Kinetic and thermodynamic studies of the adsorption of lead (II) ions onto phosphate-modified kaolinite clay

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Abstract

This study is on the kinetics and thermodynamics of the adsorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite clay obtained from Ubulu-Ukwu in Delta State of Nigeria. Increasing initial Pb^{2+} concentration increased the rate of Pb^{2+} adsorbed with increase in initial Pb^{2+} concentration from 300 to 1000 mg/L. Increasing Pb^{2+} concentration also increased the initial sorption rate h, from 1.404 to 13.11 mg g^{-1} min^{-1} for phosphate-modified kaolinite clay and 1.04–3.48 for unmodified kaolinite clay as Pb^{2+} concentration. Increase in temperature was found to increase the initial sorption rate of Pb^{2+} adsorption onto phosphate-modified adsorbent from 3.940 to 8.85 and 2.55 to 4.16 mg g^{-1} min^{-1} for the unmodified adsorbent. The overall sorption rate k, increased only slightly from 5.1×10^{-2} to 9.7×10^{-2} g mg^{-1} min^{-1} for phosphate-modified adsorbent, 3.8×10^{-2} to 5.4×10^{-2} g mg^{-1} min^{-1} for unmodified adsorbent. The adsorption reaction on both adsorbents was found to be chemically activated reaction and endothermic with energy of activation, E, at 500 mg/L of Pb^{2+} in solution as 19 and 10.68 kJ mol^{-1} for phosphate-modified and unmodified adsorbents, respectively. The positive values of both ΔH° and ΔS° obtained suggest an endothermic reaction and in increase in randomness at the solid–liquid interface during the adsorption of Pb^{2+} onto the adsorbents. ΔG° values obtained were all negative indicating a spontaneous adsorption process. The presence of Cd^{2+} decreased both initial sorption rate and the amount of Pb^{2+} adsorbed on phosphate-modified and unmodified adsorbents at equilibrium. The adsorption process follows a pseudo-second-order reaction scheme.
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1. Introduction

Lead is accumulated in the human system through a number of processes like breathing air from industrial environment (lead smelting, refining and manufacturing industries), ingesting plants or food grown on contaminated soils and breathing in fumes from hobbies that use lead (leaded-glass, ceramics). The health hazards resulting from the presence of lead in domestic and industrial wastewaters are of extreme concern to the public, government and industries for about two decades now [1]. The deleterious effects of lead on neurobehavioural development [2] and brain cell function [3] have been investigated. In view of these associate processes, the reaction pathways, and the mechanism of sorption reactions and to design appropriate sorption treatment plants, the study of the sorption kinetics of wastewater treatment have become imperative.

Numerous kinetic models have been investigated for the sorption of contaminants from wastewaters by sorbent materials. The mechanism of sorption often involves the chemical reaction between functional groups on the adsorbent and the metal ions or a cation-exchange reaction due to the high cation-exchange capacity (CEC) of the sorbent. Some other mechanisms may also be involved such as transport in the bulk of the liquid phase, diffusion across the liquid film surrounding the solid particles and diffusion in macrospores or microspores [4].

Recently, Ho and Ofomaja [5] studied the kinetics and thermodynamics of adsorption of lead on palm kernel fibre. The kinetics of the removal of lead and other metal ions by Sepiolite was also studied by Brigatti et al. [6]. The sorption of lead and other metal ions on peat [1,7–9] cassava.

Waste biomass [10], Thai Kaolin and ball clay [6], and on *Azadirachta indica* (Neem) leaf powder [11] has also been studied using the pseudo-second-order kinetics for sorption sphagnum moss peat [12–14]. Numerous studies report pseudo-first-order Lagargren kinetics for the sorption of metal ions, such as the sorption of arsenite(III) from aqueous solutions by

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haematite [15] and sorption of nickel(III) from aqueous solution by Wallastonite and China clay [16,17].

Although the kinetics of these and numerous other sorption systems have been investigated over the years, yet not much study in this regard have been carried out on clay minerals especially kaolinite and its phosphate-modified form. Phosphate has been shown to enhance the cation-exchange capacity (CEC) of kaolinite [18]. The simple but cost effective method of modifying kaolinite with phosphate has made phosphate-modified kaolinite clay a promising adsorbent in the removal of metal ions from aqueous solutions.

In this regard, this study investigates the effect of phosphate modification on the kinetics of the adsorption of lead onto kaolinite clay and the mechanism of lead ion adsorption on both phosphate-modified and unmodified kaolinite clay by the application of kinetic data obtained to fit existing kinetic models. This study will also consider the thermodynamics of the adsorption of lead onto both the phosphate-modified and unmodified kaolinite clay. These studies are carried out with the view of applying the phosphate-modified kaolinite adsorbent in the removal of lead ions from lead contaminated wastewater. The data obtained will also be useful in remediation of lead contaminated soils.

1.1. Materials and methods

Kaolinite clay was obtained from Ubulu-Ukwu, Delta State, Nigeria. On collection, stones and other heavy particles were removed from the sample. It was then sieved through a 230-mesh sieve to remove the larger non-clay fractions from the clay. A part of the raw kaolinite was kept suspended in doubly deionised water in a 1 L beaker for several hours. It was further purified using the method of Moore and Reynolds [19]. This involves the stirring of the mixture in small amount of 30% hydrogen peroxide solution till all effervescence has ceased. This treatment removes any organic substances remaining in the clay. The mixture was kept standing overnight. The supernatant was decanted and the kaolinite clay washed thoroughly with deionised water to remove traces of hydrogen peroxide before being used. The suspended Kaolin was centrifuged and oven dried at 343 K to obtain the kaolin sample. The mineralogical composition of the kaolinite clay sample was determined using a DIANO 2100E X-ray diffractometer.

The physicochemical parameters of both phosphate-modified and unmodified kaolinite clay used for this study are given by Adebowale et al. [18]. The unmodified kaolinite was found to have a specific surface area (SSA) of $12.80 \, m^2 \, g^{-1}$ and an effective cation-exchange capacity (ECEC) of 7.81 mequiv./100 g. The phosphate-modified kaolinite clay was found to have an ECEC of 13.45 mequiv./100 g.

1.2. Modification of clay sample

Clay samples (100 g) were equilibrated with 2 L of 200 mg/L of KH_2PO_4 in a rotary orbital shaker for 24 h. Thereafter, the clay samples were washed three times with 1 L portion of doubly deionised water in order to remove excess $H_2PO_4^-$ ions. Test for phosphate in solution was confirmed negative. The sample was subsequently dried in an oven at 343 K. The particle size of both phosphate-modified and unmodified adsorbent used was 100 μm.

1.3. Kinetics of Pb^{2+} adsorption

Stock solution of 1000 mg/L each of the standardized Pb^{2+} was prepared from its nitrate salt using distilled–deionised water. 300, 500 and 1000 mg/L of Pb^{2+} solutions were subsequently prepared and the solutions were adjusted to pH 6.0 ± 0.2 with either 0.1 M NaOH or HCl. Kinetic experiments were carried out by batch adsorption method at room temperature ($28.0 \pm 2 \, ^\circ C$) on a rotary shaker at 100 rpm using 120 mL capped polyethylene bottles containing 20 mL of 300, 500 and 1000 mg/L of Pb^{2+} solutions and 1 g of both phosphate-modified and unmodified kaolinite clay adsorbents. Samples were withdrawn from the shaker at different time intervals and the suspensions were centrifuged. The supernatants were then collected and analyzed for the metal ions.

The effect of temperature on the kinetics of the adsorption of Pb^{2+} was studied by adding 20 mL of 500 mg/L Pb^{2+} solution (at pH 6.0 ± 0.2) to 1 g of phosphate-modified and unmodified kaolinite clay in 120 mL capped polyethylene bottles at 298, 313 and 323 K. These were agitated in a G24 Environmental Incubator Shaker (New Brunswick Scientific model, Edison, NJ, USA) that is thermostated. Samples were withdrawn from the shaker at different time intervals. Suspensions obtained were centrifuged and the supernatants were analyzed for the metal ions.

The effect of the presence of Cd^{2+} on the kinetics of the adsorption of Pb^{2+} was studied by mixing the exact weights required to prepare 500:500 mg/L and 500:100 mg/L Pb:Cd mixed metal ion solutions in 1 L solution of distilled–deionised water. Their pH were adjusted to 6.0 ± 0.2 using 0.1 M NaOH or HCl. Twenty milliliters of the mixed metal ion solutions were then added to 1 g of phosphate-modified and unmodified kaolinite clay in 120 mL capped polyethylene bottles. These were agitated in a rotary shaker at room temperature ($28.0 \pm 2 \, ^\circ C$). Samples were withdrawn from the shaker at different time intervals. Suspensions obtained were centrifuged and the supernatants were analyzed for the metal ions.

Blank samples containing lead ions without the adsorbent were also used in this study. Samples were run in duplicates. The amounts of lead and cadmium ions adsorbed by the adsorbents were calculated by difference using the formula:

$$q_e \, (mg/g) = \frac{C_0 - C_e \, (V/1000) \, L}{W \, (g)} \quad (1)$$

where q_e is the amount of metal ion adsorbed on the adsorbent, C_0, the initial metal ion concentration (mg/L), C_e, the equilibrium concentration of metal ion in solution (mg/L), V, the volume of metal ion solution used (mL), and W, is the weight of the adsorbent used (g). The readings were obtained using a Computer-Aided Solar Series, Model 969, flame atomic absorption spectrometer (FAAS). The absorption lines used for lead and cadmium ions are 283.3 and 228.3 nm, respectively. An air–acetylene flame was used.

1.4. The pseudo-second-order model

The sorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite may involve a chemical sorption. Ho [20] developed a pseudo-second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat. This model has since been widely applied to a number of metal/sorbent sorption systems [21,22]. To investigate the mechanism of sorption and the rate constants for the adsorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite clay the pseudo-second-order equation given below was used:

$$q_t = \frac{kq_e^2 t}{1} + kt \quad (1)$$

The differential equation is as follows:

$$\frac{dqt}{dt} = k(q_e - qt)^2 \quad (2)$$

Integrating Eq. (2) for the boundary conditions $t = 0$ to t and $qt = 0$ to qt, gives:

$$\frac{1}{(q_e - qt)} = \frac{1}{q_e} + kt \quad (3)$$

When Eq. (3) is linearized it gives

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

where q_e is the amount of Pb^{2+} adsorbed at equilibrium (mg/L), qt amount of Pb^{2+} adsorbed at time t (mg g^{-1}) and k is the rate constant of the pseudo-second-order sorption (g mg^{-1} min^{-1}).

The initial sorption rate can be obtained as qt/t approaches zero:

$$h = kq_e^2 \quad (5)$$

where h is the initial sorption rate (mg g^{-1} min^{-1}).

2. Results and discussions

2.1. Mineralogical composition of kaolinite clay

The Mineralogical composition of the clay is presented in Fig. 1. It was observed that it contained basically: kaolinite (61%), illite (11%), quartz (25.5%) and hematite (2.5%).

2.1.1. Effect of initial lead concentration on kinetics

Figs. 2 and 3 show the adsorption capacity of both phosphate-modified and unmodified kaolinite clay as a function of time and initial concentration of Pb^{2+}. From the figures it was observed that the amount of Pb^{2+} uptake, q_e (mg g^{-1}) and the amount of Pb^{2+} adsorbed per time increases with contact time at all initial Pb^{2+} concentrations. When plots of q_e versus time, the rate of adsorption was obtained from the slope. The rate of adsorption of Pb^{2+} on phosphate-modified kaolinite clay for the first 8 min was found to increase from 0.3422 to 1.5521 and 0.3180 to 1.0321 mg g^{-1} min^{-1} for the phosphate-modified and unmodified kaolinite clay adsorbent,
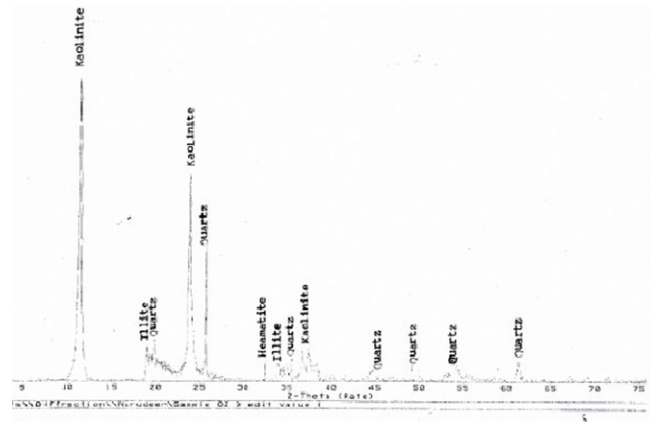

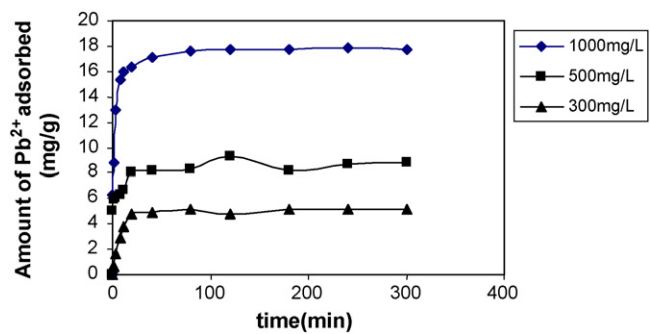Fig. 1. X-ray diffraction pattern of unmodified kaolinite clay.

Fig. 2. Effect of initial Pb^{2+} concentration on kinetics of the adsorption of Pb^{2+} on modified kaolinite clay.

respectively, with increase in initial Pb^{2+} concentration from 300 to 1000 mg/L. Between 8 and 80 min the rate of adsorption of Pb^{2+} decreased with phosphate-modified kaolinite clay given 0.0155, 0.0169, 0.0227 mg g^{-1} min^{-1} and unmodified kaolinite clay given 0.0328, 0.0188, 0.0254 mg g^{-1} min^{-1} for 300, 500 and 1000 mg/L of initial Pb^{2+} concentration. Above 80 min the rate of Pb^{2+} decreased further.

It is observed from the above that there is an initial rapid adsorption of Pb^{2+} for the first 8 min and thereafter the adsorption proceeds at a slower rate until it finally attains equilibrium. The higher initial sorption rate may be due to an increased number of vacant adsorption sites available at initial stage of the adsorption process which results in an increased concentration gradient between the solute in solution and the solute
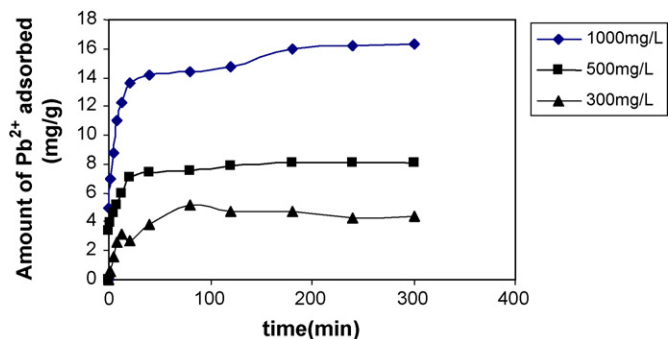

Fig. 3. Adsorption of varying concentrations of Pb^{2+} on unmodified kaolinite clay at various contact time.
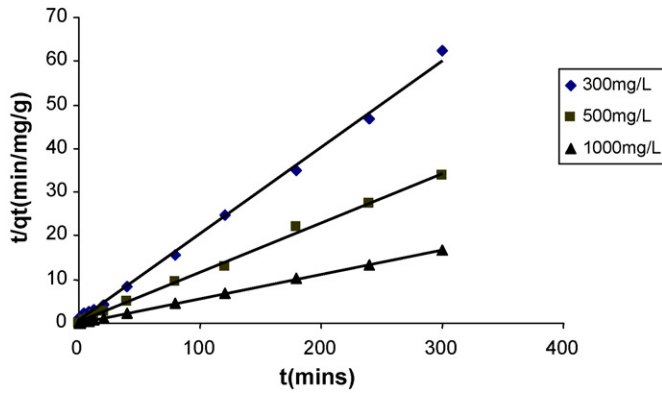
Fig. 4. Pseudo-second-order plots for adsorption of Pb ions on phosphate-modified sorbent at 298 K.

Fig. 5. Pseudo-second-order plots for adsorption of Pb ions on unmodified sorbent at 298 K.

on the adsorbent surface. This increased concentration gradient tends to increase the rate at which Pb^{2+} is adsorbed at the initial stage of adsorption. This concentration gradient is reduced with increasing contact time because of accumulation of Pb^{2+} on the vacant adsorption sites which invariably leads to decreased adsorption rate of Pb^{2+} at the later stages of adsorption (8–300 min).

The results were also analyzed using the pseudo-first- and -second-order models. Data obtained gave poor fits with the pseudo-first-order model after 8 min of reaction time but very good fits with the pseudo-second-order model at all reaction times as shown by the correlation coefficients in Tables 1 and 2. Figs. 4 and 5 show a linear variation of t/q_t with time, t (Eq. (4)) for both phosphate-modified and unmodified kaolinite clay at different initial metal ion concentration. The initial sorption rate h, pseudo-second-order rate constant k, amount of Pb^{2+} adsorbed at equilibrium q_e obtained from the pseudo-second-order model are given in Tables 1 and 2. Increasing Pb^{2+} concentration increased the initial sorption rate h (Eq. (5)) from 1.404 to 13.11 $mg\,g^{-1}\,min^{-1}$ for phosphate-modified kaolinite clay and 1.04 to 3.48 $mg\,g^{-1}\,min^{-1}$ for unmodified kaolinite clay as Pb^{2+} concentration was increased from 300 to 1000 mg/L. The amount of Pb^{2+} adsorbed at equilibrium, q_e, was also found to follow this trend with phosphate-modified clay showing an increase in q_e from 5.05 to 17.89 $mg\,g^{-1}$ and unmod-
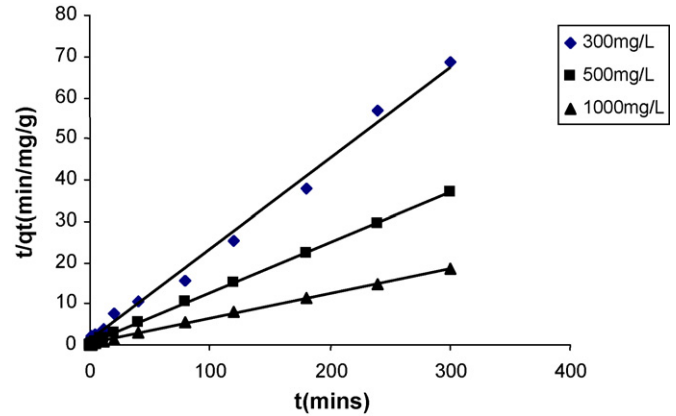
ified kaolinite clay from 4.51 to 16.37 $mg\,g^{-1}$ with increased Pb^{2+}.

Modification of kaolinite clay with phosphate tends to increase initial sorption rate h, especially at very high concentrations. The increased initial sorption rate h, and the increased amount of Pb^{2+} adsorbed, q_e, is expected as increased initial Pb^{2+} concentration produces a higher driving force that should result in a more rapid change in the rate at which Pb^{2+} is adsorbed initially onto both the phosphate-modified and the unmodified kaolinite clay adsorbents [23]. However, there was an observed decrease in the pseudo-second-order rate constant, k, for the adsorption of Pb^{2+} on both the phosphate-modified and unmodified kaolinite clay, as initial Pb^{2+} concentration was increased (Tables 1 and 2). This trend indicates that the time for the adsorption of Pb^{2+} to reach equilibrium is extended with increased initial Pb^{2+} concentration. The linearity of the plots of the pseudo-second-order model in Figs. 4 and 5 indicates that chemical reaction rather than physisorption is the main rate-controlling step throughout most of the adsorption process [30,23] and that the mechanism follows a pseudo-second-order reaction scheme. The corresponding linear plots of k, h and q_e can be expressed as a function of C_0 for the adsorption of Pb^{2+} onto phosphate-modified kaolinite as

$$k = 0.0591 - 0.00002C_0, \quad R^2 = 0.9902 \qquad (6)$$

Table 1

Pseudo-second-order rate constant for the adsorption of varying concentration of Pb^{2+} on phosphate-modified kaolinite clay

Concentration (mg/L)	R^2	q_e ($mg\,g^{-1}$)	k ($g\,mg^{-1}\,min^{-1}$)	h ($mg\,g^{-1}\,min^{-1}$)
300	0.9975	5.05	5.5×10^{-2}	1.40
500	0.9977	8.79	5.1×10^{-2}	3.94
1000	1.0000	17.89	4.1×10^{-2}	13.11

Table 2

Pseudo-second-order rate constant for the adsorption of varying concentration of Pb^{2+} on unmodified kaolinite clay

Concentration (mg/L)	R^2	q_e ($mg\,g^{-1}$)	k ($g\,mg^{-1}\,min^{-1}$)	h ($mg\,g^{-1}\,min^{-1}$)
300	0.9937	4.51	5.2×10^{-2}	1.04
500	0.9998	8.19	3.8×10^{-2}	2.55
1000	0.9987	16.37	1.3×10^{-2}	3.48

Fig. 6. Pseudo-second-order plots for the adsorption of 500 mg/L of Pb ions on modified adsorbent at varying temperature.
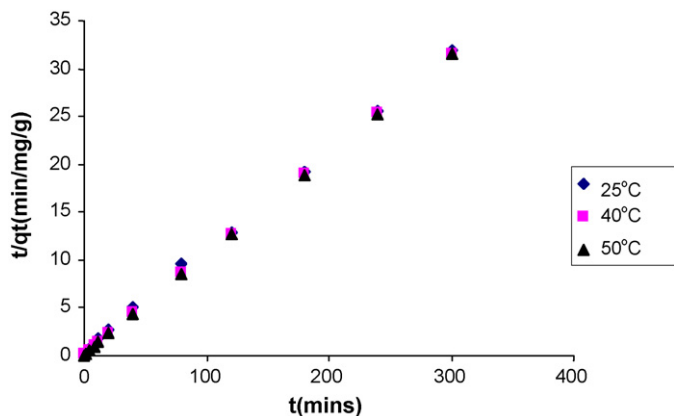

Fig. 7. Pseudo-second-order plots for adsorption of 500 mg/L of Pb ions on unmodified adsorbent at varying temperatures.

$$h = 0.015C_0 - 2.3548, \quad R^2 = 0.9704 \tag{7}$$

$$q_e = 0.0163C_0 + 1.3573, \quad R^2 = 0.9913 \tag{8}$$

and for unmodified kaolinite clay:

$$k = 0.062 - 0.00005C_0, \quad R^2 = 0.9997 \tag{9}$$

$$h = 0.0029C_0 + 0.6971, \quad R^2 = 0.9238 \tag{10}$$

$$q_e = 0.015C_0 + 1.2004, \quad R^2 = 0.9948 \tag{11}$$

2.2. Effect of temperature on kinetics lead ion adsorption

Figs. 6 and 7 show plots of the linearized form of the pseudo-second-order model for the adsorption of 500 mg/L of Pb^{2+} at different temperatures. Variation in temperature influenced the time required for the adsorption of Pb^{2+} to reach equilibrium. Increase in temperature in the range of 298 to 323 K increased the initial sorption rate h, of Pb^{2+} on both phosphate-modified and unmodified kaolinite clay adsorbent (Tables 3 and 4). The phosphate-modified adsorbent showed higher initial sorption rate h. The values of the pseudo-second-order rate constant k were found to slightly increase from 0.051 to 0.055 mg g^{-1} min^{-1} with an increase in temperature from 298 to 313 K for phosphate-modified kaolinite clay but increased
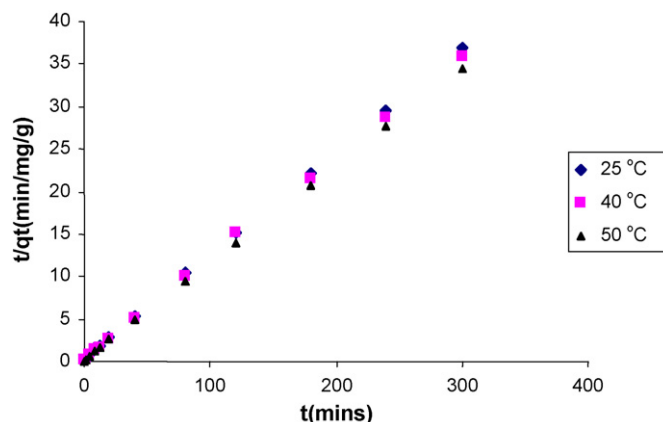
to 0.097 mg g^{-1} min^{-1} when temperature of adsorbate solution reached 323 K (Table 3). For the unmodified kaolinite clay, increase in temperature from 298 to 323 K resulted in an increase in the rate constant (Table 4). This may suggest that increasing temperature may increase the driving force of Pb^{2+} onto the adsorbents.

However, there is only a slight increase in the amount of Pb^{2+} (mg g^{-1}) adsorbed at equilibrium q_e, with increase in temperature from 298 to 323 K (Tables 3 and 4). This same observation was made by Ho et al. [14] when he studied the sorption of lead ions from aqueous solution using tree fern as a sorbent. This could indicate that increasing temperature of adsorbate solution does not necessarily increase adsorption sites on the adsorbent but produce a new pathway that increase only slightly the rate of adsorption of the adsorbate onto the adsorbent.

The relationship between the pseudo-second-order rate constant and temperature may be described by the equation:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{12}$$

where k is the pseudo-second-order rate constant of sorption (mg g^{-1} min), k_0 the temperature-independent factor (g mg^{-1} min^{-1}), E the activation energy of sorption (kJ mol^{-1}), R the gas constant (8.314 J mol^{-1} K) and T the absolute temper-

Table 3

Pseudo-second-order rate constant for the adsorption of 500 mg/L Pb^{2+} onto phosphate kaolinite clay at varying temperature

Temperature (K)	R^2	q_e (mg g^{-1})	k (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})
298	0.9977	8.79	5.1×10^{-2}	3.94
313	0.9999	9.52	5.5×10^{-2}	4.96
323	1.0000	9.54	9.7×10^{-2}	8.85

Table 4

Pseudo-second-order rate constant for the adsorption of 500 mg/L Pb^{2+} onto unmodified kaolinite clay at varying temperatures

Temperature (K)	R^2	q_e (mg g^{-1})	k (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})
298	0.9998	8.19	3.80×10^{-2}	2.55
313	0.9997	8.42	4.18×10^{-2}	2.96
323	0.9999	8.77	5.41×10^{-2}	4.16

Fig. 8. Relationship between T and K for phosphate-modified and unmodified kaolinite clay ($Pb^{2+} = 500$ mg/L).
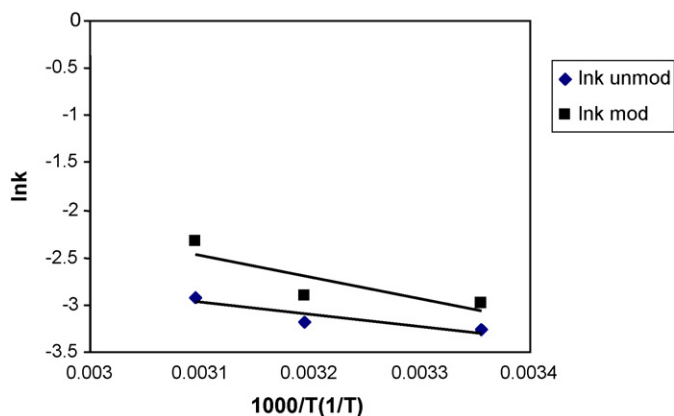

Fig. 9. Relationship between $1/T$ and $\log(q_e/C_e)$ for phosphate-modified and unmodified kaolinite clay ($Pb^{2+} = 500$ mg/L).

ature (K). When ln k is plotted against $1/T$, a straight line with slope $-E/R$ is obtained. The magnitude of activation energy may give an idea about the type of adsorption. Two main types of adsorption: physical and chemical are possible. In physical adsorption the reaction is easily reversible, equilibrium is rapidly attained and its energy requirements are small. The activation energy for physical adsorption is usually not more than 4.2 kJ mol^{-1} (1.0 kcal mol^{-1}), because the forces involved in physical adsorption are usually weak. So the activation energy is of the same magnitude as the heat of chemical reactions. This type of adsorption is usually referred to as *physisorption*. However, chemical adsorption is specific and involves forces much stronger than in physical adsorption. It is usually referred to as *chemisorption* [24].

The values of ln k (the rate constant obtained from the pseudo-second-order model) were plotted as a function of the reciprocal of the temperature (T) for the adsorption of 500 mg/L Pb^{2+}. The linear variation is shown in Fig. 8 for both phosphate-modified and unmodified kaolinite clay for the adsorption of 500 mg/L of Pb^{2+}. The values of E (11.9, 19.0, 5.12 kJ mol^{-1} for phosphate-modified kaolinite clay and 5.64, 10.68, and 4.32 kJ mol^{-1} for unmodified kaolinite clay for metal ion concentration 300, 500, 1000 mg/L (plots not shown except that for 500 mg/L) were obtained. This suggests that the adsorption of Pb^{2+} on both phosphate-modified and unmodified kaolinite is an activated chemical adsorption and that the adsorption is endothermic in nature. The values of E obtained indicate that the energy of activation increases as concentration increases up to 500 mg/L and then decreases. This may indicate that above 500 mg/L of adsorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite clay the adsorption process may begin to move towards a non-activated chemical adsorption process.

2.3. Thermodynamic parameters of adsorption

The thermodynamic parameters such as change in enthalpy, ΔH°, change in entropy, ΔS°, and change in Gibbs free energy, ΔG° of the adsorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite clay can be related to the distribution coefficient of solute between the solid and liquid phases by the equation [14,25,26]:
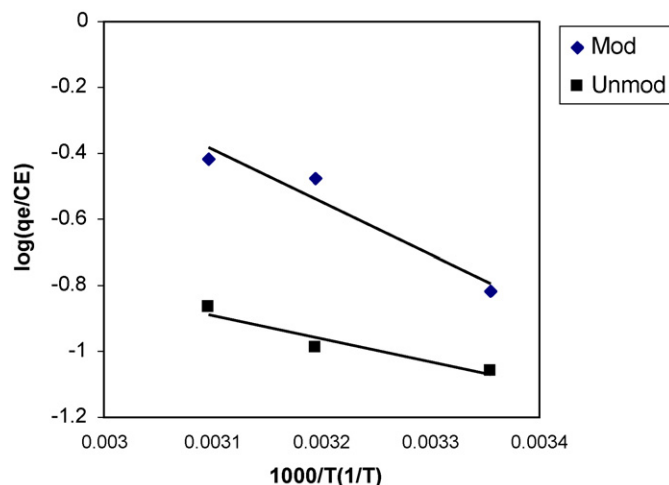
$$\log \frac{q_e(t)}{C_e(t)} = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{13}$$

$$\Delta G^\circ = -RT \ln K_c \tag{14}$$

where ΔS° and ΔH° is the standard entropy and enthalpy for the adsorption process, $q_e(t)$ is the adsorption capacity (mg g^{-1}) of the adsorbent for Pb^{2+} after time (t) of adsorption and is obtained from the slope of the plot of t/q_t versus t and $C_e(t)$ is equilibrium concentration (mg/L) of Pb^{2+} after time t of adsorption onto adsorbents. R is the ideal gas constant and T is the temperature, ΔG° is the Gibbs free energy and $K_c = C_{ad}/C_e$. Where C_{ad} is the amount of Pb^{2+} adsorbed at equilibrium, and C_e is the amount of Pb^{2+} in solution at equilibrium [24].

Adsorption of 500 mg/L Pb^{2+} onto phosphate-modified and unmodified kaolinite clay increased slightly with increasing adsorbate solution temperature from 298 to 323 K (Figs. 6 and 7). The adsorption process on both adsorbent was found to be endothermic when 500 mg/L of Pb^{2+} was used for adsorption. The plots of $\log(q_e/C_e)$ versus $1/T$ (Fig. 9) were used to obtain the values of the thermodynamic parameters (Table 7). The change in enthalpy ΔH°, during adsorption of Pb^{2+} was found to be $+30.41$ and $+13.67$ kJ mol^{-1} for phosphate-modified and unmodified kaolinite clay, respectively. The entropy change ΔS°, for phosphate-modified was $+86.86$ J mol^{-1} K and that for the unmodified was $+25.34$ J mol^{-1} K. The values of ΔH° obtained shows that the adsorption of Pb^{2+} onto both adsorbents was endothermic with adsorption onto phosphate-modified adsorbent being more endothermic. The positive values of entropy may be due to some structural changes in the adsorbate and adsorbents during the adsorption process from aqueous solution onto the adsorbents. In addition, positive value of ΔS° indicates the increasing randomness at the solid–liquid interface during the adsorption of Pb^{2+} on the adsorbents. Similar results for adsorption of metal ions onto kaolinite have been obtained [27,28,4].

The Gibbs free energy $\Delta G°$, of the adsorption process is given in Table 7 for both adsorbents. The free energy change $\Delta G°$ calculated for adsorption of Pb^{2+} on phosphate-modified are -5.06, -7.30, -7.91 KJ mol^{-1} and -3.62, -4.24, -5.13 KJ mol^{-1} for unmodified kaolinite clay at 298, 313, and 323 K, respectively. This indicates a spontaneous process which is to say that the adsorptive forces are strong enough to break the potential and shift the reaction ultimately to the right leading to binding of Pb^{2+} onto the surface constituents of both adsorbents. The increase in negative Gibbs free energy as temperature of Pb^{2+} solution increases indicates that the reaction becomes more favorable with increasing temperature of Pb^{2+} solution.

2.4. Adsorption mechanism

Prediction of the rate-limiting step and identifying the mechanism of an adsorption process are important factors to be considered for proper design purposes. For a solid–liquid adsorption process the adsorption of the solute (metal ion) is usually characterized by either mass transfer (boundary layer diffusion) or intraparticle diffusion or both [30].

The mechanism of sorption often involves the chemical reaction between surface functional groups on the adsorbents and the metal ions, thus forming metal–inorganic complexes, metal–organic complexes or a cation-exchange reaction due to high cation-exchange capacity of the adsorbent [23]. The adsorption dynamics can be described by the following three consecutive steps which are as follows:

(i) Transport of the solute from bulk solution through liquid film to the adsorbent exterior surface.
(ii) Solute diffusion into the pore of the adsorbent except for a small quantity of adsorption on the external surface; parallel to this is the intraparticle transport mechanism of the surface diffusion.
(iii) Adsorption of solute on the interior surfaces of the pores and capillary spaces of the adsorbent.

The last step is considered to be an equilibrium stage and very rapid. Thus it is assumed to negligible. The rate-determining step of an adsorption which invariably controls the overall rate of adsorption is the slowest step which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. Whatever the case, external diffusion will be involved in the adsorption process. Thus the adsorption of Pb^{2+} onto both phosphate-modified and unmodified kaolinite clay may be controlled by film diffusion at the initial stages and as surface charges are gradually used up, the adsorption process may then be controlled by intraparticle diffusion.

To identify the mechanism involved in an adsorption process the intraparticle diffusion plot is often used. Some workers have shown that the plot of q_t versus $t^{0.5}$ represents multilinearity, which is typical of adsorption processes that occur in two or more steps [29].
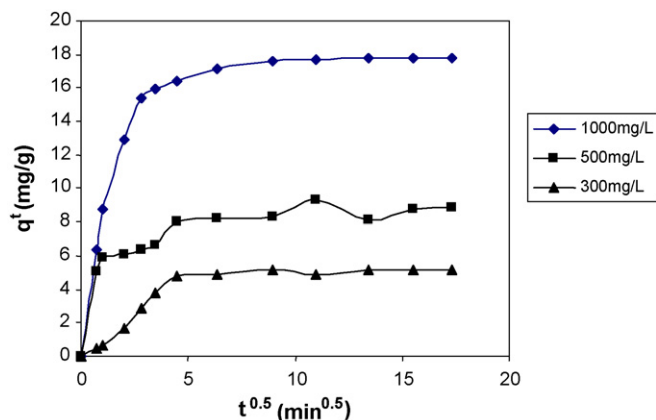

Fig. 10. Intraparticle diffusion plot for adsorption of Pb^{2+} onto phosphate-modified kaolinite clay.

The intraparticle diffusion coefficients K_i is defined by the equation:

$$K_i = \frac{q_t}{t^{0.5}} \tag{13}$$

Thus K_i (mg g^{-1} $min^{0.5}$) value can be obtained from the slope of the plot of q_t (mg g^{-1}) versus $t^{0.5}$ ($min^{0.5}$).

The presence of a 2:1 clay mineral (illite) in the sample used for this study makes it necessary to apply the intraparticle diffusion plot. Figs. 10 and 11 show the plot of q_t versus $t^{0.5}$ for the adsorption of Pb^{2+} on phosphate-modified and unmodified kaolinite clay at 298 K. It is observed that the adsorption process tends to follow two phases: a linear portion ended with a curve that gradually becomes constant. The two phases in the intraparticle diffusion plots suggest that the adsorption process proceeds by surface sorption and intraparticle diffusion. The initial curved portion of the plots indicates a boundary layer/film diffusion effect while the second linear portion is due to intraparticle/pore diffusion effect. The slope of the second linear portion of the plots as shown in Tables 5 and 6 has been defined as the intraparticle diffusion parameter K_i (mg g^{-1} $min^{0.5}$). However, the intercept of the plots reflects the boundary layer effect [30]. The larger the intercept the greater the contribution of the surface adsorption in the rate-
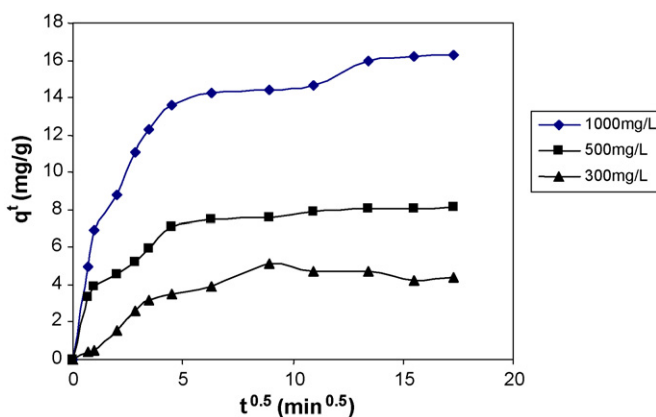

Fig. 11. Intrparticle diffusion plot for adsorption of Pb^{2+} onto unmodified kaolinite clay.

Table 5
Intercept and intra-particle diffusion parameter values obtained from plot q_t vs. $t^{0.5}$ for the adsorption of Pb^{2+} onto phosphate-modified kaolinite clay

Concentration (mg/L)	K_i (mg g^{-1} min$^{0.5}$)	Intercept values	R^2
300	0.965	1.900	0.9961
500	0.614	5.235	0.8555
1000	0.553	14.831	0.9933

Table 6
Intercept and intra-particle diffusion parameter values obtained from plot q_t vs. $t^{0.5}$ for the adsorption of Pb^{2+} onto unmodified kaolinite clay

Concentration (mg/L)	K_i (mg g^{-1} min$^{0.5}$)	Intercept values	R^2
300	0.621	1.143	0.9494
500	0.770	3.744	0.9814
1000	1.087	10.080	0.9781

limiting step. The calculated intraparticle diffusion coefficient K_i value for phosphate-modified was given as 0.965, 0.614 and 0.553 mg g^{-1} min$^{0.5}$ for initial Pb^{2+} of 300, 500 and 1000 mg/L, respectively. The unmodified kaolinite clay gave K_i values of 0.621, 0.770 and 1.087 mg g^{-1} min$^{0.5}$ for initial Pb^{2+} concentrations of 300, 500 and 1000 mg/L (Table 6). This suggests that phosphate modification of kaolinite clay reduces the effect of intraparticle diffusion on the adsorption of Pb^{2+} onto kaolinite clay with increasing initial Pb^{2+} concentration and vice versa for adsorption of Pb^{2+} onto the unmodified adsorbent. However, the intercept values from the plot of q_t versus $t^{0.5}$ were much higher than the intraparticle values for both phosphate-modified and unmodified kaolinite clay as shown in Tables 5 and 6. This indicates that the contribution of surface adsorption in the adsorption of Pb^{2+} onto both types of adsorbent is more than that of intraparticle diffusion especially the phosphate-modified adsorbent. This tend to suggest that external mass transfer of Pb^{2+} onto both phosphate-modified and unmodified adsorbent is the rate-limiting step and hence mainly governs the adsorption process.

2.5. Effect of the presence of cadmium on the adsorption of lead

The effect of the presence of cadmium on the adsorption of lead onto phosphate-modified and unmodified kaolinite clay is shown in Figs. 12 and 13. There was an 14.6% and 28.9% drop in the amount of Pb^{2+} adsorbed onto phosphate-modified and unmodified kaolinite clay at equilibrium, q_e, respectively, when 500 mg/L of both Pb^{2+} and Cd^{2+} where present in the same solution. When 100 mg/L of Cd^{2+} was present with 500 mg/L of Pb^{2+} in solution the amount of Pb^{2+} adsorbed at equilibrium, q_e, dropped by 1.7% and 23.7% for adsorption onto phosphate-modified and unmodified kaolinite clay. This indicates that the
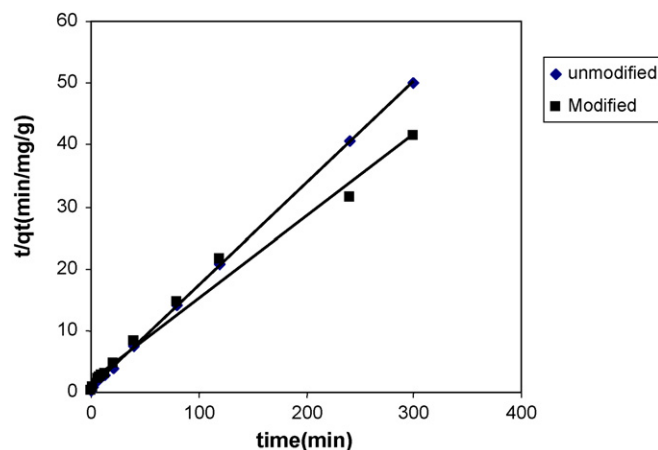

Fig. 12. Pseudo-second-order plots for the adsorption of 500:500 mg/L Pb:Cd mixed metal solution.
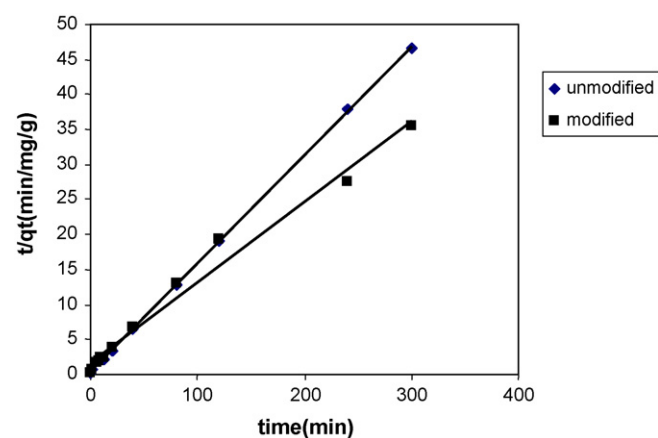

Fig. 13. Pseudo-second-order plot for the adsorption of 500:100 mg/L Pb:Cd mixed metal solution.

presence of Cd^{2+} affects to some extent the adsorption of Pb^{2+} onto both phosphate-modified and unmodified kaolinite clay because of competition between metal ions. Furthermore, changing the concentration of Cd^{2+} from 100 to 500 mg/L decreased the amount of Pb^{2+} adsorption onto both adsorbents further (Tables 8 and 9). However, in the presence of both concentrations of Cd^{2+}, phosphate-modified adsorbent showed stronger preference for Pb^{2+} than the unmodified adsorbent.

With 500 mg/L of both Pb^{2+} and Cd^{2+} in the same solution, the initial sorption rate, h, for adsorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite clay also experienced a decrease from 3.94 to 0.55 and 2.55 to 1.36 mg g^{-1} min^{-1}, respectively. For a mixed metal ion solution of 500:100 mg/L of Pb^{2+} and Cd^{2+}, respectively, it decreased to 0.66 mg g^{-1} min^{-1}

Table 7
Thermodynamic parameters for the adsorption of 500 mg/L Pb^{2+} onto phosphate-modified and unmodified kaolinite clay

		298 K	313 K	323 K	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K)
P-Mod	$-\Delta G$ (kJ mol^{-1})	5.06	7.30	7.91	+30.41	+86.86
Unmod	$-\Delta G$ (kJ mol^{-1})	3.62	4.24	5.13	+13.67	+25.34

Table 8
Pseudo-second-order rate constant for the adsorption of mixed concentrations of Pb^{2+} and Cd^{2+} ions on phosphate-modified kaolinite clay

Conc. Pb:Cd (mg/L)	R^2	q_e Pb (mg g^{-1})	k (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})
500:100	0.9817	8.64	8.8×10^{-3}	0.66
500:500	0.9854	7.51	9.8×10^{-3}	0.55

Table 9
Pseudo-second-order rate constant for the adsorption of mixed concentrations of Pb^{2+} and Cd^{2+} ions on unmodified kaolinite clay

Conc. Pb:Cd (mg/L)	R^2	q_e Pb (mg g^{-1})	k (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})
500:100	0.9998	6.48	4.6×10^{-2}	1.95
500:500	0.9998	6.04	3.7×10^{-2}	1.36

for phosphate-modified and 1.95 mg g^{-1} min^{-1} for the unmodified adsorbent. This drop in initial adsorption rate of Pb^{2+} onto both adsorbents could be as a result of competition between Pb^{2+} and Cd^{2+} in solution. The very large decrease in the initial sorption rate on phosphate-modified adsorbent can be explained to mean that Cd^{2+} competes more favorably on the phosphate-modified adsorbent surface at the early stages of the adsorption process. This could be as a result of its smaller atomic radius compared to that of Pb^{2+}.

The presence of Cd^{2+} did reduce the overall pseudo-second-order rate constant of the adsorption of Pb^{2+} onto phosphate-modified kaolinite clay from 5.1×10^{-2} to 8.8×10^{-3} and 9.8×10^{-3} g mg^{-1} min^{-1} for 500:100 and 500:500 mg/L Pb:Cd, respectively. With the unmodified adsorbent an increase in the overall rate constant k, from 3.8×10^{-2} to 4.64×10^{-2} g mg^{-1} min^{-1} was observed for 500:100 mg/L Pb:Cd and a slight decrease from 3.8×10^{-2} to 3.73×10^{-2} g mg^{-1} min^{-1} for the 500:500 mg/L mixed solution of Pb and Cd (Tables 1, 2, 8 and 9).

Increasing concentration of Cd^{2+} present in solution from 100 to 500 mg/L reduced the overall rate of the adsorption of Pb^{2+} from 4.64×10^{-2} to 3.73×10^{-2} g mg^{-1} min^{-1} for the unmodified kaolinite clay (Table 9). However, an increase from 8.8×10^{-3} to 9.8×10^{-3} g mg^{-1} min^{-1} was observed for the phosphate-modified adsorbent (Table 8). This suggest that only the initial sorption rate h, and not the overall sorption rate k, of the adsorption of Pb^{2+} onto phosphate-modified kaolinite clay is negatively affected by an increased presence of Cd^{2+} (from 100 to 500 mg/L) in a 500 mg/L solution of Pb^{2+} while both initial sorption rate and overall adsorption rate are negatively affected in the unmodified adsorbent.

3. Conclusion

The modification of kaolinite clay with phosphate enhanced the rate at which Pb^{2+} is adsorbed on kaolinite. Increasing concentration Pb^{2+} in solution increased both the amount of Pb^{2+} adsorbed on phosphate-modified and unmodified kaolinite clay and its initial sorption rates on both adsorbents. However, there was a decrease in the overall rate of adsorption of Pb^{2+} onto the adsorbents with increasing initial Pb^{2+} concentration in aqueous solution. The adsorption reaction was found to be endothermic and spontaneous. Adsorption on phosphate-modified clay was

more endothermic and spontaneous. This indicates that increase in Pb^{2+} solution temperature will enhance the initial sorption rate and the amount of Pb^{2+} adsorbed from aqueous solution by both phosphate-modified and unmodified kaolinite clay. The change in entropy for both adsorbent was observed to be positive signifying that there is increase in randomness at the solid–liquid interface during the adsorption of Pb^{2+} onto the adsorbents. The adsorption of Pb^{2+} onto phosphate-modified and unmodified kaolinite clay was found to follow the pseudo-second-order reaction. The mechanism of adsorption onto both adsorbents was deduced to be chemisorption and the rate-limiting step is being controlled mainly by external mass transfer. The increasing concentration of Cd^{2+} in solution with Pb^{2+} reduced the initial sorption rate and the amount of Pb^{2+} adsorbed onto both phosphate-modified and unmodified kaolinite clay at equilibrium. The decrease in the initial sorption rate is more with adsorption of Pb^{2+} onto phosphate-modified adsorbent and this indicates that Cd^{2+} competes more favorably with Pb^{2+} for adsorption sites on phosphate-modified kaolinite surfaces at the early stages of the adsorption process. The overall rate constant was decreased by the presence of Cd^{2+} with phosphate-modified sample being more affected.

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