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Kinetic and thermodynamic aspects of the adsorption of Pb^{2+} and Cd^{2+} ions on tripolyphosphate-modified kaolinite clay

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Abstract

Kaolinite clay obtained from Ubulu-Ukwu, Delta state in Nigeria was modified with tripolyphosphate reagent to obtain TPP-modified Kaolinite clay. The kinetics and thermodynamics of the adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay were studied. Increasing temperature and initial metal ion concentration increased the sorption capacity of the adsorbent. The rates of adsorption of both Pb^{2+} and Cd^{2+} increased with increasing temperature but decreased with increasing initial metal ion concentration and time. The pseudo-second-order initial sorption rates for the sorption of Pb^{2+} were found to be higher than those of Cd^{2+}. Pseudo-first-order model was found to only describe well, the data obtained in the first 8 min of the adsorption process. The sorption of both metal ions was endothermic and spontaneous with ΔH° values of +13.94 kJ mol^{-1} and +24.93 kJ mol^{-1} for Pb^{2+} and Cd^{2+}, respectively. Activation energy values obtained were between +8 kJ mol^{-1} and +22 kJ mol^{-1}. These values suggest that the rate-controlling step in the adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay was diffusion-controlled. The sorption of metal ions from binary solutions of both metal ions at different initial metal ion concentrations reduced the initial sorption rates of the adsorption of Pb^{2+} by TPP-Kaolinite clay and increased that for Cd^{2+}. The adsorption capacity of TPP-Kaolinite clay for both metal ions was also decreased by simultaneous presence of both metal ions.

Keywords: Kaolinite clay; Endothermic; Adsorption of metals; Tripolyphosphate

1. Introduction

Over the years, there have been increased concerns about the pollution caused by elevated levels of heavy metal ions on the environment because of their toxic nature both to man and animals. Prominent among these pollutants are Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+} and Cr^{2+} [1]. The sorption of these heavy metal ion pollutants from aqueous solutions is an important process in wastewater treatment. The use of adsorbents has been found to circumvent the production of large amounts of sludge, usually, generated using alternative wastewater treatment techniques [2,3].

The proper design of sorption processes determines the efficiency of the treatment techniques. This involves an understanding of the reaction pathways, the mechanisms of sorption reactions and the rate of solute uptake at the solid–liquid interface. The study of the kinetics and the thermodynamics of the adsorption process will therefore be vital in providing the information.

Previous researchers have provided numerous kinetic models used to describe sorption processes. These include first-order [4], and second-order [5] reversible ones, and first-order [6], and second-order [7], irreversible ones, pseudo-first-order [8] and pseudo-second-order ones [9] based on the solution concentration. In addition, other researchers have provided additional information based on the capacity of the adsorbent. These includes Lagergren's first-order equation [10], Zeldowitsch's model [11] and Ho's second-order expression [2,3,12].

Susmita Sen and Bhattacharyya [1] have reported the kinetics and thermodynamics of the adsorption of Ni^{2+} on clays; Pb^{2+} on palm kernel fibre by Ho and Ofomaja [13]; Cu^{2+} and Pb^{2+} on grafted silica [14]; Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} on Kaolinite [15]. As far as we know, there is dearth of information on the kinetics and thermodynamics of Pb^{2+} and Cd^{2+} adsorption by tripolyphosphate-modified Kaolinite clay.

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We have studied the adsorption of some heavy metal ions on sulphate and phosphate-modified kaolinite clay [16,17]. In continuation of our studies, this article considers the kinetic and thermodynamic study of the adsorption of Pb^{2+} and Cd^{2+} on tripolyphosphate-modified Kaolinite clay. A kinetic analysis was carried out using the Lagergren pseudo-first-order and Ho's pseudo-second-order kinetic models. Standard thermodynamic models were used to obtain thermodynamic parameters.

2. 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-meshsieve to remove the larger non-clay fractions from the clay. A part of the raw kaolinite was kept suspended in doubly deionized water in a 1 L beaker for several hours. It was further purified using the method of Moore and Reynolds [18]. This involves the stirring of the mixture in small amount of 30% hydrogen peroxide solution till all effervescence 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 deionized 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 physicochemical parameters of Unmodified Kaolinite clay used for this study are given by Adebowale et al. [16].

2.1. Modification of clay sample

Clay samples (100 g) were equilibrated with 2 L of a certain concentration of tripolyphosphate in a rotary orbital shaker for 24 h. Thereafter, the clay samples (TPP-Kaolinite clay) were washed three times with 1 L portion of doubly deionized water in order to remove excess tripolyphosphate ions. Test for phosphate in solution was confirmed negative. The sample was then dried at 343 K in an oven.

2.2. Kinetics of Pb^{2+} and Cd^{2+} adsorption

Stock solution of 1000 mg/L each of the standardized Pb^{2+} and Cd^{2+} were prepared from their nitrate salts using distilled-deionized water. Equilibrium study was considered within the concentration range of (60–1000 mg/L) of Pb^{2+} and Cd^{2+}. A 300 mg/L, 500 mg/L and 1000 mg/L of Pb^{2+} and Cd^{2+} solutions were subsequently prepared and the solutions were adjusted to pH 5.5 ± 0.2 with either 0.1 M NaOH or HCl. Kinetic experiments were carried out by batch adsorption method at room temperature ($25.0 \pm 2\,^{\circ}C$) on a rotary shaker at 100 rpm, using 120 mL capped polyethylene bottles containing 20 mL of 300 mg/L, 500 mg/L and 1000 mg/L of Pb^{2+} and Cd^{2+} solutions, and 0.2 g of tripolyphosphate-modified Kaolinite clay (TPP-Kaolinite clay) adsorbents. Samples were withdrawn from the shaker at different time intervals (0–300 min) and analyzed for the metal ions.

The effect of temperature on the kinetics of the adsorption of Pb^{2+} and Cd^{2+} were studied by agitating 20 mL of 300 mg/L, 500 mg/L and 1000 mg/L Pb^{2+} and Cd^{2+} solutions (at pH 5.5 ± 0.2) added to 0.2 g of tripolyphosphate-modified Kaolinite clay in 120 mL capped polyethylene bottles at 298 K, 313 K and 323 K. These were agitated in a rotary shaker. Samples were withdrawn from the shaker at different time intervals and were analyzed for the metal ions.

The effect of the simultaneous presence of both Cd^{2+} and Pb^{2+} on the kinetics of their adsorption was studied by mixing the exact weights required to prepare 500:500 mg/L, 100:500 mg/L and 500:100 mg/L Pb:Cd mixed metal ion solutions in 1 L solution of distilled-deionized water. Their pH were adjusted to 5.5 ± 0.2, using 0.1 M NaOH or HCl. Twenty millilitres of the mixed metal ion solutions were then added to 0.2 g of tripolyphosphate-modified Kaolinite clay in 120 mL capped polyethylene bottles. These were agitated in a rotary shaker at room temperature ($25.0 \pm 2\,^{\circ}C$). Samples were withdrawn from the shaker at different time intervals and were analyzed for the metal ions.

The amounts of lead and cadmium ions adsorbed by the adsorbents were calculated by difference using the formula:

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

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 (L), 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).

2.3. Pseudo-first-order model

Lagergren equation [10] also called the pseudo-first-order equation was applied, assuming that the number of metal ions outnumbers the number of adsorption sites on clay surface. The expression for the pseudo-first-order rate constant, k_1, where q_e is the adsorption capacity of the adsorbent ($\mathrm{mg\,g^{-1}}$) and qt is the amount of metal ion adsorbed at time t ($\mathrm{mg\,g^{-1}}$), is given by the differential rate law:

$$\frac{\mathrm{d}qt}{\mathrm{d}t} = k_1(qe - qt) \tag{2}$$

which on integration under the boundary conditions of $t=0$ to $t=t$ and $qt=0$ to $qt=qt$, gives a linear expression,

$$\ln(qe - qt) = \ln qe - k_1 t \tag{3}$$

The values of k_1 can be obtained from the slope of the plot of $\log(qe - qt)$ versus t.

2.4. The pseudo-second-order model

The sorption of Pb^{2+} onto phosphate-modified and Unmodified Kaolinite may involve a chemical sorption. Ho [19] 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 also to a number of metal/sorbent sorption systems. To investigate the mechanism of the adsorption and the rate constants for the adsorption of Pb^{2+} and Cd^{2+} onto tripolyphosphate-modified Kaolinite clay, the pseudo-second-order equation given below was used.

$$qt = kq_e^2 t \tag{4}$$

The differential equation is as follows:

$$\frac{dq_t}{dt} = \frac{k(q_e - q_t)^2}{1 + k_t} \tag{5}$$

Integrating Eq. (1) for the boundary conditions $t = 0$ to $t = t$ and $qt = 0$ to $qt = qt$, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_t \tag{6}$$

When this is linearized, it gives

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{7}$$

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

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

$$h = kq_e^2 \tag{8}$$

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

2.5. Thermodynamics of adsorption

The thermodynamic studies were carried out by agitating various concentrations (in the range of 60–1000 mg/L) of Pb^{2+} and Cd^{2+} solutions in 0.2 g of TPP-Kaolinite clay at 298 K, 313 K and 323 K. Samples were analyzed for metal ion after 3 h of agitation. The thermodynamic parameters for the adsorption process, ΔH°, ΔS°, and ΔG° were evaluated using the equations [1].

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

where b is the constant obtained from Langmuir plots at different temperatures, ΔS° and ΔH° the entropy and enthalpy of adsorption, R the gas constant (8.314 J mol^{-1} K) and T is the absolute temperature. The plots of $\ln b$ versus $1/T$ is linear with the slope and intercepts giving ΔH° and ΔS°, respectively. To compute ΔG°, Gibbs free energy, the Gibbs equation below was used [20],

$$\ln \frac{1}{b} = \frac{\Delta G^\circ}{RT} \tag{10}$$

or

$$\Delta G^\circ = -RT \ln b$$

For the evaluation of activation energy, ΔE, from kinetic data, Eq. (8) below was applied.

$$k = k_o \exp^{(-\Delta E/RT)} \tag{11}$$

here k is the pseudo-second-order rate constant of sorption (mg g^{-1} min), $k_{o,}$ the temperature-independent factor (g/mg min), ΔE, the change in activation energy of sorption (kJ/mol), R, the gas constant (8.314 J/mol K) and T, is the solution temperature (K). When $\ln k$ is plotted against $1/T$, a straight line with slope $-\Delta E/R$ is obtained.

3. Results and discussions

3.1. Effect of initial metal ion concentration

3.1.1. Initial sorption rate

The initial sorption rate of TPP-Kaolinite clay calculated from the slope of the plots (Figs. 1 and 2) of the amounts of metal ion adsorbed against various range of time, at temperature of 298 K (Table 1) showed that increasing initial Pb^{2+} and Cd^{2+} concentration increased initial sorption rates of these

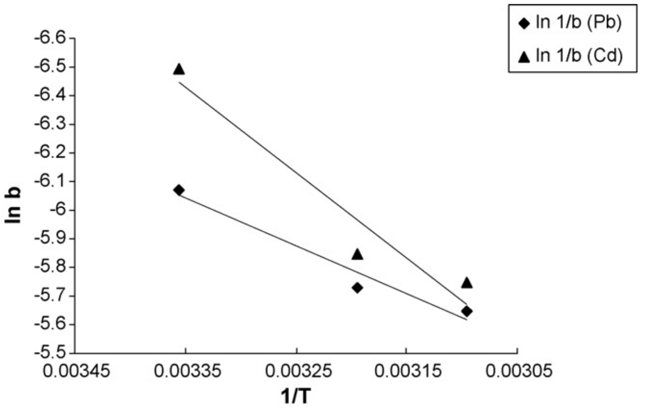

Fig. 1. Relationship between *T* and *b*.

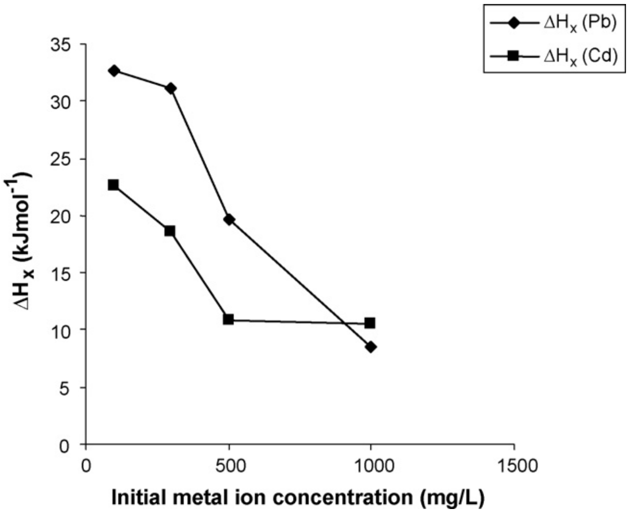

Fig. 2. The relationship between isosteric heat of adsorption TPP-Kaolinite clay surface loadings by metal ions.

Table 1
Initial sorption rate constant obtained from slopes of plots of q_t versus t

	Lead ($mg\,g^{-1}\,min^{-1}$)			Cadmium ($mg\,g^{-1}\,min^{-1}$)		
	300 mg/L	500 mg/L	1000 mg/L	300 mg/L	500 mg/L	1000 mg/L
1–8 min						
298 K	1.7695	2.590	4.6475	1.8985	2.2595	5.0225
313 K	2.4575	2.698	6.4550	2.1235	2.3160	6.1645
323 K	2.5505	3.442	7.4405	2.4050	2.5215	6.3755
9–60 min						
298 K	0.0132	0.0838	0.4219	0.0207	0.1947	0.1535
313 K	0.0206	0.0539	0.3018	0.0226	0.1448	0.2344
323 K	0.0329	0.0507	0.1654	0.0241	0.0751	0.1908
61–300 min						
298 K	0.0023	0.0047	0.0071	0.0041	0.0137	0.0192
313 K	0.0038	0.0046	0.0069	0.0018	0.0111	0.0072
323 K	0.0046	0.0046	0.0037	0.0023	0.0157	0.0064

metal ions because of increased driving force, resulting from increased metal ion concentration. The rate of sorption of Cd^{2+} (1.899–5.023 $mg\,g^{-1}\,min^{-1}$) was found to be slightly higher than that of Pb^{2+} (1.77–4.648 $mg\,g^{-1}\,min^{-1}$), as the initial concentration of these metal ions was increased from 300 mg/L to 1000 mg/L within the first 8 min of the adsorption process at 298 K. However, as temperature increases within this first 8 min of adsorption, the initial sorption rates of Pb^{2+} became higher than that those of Cd^{2+}. During the time interval (9–60 min), the sorption rates for both metal ions decreased by a factor of not less than 10 for Pb^{2+} and a factor of approximately not less than 50 for Cd^{2+}. Further decrease in the sorption rate of both metal ions from 60 min to 300 min was observed with sorption rate of Pb^{2+} on TPP-Kaolinite clay more than that of Cd^{2+}. The higher initial sorption rate observed for the sorption of Cd^{2+} over that of Pb^{2+} within the first 8 min of adsorption process at 298 K may be as a result of the smaller ionic radius of Cd^{2+} (0.97 Å) compared to that of Pb^{2+} (1.33 Å) [21]. However, after 8 min, TPP-Kaolinite clay shows higher selectivity for Pb^{2+} at a faster rate than Cd^{2+}. This is in order of the electronegativity of the metal ions: Pb^{2+} (2.33) > Cd^{2+} (1.69) [21]. This may suggest that there may be two mechanisms involved in the adsorption of these metal ions.

The initial sorption rates calculated from pseudo-second-order model showed a reverse of the trend above (Table 2) for the first 8 min of adsorption of both metal ions. The initial sorption rates for Pb^{2+} on TPP-Kaolinite clay were found to be higher than those for Cd^{2+} as initial metal ion concentrations were increased from 300 mg/L to 1000 mg/L. The difference in the trends with both methods of determining initial sorption rates of metal ions on TPP-Kaolinite clay may be because the pseudo-second-order model took into account the data from the whole range of time used in the adsorption process but the former method considers the data within a specified range of time.

3.1.2. Rate constants

Tables 2 and 4 show the rate constants k and k_1 obtained from pseudo-second-order and pseudo-first-order models, respectively and Figs. 3–6 show their different plots. While no trend is observed with these rate constants, as initial concentration of metal ion increases, they generally decreased with increasing metal ion concentration. Ho and McKay [2], Ho and McKay [3] also reported similar trend with the pseudo-second-order model when they studied the adsorption Pb^{2+} from Peat. This may have resulted from the decreasing number of active sites available for the adsorption of the metal ions. However, the

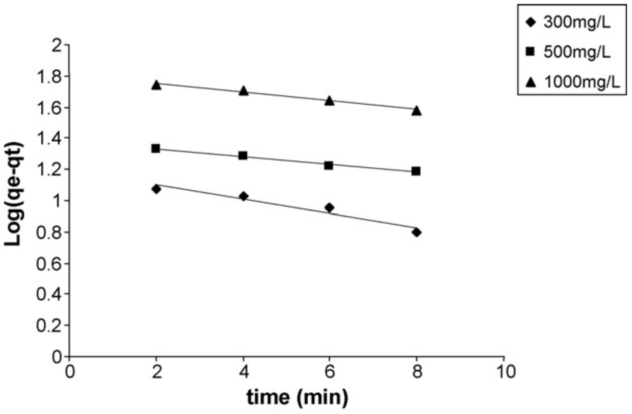

Fig. 3. Pseudo-first-order kinetic plots for the adsorption of Pb^{2+} by TPP-Kaolinite clay.

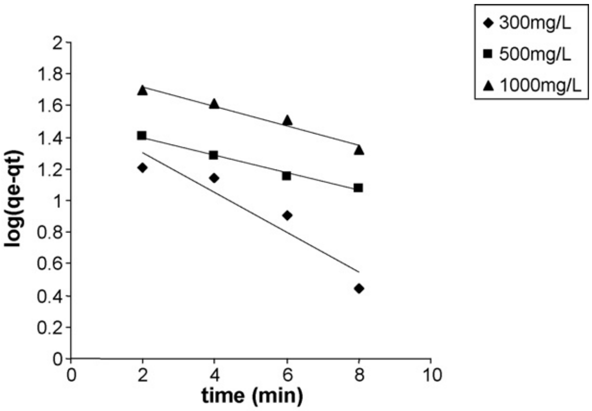

Fig. 4. Pseudo-first-order kinetic plots for the adsorption of Cd^{2+} by TPP-Kaolinite clay.

Table 2
Effects of temperature and initial metal ion concentration on pseudo-second-order kinetic parameters in the adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay

	Lead			Cadmium		
	298 K	313 K	323 K	298 K	313 K	323 K
300 mg/L						
q_e (mg g^{-1})	22.52	25.06	26.53	18.18	20.12	22.73
h (mg g^{-1} min^{-1})	11.78	14.71	19.68	3.43	4.90	6.56
k (g mg^{-1} min)	2.32×10^{-2}	2.34×10^{-2}	2.80×10^{-2}	1.04×10^{-2}	1.21×10^{-2}	1.27×10^{-2}
R^2	0.9998	0.9999	0.9996	0.9969	0.9946	0.9976
500 mg/L						
q_e (mg g^{-1})	34.96	35.46	39.53	33.67	34.48	37.59
h (mg g^{-1} min^{-1})	12.33	15.53	21.83	3.64	4.91	5.48
k (g mg^{-1} min)	1.01×10^{-2}	1.24×10^{-2}	1.4×10^{-2}	3.21×10^{-3}	4.13×10^{-3}	4.17×10^{-3}
R^2	0.9998	0.9999	0.9999	0.9986	0.9993	0.9989
1000 mg/L						
q_e (mg g^{-1})	78.74	80.65	82.65	65.36	70.92	72.99
h (mg g^{-1} min^{-1})	13.50	21.01	37.59	13.09	20.20	21.78
k (g mg^{-1} min)	2.18×10^{-3}	3.23×10^{-3}	5.5×10^{-3}	3.06×10^{-3}	4.02×10^{-3}	4.09×10^{-3}
R^2	0.9995	0.9998	0.9998	0.9984	0.9997	0.9997

Table 3
q_e obtained from kinetic test and q_{eq} from equilibrium test

	Lead q_e (mg g^{-1})			Cadmium q_e (mg g^{-1})		
	298 K	313 K	323 K	298 K	313 K	323 K
300 mg/L	21.65 (22.52)	24.50(25.06)	26.94(26.53)	17.13(18.18)	20.76(20.12)	22.84(22.73)
500 mg/L	33.44(34.96)	37.69(35.46)	41.18(39.53)	32.69(33.67)	35.47(34.48)	37.71(37.59)
1000 mg/L	76.05(78.74)	79.37(80.65)	81.74(82.65)	60.23(65.36)	69.94(70.92)	71.02(72.99)

Note: Values in bracket are q_e obtained from kinetics at same C_0 concentration of metal ions for equilibrium test.

pseudo-first-order model (Figs. 3 and 4) was only applied to the data in the first 8 min of adsorption because beyond this time, data showed large deviation from the model. Kalavathy et al. [22] in their study of the kinetics of the adsorption of Cu^{2+} onto H_3PO_4-activated rubber wood sawdust observed that the pseudo-first-order model fitted well to the data for the first 25 min. This implies that for the first 8 min, the sorption of Pb^{2+} and Cd^{2+} onto TPP-Kaolinite clay was very rapid and not concentration dependent. Perhaps, the adsorption reaction in the first 8 min is basically film-diffusion controlled. Thus, the pseudo-first-order model represents the initial stages where rapid adsorption of Pb^{2+} and Cd^{2+} onto TPP-Kaolinite clay occurs well but cannot be applied for the entire sorption period. The data were well described by the pseudo-second-order model as seen from the r^2 values in Table 2 indicating that one of the mechanisms of the adsorption of both metal ions by TPP-Kaolinite clay may be by chemisorption.

These suggest that two mechanisms could be involved in the adsorption of Pb^{2+} and Cd^{2+} onto tripolyphosphate-modified adsorbent: film-diffusion controlled mechanism and chemisorption.

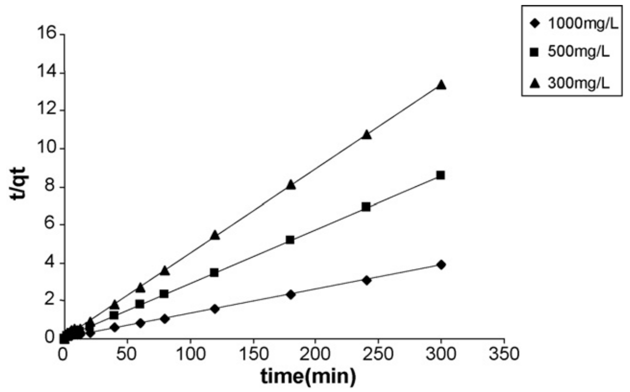

Fig. 5. Pseudo-second-order kinetic plots for the adsorption of Pb^{2+} by TPP-Kaolinite clay.

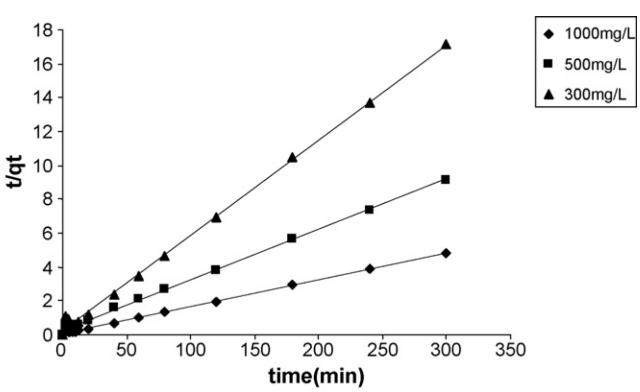

Fig. 6. Pseudo-second-order kinetic plots for the adsorption of Cd^{2+} by TPP-Kaolinite clay.

3.1.3. Adsorption capacity

From Table 2, it was observed that increasing concentrations of the metal ions at 298 K increased the adsorption capacity of TPP-Kaolinite clay. The adsorption capacity increased to almost twice its value with increased concentration. This is attributed to increasing driving force of the metal ions towards the active sites on the TPP-Kaolinite clay surface [17]. There was some good degree of agreement between the q_e obtained from kinetic test and q_{eq} from equilibrium test as can be seen from Table 3.

3.2. Effect of temperature

3.2.1. Pseudo-second-order parameters

Table 2 shows the effect temperature on pseudo-second-order parameters in the adsorption of Pb^{2+} and Cd^{2+} onto TPP-Kaolinite clay. It is observed that with increasing temperature, adsorption capacity, q_e, of TPP-Kaolinite clay, and initial sorption rate, h, were found to increase for both Pb^{2+} and Cd^{2+}. The maximum adsorption capacity of 82.65 mg g^{-1} obtained for the adsorption of Pb^{2+} on TPP-Kaolinite clay in this study is 10-fold greater than those obtained by Farrah et al. [23], Majone et al. [24] and Orumwense [25], when they studied the adsorption of Pb^{2+} on Kaolinite clay.

It is possible that increasing temperature could have increased the driving force of the metal ions towards the active sites on TPP-Kaolinite clay. The values of the initial sorption rate, h, obtained in this study were found to be higher than those obtained for the adsorption of 100–500 mg/L Pb^{2+} on the peat [2,3].

The implication of pseudo-second-order initial sorption rates is that the higher the initial sorption rate of an adsorption reaction, the faster the adsorption reaction attains equilibrium. This might be of benefit in the application of the adsorbent in the treatment of wastewater.

An increase in the pseudo-second-order rate constant, k, with increasing temperature was observed for both metal ions. This may imply that increasing temperature may increase the rate of adsorption reaction at the solid–liquid interface. However, adsorption of Pb^{2+} onto TPP-Kaolinite clay gave higher values of these parameters which show that the adsorption of Pb^{2+} onto TPP-Kaolinite clay is well favored over the adsorption of Cd^{2+} even at increasing temperatures up to 323 K.

3.2.2. Thermodynamic parameters

Table 4 shows the data of thermodynamic parameters obtained from the adsorption of Pb^{2+} and Cd^{2+} over a range of concentration (60–1000 mg/L) at different temperatures. It is observed that the adsorption of both Pb^{2+} and Cd^{2+} onto the TPP-Kaolinite clay is endothermic and spontaneous in nature. Similar observations have been made by Orumwense [25] on the adsorption of Pb^{2+} on Kaolinite, and Chantawong et al. [26] on the adsorption of Pb^{2+} on Thai Kaolin. Exothermic adsorption of lead on China clay and Wollastonite [27] has also been reported. However, it has been shown that the adsorption of Cd^{2+} on Bagasse fly ash [28] and on Kaolinite [29] is also endothermic in nature.

Fig. 7 shows the plots used in the calculation of ΔH° and ΔS°. The adsorption of Cd^{2+} by TPP-Kaolinite clay is seen to be more endothermic than that of Pb^{2+} by TPP-Kaolinite clay, with ΔH° for Cd^{2+} being +24.93 kJ mol^{-1} and that for Pb^{2+} being +13.941 kJ mol^{-1}. From the magnitude of the adsorption enthalpy, ΔH°, of both metal ions, there is the possibility of a moderately strong bonding between the adsorbate and adsorbent as observed by Gupta et al. [30] and Manohar et al. [35]. The adsorption of Pb^{2+} and Cd^{2+} on TPP-Kaolinite clay could be a combination of two processes: (a) the desorption of H^+ and Na^+ attached to active sites on the surface active sites of the adsorbent and (b) the adsorption of adsorbate species. This may also explain in part the endothermic nature of the adsorption process.

ΔG° obtained for all the various adsorbents were found to be small and negative indicating that the adsorption of both metal ions onto TPP-Kaolinite clay was spontaneous (Table 4). However, increasing temperature does not seem to significantly change ΔG°. Data of ΔS° obtained for the adsorption of both metal ions by TPP-Kaolinite clay are shown in Table 2. It was found that adsorption of Pb^{2+} has a negative ΔS° and that for Cd^{2+} was positive. Gupta et al. [31] reported a value range of negative ΔS° for the adsorption of Cd^{2+} and Pb^{2+} by Duolite C-433 synthetic resin. The negative value obtained for Pb^{2+} indicates a stable configuration of the metal ion on the TPP-Kaolinite clay adsorbent surface [1], while the positive value for Cd^{2+} suggests some structural changes in the adsorbent and adsorbate [35].

The positive values of activation energy, ΔE, calculated for the adsorption of both metal ions on TPP-Kaolinite clay (Table 5) suggest that a rise in temperature favors the adsorption of both metal ions and the adsorption process is endothermic in nature. Table 4 also showed that the adsorption Pb^{2+} by the adsorbent, required higher activation energy than for the adsorption of Cd^{2+}, as concentration and temperature of the metal ion solution increases. The values of the ΔE for the adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay in this study fall within the range of diffusion controlled adsorption processes (8–22 kJ mol^{-1}) as reported by Glasstone et al. [32]. This implies that the sorption rate-controlling step in the adsorption of Pb^{2+} and Cd^{2+} by TPP-

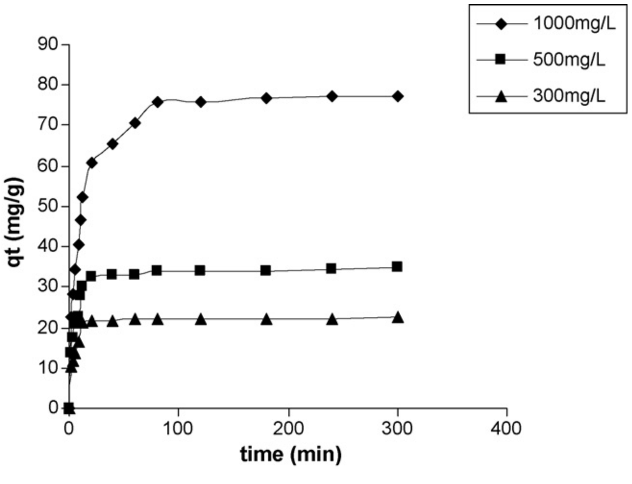

Fig. 7. Plot of q_t versus time for the adsorption Pb^{2+} onto TPP-modified clay.

Table 4
Thermodynamic parameters for the adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite Clay

Metal ion	T (K)	q_{eq} (mg g^{-1})	ΔH°_{mean} (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔS° (J mol^{-1})
Lead	298	126.58	+13.94	−15.04	−3.54
	313	149.25		−14.92	
	323	208.33		−15.16	
Cadmium	298	113.64	+24.93	−16.09	+30.06
	313	120.48		−15.21	
	323	131.58		−15.43	

Table 5
Pseudo-first-order rate constant, k_1, and activation energy, ΔE, for the adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay

TPP	Lead			Cadmium		
	k_1 (min^{-1})	R^2	ΔE (kJ mol^{-1})	k_1 (min^{-1})	R^2	ΔE (kJ mol^{-1})
300 mg/L	0.105	0.9224	+5.47	0.288	0.8878	+6.52
500 mg/L	0.058	0.9950	+10.39	0.128	0.9918	+8.82
1000 mg/L	0.064	0.9930	+28.69	0.141	0.9662	+9.30

Kaolinite clay may likely be a diffusion-controlled process. This does not preclude the fact that the adsorption of these metal ions on the adsorbent may also be chemical in nature.

To ascertain the nature of the adsorbent surface and the nature of the adsorbed phase, we need information concerning the magnitude of the heat of adsorption as it varies with surface loading. The heat of adsorption, determined at constant amounts of adsorbate loadings is known as the isosteric heat of adsorption (ΔH_x) and is calculated using the Clausius–Clapeyron equation [33].

$$\frac{\mathrm{d}\ln C_e}{\mathrm{d}T} = \frac{\Delta H_x}{RT^2} \tag{12}$$

or

$$\Delta H_x = -R\left[\frac{\mathrm{d}(\ln C_e)}{\mathrm{d}(1/T)}\right] \tag{13}$$

ΔH_x is calculated from the plot of $\ln C_e$ versus $1/T$ for different amount of Pb^{2+} and Cd^{2+} loadings. The ΔH_x values are shown in Fig. 8 as a function of adsorbate loadings. From Fig. 8, it is seen that the isosteric heat of adsorption varied with the surface loading, indicating that the TPP-Kaolinite clay adsorbent used in this studies has an energetically heterogeneous surface. The variation in ΔH_x can also be attributed to the presence of some lateral interactions between adsorbed Pb^{2+} and Cd^{2+} species [35].

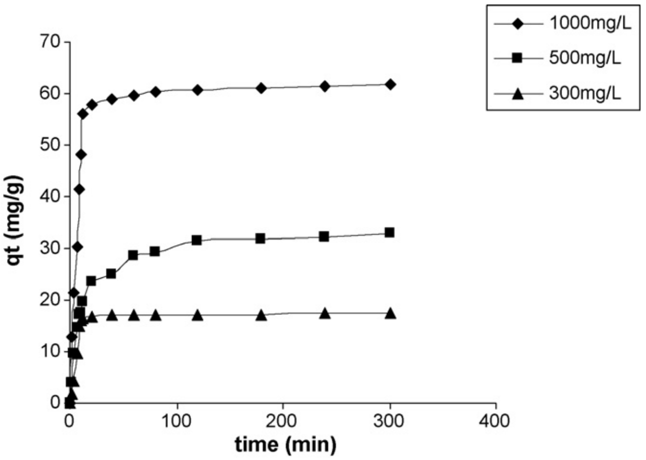

Fig. 8. Plot of q_t versus time for the adsorption Cd^{2+} onto TPP-modified clay.

3.3. *Effect of binary metal ion solutions*

Table 6 shows the data obtained from the kinetics of the adsorption binary solutions of various concentrations of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay, using the pseudo-second-order model. The presence of Cd^{2+} at both 500 mg/L and 100 mg/L in 500 mg/L Pb^{2+} reduced the initial sorption rates of Pb^{2+} by TPP-Kaolinite clay from 12.33 mg g^{-1} min^{-1} to 6.27 mg g^{-1} min^{-1} and 9.58 mg g^{-1} min^{-1}, respectively when results were compared with that of the adsorption of 500 mg/L Pb^{2+} at 298 K in Table 1. However, the simultaneous presence of both 500 mg/L and 100 mg/L of Pb^{2+} in 500 mg/L of Cd^{2+} increased the initial sorption rate of Cd^{2+} by TPP-Kaolinite clay from 3.64 mg g^{-1} min^{-1} to 3.70 and 8.04 mg g^{-1} min^{-1}, respectively. This might be related to the smaller ionic size of Cd^{2+} compared to that of Pb^{2+} which enables it to effectively compete for active sites at the initial stage of the adsorption process and thus, enhanced initial sorption rate.

Srivastava et al. [34] showed that metals that form hydrolysis products more readily (Pb and Cu) adsorb to variable charge surfaces from about pH 5.0 and above. Because of its lower tendency to form hydrolysis products, Cd^{2+} does not compete effectively for variable charge surfaces, and so its adsorption is more restricted to permanent charge sites; hence we see an increased uptake of Cd^{2+} at these sites when other metals are present. It is possible that TPP-Kaolinite clay possess more permanent charged sites than variable charged sites. Thus, Cd^{2+} would tend to be adsorbed more on these sites than Pb^{2+} when both are simultaneously present in the solution. This tends to suppress the adsorption of Pb^{2+} onto such sites and subsequently

Table 6
Effect of the adsorption of binary solutions of Pb^{2+} and Cd^{2+} on the pseudo-second-order kinetic parameters

Kinetic parameters	Lead			Cadmium		
	500:500[a]	500:100[a]	100:500[a]	500:500[a]	500:100[a]	100:500[a]
q_e (mg g^{-1})	32.47	33.56	4.89	26.46	2.22	22.12
h (mg g^{-1} min^{-1})	6.27	9.58	0.91	3.70	0.21	8.04
k (g mg^{-1} min)	5.95×10^{-3}	8.51×10^{-3}	3.83×10^{-2}	5.29×10^{-3}	4.18×10^{-2}	1.64×10^{-2}
R^2	0.9991	0.9998	0.9995	0.9991	0.9942	0.9994

[a] Pb:Cd ratio in mg/L.

reduced the overall adsorption capacity of TPP-Kaolinite clay for Pb^{2+}. This may also explain in part the increase in the initial sorption rate of Cd^{2+} on TPP-Kaolinite clay in binary solutions of the metal ions.

Nonetheless, the initial sorption rates of Pb^{2+} were found to be higher than those of Cd^{2+} (Table 6) when both are simultaneously present in solution. However, in the overall adsorption process the pseudo-second-order adsorption rate constant, k, of Pb^{2+} by TPP-Kaolinite clay is higher than that of Cd^{2+} in an equal concentration (500:500 mg/L) of binary solution of both metal ions as shown in Table 6. With 100 mg/L of either metal ion in 500 mg/L of each metal ion, the overall adsorption rate, k, of Cd^{2+} was greater for a single metal ion solution of Pb^{2+}. This might mean that the adsorption of Cd^{2+} from a binary solution of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay may have reached equilibrium faster than that for Pb^{2+}, provided they are both present in the same concentration in the solution.

The simultaneous presence of both metal ions at different concentrations was also found to reduce the adsorption capacity, q_e, of TPP-Kaolinite clay for both metal ions as shown in Table 6. The adsorption of Cd^{2+} was more negatively affected by this factor than Pb^{2+}. This further strengthens the point that the TPP-Kaolinite clay adsorbent shows higher selectivity towards Pb^{2+} than towards Cd^{2+} even in the presence of both metal ions. This was also reported by Srivastava et al. [34].

4. Conclusion

- The rate of adsorption of Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay were found to increase, with increasing temperature but decreased with initial metal ion concentration and time.
- The adsorption of both Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay was found to be endothermic with negative ΔG° which suggest that adsorption Pb^{2+} and Cd^{2+} by TPP-Kaolinite clay is spontaneous in nature. The adsorption of Pb^{2+} by TPP-Kaolinite clay gave a negative ΔS° value indicating a more stable formation of TPP-Kaolinite-clay-Pb^{2+} complex while the adsorption of Cd^{2+} gave a positive ΔS° which suggest a structural change in the adsorbent and adsorbate after adsorption reaction.
- The isosteric heat of adsorption was found to vary with the surface loading, indicating that the TPP-Kaolinite clay adsorbent used in this study has an energetically heterogeneous surface.
- Calculated ΔE values obtained for the adsorption of Pb^{2+} and Cd^{2+} in this study suggest that the rate controlling step of the adsorption of these metal ions by TPP-Kaolinite clay could possibly be a diffusion-controlled reaction.
- Binary solutions of both metal ions at different concentrations reduced both the rate of adsorption of Pb^{2+} and the sorption capacity of TPP-Kaolinite clay for both Pb^{2+} and Cd^{2+}. However, the rate of adsorption of Cd^{2+} was enhanced in binary solutions of both metal ions.

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