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Pb/Ca ion exchange on kaolinite clay modified with phosphates

Emmanuel I. Unuabonah · Bamidele I. Olu-Owolabi · Abiola N. Oladoja · Augustine E. Ofomaja · Zhang L. Yang

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Abstract
Purpose Pollution of soils by heavy metal ions has attracted global concern because of the subsequent translocation into food chain which when taken up to a certain level can cause serious health problems. The influence of preadsorbed calcium by kaolinite clay modified with orthophosphate and tripolyphosphate reagents on the mobility of Pb^{2+} in kaolinitic soil system is studied. This is with the view to understand the fate of Pb^{2+} in phosphate-fertilized kaolinitic soils that are subsequently limed.
Materials and methods Potassium dihydrogen phosphate (98%) and sodium tripolyphosphate (87%) were purchased from Aldrich and Merck, respectively. They were used to modify locally obtained kaolinite clay. These adsorbents were further pretreated with 0.1 M $Ca(NO_3)_2$. These phosphate-modified kaolinite clay adsorbents pretreated with Ca^{2+} were used in the adsorption of Pb^{2+} from aqueous solution in a batch mode.
Results and discussion X-ray diffraction spectra of the various adsorbents indicated that modification of kaolinite clay with the reagents were effective on the surface of the clay mineral and not on the crystal structure of the clay mineral. Treatment with 0.1 M $Ca(NO_3)_2$ gave K–Ca (for unmodified kaolinite clay), K–O–Ca (for potassium-dihydrogen-phosphate-modified kaolinite clay), and K–TPP–Ca (for sodium-tripolyphosphate-modified Kaolinite clay) samples. The pH_{PZC} of the adsorbents before pretreatment with Ca^{2+} decreased when compared with the unmodified kaolinite clay. Further pretreatment of these adsorbents with Ca^{2+} largely decreased the adsorption capacity of all three adsorbents for Pb^{2+} from aqueous solution due to the higher reactivity of Ca^{2+} compared with Pb^{2+}. Data from all three adsorbents failed the nonlinear single Langmuir model fit while data from K–O–Ca adsorbent failed the competitive Langmuir model fit. ΔS^o data were used to support the proposed structures of adsorbed Pb^{2+} on the various

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E. I. Unuabonah (✉)
College of Natural Science, Department of Chemical Sciences,
Redeemer's University,
km 46 Lagos-Ibadan Expressway,
Redemption City, Ogun State, Nigeria
e-mail: iyaemma@yahoo.com

B. I. Olu-Owolabi
Department of Chemistry, University of Ibadan,
Ibadan, Nigeria

A. N. Oladoja
Department of Chemistry, Adekunle Ajasin University,
Akoko-Akungba, Nigeria

A. E. Ofomaja
Department of Chemistry, University of Benin,
Benin City, Nigeria

Z. L. Yang
Institute of Soil Science,
Nanjing, People's Republic of China

Present Address:
E. I. Unuabonah
DST/NRF Center of Excellence in Strong Materials,
University of the Witwatersrand,
Johannesburg, South Africa

Present Address:
A. E. Ofomaja
Center of Materials and Process Synthesis (COMPS),
Department of Chemical and Metallurgical Engineering,
University of the Witwatersrand,
Johannesburg, South Africa

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adsorbents. ΔH^o for Pb/Ca exchange was endothermic in nature for K–O–Ca adsorbent and K–TPP–Ca adsorbents. However, it was exothermic for K–Ca adsorbent. ΔG^o for Pb/Ca exchange on modified adsorbents was nonspontaneous but was spontaneous for K–Ca adsorbent. With increasing temperature, ΔG^o for the ion exchange reaction became more spontaneous for all adsorbents.

Conclusions Pb/Ca ion exchange on phosphate-modified kaolinite clay adsorbents is endothermic in nature and nonspontaneous. However, with increase in temperature, spontaneity of the ion exchange reaction increased. This study suggests that liming of kaolinitic soils will decrease strongly the adsorption capacity of the soil for Pb^{2+}, especially when they have initially adsorbed phosphates.

Keywords Adsorption capacity · Equilibrium · Ion exchange · Kaolinite · Lead · Phosphate · Thermodynamics

1 Introduction

The extent of interaction between soil and metal cations has practical applications in plant nutrition and pollution control. The fate of some toxic metal cations, such as lead, in soils and its subsequent translocation into the food chain has generated global concerns (Bhattacharyya and Gupta 2006; Srivastava et al. 2005; Erdem and Ozverdi 2005).

Lead toxicity has been implicated in damage to the central nervous system, leading to encephalitis (i.e., inflammation of the brain), intelligent quotient deficits, and reduced nerve conduction (Dietrich et al. 1990). It has lead to physiological dysfunction of the human body with the resultant effect of kidney malfunction, liver disease, loss of appetite, and mild anemia (Ademoroti 1996). Lead pollution in our environment arises from automobile exhaust which deposits lead particles on plant material, and it is eventually leached off into soil and water bodies during rainfall. Other sources include application of fertilizers, pesticides, sewage sludge, and mining and smelting operations.

Sodium dihydrogen phosphate and sodium tripolyphosphate are components of sewage and agricultural runoff which contribute to the increasing eutrophication of estuaries. Phosphates are further introduced into water and soil bodies via domestic detergents and fertilizers. The adsorption of phosphate by sediment, soil, and clay minerals has been extensively studied during the past 30 years (Lake and Maclntyre 1977).

In Nigeria, most soils are known to have high kaolinite mineral content. Studies have shown that over 20 states in Nigeria have reserves of kaolinite clay worth millions of tons (Aliyu et al. 1996). Typically, kaolinite has low cation exchange capacity (CEC; 3–15 meq/100 g of clay; Grim 1968), while values quoted for the specific surface area (SSA) of kaolinite ranges from 10 to 20 m^2/g (Yong et al. 1992). Our previous studies have shown that the cation exchange capacity of kaolinite clay obtained from Ubulu-Ukwu, Delta state of Nigeria, can be significantly increased by surface modification with sodium dihydrogen phosphate and sodium tripolyphosphate reagents (Adebowale et al. 2006; Unuabonah et al. 2007a).

Numerous studies are available about the exchange coefficients and thermodynamic parameters for various binary or ternary soil exchange systems one of which is Bansal (1982) who studied the exchange equilibria involving Ni^{2+} ions on K- and Ca kaolinite. He observed that the equilibrium constants and standard free energy values suggested a higher preference for Ni^{2+} ions on kaolinite surface with the standard entropy and enthalpy changes of Ni^{2+} suggesting a stronger binding of Ni^{2+} on kaolinite surface. Udo (1978) on the other hand examined the thermodynamics of Ca/K and Ca/Mg exchange on a kaolinitic soil clay and observed a preference for K in the Ca/K system and Ca in the Ca/Mg system. Bittell and Miller (1974) studied lead, cadmium, and calcium selectivity coefficients on montmorillonite, illite, and kaolinite clay minerals and observed that the selectivity of montmorillonite clay for Pb(II) is higher than that of kaolinite clay. Recently, Appel et al. (2002) studied the heats of exchange of K/Ca and K/Pb exchange in two tropical soils using flow calorimetry and observed that heat of exchange in K/Ca system was higher than for K/Pb in both ultisol and oxisol studied. Kazutoshi et al. (2004), using ion exchange selectivity coefficient, were able to show that solution systems composed of Mn-clay minerals and Ca-clay minerals can be regarded as having thermodynamically ideal behavior and that Mn^{2+} can be adsorbed uniformly on the surface of the clay minerals with selectivity similar to that of alkaline earth ions. Also, Dontsova et al. (2005) studied the exchange reaction of Ca/NH_4^+ and Mg/NH_4^+ on soil clays, while Li et al. (2006) studied the effect of K^+- and Ca^{2+}-premodified montmorillonite clay on the adsorption of pesticides.

Whereas there are more detailed reports on the adsorption of metal cations by clay mineral phases, there is still the lack of information on the Pb/Ca ion exchange properties of potassium dihydrogen-phosphate- and sodium-tripolyphosphate-modified kaolinite clay. This is in view of understanding the fate of Pb^{2+} on limed soils that are kaolinitic in nature and have been previously treated with phosphate fertilizers since the clay portions of soils are usually more involved in the mobility of ions in soils.

This paper therefore considers the further pretreatment of potassium-dihydrogen-phosphate- and sodium-tripolyphosphate-modified kaolinite clay with calcium and the effect of

this pretreatment and temperature on their adsorptive capacities for lead.

2 Materials and methods

Kaolinite clay used in this study was obtained from Ubulu-Ukwu in the Delta State of Nigeria. The raw kaolinite clay sample was purified according to the method stated by Adebowale et al. (2005). This involves the stirring of the mixture in small amount of 30% hydrogen peroxide solution until 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 distilled deionized water to remove traces of hydrogen peroxide before being used. The suspended kaolinite was centrifuged and oven-dried at 343 K to obtain the kaolinite sample.

2.1 Modification of sample

Fifty grams of the raw kaolinite clay was added to 500 ml of 200 mg/l of potassium dihydrogen phosphate and 0.1 M of sodium tripolyphosphate reagents in 1-l vessels. The suspensions were stirred on a magnetic stirrer for 6 h after which they were centrifuged. The supernatant was discarded, and the modified samples were washed with distilled deionized water until test for phosphate was negative. They were then dried in the oven at 343 K. These modified samples were dissolved in 500 ml of 0.1 M of $CaCl_2$ solutions and stirred for 3 h in a magnetic stirrer. The suspensions were again centrifuged and supernatant discarded. The samples obtained (K–Ca for kaolinite clay pretreated with Ca, K–O–Ca for Ca-pretreated potassium dihydrogen-phosphate-modified kaolinite, and K–TPP–Ca for Ca-pretreated sodium-tripolyphosphate-modified kaolinite) were washed several times with distilled deionized water until Ca^{2+} was found to be negative in solution using a flame photometer. They were all dried in an oven at 343 K. The dried samples were gently crushed and packed into plastic containers for further use.

2.2 Physicochemical properties

2.2.1 X-ray diffraction

Once dried, the various samples were sieved into desired particle size (+220 μm). The X-ray diffraction (XRD) of both unmodified and phosphate-modified adsorbents were determined with the Philips Analytical X-ray spectrometer (PW 1710) using CuKα. The XRD pattern was recorded from 1.5° to 50° 2θ per second with a scanning speed of 0.02° 2θ per second.

2.2.2 Point of zero change

The points of zero charge (PZC) of both adsorbents were obtained using the method of Kinniburgh et al. (1976). For point of zero charge determination, 1 g of the adsorbent prepared above was suspended in 10^{-3}mol/dm^3 $NaNO_3$ solution for 24 h. Sixty milliliters of the suspension was measured into eight plastic containers. The content of the plastics were adjusted to different pH values (2.06, 3.51, 4.69, 5.39, 6.58, 7.19, 8.44, and 9.79). The suspension in each of the container was divided into four equal parts with the aid of a pipette. A 0.3 g of $NaNO_3$ was added to two sets while the other pair contained no added nitrate. They were left for 6 h, and after this, the pH of the reference and the test suspensions was taken as initial and final pH values, respectively. The pairs containing no added nitrate were taken as the reference while those with added nitrate were taken as test samples. The results were plotted as ΔpH against final pH (pH_f).

2.2.3 Specific surface

The SSA of the adsorbents was determined using the method of Sear's (1956). A sample of 0.5 ml of adsorbent particles was diluted with carbon-dioxide-free water to 2–3% weight per volume particles in solution. A 0.1 M Hydrochloric acid was used to adjust the particle solution to pH3.0. After the solution volume was diluted to 2.25 ml, 0.5 g of pure crystalline sodium chloride was added. The solution was mixed to dissolve the sodium chloride, and the pH was adjusted to 4.0 with 0.1 M sodium hydroxide. Finally, the solution was titrated to pH9.0 with 0.1 M sodium hydroxide. The volume of sodium hydroxide used when the mixture remained at pH9.0$\pm$0.05 for 1 min was noted and used to calculate the surface area of the particles of the various adsorbents. The surface area is determined by the equation: $A=26.4(V_t-V_b)$, where A is the square meter per gram or milliliter determined by the method; V_t is the number of milliliters of 0.1 M sodium hydroxide required to titrate the sample from pH4.0 to pH9.0, and V_b is the titration blank in the absence of adsorbent particle.

2.2.4 Cation exchange capacity

The CEC of all clay samples was determined using the ammonium acetate method of Chapman (1965). The CEC of the unmodified kaolinite clay sample has been previously determined by Adebowale et al. (2005) by the same method. In this method, 50 ml of 1 M sodium acetate (CH_3COONa) was added to 2 g of the adsorbent in 120-ml plastic bottle. The suspension was then agitated for 1 h at 200 rpm. This was then filtered and the residue washed with distilled deionized water several times to remove

excess sodium acetate from the adsorbents. They were filtered and air-dried. The samples were then added to 50 ml of 1 M ammonium acetate (pH7.0) and agitated for 30 min. This step was repeated three times, and each time the supernatant was collected and analyzed for Na^+ using flame photometry.

2.3 Exchange reaction

Weighed into plastic sample bottles was 0.2 g each of the Ca-saturated soil samples. To each bottle, 10 ml of the appropriate equilibrating solution at pH5.0±0.2 was added, and the bottle was capped tightly. The suspensions were shaken for 3 h at 298 K with an end-over shaker having a water bath that is temperature-regulated. Finally, they were centrifuged at 20,000 rpm for 15 min. The samples collected were then analyzed for Pb(II) using inductively coupled plasma atomic emission spectroscopy IRIS Advantage model (made by Thermo Fisher). This procedure was repeated at 313 and 323 K. All the experiments were performed in duplicate, and the average values were used for data analysis (Kazutoshi et al. 2004).

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

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Where q_e is the adsorption capacity of various adsorbents; C_0 is the initial concentration of Pb^{2+} (mg/l); C_e is the equilibrium concentration of Pb^{2+} (mg/l); V is the volume of sample used; W is the weight of adsorbent used.

2.4 Theoretical considerations

2.4.1 Thermodynamics

The thermodynamic parameters, ΔH^o, ΔS^o, and ΔG^o, for the ion exchange process were calculated using the relation (Thomas and Crittenden 1998).

$$\ln\ k_{eq} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{2}$$

where

$$k_{eq} = \frac{\text{Pb adsorbed (mmol/kg)}}{\text{Ca preadsorbed (mmol/kg)}} \div \frac{\text{Pb in solution (mmol/l)}}{\text{Ca in solution (mmole/l)}} \tag{3}$$

$$\Delta G^o = -RT \ln K_{eq} \tag{4}$$

Where:

ΔG^o	Standard Gibbs free energy change
ΔH^o	Standard enthalpy change
ΔS^o	Standard entropy change
R	Gas constant
K_{eq}	Equilibrium constant

The mean of all K_{eq} for all concentrations of Pb^{2+} at a particular temperature was taken and used as K_{eqm} (Sparks 2003).The plot of ln K_{eq} versus $1/T$ yields straight lines with the slope and the intercept giving values of ΔH^o and ΔS^o. In deriving the values of the thermodynamic parameters, it is assumed that the enthalpy does not change with temperature.

2.4.2 Competitive Langmuir model

Boyd et al. (1947) developed an adsorption equation for the simultaneous competitive adsorption of two equally charged cations, A and B, using the simple Langmuir equation developed by Langmuir (1918).

$$(X_A/m) = \frac{bK_A/K_B(C_A/C_B)}{1 + K_A/K_B(C_A/C_B)} \tag{5}$$

X_A/m	Amount of adsorbate adsorbed per kilogram of adsorbent
C_A	The equilibrium ion concentration of adsorbate A
C_B	The equilibrium ion concentration of adsorbate B
K	A constant related to the bonding energy of the adsorbate to the adsorbent
b	The adsorption capacity of the adsorbent

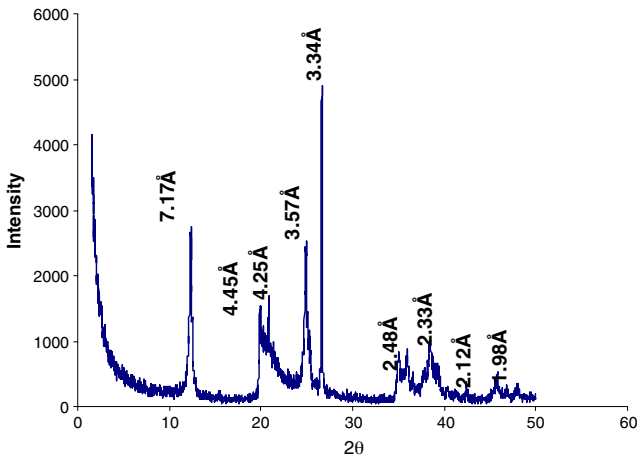

Fig. 1 X-ray diffraction fraction pattern for unmodified kaolinite clay adsorbent

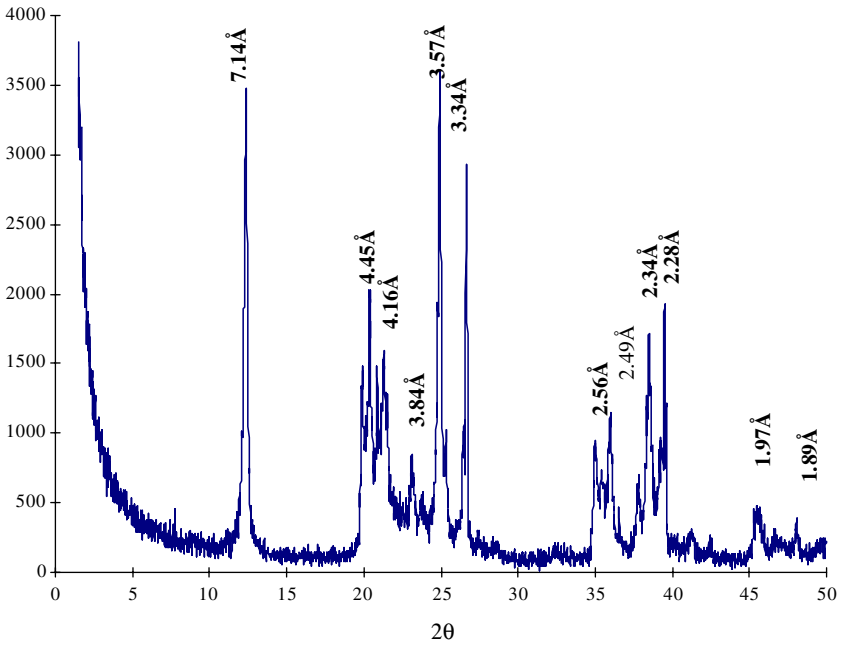

Fig. 2 X-ray diffraction fraction pattern for sodium-dihydrogen-phosphate-modified kaolinite clay adsorbent

The linear form of Eq. 5 is

$$\frac{(C_A/C_B)}{(x_A/m)} = \frac{K_B}{K_A b} + \frac{C_A}{bC_B} \tag{6}$$

From Eq. 6, it can be seen that the amount adsorbed (X_A/m), must depend upon the ratio of the equilibrium concentrations of the exchanging cations and not upon the actual concentrations of the exchanging cations in solution. However, depending upon experimental conditions, the value of the equilibrium (C_A/C_B) ratio can be varied from a small to a large number.

2.4.3 Simple Langmuir model

The simple Langmuir model (SLM) used in analysis of data was that proposed by Langmuir (1918). The linear form of the equation can be represented by:

$$\frac{C_e}{(x/m)} = \frac{1}{kb} + \frac{C_e}{b} \tag{7}$$

where C_e is the equilibrium concentration (mg/l); b (mg/g) is the adsorption capacity of the adsorbent; k (l/g) is Langmuir constant; x/m (mg/g) is the amount of Pb^{2+} adsorbed at equilibrium.

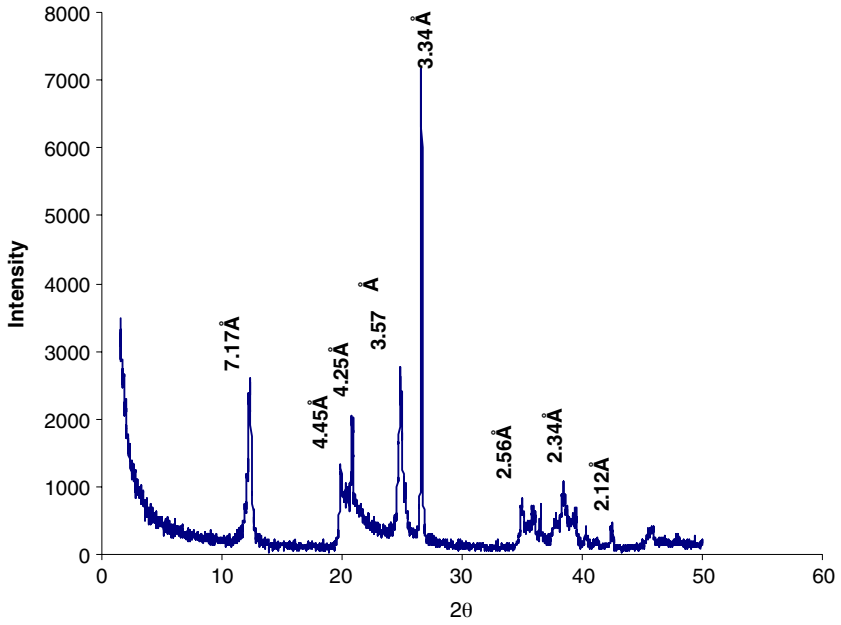

Fig. 3 X-ray diffraction fraction pattern for unmodified tripoly-phosphate modified kaolinite clay adsorbent

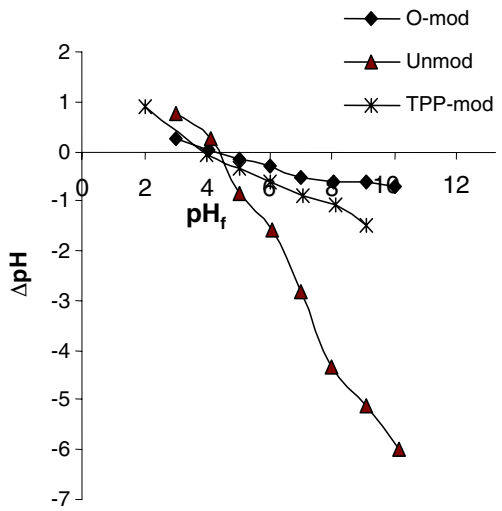

Fig. 4 pH_{PZC} plot for the various modified kaolinite clay adsorbents

3 Results and discussion

3.1 Physicochemical properties

The prominent peaks found in the unmodified adsorbent were 7.17 (001), 4.25, 3.57 (002), 3.34, 2.56, 2.49, 2.33, 2.12, and 1.98 Å which correspond to kaolinite, quartz, kaolinite, illite + quartz, goethite, goethite, gibbsite, gibbsite, and dickite, respectively (Moore and Reynolds 1989). X-ray diffraction results obtained for modified kaolinite clay analogs showed that modification with potassium dihydrogen phosphate and sodium tripolyphosphate did not change the crystal spacing on the lattice structure of the clay mineral to any significant degree, as similar peaks with those for the unmodified were obtained (Figs. 1, 2, and 3).

However, there were shifts in the intensity of the peaks for the various adsorbents. This strongly suggests that the modification with these reagents were effective only on the surface of the clay adsorbent and not on the crystal of the clay mineral. However, even though both modified and unmodified adsorbents showed almost the same peaks, the modified adsorbents showed peak intensities different from that of the unmodified, which is an indication of the modification of the kaolinite clay mineral.

The above data further suggest that this kaolinite clay is a mixed kaolinite–illite clay mineral. Our previous work has shown that the percentage of illite in this mixed clay mineral is ≈11% (Unuabonah et al. 2007b). The CECs of the unmodified, O-modified, and TPP-modified kaolinite clay adsorbents were found to be 7.81, 13.7, and 78.9 meq/100 g of the adsorbents.

The pH at which there is a net zero charge on a solid surface in the absence of specific sorption is called the point of zero charge (pH_{PZC}). Above the pH_{PZC}, adsorption of cations is enhanced, and below the pH_{PZC} it is reduced. The kaolinite clay surface became increasingly negative as the initial solution pH was increased from 1.06 to 9.79. On addition of $NaNO_3$ to the adsorbents in solution, the ΔpH became negative after initial pH of 1.06 (Fig. 4). Below this pH (1.06), ΔpH had a positive value. Extrapolation of the plot of ΔpH versus pH_f to the ΔpH=0 line indicated the pH_{PZC} of the various adsorbents. It was observed that the point of zero charges of the modified adsorbents (O-modified=4.25 and TPP-modified=3.80) were both lower than that for the unmodified kaolinite clay (4.40). This suggests that modification with the phosphate-modifying reagents enhances the adsorption capacity of kaolinite for metal ions from aqueous solutions even at lower pH.

The SSA of O-modified (9.24 $m^2 g^{-1}$) was observed to be lower than that of the unmodified adsorbent (10.56 $m^2 g^{-1}$). The observed small decrease in SSA did not in any way affect the efficiency of these adsorbents as they were more efficient than the unmodified adsorbent in the adsorption of Pb^{2+} and Cd^{2+} (Adebowale et al. 2006). This is because the decrease in surface area was well compensated for by the increase in active sites available for the adsorption of metal ions, on the surface of the modified adsorbents. However, for TPP-modified, a small increase in SSA (13.2 $m^2 g^{-1}$) was observed. This increase might be because of the more dispersed nature of the particles of TPP-modified kaolinite clay which allows for easy interaction between the particles and the chemical species for SSA measurement. This highly dispersed nature of TPP-modified kaolinite clay sample as compared with unmodified or O-modified (which had the better flocculation rate of the three) was observed from the very low flocculation rate of this sample even when left standing for 24 h.

3.2 Adsorption capacity

Table 1 indicates that both K–O–Ca and K–TPP–Ca showed increasing adsorption capacity as temperature from 298 to 323 K. However, with K–Ca, the reverse trend was

Table 1 Some physicochemical parameters of unmodified and modified kaolinite clay adsorbents

	CEC (meq/100g)	SSA (m^2/g)	pHpzc	Adsorption Capacity (mmol/kg)
Raw kaolinite	7.81	10.56	4.40	78.07 (16.16)[a]
O-modified kaolinite	13.70	9.24	4.25	93.09 (19.27)[a]
TPP-modified kaolinite	78.90	13.2	3.80	611.5 (126.58)[a]

[a] Data in brackets are adsorption capacities (mg/g)

Table 2 Linear CLM parameters for the various kaolinite clay samples

	298K			313K			323K		
	K–Ca	K–O–Ca	K–TPP–Ca	K–Ca	K–O–Ca	K–TPP–Ca	K–Ca	K–O–Ca	K–TPP–Ca
b (mmol kg^{-1})	27.40 (↓ 64.9%)	6.24 (↓ 93.3%)	21.98 (↓ 96.4%)	27.10 (↓ 65.3%)	6.39 (↓ 93.1%)	28.25 (↓ 95.4%)	26.24 (↓ 66.4%)	8.73 (↓ 90.6%)	29.24 (↓ 95.2%)
K (l mmol^{-1})	91.25	0.366	17.50	46.13	0.421	70.8	42.33	0.556	114.00
r^2	0.9959	0.9681	0.9690	0.9920	0.9926	0.9961	0.9706	0.8474	0.9997

↓ decrease in adsorption capacity of adsorbent

observed. In our previous studies, it was observed that adsorption of Pb^{2+} onto unmodified kaolinite clay gave an adsorption capacity of 78.07 mmol/kg (16.16 mg/g), while sodium-dihydrogen-phosphate-modified kaolinite clay gave an adsorption capacity of 93.09 mmol/kg (19.27 mg/g). However, sodium-tripolyphosphate-modified kaolinite clay gave 611.5 mmol/kg (126.58 mg/g). In the presence of 0.1 M $Ca(NO_3)_2$, all three adsorbents had reduced adsorption capacity for Pb^{2+} with unmodified kaolinite giving 49.57 mmol/kg (10.26 mg/g), sodium-dihydrogen-phosphate-modified 63.96 mmol/kg (13.24 mg/g), and sodium-tripolyphosphate-modified 303.82 mmol/kg (62.89 mg/g; Unuabonah et al. 2007a; Adebowale et al. 2006). However, in our present study, we observed that pretreatment of all three adsorbents with 0.1 M Ca^{2+} indicated a further decrease in adsorption capacity of all three adsorbents for Pb^{2+} (Table 2) in the order

$$K - TPP - Ca < K - O - Ca < K - Ca$$

Proposed reaction schemes for the formation of the phosphate adsorbents are shown in Figs. 5 and 6. It is proposed that the phosphate anion may have been held to kaolinite by its less-hindered oxygen as shown in Figs. 5 and 6. Both proposed reaction schemes (see Figs. 5 and 6) were borne from our observation that the adsorption of the phosphates was with a small decrease in equilibrium solution pH by approximately 0.64 for potassium dihydrogen phosphate (Unuabonah et al. 2007a, 2007b) and 0.18 for pentasodium tripolyphosphate.

This highest drop in adsorption capacity shown by K–TPP–Ca adsorbent is possibly due to the strong affinity Ca^{2+} has for the phosphate adsorption site with all possible adsorption sites being occupied by Ca^{2+} (see Fig. 6). However, the lower percentage drop in adsorption capacity shown by K–O–Ca adsorbent might be perhaps because Pb^{2+} finds it a little easier to exchange with Ca^{2+} on the ionic site, $-O-Ca^{+}$ on the adsorbent (see Fig. 5), than with –O–Ca–O– in the K–TPP–Ca adsorbent. Although these reaction mechanisms have been proposed, more studies are required to authenticate this mechanism and to further understand the ion exchange reaction of Pb^{2+} and Ca^{2+} on phosphate-modified kaolinite clay.

The result obtained above might imply that soils with high kaolinite clay mineral already loaded with phosphate and sodium tripolyphosphate from phosphate fertilizer applications and wastewater from laundry washes using detergents are most likely to fix Ca^{2+} and perhaps make it less available for bioaccumulation by plants. Besides, soils loaded with both phosphates and Ca^{2+} are likely to allow for leached Pb^{2+} in aqueous solutions into water bodies because Pb^{2+} competes less efficiently with already-adsorbed Ca^{2+} for adsorption sites on both adsorbents. One would expect that Pb should show stronger preference

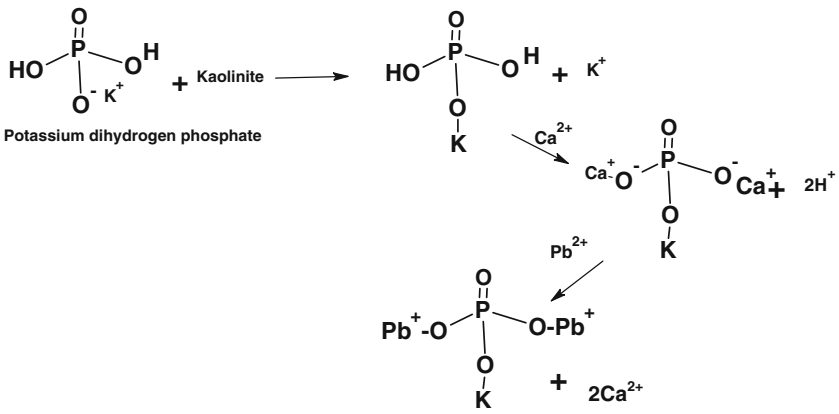

Fig. 5 Proposed reaction scheme for the formation K–O–Ca adsorbent

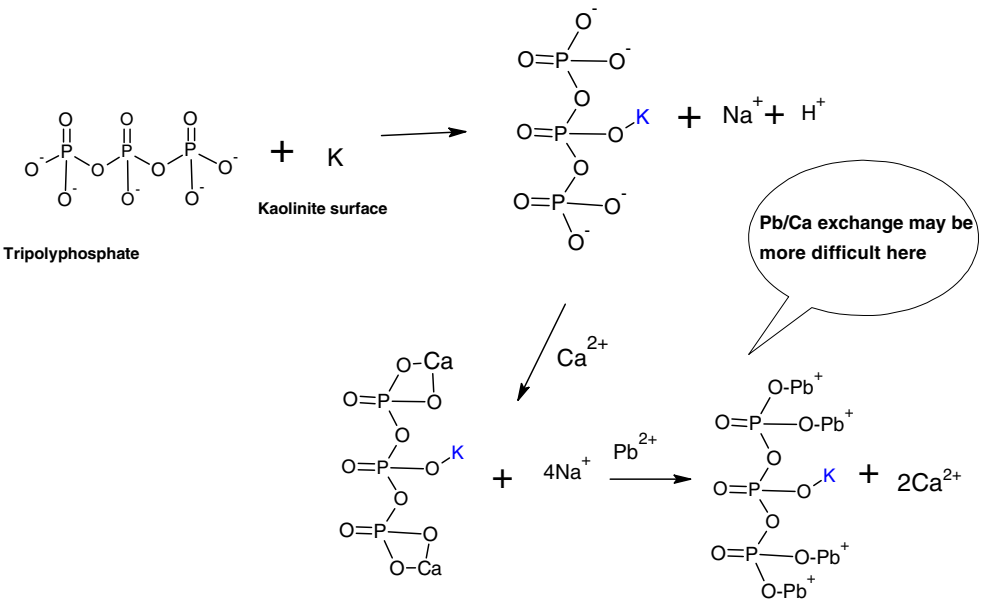

Fig. 6 Proposed reaction scheme for the formation of K–TPP–Ca adsorbent

for the adsorption sites on the adsorbents because of its smaller atomic size of 1.75 Å as compared to that of Ca which is 1.973 Å. The stronger preference these adsorbents have for Ca^{2+} in Pb/Ca exchange reaction may be due to the higher reactivity of Ca^{2+} when compared with Pb^{2+} in the reactivity series. The more reactive the metal, the more stable its compound is likely to be.

3.3 Thermodynamic parameters

The equilibrium constant, K_{eq}, ΔG^o, ΔH^o, and ΔS^o thermodynamic parameters were calculated from Eq. 1–3. Figure 7 shows the plot for obtaining ΔH^o and ΔS^o. Data for these thermodynamic equilibrium parameters are shown in Table 3. It is observed that the equilibrium constant values obtained in this work were generally positive, indicating that the exchange reactions were well favored and equally feasible. The K_{eq} values increased with increasing temperature for K–O–Ca and K–TPP–Ca adsorbents which suggests that the exchange reaction could be endothermic in nature. However, on K–Ca adsorbent, a reverse trend was observed which could indicate an exothermic reaction. The formation of K–Ca is thermodynamically more stable than K–Pb, and for this reason at high temperatures, when plenty of energy is offered to the system, a decrease in Pb^{2+} adsorption is observed (K–Ca is favored; Doula et al 2000).

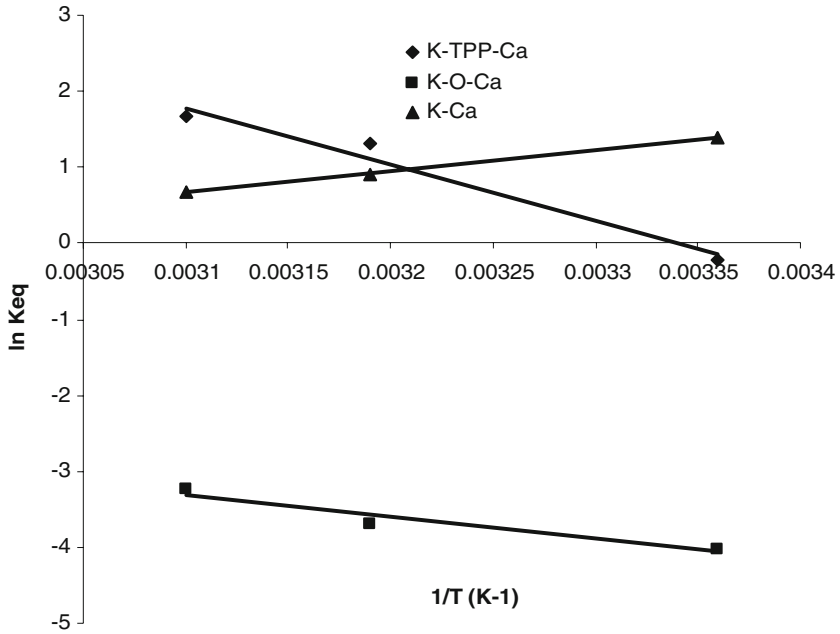

Fig. 7 Plot of ln K_{eq} vs 1/T for obtaining ΔH^o and ΔS^o

Table 3 Thermodynamic parameter for the various kaolinite clay

	298K			313K			323K		
	K–TPP–Ca	K–O–Ca	K–Ca	K–TPP–Ca	K–O–Ca	K–Ca	K–TPP–Ca	K–O–Ca	K–Ca
k_{eq} (l mmol^{-1})	0.806	0.018	4.059	3.677	0.025	2.459	5.274	0.039	1.963
ΔG^o (kJ mol^{-1}K^{-1})	+2.14	+9.95	−3.47	−3.39	+9.60	−2.34	–4.47	+8.71	−1.81
	K–TPP–Ca			K–O–Ca			K–Ca		
ΔH^o (kJ mol^{-1})	+61.91			+23.60			–23.40		
ΔS^o (J mol^{-1})	+206.76			+45.56			–67.01		
r^2	0.9727			0.9327			0.9984		

K_{eq}mean equilibrium

However, these results were further confirmed by their standard enthalpy, ΔH^o, values which were positive for K–O–Ca and K–TPP–Ca, suggesting that the exchange reaction on both adsorbents was endothermic in nature (see Table 3) with Pb/Ca exchange on K–TPP–Ca adsorbent being more endothermic. Pb/Ca exchange K–Ca was exothermic in nature.

The smaller than unity the equilibrium constant, the greater is this reluctance or the stronger is the binding strength of Ca with the modified soil exchange sites. Thus, we find in Table 3 that for the three modified soil samples the order of decreased K_{eq} is

$$K - Ca > K - TPP - Ca > K - O - Ca$$

This trend therefore suggests that kaolinite clay pretreated with Ca^{2+} has a better ion exchange potential for Pb/Ca exchange reaction than sodium dihydrogen-phosphate-modified and sodium-tripolyphosphate-modified that are further pretreated with Ca^{2+}. This might be perhaps because Ca^{2+} forms a more stable complex with phosphate on the surface of the adsorbent than Pb^{2+}. Besides, this is also likely because of the higher reactivity of Ca^{2+} compared with that of Pb^{2+}.

ΔG^o values were all small and positive for exchange reaction on K–O–Ca sample which indicates that the exchange reaction Pb/Ca on K–O–Ca soil sample is probably nonspontaneous. However, for K–TPP–Ca soil sample, ΔG^o for the exchange reaction was positive at 298 K but became negative at 313 and 323 K. This suggests that the Pb/Ca exchange becomes spontaneous at 313 K. This suggests that increasing temperatures favors the ion exchange adsorption of Pb^{2+} onto K–TPP–Ca soil sample. This is corroborated by the positive enthalpy of the ion exchange process (see Table 3). For K–Ca adsorbent, Pb/Ca exchange reaction was spontaneous at temperatures in this study, and the spontaneity of the exchange reaction increased with increasing temperature from 298 to 323 K. The exchange reaction became more spontaneous for K–TPP–Ca and K–O–Ca adsorbents but less spontaneous with temperature increase for K–Ca (see Table 3).

Standard entropy, ΔS^o, values were positive for exchange reaction on K–O–Ca and K–TPP–Ca samples, suggesting that the adsorption of Pb onto the three modified soil samples produced a state less ordered in their molecular arrangement and therefore an increase in entropy. K–TPP–Ca showed very high positive ΔS^o value. This could also suggest that some structural changes may have occurred on the adsorbent (Manohar et al. 2002). However, for K–Ca, the exchange reaction gave negative ΔS^o values which suggests that the product of the exchange reaction is well ordered in their molecular arrangement. These results may have further supported the proposed structures of adsorbed Pb on the phosphate-modified kaolinite clay adsorbents shown in Figs. 5 and 6. This might be so because the charged Pb on these adsorbents may have caused the structural changes that could have given rise to positive ΔS^o

Table 4 Linear SLM parameters for the various kaolinite clay samples

	298K			313K			323K		
	K–Ca	K–O–Ca	K–TPP–Ca	K–Ca	K–O–Ca	K–TPP–Ca	K–Ca	K–O–Ca	K–TPP–Ca
b (mmol kg^{-1})	49.57 (↓ 63.8%)	23.41 (↓ 74.9%)	23.64 (↓ 103.7%)	26.39 (↓ 63.6%)	26.62 (↓ 71.4%)	27.70 (↓ 93.5%)	24.51 (↓ 62.0%)	27.18 (↓ 70.8%)	28.90 (↓ 94.09%)
K (l mmol^{-1})	30.92	18.46	14.59	12.63	37.28	51.57	15.69	52.75	86.50
r^2	0.9990	0.9954	0.9656	0.9972	0.9917	0.9998	0.9978	0.9939	0.9999

– means that data failed the model test

values obtained for K–O–Ca and K–TPP–Ca adsorbents. On the contrary, for K–Ca, the lead was adsorbed on kaolinite clay without any charge which may have given rise to the negative ΔS^o values obtained for this adsorbent (Eq. 8).

3.4 Data fitting

Fitting adsorption data obtained from the adsorption of Pb^{2+} onto the various adsorbents into linear forms of the competitive Langmuir model and the SLM (Eqs. 6 and 7) suggest that the adsorption of Pb^{2+} onto the various adsorbents is better described by the simple linear Langmuir model (Tables 2 and 4). This is seen from the better correlation values shown by the simple Langmuir model for the adsorbents at all temperatures used in this study (see Tables 1 and 2).

However, the linear method of fitting experimental data is usually associated with errors. To reduce these errors and have better qualitative results, the nonlinear method is applied. Figures 8, 9, and 10 show nonlinear model curves for the experimental data obtained. It is observed that data from K–O–Ca failed the nonlinear model test for CLM (see Fig. 10) while data from all three adsorbents failed the nonlinear test for the simple Langmuir model (curves not shown). Data from K–TPP–Ca adsorbent may have had a good degree of fit to the single site CLM perhaps because Pb^{2+} may have been adsorbed on same type of adsorption site (sites on which Ca^{2+} is held) on the adsorbent as shown in Fig. 6.

No plausible reason can yet be given for the poor fit of data from K–O–Ca to nonlinear CLM. However, it is possible that Pb^{2+} adsorption may have occurred within the clay surface—that surface that was not modified, giving rise to adsorption of two types of adsorption sites. This may not be possible with the K–TPP–Ca due to the bulky nature of the tripolyphosphate reagent.

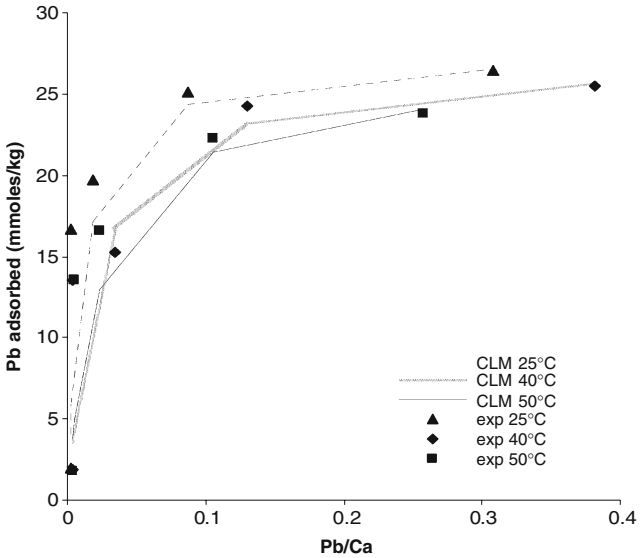

Fig. 8 Data fit for Pb(II) adsorption data from K–Ca kaolinite clay using nonlinear competitive Langmuir model (*CLM*)

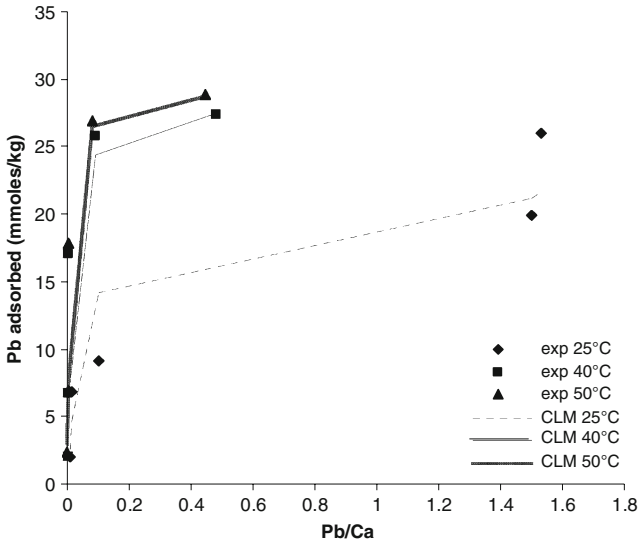

Fig. 9 Data fit for Pb(II) adsorption data from K–TPP–Ca (TPP-mod) kaolinite clay using nonlinear competitive Langmuir model (*CLM*)

For the K–Ca adsorbent, it has been proposed that at pH ~ 5.0 (pH at which exchange reaction was carried out in this study) Pb^{2+} is adsorbed onto permanently charged sites (which are of same type) by ion exchange reactions (Srivastava et al 2005).

$$M^{2+} + 2X - - - - - - - Ca^{2+} \longrightarrow X_2M + Ca^{2+} \quad (8)$$

Where M^{2+} represents Pb(II); X^- is a permanent charge site, and X_2M is an outer-sphere complex.

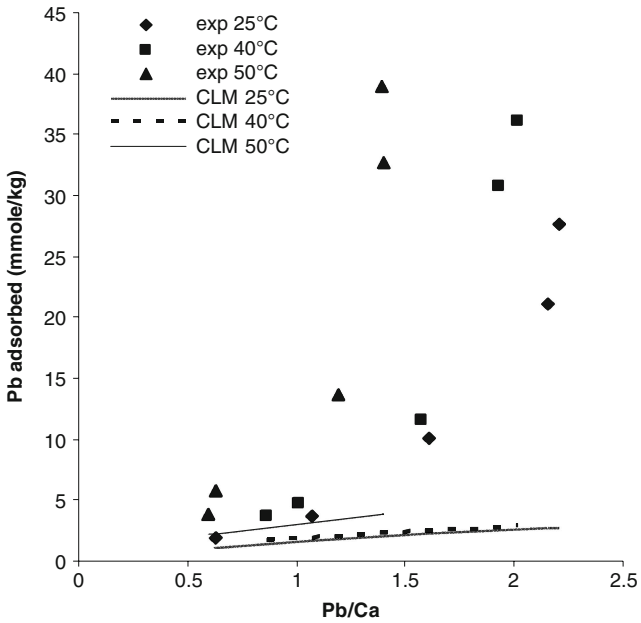

Fig. 10 Data fit for Pb(II) adsorption data from K–O–Ca kaolinite clay using nonlinear competitive Langmuir model (*CLM*)

Furthermore, the failure of adsorption data from all three adsorbents to fit well with nonlinear forms of SLM suggests that SLM does not support ion exchange mechanism.

4 Conclusions

The modification of kaolinite clay with potassium dihydrogen phosphate and sodium tripolyphosphate reagents was not effective within the crystals of the clay mineral but on the surface of the clay mineral. This was confirmed from the X-ray diffraction patterns of the modified clay adsorbents with the unmodified adsorbent. Modification was observed to decrease the pH_{PZC} of kaolinite clay adsorbent.

This study reveals that potassium-dihydrogen-phosphate- and sodium-tripolyphosphate-modified kaolinite clay shows very strong affinity for Ca^{2+} than for Pb^{2+} with the later adsorbent showing stronger affinity for Ca^{2+}. This was found to largely decrease their adsorption capacity. Thus liming of kaolinitic soils will decrease strongly the adsorption capacity of the soil for Pb^{2+}, especially when they have initially adsorbed phosphates from phosphate fertilizers. Proposed reaction scheme suggests that the phosphates were held on kaolinite clay by their less-hindered site while ΔS^o data were used to support the proposed structures of Pb^{2+} on the various adsorbents. Although adsorption of phosphates on kaolinite was proposed to by its less-hindered site, further studies will be required to study interactions between adsorbed phosphates and kaolinite clay and also Pb/Ca ion exchange reactions on these phosphatic surfaces.

Contrary to the endothermic nature of the unmodified adsorbent for adsorption of Pb^{2+} in our previous study, our present study showed that Ca-pretreated kaolinite clay adsorbed Pb^{2+} from aqueous solutions exothermically while the other adsorbents maintained their endothermic nature of adsorption of Pb^{2+}. However, the adsorption capacity of the unmodified kaolinite was decreased at all temperatures used in this study due to the pretreatment with Ca.

Pb/Ca exchange reaction on all adsorbents became more spontaneous as temperature of adsorbate solution increased from 298 to 323 K. However, the exchange reaction was more spontaneous with K–Ca adsorbent.

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References

Adebowale KO, Unuabonah IE, Olu- Owolabi BI (2005) Adsorption of some heavy metal ions on sulphate and phosphate-modified kaolin. App Clay Sci 29(2):145–148

Adebowale KO, Unuabonah EI, Olu-Owolabi BI (2006) The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay. J Hazard Mat B134:130–139

Ademoroti CMA (1996) Environmental chemistry and toxicology. Foludex, Ibadan, pp 192–194

Aliyu AA, Aluko BA, Biliaminu KO (1996) Priority investment projects in the solid minerals sector. Raw materials Research and Development Council, Abuja, pp 12–14

Appel C, Rhue D, Ma L, Reve B (2002) Heats of K/Ca and K/Pb exchange in two tropical soils as measured by flow calorimetry 1. Soil Sci 167(12):773–781

Bansal OP (1982) Thermodynamics of K–Ni and Ca–Ni exchange reactions on kaolinite clay. J Soil Sci 33:63–71

Bhattacharyya KG, Gupta SS (2006) Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution. Sep Purif Technol 50:388–397

Bittell JE, Miller RJ (1974) Lead, cadmium, and calcium selectivity coefficients on a montmorillonite, illite, and kaolinite. J Environ Qual 3:250–253

Boyd GE, Schubert J, Adamson AW (1947) The exchange adsorption of ions from aqueous solutions by organic zeolites, 1, ion exchange equilibria. J Am Chem Soc 69:2818–2829

Chapman AD (1965) Cation exchange capacity. In: Black CA (ed) Methods of soil analysis. Part 2. Chemical and mineralogical properties. Agronomy no. 9. American Society of Agronomy, Madison, pp 891–901

Dietrich KN, Succop PA, Bornschein RL, Krafft KM, Berger O, Hammond PB, Buncher CR (1990) Lead exposure and neurobehavioural development in later infancy. Environ Health Pers 89:13–19

Dontsova KM, Norton LD, Johnston CT (2005) Calcium and magnesium effects on ammonia adsorption by soil clays. Soil Sci Soc Am J 69:1225–1232

Doula M, Ioannou A, Dimirkou A (2000) Thermodynamics of copper adsorption–desorption by Ca–kaolinite. Adsorption 6:325–335

Erdem M, Ozverdi A (2005) Lead adsorption from aqueous solution onto siderite. Sep Purif Technol 42:259–264

Grim RE (1968) Clay mineralogy, 2nd edn. McGraw-Hill, New York, pp 51–59

Kazutoshi S, Shin-Ichiro W, Masahiro S (2004) Ca^{2+}–Fe^{2+} and Ca^{2+}–Mn^{2+} exchange selectivity of kaolinite, montmorillonite, and illite. Soil Sci 169(2):125–132

Kinniburgh DG, Jackson ML, Syers JK (1976) Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of Fe and Al. Soil Sci Soc Am J 40:796–779

Lake CO, Maclntyre WG (1977) Phosphate and tripolyphosphate adsorption by clay minerals and estuarine sediments. Bulletin 109. Gloucester Point, Virginia 23062

Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica, and platinum. J Am Chem Soc 40:1361–1403

Li H, Teppen BJ, Laird DA, Johnston CT, Boyd SA (2006) Effects of increasing potassium chloride and calcium chloride ionic strength on pesticide sorption by potassium- and calcium-smectite. Soil Sci Soc Am J 70:1889–1895

Manohar DM, Krishnan KA, Anirudhan TS (2002) Removal of mercury(II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercaptobenzimidazole-clay. Water Res 36:1609–1619

Moore DM, Reynolds RC Jr (1989) X-ray diffraction and the Identification and analysis of clay minerals. Oxford University Press, Oxford, pp 179–201

Sears GW (1956) Determination of specific surface area of colloidal silica by titration with sodium hydroxide. Anal Chem 28:1981–1983

Sparks DL (2003) Environmental soil chemistry. Academic, New York, p 190

Srivastava P, Singh B, Angove M (2005) Competitive adsorption behavior of heavy metals on kaolinite. J Colloid Interf Sci 290:28–38

Thomas WJ, Crittenden B (1998) Adsorption technology and design. Butterworth/Heinemann, Oxford, pp 38–50

Udo EJ (1978) Thermodynamics of potassium–calcium and magnesium–calcium exchange reaction on kaolinitic soil clay. Soil Sci Soc Am J 42:556–560

Unuabonah EI, Olu-Owolabi BI, Adebowale KO, Ofomaja AE (2007a) Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated kaolinite clay. Colloids Surfaces A Physicochem Eng Aspects 292:202–211

Unuabonah EI, Adebowale KO, Olu-Owolabi BI (2007b) Kinetic and thermodynamic studies of the adsorption of lead(II) ions onto phosphate-modified kaolinite clay. J Hazard Mater 144(1–2): 386–395

Yong RN, Mohaned AMO, Warkentin BP (1992) Principles of contaminant transport in soils. Elsevier, New York