1 was chosen for the following experiments.

From Table 1, it can be found that the R^2 values (0.9773, 0.9493 and 0.9623 for 0.04, 0.08 and 0.1, respectively) of the

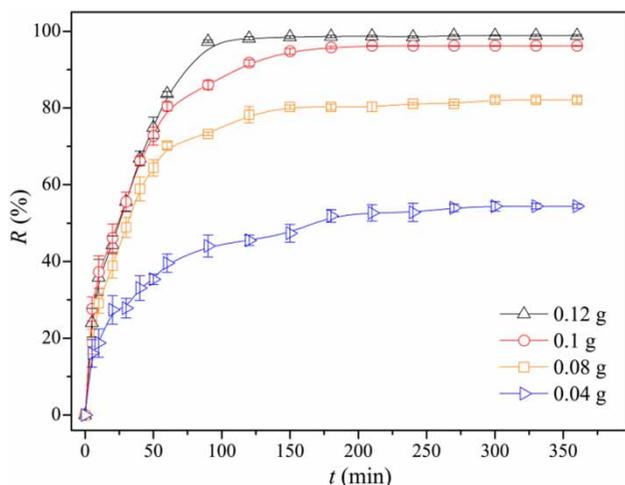


Figure 4 | The effect of dosage and contact time on the uptake of Pb^{2+} onto SFP.

Table 1 | Pseudo-first order and pseudo-second order kinetic parameters for the adsorption of Pb^{2+} onto SFP

Dosage (g)	$q_{e \text{ exp}}$ (mg/g)	Pseudo-first order		Pseudo-second order		
		$q_{e \text{ cal}}$ (mg/g)	R^2	$k_2 \times 10^{-3}$ (g/(mg min))	$q_{e \text{ cal}}$ (mg/g)	R^2
0.04	67.4	48.5	0.9773	0.19	72.4	0.9939
0.08	50.7	30.8	0.9493	0.33	55.3	0.9984
0.1	48.1	59.3	0.9623	0.38	51.2	0.9979

pseudo-first order model were lower than those of the pseudo-second order model (0.9939, 0.9984 and 0.9979). The theoretical $q_{e \text{ cal}}$ s calculated from the pseudo-first order equation were 48.5, 30.8 and 59.3 mg/g for 0.04 g, 0.08 g and 0.1 g, respectively, which were markedly different from experimental data (67.4, 50.3 and 48.1 mg/g). However, for the pseudo-second order model, the values of $q_{e \text{ cal}}$ were in good agreement with experimental data. These results indicated the good applicability of the pseudo-second order model for Pb^{2+} removal by SFP under the experimental condition. On the other hand, the overall rate of Pb^{2+} adsorption on SFP was controlled by a chemical process, which was in accordance with the results obtained by an other study (Yan et al. 2014).

Equilibrium studies

The analysis of equilibrium data is essential to understand the adsorption process and to be able to compare different adsorbents under different operational conditions. The relationship between various initial Pb^{2+} concentrations and equilibrium adsorption capacities was investigated. It is obvious from Figure 5 that the equilibrium adsorption capacities of SFP ranged from 33.71 mg/g to 120.7 mg/g, 35.78 mg/g to 157.1 mg/g, and 36.84 mg/g to 174.1 mg/g at 298 K, 308 K, and 318 K, respectively. Especially, the equilibrium adsorption capacities of SFP were in the order of $q_{e \text{ 318}} > q_{e \text{ 308}} > q_{e \text{ 298}}$ in the whole adsorption process, suggesting an endothermic process for Pb^{2+} adsorption onto SFP.

The calculated isotherm constants are summarized in Table 2. It can be discovered that the adsorption processes in all conditions were accurately described by the Langmuir

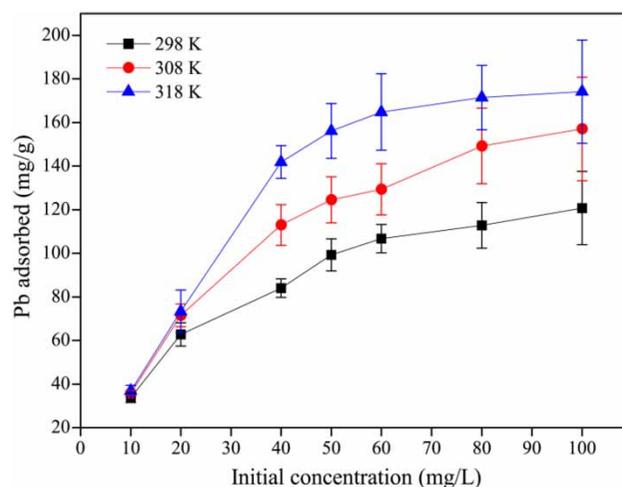


Figure 5 | Effect of initial concentration on the uptake of Pb^{2+} onto SFP.

Table 2 | Langmuir, Freundlich and D-R parameters for the adsorption of Pb²⁺ onto SFP

T (K)	Langmuir			Freundlich			D-R	
	q_{\max} (mg/g)	b (L/mg)	R^2	K_F	$1/n$	R^2	E (kJ/mol)	R^2
298	126.5	0.1941	0.9917	38.01	0.2879	0.9583	19.61	0.9385
308	161.3	0.3100	0.9915	56.57	0.2674	0.9142	22.36	0.8943
318	175.4	1.295	0.9999	80.32	0.2461	0.8309	23.57	0.8588

model due to the higher values of R^2 , indicating that the Pb²⁺ removal by SFP corresponded to a homogeneous system. The maximum adsorption capacities (q_{\max}) predicted from the Langmuir equation were in the range of 126.5–175.4 mg/g, which were similar to or even greater than those of other adsorbents (Table 3), implying that SFP possessed a significant potential for Pb²⁺ removal from practical wastewater. The Langmuir constant b is commonly used to calculate the dimensionless separation factor, R_L ($R_L = (1 + bC_0)^{-1}$), which can evaluate the favorability of adsorption. The adsorption process is favorable if the R_L values lie between 0 and 1, while the process is unfavorable if the values of $R_L > 1$ (Meitei & Prasad 2014). In this case, the calculated R_L values at different temperatures were all within the range of 0–1 (0.049–0.340 for 298 K, 0.031–0.243 for 308 K and 0.007–0.072 for 318 K), indicating the favorable nature for adsorption of Pb²⁺ from wastewater by SFP. Additionally, the $1/n$ values obtained from the Freundlich equation were 0.2879, 0.2674 and 0.2461 for

298 K, 308 K and 318 K, respectively, which all lie between 0 and 1, reflecting the favorable adsorption and high affinity between the optimum hydroxyapatite prepared from alkaline residue (O-HAP) and Pb²⁺ (Zhao *et al.* 2010), demonstrating the results from R_L studies.

The E calculated from D-R equations gives important information about the adsorption type. The adsorption type is physisorption if $E < 8$ kJ/mol, while the process is chemical in nature if the values of $E > 16$ kJ/mol, and $8 < E < 16$ kJ/mol indicates ion exchange (Hamayun *et al.* 2014). In present work, the E values were all greater than 16, suggesting that the removal of Pb²⁺ by SFP was a stronger chemical process, which was consistent with the results of kinetic studies.

Thermodynamics

The thermodynamic parameters are listed in Table 4. As the temperature rose from 298 to 318 K, the absolute values of ΔG° increased, reflecting more efficient adsorption at higher temperature. The positive values of ΔS° revealed the increase of randomness at the interface of the solid-solution during the adsorption of Pb²⁺ on the active sites of SFP. Furthermore, the positive values of ΔH° confirmed that this adsorption process was exothermic in nature. In addition, according to the ΔH° value, the procedure can be classified as a physical ($2.1 < \Delta H^\circ < 20.9$ kJ/mol) or a chemical ($20.9 < \Delta H^\circ < 418.4$ kJ/mol) process (Sağ & Kutsal 2000). In this case, the ΔH° was 58.60 kJ/mol, indicating that the nature of Pb²⁺ adsorption is chemisorption, which is consistent with the results of kinetics study and D-R model.

Table 3 | Comparison of adsorption capacity (q_{\max}) of various adsorbents for Pb²⁺ adsorption

Adsorbents	q_{\max} (mg/g)	References
SFP	126.5–175.4	This study
Carbonate hydroxyapatite	101	Liao <i>et al.</i> (2010)
Non-activated charcoal of oak wood origin	31.08	Machida <i>et al.</i> (2005)
FGD gypsum	161.3	Yan <i>et al.</i> (2015)
Chitosan-based granular adsorbent	178.57–465.12	Zhu <i>et al.</i> (2015)
Functionalized chrysotile nanotubes	83.96	Sun <i>et al.</i> (2015)
Water hyacinth based activated carbon	118.8	Huang <i>et al.</i> (2014)
Mercapto groups functionalized CeO ₂ nanofiber	90.9	Yari <i>et al.</i> (2015)
Modified hide waste	14.60–32.36	Kong <i>et al.</i> (2014)

Table 4 | Thermodynamic parameters for the adsorption of Pb²⁺ on SFP

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
298	–3.57	58.60	0.21
308	–5.13		
318	–7.74		

Effect of competing ions

Alkali and alkali-earth metal ions such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} , which exist widely in natural water sources, may compete with Pb^{2+} for the available adsorptive sites (Dong *et al.* 2010). Hence, it is important to investigate the interference of competing ions for Pb^{2+} adsorption onto SFP. Figure 6 shows the effect of various ions of different concentrations on Pb^{2+} adsorption by SFP. Under the given experimental conditions, K^+ , Na^+ , Ca^{2+} and Mg^{2+} have shown negligible effect on the removal of Pb^{2+} . These results confirm that SFP has the capability of selectively and efficiently removing Pb^{2+} from aqueous solution when the above competing ions are in the range of 0–200 mg/L.

Regeneration

At present, the significance of removing heavy metal ions relates to the process of desorption and reuse in industry processes rather than simple adsorption and disposal (Kumar *et al.* 2007). In order to assess the reusability of SFP, continuous adsorption/desorption cycles were conducted by mixing 0.1 g SFP and 100 mL wastewater (50 mg Pb^{2+} /L) at a speed of 200 rpm. At every 3 h sampling time interval, the entire solution was withdrawn from the conical flask to analyze Pb^{2+} concentration, followed by the addition of 50 mL HNO_3 (1.0 M) to desorb the saturated SFP. Such adsorption/desorption cycles were carried out using the same SFP batch eight consecutive times. As seen from Figure 7, Pb^{2+} removal was higher than 90% during the initial five cycles but sharply declined to 72.13% at the eighth cycle. In general, the relatively good regenerability was more conducive to its practical application.

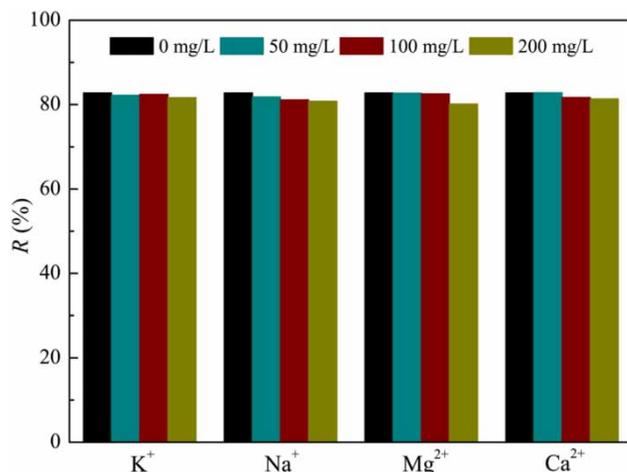


Figure 6 | Effect of competing ions on the removal of Pb^{2+} by SFP from aqueous solution.

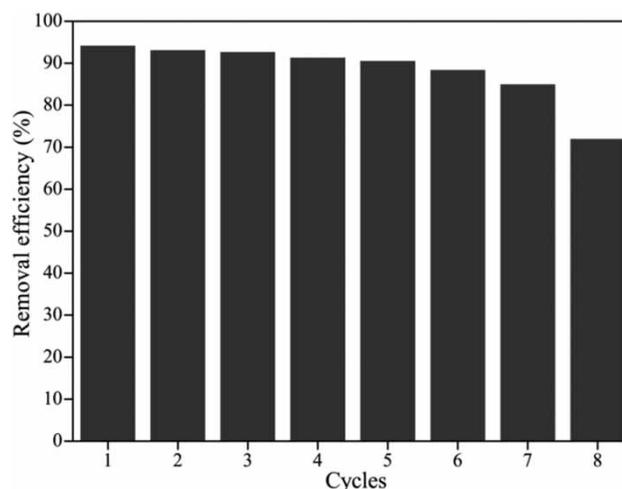


Figure 7 | Sustained removal of Pb^{2+} by SFP.

CONCLUSIONS

The present study indicated that the spinel ferrite synthesized using the steel pickling sludge as raw material showed excellent adsorption performance for Pb^{2+} from aqueous solution. Increasing the solution's initial pH increased the negative surface charge of spinel ferrite, and the negative surface enhanced the removal efficiency of Pb^{2+} . When the dosages of adsorbent and initial pH were, respectively, fixed at 0.1 g and 5.8 ± 0.2 , the process of adsorption was relatively rapid and approached equilibrium within 180 min. The kinetic data correlated well with the pseudo-second order model, indicating that the chemical reaction was the rate-limiting step. Equilibrium study showed an excellent fit between experimental data and the Langmuir isotherm model, and the maximum adsorption capacities predicted from the Langmuir equation were relatively greater than for other adsorbents. The negative ΔG° values and positive ΔH° and ΔS° values signified that the adsorption reaction was spontaneously endothermic and increased randomness at the solid/liquid interface. Thus, the spinel ferrite from steel pickling sludge can be considered as a promising candidate for Pb^{2+} removal from wastewater.

ACKNOWLEDGEMENTS

The authors would like to acknowledge National Natural Science Foundation of China (No. 51278248), Environmental Protection Department of Jiangsu Province, China (No. s201118) and Jiangsu Provincial Education Ministry of China (No. KYZZ_0129) for their financial support.

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First received 26 August 2015; accepted in revised form 28 October 2015. Available online 14 November 2015