

The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay

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Abstract

Modification of kaolinite clay mineral with orthophosphate (p-modified sample) enhanced adsorption of Pb and Cd ions from aqueous solutions of the metal ions. Increasing pH of solutions of metal ions, increasing adsorbent dose and increasing concentration of metal ion, increased the adsorption of metal ions. Adsorption of both metal ions simultaneously on both unmodified and p-modified samples indicates that adsorption of one metal ion is suppressed to some degree by the other.

The presence of electrolyte and their increasing concentration reduced the adsorption capacities of both unmodified and p-modified samples for the metal ions. Ca-electrolytes had more negative effect on the adsorption capacities of the adsorbents than Na-electrolytes. Ca-electrolytes reduced adsorption capacities of the adsorbents for Pb and Cd ions. From Langmuir plots it was observed that these electrolytes increased the binding energy constant of the metal ions onto the adsorbents especially on the p-modified samples.

The rate of adsorption of Pb and Cd ions on p-modified adsorbent were increased and equilibrium of metal ion solution were more quickly reached (8 min for Pb ions and 12 min for Cd ions) with p-modified adsorbent as against 20 min for adsorption of both metal ions on unmodified adsorbent when 200 mg/L of metal ion solutions were used during the kinetic studies.

When adsorption data were fitted against Langmuir, Freundlich, Toth and Langmuir–Freundlich isotherms, satisfactory fits were found with the Freundlich isotherm. However, at low concentration of metal ions, data also showed satisfactory fits to Langmuir isotherm.

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1. Introduction

The important sources of accumulation of heavy metals in soils include input from municipal and industrial wastes; and application of fertilizers and pesticides on farmlands [1]. These practices have led to increased concern on the environmental impacts of these metals in soils. The environmental impacts of metals on plants; health of humans and wildlife have been studied [2–8].

Several methods have evolved over the years on the removal of these metal ions present in industrial wastewaters and soils. These are chemical precipitations, conventional coagulation, reverse osmosis, ion exchange and adsorption on activated carbon. The selection of the method is based on the concentration

of the metal ions, efficiency/cost ratio and the adsorption capacity of the adsorbent. Out of these methods, adsorption appears to be the most widely used for the removal of heavy metals [9–11]. Natural substances like activated carbon and zeolites have assumed a wide application in this regard, but their high cost limits their utilization. Peat and modified peat adsorbents have been used to remove metals from aqueous solutions [12–14]. The possibility of using other cheaper adsorbents like kaolinite clay might be worthwhile.

Kaolin ($\text{Al}_2\text{Si}_2\text{O}_5\text{OH}_4$) is a highly weathered clay mineral. It is common in tropical soils and the second most abundant clay mineral in ocean sediments [15]. It has been found in substantial quantities in many parts of Nigeria. Typically, kaolinite has low cation exchange capacity (CEC) [3–15 meq/100 g of clay] [15], while values quoted for the specific surface area (SSA) of kaolinite ranges from 10 to 20 m²/g [16]. However, clay could be modified to improve its sorption capacity. Cadena et al. [17] used bentonite, tailored by replacing the natural exchangeable

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cations in the clay with organophillic cation, tetramethylammonium ion (TMA^+) in order to adsorb Pb and Cr(IV) ions. Pradas et al. [18] examined the modification of natural bentonite with less complex treatments such as acid and heat treatments. Manohar et al. [19] reported the use of 2-mercaptobenzimidazole in the removal of mercury in aqueous solutions. Natural peat was modified with resin particles [14].

Recent research suggest that chemically modified clay minerals represent a new and promising class of adsorbents for water purification and industrial wastewater treatment with wider applications in soils [20]. Modification with phosphate has gained a renewed attention because apart from being environmentally friendly it also improves the structure and soil moisture-holding capacity when added to sandy soil [21]. Modification by the addition of phosphates can be achieved by either physical or chemical means. Impregnation of organic/inorganic molecules on solid surfaces (physical process) and grafting of organic/inorganic molecules on solid surface (chemical process).

It has been observed that increasing pH favors the adsorption of metal ions because of less competition between H^+ and metal ions for adsorption sites [22]. The effect of electrolyte and their ionic strength is known to affect the adsorption of metal ions from aqueous solutions. Investigations by Naidu et al. [23] showed that increasing ionic concentration of Ca^{2+} and Na^+ electrolytes decreased cadmium ion adsorption onto variable charge soils. For variable charge surfaces it has also been observed that there is a characteristic pH above which adsorption of metal ion decreases with ionic strength and below which the reverse is seen to occur [24]. Increasing solid–liquid ratio (adsorbent weight) reduces adsorption of metal ions because of aggregation and thus flocculation of adsorbent particles. A decrease in this ratio allows dispersion of the particles which increases the available sorption sites between the particles [25]. However, no study has been reported on the effect of these operating variables in the adsorption of metal ions onto phosphate-modified kaolinite clay.

This paper, therefore investigates the effect of phosphate ion modification of indigenous kaolinite clay on the selectivity of the modified kaolin for Pb^{2+} and Cd^{2+} ions in aqueous solutions. Reaction variables like initial metal ion concentration, adsorbent dose, pH, electrolytes and their ionic strength, and contact time will be optimized with respect to the efficiency of metal ion removal. It is hoped that the data generated from this work will be useful in the application of modified kaolin in cleanup of metal ions from industrial wastewater and in agriculture.

2. Materials and methods

2.1. Materials

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 de-ionised water in a 1 L beaker for several hours. It was further purified using the method of Moore and Reynolds, [26]. 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 de-ionised 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 surface area of the kaolin sample was determined by the methylene blue adsorption method [27]. The silica and alumina content of the sample was determined using the atomic absorption spectrophotometer (AAS) while $\% \text{Fe}^{2+}$ and $\% \text{Fe}^{3+}$ were determined by the method described by Vogel [28]. The effective cation exchange capacity (ECEC) was obtained by the method of Juo et al. [29]. The mineralogical composition of the clay sample was determined with a DIANO 2100*E X-ray diffractometer.

2.2. Modification of clay sample

Clay samples (1 g) were equilibrated with 20 mL 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 30 mL portion of doubly de-ionised water in order to remove excess H_2PO_4^- ions. Test for phosphate in solution was confirmed negative. The infra-red spectrograph of both modified and unmodified samples were obtained using a Perkin-Elmer infra-red (IR) spectrometer.

2.3. Effect of liquid–solid ratio on modification

Various weights of the adsorbent (0.1–1.0 g) were placed in 120 mL polyethylene bottles. Phosphate solutions (30 mL of 200 mg/L) were added and the suspension agitated in a rotary orbital shaker (100 rpm) for 3 h. The supernatant obtained were centrifuged and concentration of phosphate left in solution was determined by the method of Harwood and Hatting [30]. The concentration of the acid in solution was determined using a SPECORD UV–vis spectrophotometer at 400 nm.

2.4. Effect of operating variables

2.4.1. Effect of pH

A 300 mg/L solution of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ were prepared from a stock solution of 1000 mg/L each of both salts using distilled–de-ionised water. Metal ion solution (20 mL of 300 mg/L) was added to 1 g of both modified and unmodified clay samples weighed into 120 mL polyethylene bottles. The solutions were adjusted to 3.5–7.5 using either 0.1 M NaOH or HCl. The suspensions were agitated for 3 h. The supernatants obtained after centrifugations were analyzed for the respective metal ions using an atomic absorption spectrometer, AAS (Computer-Aided Solar Series, Model 969) while the amount adsorbed was calculated by difference.

2.4.2. Effect of initial metal ion concentration

Stock solutions of 1000 mg/L each of the standardized Pb^{2+} and Cd^{2+} were prepared from their nitrates using distilled–de-

ionised water. The solutions were adjusted to pH 6.0 ± 0.2 with either 0.1 M NaOH or HCl. Batch sorption experiments were performed at room temperature ($28.0 \pm 2^\circ\text{C}$) on a rotary shaker at 100 rpm using 120 mL capped polyethylene bottles containing 20 mL of 60–1000 mg/L of metal ion solutions and 1 g of the adsorbent. After agitation, the suspensions were centrifuged at 1500 rpm for 30 min. The supernatants were then collected and analyzed for the metal ions. The amounts of metal ion adsorbed by the sorbents were calculated by difference.

2.4.3. Effect of electrolyte

Twenty milliliter of the various electrolytes (NaNO_3 , NaCl , $\text{Ca}(\text{NO}_3)_2$, CaCl_2) in three concentrations (0.1, 0.01, and 0.001 M) were separately added to 20 mL of each of the metal ion solutions of concentration range 60–1000 mg/L. These solutions were then added to 2 g of modified and unmodified Kaolinite clay adsorbents. The solutions were adjusted to pH 6.0 ± 0.2 with either 0.1 M NaOH or HCl. These solutions were agitated in a rotary shaker and were subsequently centrifuged. The supernatants collected were analyzed for Pb^{2+} and Cd^{2+} . The amounts of metal ions adsorbed were calculated by difference.

2.4.4. Effect of binary solutions of metal ions

For the binary solution of the metal ions, 20 mL each of the same concentration of Pb^{2+} and Cd^{2+} metal ion solutions were mixed together and added to 1 g of modified and unmodified Kaolinite clay adsorbents. The solutions were adjusted to pH 6.0 ± 0.2 with either 0.1 M NaOH or HCl. All the suspensions were agitated for 3 h in a rotary shaker at 100 rpm and they were subsequently centrifuged at 1500 rpm for 30 min. The supernatants was collected and analyzed for metal ions (Pb^{2+} and Cd^{2+}). The amounts of metal ions adsorbed by the clay samples were calculated by difference.

2.4.5. Effect of time

Weights of 0.2 g of the samples were placed in 120 mL polyethylene bottles containing 20 mL of metal ions. The solutions were adjusted to pH 6.0 ± 0.2 with either 0.1 M NaOH or HCl. These were agitated at 100 rpm at different times within the range of 1–80 min after which they were centrifuged and the supernatant solution taken for metal ion analysis using AAS. The amounts of metal ions adsorbed by the clay samples were calculated by difference.

All experiments were carried in duplicates and the data obtained were used for analysis.

The batch experimental test method was used for all experiments and the temperature at which experiments were carried was $28 \pm 2^\circ\text{C}$. Calculation of amount of metal ion adsorbed by both modified and unmodified adsorbents after AAS reading of equilibrium solution was obtained by calculating the difference using the formula:

$$q_e(\text{mg/g}) = \frac{C_o - C_e (V/1000)L}{W(\text{g})}$$

where q_e is the amount of metal ion adsorbed on the adsorbent, C_o , the initial metal ion concentration (mg/L), C_e , the equilibrium concentration of metal ion solution (mg/L), V , the volume

of metal ion solution used (L), and W is the weight of adsorbent used (g).

2.5. Theory of adsorption isotherms

2.5.1. Langmuir isotherm

The Langmuir isotherm has been used extensively by many authors for the sorption of heavy metal ions in clay, metal oxides, soils, etc. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (\text{non-linear form}) \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (\text{linear form}) \quad (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e , the equilibrium concentration of solute in the bulk solution (mg/l), Q^0 , the monolayer adsorption capacity (mg/g) and b is the constant related to the energy of adsorption. It is the value reciprocal of the concentration at which half the saturation of the adsorbent is attained.

The effect of isotherm shape can be used to predict whether a sorption system is “favorable” or “unfavorable” both in fixed-bed systems [31] as well as in batch processes [32]. According to Hall et al. [33] the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R , which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0} \quad (3)$$

where K_R is a dimensionless separation factor, C_0 , the initial metal ion concentration (mg/L) and K_a is Langmuir constant (L/mg). The parameter K_R indicates the shape of the isotherm accordingly:

Values of K_R	Type of Isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

2.5.2. Freundlich isotherm

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The Freundlich equation may be written as

$$q_e = K_F C_e^{1/n} \quad (\text{non-linear form}) \quad (4)$$

$$\text{Log} q_e = \log K_F + 1/n \log C_e \quad (\text{linear form}) \quad (5)$$

Table 1
Band assignments of unmodified and modified kaolinite sample

IR frequencies (cm ⁻¹)		Band assignments
Unmodified	Modified	
3668.3	3667	Inner surface–OH stretching vibration
2919	2917	CH ₃ –Nujol mull
Absent	2440	P–OH stretching vibration
1034.4	1072.4	Si–O bending vibrations
918.7	921.5	Al–OH bending vibration
792	791	Si–O–Al ^{IV} compounded vibrations
693.8	689	Si–O stretching vibration

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e , the equilibrium concentration of solute in the bulk solution (mg/l), K_F , the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant indicative of the intensity of the adsorption.

2.5.3. Toth isotherm

This is Langmuir-based isotherm. It belongs to the left-handed widened Gaussian energy distribution and assumes a continuous distribution of site affinities [34]:

The equation may be written as

$$q_e = KC_e Q^0 / (1 + (KC_e)^n)^{1/n} \quad (6)$$

where q_e , k , C_e , Q^0 , Q and $1/n$ are same as those in Langmuir and Freundlich isotherms.

2.5.4. Langmuir–Freundlich isotherm

That is an isotherm that fuses both Langmuir and Freundlich isotherms together. It is expected to describe heterogeneous surfaces much better. The equation can be written as

$$q_e = (KC_e)^n Q^0 / 1 + (KC_e)^n \quad (7)$$

where q_e , k , C_e , Q^0 , Q and $1/n$ are same as those in Langmuir and Freundlich isotherms.

3. Results and discussions

3.1. Physicochemical properties

Our earlier work on the mineralogical composition of clay revealed that it consists mainly of kaolinite mineral (61%) with some other minor components [35].

The infra-red spectra of both the unmodified and modified samples were obtained while the band assignments are presented in Table 1. The absorption band at 3668.3 cm⁻¹ for the unmodified sample represents the inner surface –OH stretching vibration and those at 1034.4 and 918.7 cm⁻¹ represents the Si–O and Al–OH bending vibrations, respectively.

An increase in wavelength from 1034.4 and 918.7 cm⁻¹ in the unmodified sample to 1072.4 and 921.5 cm⁻¹, respectively, in the modified sample was observed. The latter peaks were broader and more intense. This suggests that the modification may have been effected at the Si–O⁻ and Al–OH linkages that are negatively charged. The band shift (from 1034.4 to 1072.4 cm⁻¹)

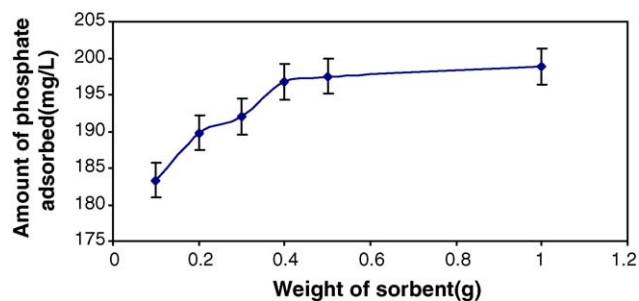


Fig. 1. Effect of liquid–solid ratio on the adsorption of phosphate.

and the presence of a strong absorption at 1072.4 cm⁻¹ suggest the presence of a PO₄²⁻ ion after modification. A similar observation was reported by Colthup et al. [36].

There is also the persistence of the 3668.3 cm⁻¹ peak (inner surface OH⁻) although more intense in the modified sample. This suggests that modification was not effected on this position in the crystal lattice of the clay mineral. This supports Kuo and Lotse [37] who suggested that the phosphate anion displaces a water molecule coordinated to aluminum in the clay mineral. However, a decrease in pH of equilibrium solution from 5.55 to 4.81 after phosphate modification of clay mineral may suggest that K⁺ from the potassium dihydrogenphosphate salt could have displaced H⁺ from the outer/edge OH– groups of the clay mineral.

The small shift in the 693.8 cm⁻¹ peak in the unmodified sample to 689 cm⁻¹ in modified sample also confirms the involvement of the Si–O bond linkage in the modification. The modified kaolinite clay shows a P–OH stretching vibration at 2440 cm⁻¹ [38] which was absent in the unmodified sample. This might indicate the presence of free –OH sites on the modified kaolinite clay.

It is therefore thought that phosphate adsorption would therefore lead to the formation of an outer octahedral complex of aluminum phosphate resulting in the formation of covalent bond between Al of the surface and O of the phosphate [37,39,40] with the resultant displacement of a water molecule.

3.2. Effect of solid–liquid ratio on phosphate adsorption

The effect of solid–liquid ratio on phosphate adsorption is shown in Fig. 1. As the weight of the kaolinite clay increases there is a corresponding increase in the amount of phosphate adsorbed. A plateau is observed at 1 g. The presence of phosphate adsorbed increased the amount of Pb²⁺ and Cd²⁺ adsorbed (Fig. 2). This could be due to increase in surface negative charge as well as a decrease in the electrostatic potential near the solid surface.

3.3. Effect of pH

Fig. 3 showed that increasing pH enhanced the uptake of the metal ions, with the modified adsorbents showing better performance and Pb ions being more adsorbed onto both adsorbents than Cd ions. This enhanced metal ion uptake by kaolinite

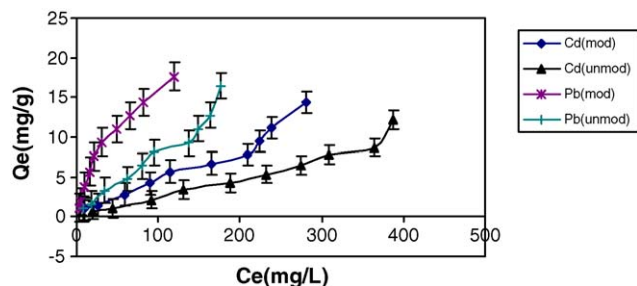


Fig. 2. Adsorption isotherms of single metal ions for modified and unmodified adsorbents (pH 6.0, wt. = 1 g, vol. = 20 mL).

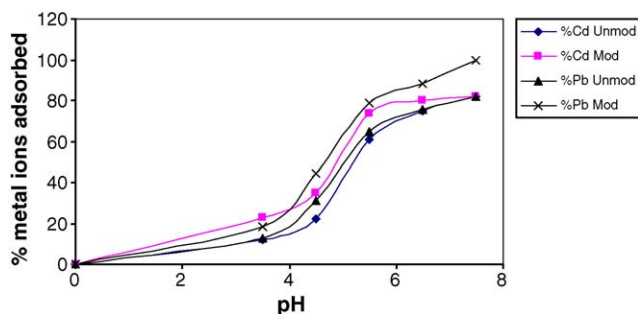


Fig. 3. Effect of pH on adsorption of 300 mg/L of Pb²⁺ and Cd²⁺ ions (wt. = 1.0 g, vol. = 20 mL).

was also reported by Orunwense [41] and Coston et al. [42] for lead ions and Sparks et al. [43]. This may be as a result of increased overall negative charge on both the unmodified and p-modified kaolinite samples especially between pH 4 and 7.0. In addition, increasing pH decreases the concentration of H⁺ therefore reducing the competition between metal ions and protons for adsorption sites on the particle surface. Another factor that could also contribute to enhancing metal ion adsorption is the increasing pH which encourages metal ion precipitation from the solution in the form of hydroxides.

In Fig. 4, it was observed that as metal ion concentration increases, the equilibrium pH of the metal ion in solution (Pb²⁺ and Cd²⁺) decreased from the initial pH value of 6.0–4.08 and 4.32 for Pb²⁺; and pH 4.45 and 4.81 for Cd²⁺ on both unmodified and p-modified adsorbent, respectively. This decrease is in the range of 1–1.82 pH unit as the amount of adsorbed metal ions increased, which agrees with findings by Singh et al. [44].

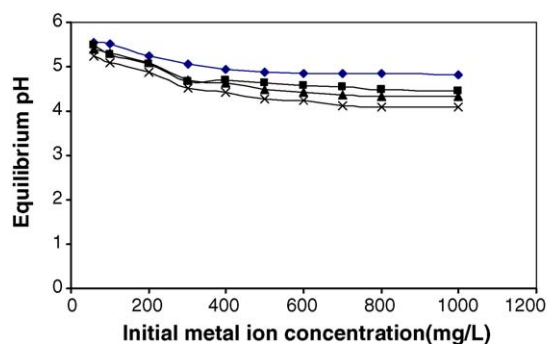


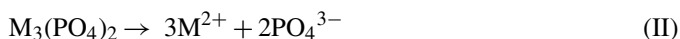
Fig. 4. Effect of initial metal ion concentration on equilibrium solution pH where CP and CU = Cd adsorbed on modified and unmodified adsorbents LP and LU = Pb adsorbed on modified and unmodified adsorbents, respectively.

This decrease in pH became fairly constant with increase in metal ion concentrations for both p-modified and unmodified adsorbents. For the p-modified adsorbent it is expected that the divalent cations of Pb and Cd will displace two H⁺ from both p-modified and unmodified substrates for each of the metal cation adsorbed, while one H⁺ is displaced for each monovalent metal ion specie (MOH⁺) adsorbed. It is therefore suggested that more monovalent species of Pb and Cd were retained as concentration of metal ions increased. This explains the almost constant pH values obtained with increasing metal ion concentrations.

The p-modified adsorbents tend to give slightly higher equilibrium pH values when compared with those of the unmodified adsorbents. This may be due to the initial displacement of H⁺ during phosphate modification. To confirm this, the pH of phosphate solution used for modification was determined before and after the modification process. It was found that the pH of the phosphate solution before modification was 5.55 and the equilibrium solution after modification gave a pH of 4.81.

This findings and the result from IR analysis does not completely favor the idea by Hsu [45] that the mechanism of phosphate retention is due to an adsorption reaction in which Al (or iron) remains as the constituent of the original adsorbent but reacts with phosphate by displacement of a water molecule neither does it also completely favor the suggestion of adsorption of phosphate by exchange of edge hydroxyl groups of the crystal lattice as proposed by Muljadi et al. [46]. It therefore seems that a combination of both displacement of water molecule and exchange of H⁺ from edge hydroxyl group by K⁺ from the potassium dihydrogen phosphate salt are the most likely mechanisms of phosphate adsorption onto kaolinite clay mineral.

The possibility of Pb²⁺ and Cd²⁺ ions being precipitated as hydroxides at pH of experiment during adsorption was examined. Using the solubility product constant (K_{sp}), the pH at which the hydroxides of the metal ions starts to formulate was calculated using the equation below:



$$K_{sp} = [PO_4^{3-}]^2[M^{2+}]^3 = [M^{2+}][OH^-]^2 \quad (III)$$

$$pH = 14 - \log \left[\sqrt{M^{2+}} / \sqrt{K_{sp}} \right] \quad (IV)$$

The K_{sp} values of Pb(OH)₂ and Cd(OH)₂ 1.2×10^{-15} and 5.27×10^{-15} , respectively [47].

The pHs for precipitation of Pb²⁺ and Cd²⁺ from a 1000 mg/L solution of these cations are 7.69 and 7.89, respectively. However, there could be precipitates of the metal ions in the hydroxide form at pH of the experiment as shown in Fig. 5. To ascertain this, the pH of 500 mg/L of Pb²⁺ and Cd²⁺ were varied between 5 and 9 and the solutions were left standing for 3 h after which the solutions were analyzed for the various metal ions. At pH 6 the percentage amount of Pb and Cd precipitate formed is 6.75 and 7.46, respectively. This may have contributed to the amount of Pb²⁺ and Cd²⁺ ions adsorbed.

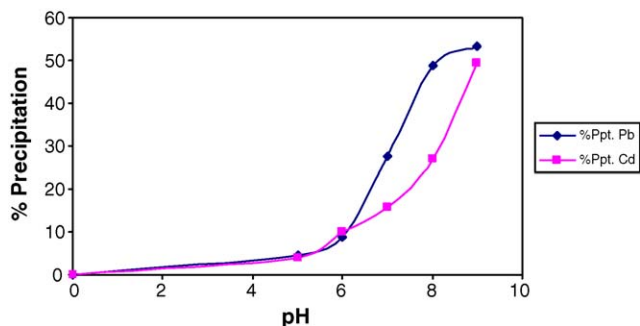


Fig. 5. Percentage precipitation of metal ions.

The phosphates of the metal ions are not expected to be formed in solution of the metal ions at the pH of adsorption during this experiment. This was confirmed by testing for phosphate ions in the equilibrium solutions and the results were negative.

3.4. Effect of initial metal ion concentration

It was observed from Fig. 2 that increasing initial metal ion concentration from 60 to 1000 mg/L resulted in an increase in the metal ions adsorbed for both p-modified and unmodified sorbent.

At very low initial concentrations 94.7% of Pb ions were adsorbed on p-modified kaolinite clay compared with 85.5% of Pb ions on the unmodified sorbent. However, 88.1% Cd ions were adsorbed on p-modified kaolinite clay whereas 58.1% of Cd ions were adsorbed on unmodified kaolinite clay samples. Although not shown, the fraction of metal ions adsorbed decreased with increasing metal ion concentration. This indi-

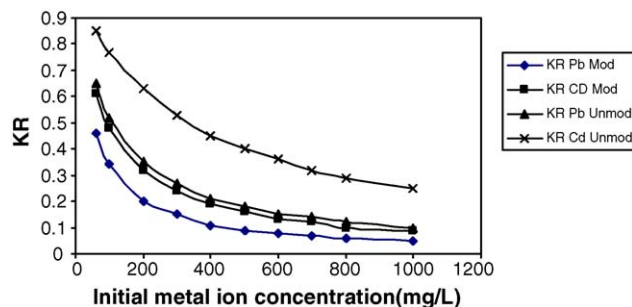


Fig. 6. Effect of initial metal ion concentration on separation factor (K_R).

cates a decrease in the active sites on the sorbents as more metal ions are adsorbed.

With increasing metal ion concentration, there is increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on both the modified and unmodified adsorbents.

Plots of the K_R (separation factor) values for the metal ions as given in Fig. 6 indicated that sorption is more favorable for higher initial metal ion concentrations with respect to lower ones. The sorption of both metals is more favorable on the p-modified sorbent than on the unmodified adsorbent.

3.5. Effect of background electrolyte

Table 2 shows adsorption capacities (Q^0) and the binding energy constant (b) of p-modified and unmodified adsorbents for Pb and Cd ions in solutions of different electrolytes and at different concentrations of these electrolytes. It was observed that in the presence of Na- and Ca-electrolyte and with increasing

Table 2

Data showing the effects of electrolyte on the adsorption capacities of modified and zero electrolyte metal solution and the binding energy constants of Pb^{2+} and Cd^{2+} on the adsorbents

Parameters	NaNO ₃ (M)			NaCl (M)			Ca(NO ₃) ₂ (M)			CaCl ₂ (M)			Unmodified kaolinite clay
	0.1	0.01	0.001	0.1	0.01	0.001	0.1	0.01	0.001	0.1	0.01	0.001	
Lead													
Modified sample													
Q^0 (mg/g)	17.54	17.89	18.01	17.42	17.54	17.76	13.24	14.02	17.01	12.66	13.68	14.45	19.27
b (L/g)	0.0298	0.0437	0.0620	0.0647	0.0641	0.0708	0.0163	0.0238	0.0198	0.0058	0.0090	0.0143	0.020
R^2	0.8502	0.9206	0.9556	0.9165	0.8850	0.9135	0.9698	0.9437	0.9378	0.9391	0.9729	0.9708	0.9799
Unmodified sample													
Q^0 (mg/g)	13.19	13.97	14.33	14.90	15.58	16.13	10.26	11.24	12.97	8.36	8.95	11.11	16.16
b (L/g)	0.0193	0.0379	0.0399	0.0298	0.0355	0.0361	0.0140	0.0180	0.0190	0.0090	0.0150	0.0150	0.0090
R^2	0.9233	0.9170	0.9291	0.9144	0.9232	0.9307	0.9747	0.9589	0.9302	0.9299	0.9077	0.9654	0.9059
Cadmium													
Modified sample													
Q^0 (mg/g)	7.37	8.39	8.72	8.64	9.58	10.34	7.19	8.62	8.88	6.74	8.83	9.33	15.60
b (L/g)	0.032	0.029	0.028	0.033	0.029	0.032	0.017	0.021	0.034	0.024	0.018	0.020	0.011
R^2	0.9600	0.9823	0.9861	0.9758	0.9694	0.8708	0.9658	0.9653	0.7520	0.9237	0.9500	0.8665	0.9835
Unmodified sample													
Q^0 (mg/g)	7.23	9.96	10.49	7.78	9.13	10.00	6.93	8.64	9.68	6.68	7.23	9.62	10.75
b (L/g)	0.014	0.013	0.014	0.028	0.026	0.024	0.005	0.007	0.012	0.002	0.007	0.007	0.003
R^2	0.9726	0.9763	0.8945	0.9165	0.9843	0.9857	0.9430	0.9023	0.9758	0.8016	0.9228	0.8813	0.9591

Q^0 : maximum adsorption capacity; b : binding energy constant; R^2 : correlation coefficient.

concentrations of both electrolytes, there was a decrease in the adsorption capacities of both adsorbent for the metal ions. Pb ions are more adsorbed on both types of adsorbents than Cd ions over the wide range of electrolyte concentration applied (Table 2) and the p-modified adsorbent show better adsorption capacities when compared with the unmodified adsorbent in the presence of these electrolytes.

The percentage decrease in adsorption capacity of p-modified kaolinite clay in the presence of increasing concentration of Na-electrolytes when calculated were 7.84–9.60 compared with a range of 0.19–18.38 for unmodified adsorbents for Pb ions. However, in the presence of increasing concentration of Na-electrolytes for Cd ions, the range of decrease of adsorption capacity of p-modified kaolinite clay was between 2.42 and 32.74 compared with a range of 33.72–52.76 for the unmodified kaolinite clay. A similar trend was observed in the presence of increasing concentration of Ca-electrolytes. However, a more pronounced decrease was observed with this electrolyte. The negative effect exerted by Ca-electrolytes on the adsorption capacities of the adsorbents was more pronounced than Na-electrolytes. It also reveals that Cd ions compete poorly with Ca ions for adsorption sites especially on p-modified adsorbent.

Although not shown, experimental values revealed that the negative effect of increasing concentration of electrolytes on the adsorption capacities of the adsorbents for Pb and Cd ions, decreased with increasing Pb and Cd ion concentration. This is due to the stronger preference both p-modified and unmodified adsorbents show towards Pb and Cd ions than for Na⁺ and Ca²⁺.

In considering the effect of the anions of the electrolytes on the adsorption capacities of the adsorbents, it is observed that the chloride of Na had a less negative effect on the adsorption capacities of the adsorbents when compared with its nitrate form. This therefore supports the view by Suraj et al. [48] that there could be the formation and adsorption of monovalent chloride complexes of the metal ions that could raise the maximum uptake of metal ion by the adsorbents. However, the anions of Ca show a reversed effect. This suggest further, that with increase in the concentration of chloride anions in metal ion solution (as it is in CaCl₂ compared to NaCl) there is the possibility that the metal ions will form uncharged or negatively charged chloride complexes (e.g. MCl₂⁰, MCl₃⁻, MCl₄²⁻) that will invariably reduce the adsorption capacity of the sorbent [49,50] although Neal and Sposito [51] had suggested that species other than Pb and Cd ions do not significantly sorb.

Therefore, the decrease in adsorption capacities observed when increasing concentrations of electrolytes were used, may be primarily due to the competition between cations of the electrolytes and metal ions for certain surface sites. This is possibly the reason for a decrease in pH of sample solutions (from 6.0 to an average of 4.35) and subsequently a decrease in adsorption of metal ion. Sparks et al. [43] showed that the cations of these electrolytes compete much more effectively for permanent negatively charged sites (silanol sites, Si–O) on the kaolinite faces than on the aluminol sites (Al–OH). It is also suggested that increasing electrolyte concentration can cause screening of sur-

face negative charges by the electrolyte ions leading to a drop in the adsorption of the metal ions [52].

The difference in the adsorption capacities of the adsorbents for the metal ions in the presence of these Na- and Ca-electrolytes is due to the difference between Na⁺ and Ca²⁺ with respect to competition with Pb and Cd ions sorption sites. This indicates that the adsorbents show stronger preference for Ca²⁺ (a divalent cation) than for Na⁺ (a monovalent cation) with the resultant effect of a further drop in monolayer adsorption capacities of the adsorbents for the metal ions when Ca-electrolytes were used.

From the Langmuir equation the binding energies of the metal ions onto the adsorbents were enhanced by modification. Sodium-electrolytes enhance the binding energy more than Ca-electrolytes. This may therefore suggest that the presence of Na- and Ca-electrolytes may generally reduce reversibility of the adsorbed metal ions (Pb²⁺ and Cd²⁺). This reduction in reversibility may be more pronounced with the p-modified adsorbent.

3.6. Effect of binary solutions

The effect of the presence of one heavy metal ion in solution of another (binary solution of metal ions) on the adsorption of heavy metal ions onto both modified and unmodified adsorbents is shown in Fig. 7. It may be represented by the ratio of the sorption capacity for one metal ion in the presence of the other metal ion, Q^{mix} , to the sorption capacity for the same metal when it is present alone in the solution, Q^0 , so that for:

$$\frac{Q^{\text{mix}}}{Q^0} > 1$$

the sorption is promoted by the presence of other metal ions:

$$\frac{Q^{\text{mix}}}{Q^0} = 1$$

there is no observable net interaction:

$$\frac{Q^{\text{mix}}}{Q^0} < 1$$

sorption is suppressed by the presence of other metal ions.

The values of $\frac{Q^{\text{mix}}}{Q^0}$ are found to be less than one as shown in Table 3 which suggest that sorption of either metal ion is

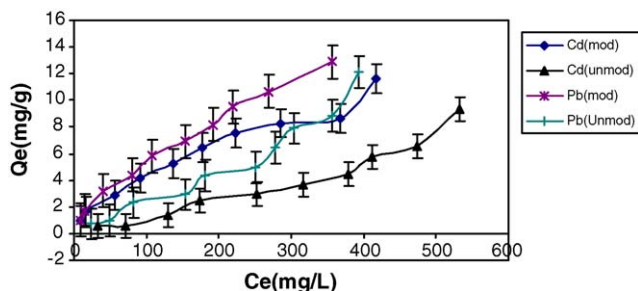


Fig. 7. Adsorption isotherm of binary metal ion solutions for modified and unmodified sorbents (pH 6.0, wt. = 1 g, vol. = 20 mL).

Table 3
Binary solutions of lead and cadmium ions

Metal ion	Sorbent type	Q^{mix} (mg/g)	Q^{mix}/Q^0	b (L/g)	R^2
Lead	Modified	18.25	0.95	0.005	0.8747
	Unmodified	15.04	0.93	0.002	0.9359
Cadmium	Modified	14.03	0.90	0.006	0.8827
	Unmodified	9.23	0.86	0.002	0.8356

suppressed by the presence of the other metal ion [53]. However, the % drop in adsorption capacities of both p-modified and unmodified adsorbents for the binary metal ion solutions are less than those obtained during adsorption of metal ions in the presence of electrolytes. This may therefore suggest that the negative effect of an electrolyte on the adsorption capacities of both p-modified and unmodified kaolinite clay for Pb and Cd ions is more pronounced than the negative effect produced by binary solution of both metal ions during their adsorption onto the adsorbents.

3.7. Effect of time on adsorption

From Fig. 8, it was observed that modification of kaolinite clay enhanced adsorption of the metal ions as well as altered the rate of adsorption these metal ions by the adsorbent. Unlike the unmodified adsorbents, there was a sharp increase in the adsorption of both metal ions on the p-modified adsorbents within the first 5 min of the reaction. For adsorption of lead on p-modified adsorbent, equilibrium was reached after 8 min with 94.8% adsorption while for the unmodified adsorbent, equilibrium was attained after 20 min with 78.7% adsorption. However, for cadmium adsorption, equilibrium condition was attained after 12 min for the p-modified adsorbent and 20 min for the unmodified adsorbent with 87.5 and 68.6% adsorption, respectively.

This accelerated adsorption of these metal ions onto phosphate-pre-treated kaolinite clay may be as a result of the blocking of some pores on the surface of the kaolinite clay mineral by phosphate anion [54,55]. This is because the size of phosphate anion (0.22 nm in radius) is larger than the sizes of Pb^{2+} (0.133 nm) and Cd^{2+} ions (0.097 nm). It is therefore possible for phosphate ions to diffuse into and block the pores after pre-treatment. As a result, Pb and Cd ions may not be able to diffuse further into the pores and this will increase the overall

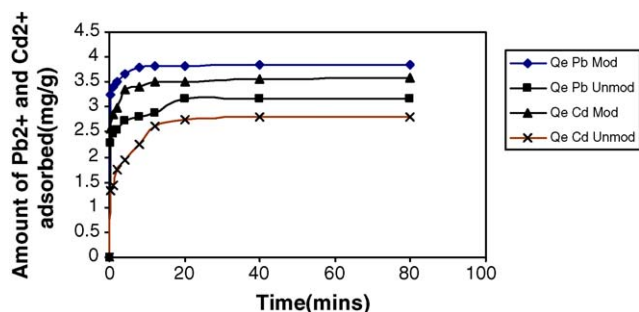


Fig. 8. Effect of time on adsorption of 200 mg/L Pb^{2+} and Cd^{2+} onto modified and unmodified adsorbents.

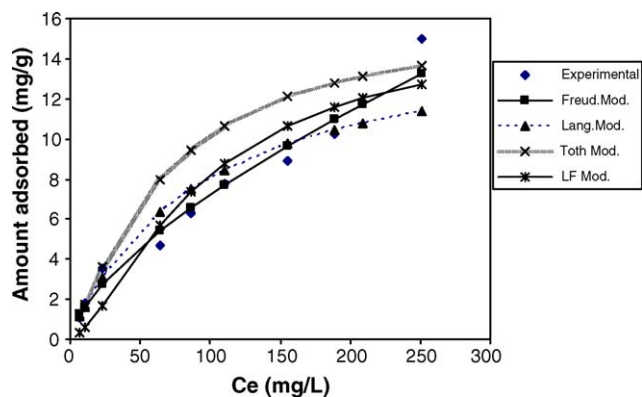


Fig. 9. Model isotherm of the adsorption of cadmium ions on modified adsorbent.

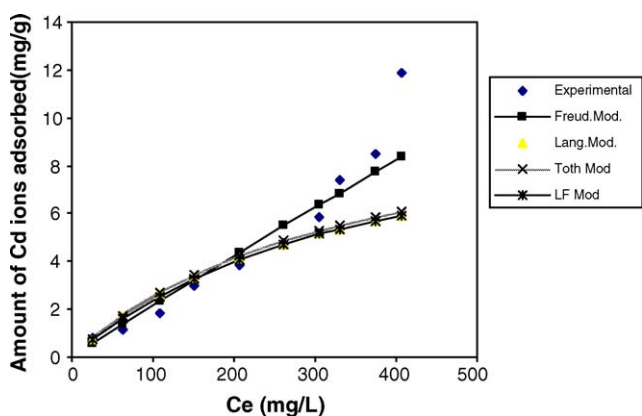


Fig. 10. Model isotherm of the adsorption of cadmium ions on unmodified adsorbents.

rate of adsorption. A similar observation was reported by Wang and Xing [56].

3.8. Data modelling

Data obtained from adsorption of metal ions in the absence of electrolytes are fitted against non-linear Langmuir, Freundlich, Toth and Langmuir–Freundlich isotherms. This is shown in Figs. 9–12. Data from adsorption of lead ions on p-modified

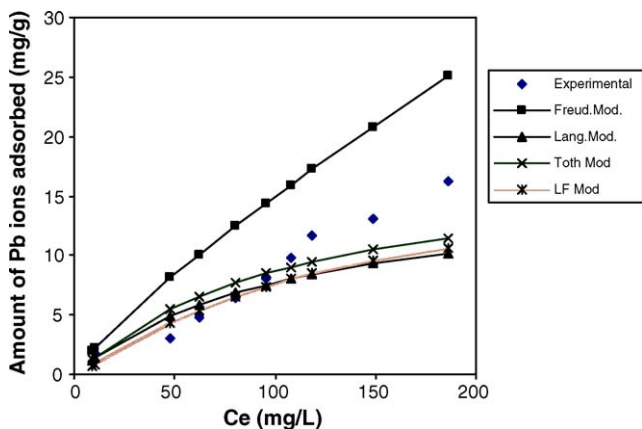


Fig. 11. Model isotherm of the adsorption of lead ions on unmodified adsorbent.

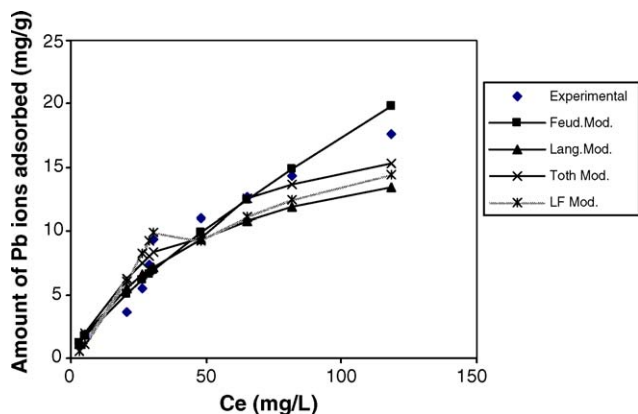


Fig. 12. Model isotherm of the adsorption of lead ions on modified adsorbent.

Table 4
Correlation coefficients (R^2) of modeled adsorption data

	Modified		Unmodified	
	Lead	Cadmium	Lead	Cadmium
Experimental	0.9790	0.9799	0.9177	0.9193
Freundlich model	0.9953	0.9840	0.9911	0.9999
Langmuir model	0.9211	0.9019	0.8837	0.9636
Toth model	0.9170	0.8753	0.8844	0.9634
Langmuir–Freundlich model	0.9436	0.9299	0.7559	0.9678

adsorbents showed satisfactory fits to all model but adsorption on unmodified adsorbents show poor fit to Langmuir, Toth and Langmuir–Freundlich models (Table 4). For cadmium ions data from both adsorbent showed satisfactory fits to all models except for adsorption on modified adsorbent which showed a poor fit to the Toth model. At low concentrations, both metal ions showed better fits to Langmuir than the Freundlich model. This implies that at low concentration of the metal ions certain sites are responsible for their adsorption and adsorption of these ions assumes monolayer coverage of the surface. However, adsorption data for adsorption of both metal ions on both p-modified and unmodified adsorbents produced very good fits to the Freundlich model at high concentrations. This suggests that more than one type of active site may also be involved in the adsorption of the metal ions at high concentrations.

However, from the correlation coefficient shown in Table 4 there is strong indication that the adsorption data obtained fits the Freundlich model better than other models when the whole range of initial metal ion concentration is considered.

4. Conclusions

The modification of kaolinite clay mineral was found to be on both silanol (Si–O) and aluminol (Al–OH) sites of the clay mineral and not on the edge — hydroxyl groups on the surface of the sorbent.

The presence of Na- and Ca-electrolytes reduced the adsorption of the metal ions on both p-modified and unmodified adsorbents.

Adsorption reaction carried out on binary solutions of both metal ions reveals that adsorption of both metal ions is suppressed by the presence of either metal ion.

Modeling data obtained with Langmuir, Freundlich, Toth and Langmuir–Freundlich isotherms, indicated that very good fits were produced with the Freundlich model at high metal ion concentration. Poor fit was however obtained with Toth and Langmuir–Freundlich models. This implies that the sites on both modified and unmodified kaolinite clay adsorbents available for the adsorption of high concentrations of Pb^{2+} and Cd^{2+} may be heterogeneous in nature.

In view of the above, the phosphate-modified adsorbent has the potential of holding heavy metal ions from industrial wastewaters even in the presence of low concentrations of electrolytes. It also offers an application in the in situ treatment of heavy metal contaminated soils.

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