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Abstract: The kinetics and thermodynamics of Pb(II) adsorption on vermiculite have been studied by the sets of experiments at various conditions (temperature, initial lead concentration and adsorption time). The structures of the vermiculite before and after Pb(II) adsorption were measured using X-ray diffraction (XRD), thermogravimetric analysis (TA), and X-ray photoelectron spectroscopy (XPS). Adsorption of Pb(II) was strongly affected by pH. First order kinetics model best described the reaction rate, and the adsorption capacity calculated by the model was consistent with that actual measurement. Isotherms for the adsorption of Pb(II) on vermiculite were developed and the equilibrium data fitted well to the Langmuir and Freundlich models. Thermodynamic parameters such as enthalpy, entropy, and free energy were calculated using the Van't Hoff equations. The thermodynamics of Pb(II) on vermiculite indicates the spontaneous and endothermic nature of adsorption. Quantitative desorption of Pb(II) from vermiculite was found to be more than 40% which facilitates the sorption of metal by ion exchange

Keywords: Kinetics, thermodynamics, adsorption, lead, vermiculite

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INTRODUCTION

Recently, lead has been introduced into natural water supplies from a variety of sources such as storage batteries, lead smelting, tetraethyllead manufacturing, mining, plating, ammunition, and the ceramic glass industries. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis. Lead ions have an affinity for ligands containing thiol and phosphatic groups and they inhibit the biosynthesis of heme, causing damage both to the kidney and the liver. However, lead can remain immobilized for years, and hence it is difficult to detect the metabolic disorders it causes. Several methods such as ion exchange, solvent extraction, reverse osmosis, precipitation, and adsorption have been proposed for the treatment of wastewater contaminated with heavy metals (1). Among the treatment processes available, activated carbon has been used as a sorbent for sorption of heavy metals like lead in wastewater (2). In spite of its effectiveness in the removal of heavy metals, the high cost of activated carbon has restricted its widespread use (3).

Therefore, numerous approaches have been studied for the development of cheaper and environmentally friendly metal adsorbents such as fly ash (1, 4–6), peat (7, 8), microbial biomass (9), biosorbents (10–12), waste slurry (13, 14), synthetic resin (15), clays, and related minerals (16–19). Vermiculite is relatively inexpensive and easily available in China. It consists of unit layers composed from two silica tetrahedral sheets attached to a central magnesium octahedral sheet. Al^{3+} substitution for Si^{4+} in tetrahedral layers, and Al^{3+} and/or Fe^{3+} substitutions for Mg^{2+} in octahedral layers are responsible for the negative charge of the structure. The use of vermiculite in wastewater treatment has been studied in recent years and experimental results have shown vermiculite to be a suitable adsorbent for the removal of heavy metals from wastewaters. Bandyopadhyay et al. (20) studied Cu(II) removal by vermiculite from Bihar, India, under conditions of constant ionic strength. They reported 80% Cu(II) removal at pH 6 with an equilibrium time of 12 hours, and the adsorption followed the Freundlich isotherm. Bors et al. (21) studied iodide, cesium, and strontium adsorption by untreated and a treated-organophilic vermiculite. They concluded that the cation adsorption was substantially reduced for the organophilic vermiculite. Mathialagan et al. (22) used natural vermiculite to achieve 96% removal of Cd(II) from aqueous solutions. They found that the optimum pH for adsorption was 6. The adsorption reached equilibrium in about four hours following Ho's pseudo second order model, and the adsorption followed the Freundlich isotherm model. Although previous researches have highlighted the utility of this low cost and environmentally friendly clay for studies of the adsorption of heavy metals from aqueous solutions (20–25), little attention has been paid to the mechanism of kinetics and thermodynamics for the metal adsorption on vermiculite.

The objective of this study is to investigate the sorption behavior of Pb(II) on vermiculite. To understand the mechanisms of Pb(II) adsorption on vermiculite, X-ray diffraction (XRD), thermogravimetric analysis (TA), and X-ray photoelectron spectroscopy (XPS) were used. The adsorption experiments were performed at different temperature, different initial Pb(II) concentration, and different adsorption time. A particular objective of this study was to evaluate the kinetic (rate constants) and thermodynamic (entropy, enthalpy, free energy) parameters for Pb(II) adsorption on vermiculite.

EXPERIMENTAL PROCEDURE

Adsorbent

Vermiculite used in this work was supplied by the Xinjiang Yuli Xinlong Vermiculite Company, China. Vermiculite was initially rinsed with deionzed water several times, and dried in an oven at 80°C, then sieved to a size fraction of smaller than 0.16 mm.

Apparatus

The X-Ray diffraction experiments were performed with X'Pert Pro MPD X-ray diffractometer (Philips, Netherlands). The voltage and anode current were 40 kV and 40 mA, respectively. The Cu $K_\alpha = 0.15405$ nm and continuous scanning mode were 0.01 step size. The thermogravimetric analysis of the composites from 30 to 1000°C was determined with a EXSTAR 600 instrument (Japan) at a heating rate of 10°C/min. High-resolution XPS spectra were taken with a pass energy of 25 eV using Mg KR X-rays (Perkin-Elmer PHI model 04-51 X-ray source). An Atomic absorption spectrometer (AAS, Spectr AA 220FS, Varian, America) was used for the determination of lead concentration.

Reagents

A stock lead solution (1000 mg l^{-1}) was prepared from analytical grade lead nitrate and diluted to the required concentration. All other chemicals were analytical grade.

Batch Adsorption Experiments

Batch pH experiments were studied by agitating 50 ml of 20 mg l^{-1} solution of Pb(II) with 4.0 g l^{-1} vermiculite, which were adjusted to initial pH varying between 1.0 and 5.5, and the stirring rate was 1200 r/min during the experiments. In preliminary studies, it was found that Pb(II) adsorption on vermiculite was very fast because of more than 90% Pb(II) adsorbed on vermiculite in initial 10 minutes, and the Pb(II) adsorption did not increase at adsorption time of more than 30 minutes. Therefore, a 30 minute adsorption time was selected. The suspensions were then filtered for analyzing the lead concentration by AAS.

Batch kinetic experiments were studied by agitating 50 ml of 20 mg l^{-1} solution of Pb(II) with 4.0 g l^{-1} vermiculite at pH 5.0. The stirring rate was 1200 r/min during the experiments. Samples were collected at 1, 3, 5, 10, 20, 30, 60 minutes.

Batch adsorption isotherms were studied by agitating 50 ml of different initial concentration of Pb(II) (20, 50, 100, 150, 200 mg l^{-1}) with 4.0 g l^{-1} vermiculite at pH 5.0 at temperatures 10, 35, 60, and 80°C for 30 minutes. The stirring rate was 1200 r/min during the experiments.

Adsorption of Pb(II) on the walls of glass flasks and plastic bottles was found to be negligible by running blank experiments. Each experiment was carried out in duplicate and the average results were presented in this work.

Desorption Studies

After adsorption experiments, vermiculite adsorbed Pb(II) was separated out by filtration and the filtrate was discarded. The vermiculite was given a gentle wash with deionized water to remove any unadsorbed Pb(II). Desorption studies were carried out using those vermiculite samples agitated with 50 ml different desorption agent including HNO_3, NaCl, and H_2O.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 showed the X-ray diffraction patterns for vermiculite with and without different concentrations of Pb(II). The XRD pattern for natural vermiculite show strong peaks at 1.45 and 1.28 nm, the former corresponding to vermiculite and the latter to a mica-type mineral, indicating that the sample was a mixture of clay minerals, and the main phase was vermiculite. Previous authors also observed these peaks in ethyleneglycolated vermiculite from Vali (26) interpreting the peak at 1.43 nm as vermiculite and the peak at 1.2 nm as a biotite–vermiculite mixed layer mineral with 50–70% biotite component. The peaks at 1.4 nm decreased in intensity and the interlayer distance for vermiculite increased with the increasing of Pb(II) concentration (Fig. 1 and Table 1), suggesting that a cationic exchange between the Pb(II) and the cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) in the clay had occurred.

TG and DTG Analysis

The thermogravimetric analysis showed a thermal degradation characteristic for vermiculite before and after adsorption of Pb(II). As it followed from

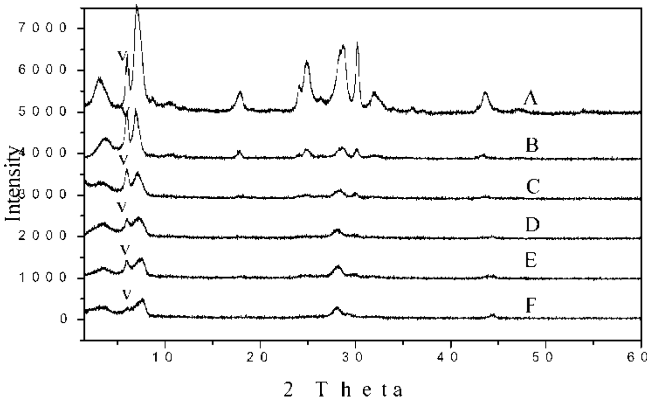

Figure 1. XRD pattern for vermiculite with and without various concentrations of Pb(II). (A) vermiculite, (B) vermiculite with 0.02 mol l^{-1} Pb(II), (C) vermiculite with 0.04 mol l^{-1} Pb(II), (D) vermiculite with 0.06 mol l^{-1} Pb(II), (E) vermiculite with 0.08 mol l^{-1} Pb(II), (F) vermiculite with 0.10 mol l^{-1} Pb(II), (V) peak for vermiculite.

TG and DTG results (Fig. 2), for natural vermiculite, three loss zones were observed in the temperature ranges from 50 to 200°C. The weight losses were 5.04% in the range 49–65°C, 2.38% in the range 82–99°C, and 0.50% in the range 145–168°C respectively, corresponding to the release of physically adsorbed water and a part of water molecules in the layer. In the range of 500–850°C, the weight loss observed was 0.35%, which was ascribed to the release of OH groups. The weight loss above 850°C was 3.72%, corresponding to the formation of new phases enstatite. It was reported by J. Poyato (27) that on further heating up to 1100°C the increase in the crystallinity of enstatite phase and also formation of the spinel phase took place.

For the vermiculite adsorbed Pb(II), only two loss zones were observed in the range 50–200°C, and the weight loss was 4.66% in the range 40–121°C, which was different in comparison to the vermiculite before adsorption of Pb(II). This change can be attributed to the dehydration of Pb(II). The weight loss was 0.39% in the range of 294–350°C; this was not observed for natural vermiculite. It could be suggested that the release of OH groups

Table 1. Interlayer distance for vermiculite sorption of Pb(II) at various concentrations

Pb(II) concentration (mol l^{-1})	0.00	0.02	0.04	0.06	0.08	0.10
Interlayer distance for vermiculite (d_{001}/Å)	14.46	14.76	14.82	14.80	14.84	14.91

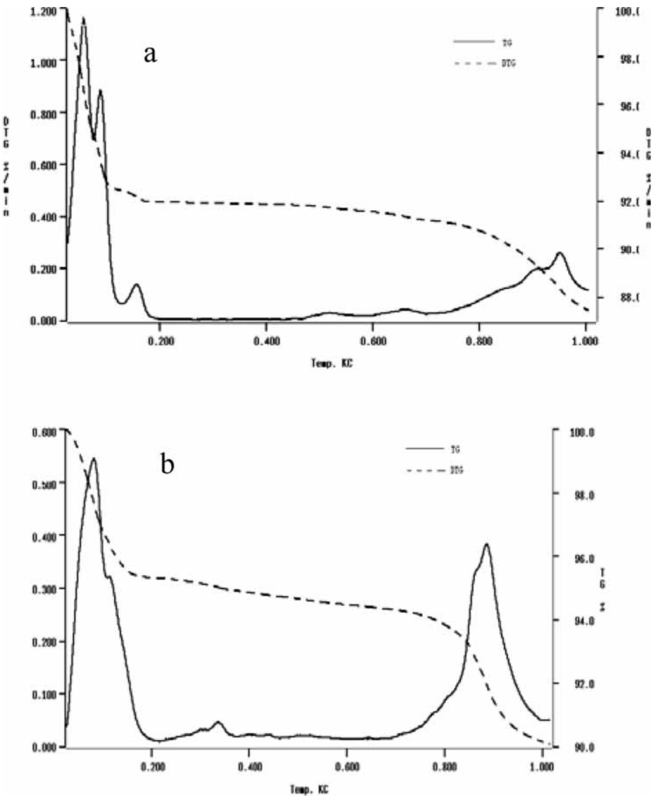

Figure 2. Results of TG and DTG for a- natural vermiculite, b- vermiculite adsorbed Pb(II).

related to hydrolysate for Pb(II) had occurred. The weight loss in the range of 832−921°C was 4.35%, which was more than the weight loss for natural vermiculite.

XPS Analysis

XPS was utilized to characterize the compositions of vermiculite surfaces before and after adsorption of Pb(II), especially the forms of Pb(II) on vermiculite after adsorption. From Fig. 3, the peak for binding energy of 140 eV was not symmetrical, which suggested that more than one peak overlapped. Software named Peakfit Demo was used to separation the peak. From the result of peak separation (Fig. 4), it can be see that at least two peaks were separated out, indicating that there were more Pb(II) forms adsorption on vermiculite, such as Pb^{2+}, $PbOH^{+}$, -Si-O-Pb-, -Al-O-Pb-, -Si-O-PbOH, -Al-O-PbOH.

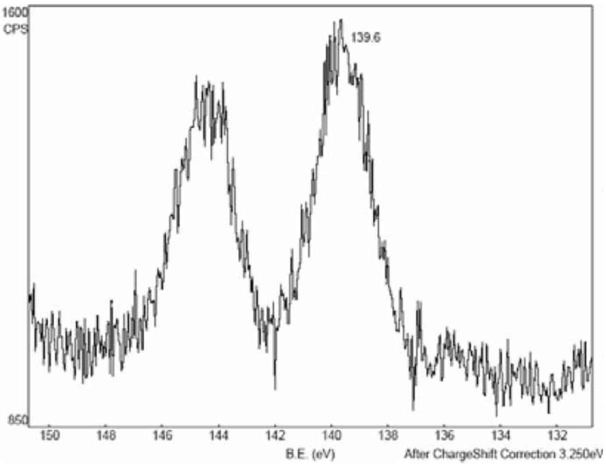

Figure 3. XPS Pb4f spectra obtained from vermiculite4 after adsorbed Pb(II).

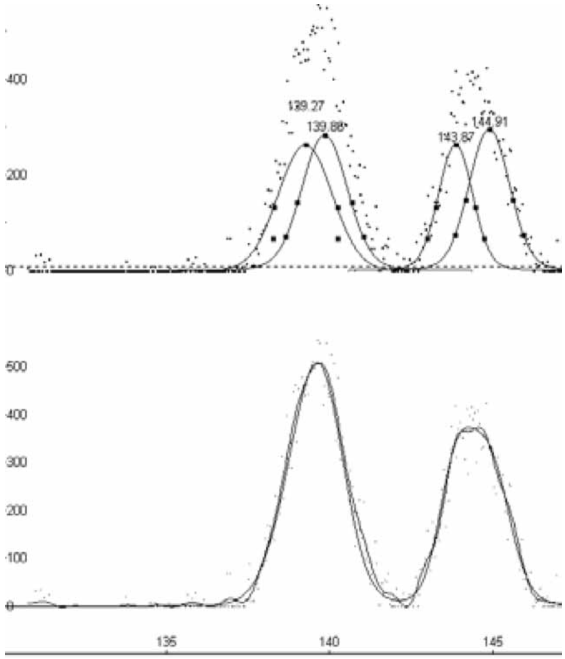

Figure 4. Result of peak separation.

Effects of Initial pH on Pb(II) Removal

pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metal: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation are strongly influenced by pH and, on the other hand, it strongly influences the speciation and adsorption availability of heavy metals (28). Figure 5 presented the effect of initial pH on the removal of Pb(II) by vermiculite. The Pb(II) adsorption on vermiculite was lower with pH < 4. At pH 1.0, only 49.67% of the Pb(II) was adsorbed. At pH 3.1, the Pb(II) adsorption increased to 93.27%. From pH 4.0 to pH 5.5, the Pb(II) adsorption reached a plateau value and remained constant, ranging from 96% to 98%. A similar result was found by Mathialagand et al. (22), who studied Cd^{2+} removal by vermiculite at different pH. They reported that the Cd^{2+} adsorption ranged from 95% to 96% at pH > 4. In the present study, it was found that Pb(II) started precipitating as $Pb(OH)_2$ above pH 5.5, so pH 5.0 was selected for all the experiments.

The increase in adsorption capacity of Pb(II) with increasing pH is the results of two possible mechanisms, which are cation exchange and surface complexation mechanisms. Vermiculite has two types of charges, one is a permanent layer charge originating from isomorphic substitutions of Al^{3+} for Si^{4+}; the other is a pH-dependent charge on the edges. When the pH was lower, H^+ ions competed more with Pb(II) for exchange with other cations on the vermiculite. At the same time, the number of sites available for Pb(II) adsorption on the surface was decreased because of large surface

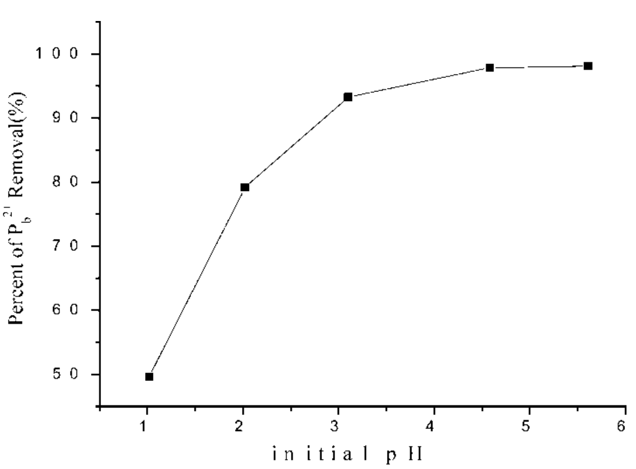

Figure 5. The effect of pH on adsorption of Pb(II) on vermiculite. Conditions: vermiculite dosage 4.0 g l^{-1} for Pb(II) 20 mg l^{-1}; contact time 30 min.

functionalities, such as -Al-OH, -Si-OH, adsorbed H^+ ions. With the higher pH, H^+ ions competed less with Pb(II), and the number of sites increased because more of the protons adsorbed on -Al-OH, -Si-OH were forced from the surface to the bulk solution.

Adsorption Kinetics

The kinetics of Pb(II) adsorption and the heterogeneous equilibrium between the Pb(II) solution and the vermiculite may be expressed as (28):

$$\mathrm{S} + \mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{SM} \tag{1}$$

where M represents the dissolved Pb(II) concentration, S is the available surface sites, and SM is the adsorbed state. k_1 and k_2 are forward and backward rate constants, respectively.

If a is the initial concentration of lead and x is the amount transferred from liquid phase to solid phase at any time t, then the rate is:

$$\frac{dx}{dt} = \frac{-d(a-x)}{dt} = k(a-x) \tag{2}$$

or

$$k = \frac{1}{t}\ln\frac{a}{a-x} \tag{3}$$

where k is the overall reaction rate constant. Since k_1 and k_2 are the rate constants for the forward and reverse processes, the rate can be expressed as:

$$\frac{dx}{dt} = k_1(a-x) - k_2x \tag{4}$$

if X_e represents the concentration of lead adsorbed at equilibrium, then at equilibrium, $k_1(a - X_e) - k_2X_e = 0$ because under these conditions

$$\frac{dx}{dt} = 0 \quad \text{or} \quad k_c = \frac{X_e}{a - X_e} = \frac{k_1}{k_2} \tag{5}$$

where k_c is the equilibrium constant. Now under equilibrium conditions, the overall rate becomes

$$k_1 + k_2 = \frac{1}{t}\ln\frac{X_e}{X_e - x} \tag{6}$$

The above equation can be written in the form of

$$\ln\frac{X_e - x}{X_e} = -(k_1 + k_2)t = -kt \tag{7}$$

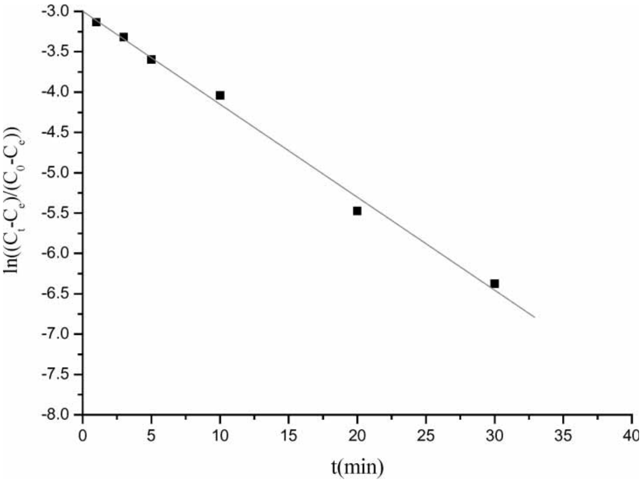

Figure 6. Kinetics of Pb(II) adsorption on vermiculite. Conditions: vermiculite dosage 4.0 g l^{-1}; pH 5.0.

Further,

$$k = k_1 + k_2 = k_1 + \frac{k_1}{k_c} \tag{8}$$

X_e can be calculated using the expression

$$X_e = C_0 - C_e$$
$$X = C_0 - C_t$$

Where C_0 is the initial concentration of lead, C_t is the concentration of lead present at any time (t), and C_e is the concentration of lead present at equilibrium.

In the present study the kinetic behavior was studied for the initial Pb(II) concentration of 200 mg l^{-1} by plotting $ln((C_t - C_e)/(C_0 - C_e))$ vs t. Figure 6 showed the kinetic behavior of Pb(II) uptake by vermiculite, which was found to be linear with a correlation coefficient of more than 0.99. It was apparent that the sorption was relatively fast with more than 90% of Pb(II) adsorbed in initial 10 minute. The overall rate constant k was 0.1152 min^{-1} by considering the slope of straight line in Fig. 6, the equilibrium constant k_c and the forward and backward rate constants k_1 and k_2 were 28.41, 0.1113 min^{-1} and 0.003918 min^{-1} using Eqs. (5) and (8). It can be seen that the forward rate constant for the adsorption of lead was much higher than the backward rate constant. Sekar (28) reported that the overall rate constant k for 20 mg l^{-1} lead adsorbed on activated carbon was 0.05103 min^{-1}, and the forward and backward rate constants were 0.0464 min^{-1} and 0.00459 min^{-1}, which were smaller than the results obtained by the present study. This may be due to the difference in the adsorbent employed in the experiments.

Adsorption Thermodynamics

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The Langmuir equation can be described by the linearized form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \tag{9}$$

where Q_{max} is the maximum adsorbed material in mg per g of the adsorbent and b is the Langmuir isotherm constant.

The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent Q_e and the concentration of the metal in solution at equilibrium. The Freundlich equation can be described by the linearized form:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \tag{10}$$

where K_F and $1/n$ are Freundlich constants related to the adsorption capacity and the adsorption efficiency, respectively.

In the present study, the adsorption data obtained from the initial Pb(II) concentration from 20 to 200 mg l^{-1} at pH 5.0 show that the adsorption obeys both Langmuir and Freundlich model, see Figs. 7 and 8. Regression analysis of the linearized isotherms of Freundlich (log Qe versus log Ce) and Langmuir (Ce/Qe versus Ce), using the slope and the intercept, gave the sorption constants (K_F, $1/n$ and Q_{max}, b) and correlation coefficients (R^2). The fitting parameters offer Freundlich and Langmuir equations at different temperatures were summarized in Table 2.

Effect of Temperature on the Adsorption

Increase of temperature from 10°C to 80°C increased the sorption of Pb(II) from 86.96 mg g^{-1} to 109.9 mg g^{-1}, indicating that the process was endothermic. The mechanism of adsorption may be determined through thermodynamic quantities such as change in free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS). The thermodynamic equilibrium constant K for the sorption was determined by Khan and Singh (29) from the intercept of the plots of *ln (Qe/Ce)* versus Qe. Then, the ΔG, ΔH and ΔS are

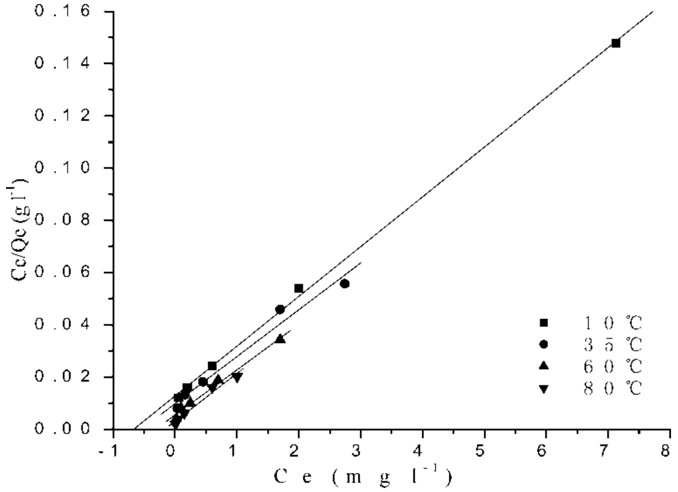

Figure 7. Langmiur isotherms of Pb(II) on the vermiculite at different temperatures. Conditions: pH 5.0; vermiculite dosage 4.0 g l^{-1}; contact time 30 min.

calculated from the Van't Hoff Equation (29):

$$\Delta G = -RT \ln K \tag{11}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

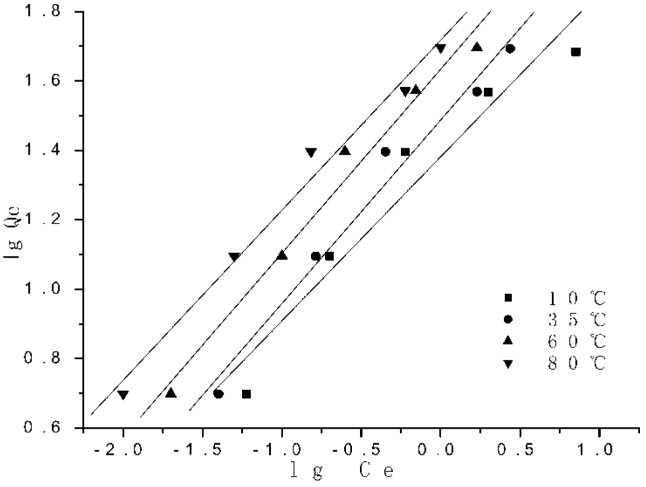

Figure 8. Freundlich isotherms of Pb(II) on the vermiculite at different temperatures. Conditions: pH 5.0; vermiculite dosage 4.0 g l^{-1}; contact time 30 min.

Table 2. Adsorption parameters of the Pb(II) on the vermiculite at different temperatures

	Langmuir constants			Freundlich constants		
T (°C)	R^2	Q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	K_F	$1/n$
10	0.9989	86.96	0.2164	0.9374	24.05	0.4723
35	0.9731	94.61	0.2864	0.9784	30.67	0.5281
60	0.9901	104.5	0.3964	0.9811	43.00	0.5298
80	0.9714	109.9	0.5916	0.9848	52.10	0.4896

In the present study, the values of the observed equilibrium constant (K) for the sorption were calculated with respect to temperature by plotting *ln(Qe/Ce)* versus *Qe* and extrapolating to zero *Qe* (Fig. 9). Thermodynamic parameters were calculated from the variations of the thermodynamic equilibrium constant K by plotting of ln K versus $1/T$ (Fig. 10). Then the slope and intercept were used to determine ΔH and ΔS, and the Vant't Hoff equation (Eq. (11) was applied to calculate ΔG (Table 3). For the adsorption process, the ΔH was 3.103 kJ mol^{-1}, which indicate that increased temperature favors adsorption and the adsorption process is an endothermic reaction in nature. The ΔS was 23.83 J mol^{-1} K^{-1}, and the ΔG were -3.720 kJ mol^{-1}, -4.115 kJ mol^{-1}, -4.776 kJ mol^{-1}, -5.412 kJ mol^{-1} at 10°C, 35°C, 60°C, 80°C, respectively. The positive value of ΔS suggest an increased

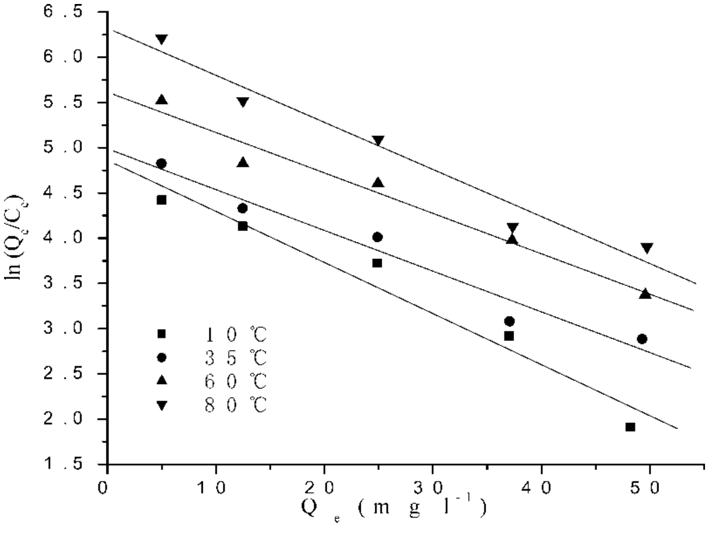

Figure 9. Plots of ln(Qe/Ce) vs. Qe for the Pb(II) adsorption on the vermiculite at different temperature.

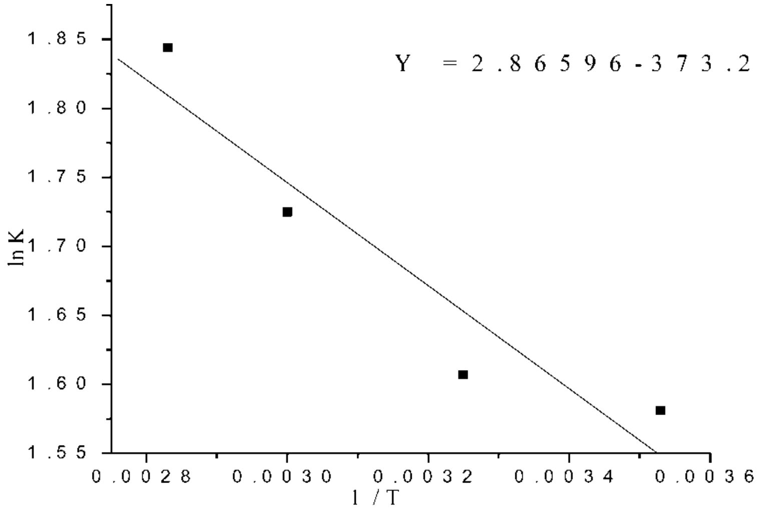

Figure 10. Van't Hoff plot for the Pb(II) adsorption on the vermiculite.

randomness at the solid/solution interface during the adsorption of Pb(II) on vermiculite. The negative values of Δ*G* indicate the sorption process to be feasible and adsorption to be more spontaneous with increasing temperature. A similar result was found by Sekar et al. (28), who studied Pb(II) adsorption on activated carbon at different temperature. They reported that the negative values of Δ*G* indicate the process to be spontaneous, and the positive values of Δ*H*, Δ*S* indicate that the adsorption process is endothermic, random at the solid solution interface. Lyubchik et al. (29) studied the temperature effect on Cr(III) adsorption on activated carbon. They found that the values of Δ*H*, Δ*S* were positive and the values of Δ*G* were negative indicating an endothermic and spontaneous process, which were also similar to the results obtained in the present study.

This observation can be explained by the fact that for the vermiculite, which is rich in surface functionalities, such as Si-OH, Al-OH, there is

Table 3. Thermodynamic parameters of the Pb(II) adsorption on vermiculite at different temperatures

T (°C)	Thermodynamic equilibrium constant (K)	Δ*G* (kJ mol^{-1})	Δ*S* (J mol^{-1} K^{-1})	Δ*H* (kJ mol^{-1})
10	4.860	−3.720	23.83	3.103
35	4.988	−4.115		
60	5.613	−4.776		
80	6.322	−5.412		

more than one mechanism for Pb(II) adsorption. Along with the usual physisorption, the chemisorption of Pb(II) at the active sites on the vermiculite surface also took place. Increasing temperature not only increased the active surface centers available for adsorption, but also decreased the activation energy for the adsorption. All of these favor chemsorption.

Desorption Studies

Desorption studies can help to elucidate the adsorption mechanism. The desorption process allows the recovery of precious metals from wastewater and regeneration of the vermiculite. The effect of HNO_3 concentration on the desorption of Pb(II) was represented in Fig. 11. The maximum desorption of more than 40% was obtained with 1 mol l^{-1} HNO_3, while desorption using distilled water (H_2O) and 1 mol l^{-1} NaCl was 5% and 20% respectively, which clearly indicates that effective desorption of Pb(II) was observed with HNO_3. The effectiveness of HNO_3 solution is due to H^+ competing with Pb(II), which promotes displacement of Pb(II) species into solution.

CONCLUSIONS

From the foregoing experiment we have concluded that natural vermiculite is an efficient adsorbent for removing Pb(II) from aqueous solution. The following conclusions were drawn.

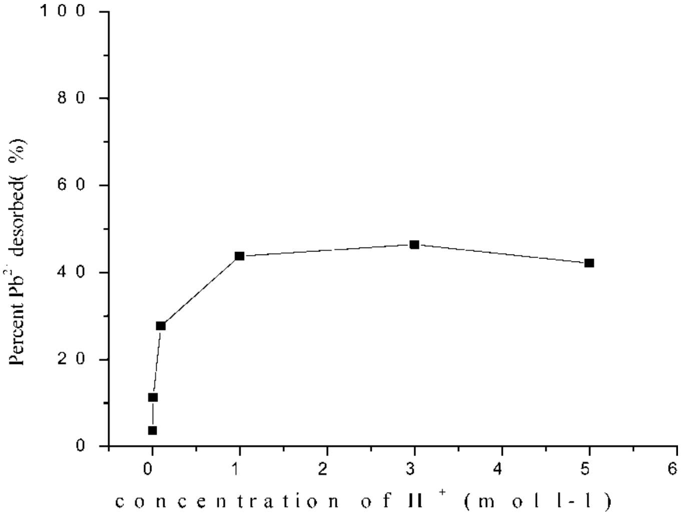

Figure 11. Desorption of Pb(II) on the vermiculite at different H^+ concentration. Conditions: vermiculite adsorbed Pb(II) dosage 4.0 g l^{-1}; contact time 30 min.

1. The pH studies indicated that Pb(II) adsorption on vermiculite increased from 49% to 98% when the pH was varied from 1.0 to 5.5. The optimum pH was 5.0 and the Pb(II) removal at this pH was 98%.
2. First order kinetics model best described the kinetics of adsorption of Pb(II) onto vermiculite, for which the correlation coefficient was $>$ 0.99. Kinetic data would be useful for the fabrication and designing of wastewater treatment plants.
3. Adsorption of Pb(II) onto vermiculite from 20 to 200 mg l^{-1} followed both Langmiur and Freundlich isotherm models. The equilibrium adsorption capacity increased with increasing temperature from 10 to 80°C, which indicated that the adsorption process was endothermic. For the adsorption process, the ΔH was 3.103 kJ mol^{-1}, the ΔS was 23.83 J mol^{-1} K^{-1}, and the ΔG were -3.720 (10°C), -4.115 (35°C), 4.776 (60°C), -5.412 (80°C) kJ mol^{-1} respectively.
4. The structure transformation for the vermiculite before and after adsorption of Pb(II) was measured by XRD, TA, and XPS. Results of XRD suggested that a cationic exchange between the Pb(II) and the cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in the clay had occurred. Results of XPS indicated that at least two Pb(II) forms adsorbed on vermiculite.

NOMENCLATURE

M	dissolved lead concentration, g l^{-1}
S	available surface sites of vermiculite
SM	adsorbed state of vermiculite
k_1	forward rate constant, min^{-1}
k_2	backward rate constant, min^{-1}
a	initial concentration of lead
x	amount transferred from liquid phase to solid phase
k	overall reaction rate constant, min^{-1}
X_e	concentration of lead adsorbed at equilibrium, mg g^{-1}
k_c	equilibrium constant
C_0	initial concentration of lead, mg l^{-1}
C_t	concentration of lead present at any time, mg l^{-1}
C_e	concentration of lead present at equilibrium, mg l^{-1}
Q_{max}	adsorption capacity, mg g^{-1}
b	Langmuir constant, l mg^{-1}
Q_e	amount adsorbed at equilibrium time, mg g^{-1}
K_F, n	Freundlich constants
K	equilibrium constants
ΔG	change in free energy, kJ mol^{-1}
ΔH	change in enthalpy, kJ mol^{-1}
ΔS	change in entropy, J mol^{-1} K^{-1}

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