Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: Equilibrium and thermodynamic studies

E.I. Unuabonah [a,*], K.O. Adebowale [b], B.I. Olu-Owolabi [b], L.Z. Yang [c], L.X. Kong [c]

[a] College of Natural and Applied Sciences, Department of Chemical Sciences, Bells University of Technology, Ota, Nigeria
[b] Faculty of Science, Department of Chemistry, University of Ibadan, Ibadan, Nigeria
[c] Institute of Soil Science, Chinese Academy of Sciences, Nanjing, PR China

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ABSTRACT

Kaolinite clay sample obtained from Ubulu-Ukwu in Delta State of Nigeria was modified with sodium tetraborate to obtain NTB-modified kaolinite clay. XRD measurements of NTB-modified kaolinite adsorbent showed no observable change in the d-spacing of its crystal lattice. Also, the data of XRD confirmed that this kaolinite clay sample is a mixture of kaolinite and Illite clay minerals. The SEM of modified and unmodified samples showed irregular crystal structures. FTIR results proved the surface modification of the kaolinite at $-Al-O$ and $-Si-O$ centers. The NTB-modified adsorbent presented with broader peaks of inner $-OH$. Modification of kaolinite clay sample with sodium tetraborate decreased its PZC from pH 4.40 to 3.70 while its Specific Surface Area (SSA) was increased from 10.56 m^2 g^{-1} to 15.84 m^2 g^{-1}.

Modification with sodium tetraborate reagent increased the adsorption capacity of kaolinite clay from 16.16 mg/g to 42.92 mg/g for Pb (II) and 10.75 mg/g to 44.05 mg/g for Cd (II) at 298 K. Increasing temperature was found to increase the adsorption of both metals onto both adsorbents suggesting an endothermic adsorption reaction. The simultaneous presence of electrolyte in aqueous solution with Pb and Cd (II) was found to decrease the adsorption capacity of NTB-modified adsorbent for Pb and Cd (II). Using the Pearson's Hard and Soft Lewis Acid and Base (HSAB) theory the higher selectivity of unmodified kaolinite clay adsorbent for Pb and NTB-modified kaolinite clay for Cd (II) was justified.

The thermodynamic calculations for the modified kaolinite clay sample indicated an endothermic nature of adsorption (ΔH_{mean} +4.35 kJ mol^{-1} for Pb(II) and +3.79 kJ mol^{-1} for Cd (II)) and an increase in entropy as a result of adsorption of Pb (II) and Cd (II) (ΔS_{mean} −21.73 J mol^{-1} K for Pb (II) and −18.30J mol^{-1} K for Cd (II)). The small positive values of free energy change (ΔG_{mean}) indicated that the adsorption of Pb (II) and Cd (II) onto the modified adsorbent may require some small amount of energy to make it more feasible.

Modeling equilibrium adsorption data obtained suggested that NTB-modified adsorbent sample has homogeneous adsorption sites and fit very well with Langmuir adsorption model.

Regeneration studies suggest that ≈85% of the metals were desorbed from both adsorbents. On reuse of the adsorbents only ≈80% of metals were adsorbed. NTB-modified kaolinite clay sample show some very good potentials as a low-cost adsorbent for the adsorption of Pb (II) and Cd (II) from aqueous solutions.

1. Introduction

There is an increasing public concern regarding the contamination in drinking water. This has lead to tighter controls from various state and federal environmental protection agencies on industries in their discharge of liquid waste into water bodies. Increasing industrialization in Africa is generating large volumes of wastes containing toxic metals. These metals when discharged into the environment may get into the food chain causing deleterious effects on humans as well as animals. Chemical Precipitation is the most common method employed by many industries here in Africa in treating metal-bearing effluents. However, this method involves huge financial cost and produces pollution.

Adsorption is one of the few alternatives available for recovery of metal ions from aqueous solutions including wastewater. This method have been found to be both efficient and cost effective in that the process does not involve the production of sludge as in the case of the former method which adds to the cost of recovery of the metal ions (Ho and McKay, 1999).

Activated carbon has been long recognized as an effective adsorbent because it possesses high surface area and can be easily regenerated for reuse (Cooper and Burch, 1999). Its increasing cost has necessitated the sourcing of alternatives that are cheap and equally efficient. In recent years numerous low cost adsorbents have been proposed as potential replacement for the effective but expensive

* Corresponding author. Tel.: +234 805 3175 971.
E-mail address: iyaemma@yahoo.com (E.I. Unuabonah).

activated carbon. A wide range of low cost adsorbents have been tested for their capacity to adsorb heavy metal ions from aqueous solutions, as documented in a recent review (Bailey et al., 1999). Among these low cost adsorbents are the clay minerals (aluminosilicates) which have been found to be also very useful in the recovery of metal ions. There are three main classes of clays: Kaolinite, Micas (such as Illite) and Smectite (such as Montmorillonite). Of these three classes, Montmorillonite clay has the smallest crystals, the largest surface area and largest Cation Exchange Capacity. Montmorillonite clay has been shown to have adsorption capacities five times that of Kaolinite (Griffin et al., 1977).

Clay minerals have different adsorption capacities for metal ions depending on the conditions in which the adsorption reactions were carried out. Clay minerals could be modified like other adsorbents mentioned earlier. Several methods have been employed to improve on the Cation Exchange Capacity (CEC) of clay minerals. These includes activation (Suraj et al., 1998), pillaring or intercalation (Frost et al., 2002, Frost et al., 1997, Frost et al., 1999) and chemical modification of the surface using inorganic complex forming ions (Sidheswara et al., 1990) or organic based complex forming ions (Sang-Mo and Dixon, 2002). Montmorillonite clay has also been modified with hydroxylaluminium and hydroxoaluminosilicate (Saha et al., 2001). kaolinite clay has also been modified with orthophosphate and tripolyphosphate (Adebowale et al., 2006; Unuabonah et al., 2007b). Manohar et al. (2002) and Dais Filho et al. (1995), have reported that 2-mercaptobenzothiazole impregnated clay surface can be used for the removal of some heavy metal ions from water samples.

This study seeks to introduce a new low-cost adsorbent, sodium tetraborate-modified kaolinite clay adsorbent. Some of the characteristics of this adsorbent in the adsorption of Pb (II) and Cd (II) are studied in this paper with the view to discovering its metal ion recovery potential from industrial effluents with relatively high concentrations of these metal ions.

2. Materials and methods

2.1. Purification and characterization of Kaolinite clay

Kaolinite Clay was obtained from Ubulu-Ukwu, Delta State, Nigeria. On collection, it was purified by method described by the Adebowale et al., 2005. Once dried, it was sieved to +220 μm particle size.

2.2. Preparation of sodium tetraborate (NTB)-modified kaolinite

The Kaolinite clay sample was first treated with 2 M HNO₃ for 3 h and was then washed several times with distilled-deionized water until filtrate attained pH 7.0 and then dried in the oven at 333 K for 48 hrs. To 50 g of Kaolinite sample, 500 ml of a certain concentration of sodium tetraborate (NTB) reagent was added. This suspension was stirred on a power stirrer with impeller blades for 6 h. The suspension which had a pH of 9.61 was washed several times with distilled-deionized water until pH 8.98. The sample was then centrifuged at 1500 rpm for 30 min, dried in an oven at 333 K and sieved to +220 μm particle size and the sample was subsequently referred to as NTB-modified Kaolinite clay adsorbent.

2.3. Characterization of adsorbents

The cation exchange capacity (CEC) of NTB-modified kaolinite clay sample 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 same method.

The Specific Surface Area (SSA) of the unmodified and NTB-modified kaolinite clay was determined using the Sear's method (Sears, 1956). 0.5 g of the sample was acidified with 0.1 M HCl to a pH 3–3.5. The volume was made up to 50 mL with distilled water after addition of 10.0 g of NaCl. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 298±0.5 K to pH 4.0, and then to pH 9.0. The volume, V, required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation:

$$S(\text{m}^2/\text{g}) = 32V - 25 \tag{1}$$

The Infrared spectra of the adsorbents were obtained by method described by Unuabonah et al., 2007b. The Point of Zero Charge (PZC) of both adsorbents was determined using the method described by Ofomaja, 2007. The X-ray diffraction (XRD) spectra of the adsorbents were obtained using a Philips X-ray Diffraction instrument

with filtered Cu Kα radiation operated at 40 kV and 40 mA. The XRD pattern was recorded from 1.5 to 50° of 2θ per second with a scanning speed of 0.02° of 2θ per second. A Philip XL30 Scanning Electron Microscope/EDAX was used to obtain microgram scans of both Unmodified and NTB-modified kaolinite clay samples. Fourier transform infrared spectrometer (Nexus 870 FT-IR) was used for the Infrared Spectroscopic analysis of the samples.

2.4. Effect of adsorbent dose

In 120 ml polyethylene bottles containing 300 mg/L of 20 ml of metal ion solution 0.2–1.0 g of the NTB-modified and unmodified kaolinite clay sample were introduced. The samples were agitated for 5 h. The pH of metal ion solutions was kept at 5.5±0.2. After agitation, the suspensions were centrifuged at 1500 rpm for 15 min and supernatant kept for Pb (II) and Cd (II) analysis. The amounts of metal ion adsorbed by the adsorbents were calculated by difference.

2.5. Effect of pH

Twenty millilitres of 200 mg/L of metal ion solutions were added to 0.2 g of both the NTB-modified and unmodiified kaolinite clay samples in 120 ml polyethylene bottles. The pHs of the suspensions were adjusted within the pH range of 3.0±0.2 to 5±0.2 using either 0.1 M NaOH or 0.1 M HCl. These samples were agitated for 5 h. After agitation, the suspensions were centrifuged at 1500 rpm for 15 min and supernatant kept for Pb (II) and Cd (II) analysis. The amounts of metal ion adsorbed by the adsorbents were calculated by difference.

2.6. Adsorption equilibrium study

The pH of the metal ion solutions for sodium tetraborate adsorbent (NTB-modified sample) were adjusted to 5.5 0.2. Batch adsorption experiments were performed at room temperature (28.0±2 °C) on a rotary shaker at 100 rpm using 120 ml capped polyethylene bottles containing 20 ml of 60–400 mg/L of metal ion solutions and 0.2 g of unmodified and NTB-modified adsorbents for 5 h. After agitation, the suspensions were centrifuged at 1500 rpm for 15 min and supernatant kept for Pb (II) and Cd (II) analysis. The amounts of metal ion adsorbed by the adsorbents were calculated by difference. In Adebowale et al. (2006), data for previous adsorption studies on the unmodified kaolinite clay sample has been shown.

2.7. Adsorption Isotherms

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

$$q_e = \frac{Q^o bCe}{1 + bCe} \quad \text{(Non-linear form)} \tag{2}$$

$$\frac{1}{q_e} = \frac{1}{Q^o bCe} + \frac{1}{Q^o} \quad \text{(Linear form)} \tag{3}$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), Ce is the equilibrium concentration of solute in the bulk solution (mg/L), Q^o is the monolayer adsorption capacity (mg/g) and b is the constant related to the energy of adsorption ($L g^{-1}$). It is the value reciprocal of the concentration at which half the saturation of the adsorbent is attained.

For the following other equilibrium isotherm models were used for adsorption data fittings

Freundlich isotherm model

$$q_e = K_f Ce^{1/n} \tag{4}$$

Toth isotherm model

$$q_e = \frac{KCeQ^o}{\left\{1 + (KC_e)^n\right\}^{1/n}} \tag{5}$$

Lagmuir–Freundlich isotherm model

$$q_e = \frac{(KCe)^n Q^o}{1 + (KC_e)^n} \tag{6}$$

Where q_e, K, Ce, Q^o, and $1/n$ are same as those in Langmuir and Freudlich isotherms.

2.8. Effect of ionic strength of electrolyte

The effect of electrolyte was studied using NaNO₃, NaCl, CaCl₂ and Ca(NO₃)₂ in three concentrations (0.1, 0.01 and 0.001 M). The various weights required for the preparation of each concentration of electrolyte were added to the weights of metal ion salts required to prepare the various concentrations of the metal ion. These were mixed and made up to standard mark using distilled–deionized water. Subsequently, 20 ml of

these solutions were added to 0.2 g NTB-modified adsorbents respectively. The pHs of suspensions were adjusted to pH values used for equilibrium studies agitated for 5 hrs. They were subsequently centrifuged for 15 min at 1500 rpm. The supernatants collected for metal ions (Pb (II) and Cd (II)) analysis. The amounts of the metal ion adsorbed by the adsorbents were calculated by difference.

2.9. Thermodynamic study

The thermodynamics of the adsorption of Pb (II) and Cd (II) onto NTB-modified kaolinite clay adsorbent was studied when 0.2 g of NTB-modified adsorbent was added to 20 ml of various concentrations (60–400 mg/L) of metal ion solutions at pH 5.5±0.2. These were agitated and samples were collected after 5 hrs. These samples were subsequently filtered and filtrate collected for metal ion analysis. The above procedure was carried out at 298 K, 313 K and 323 K.

2.10. Desorption study

Twenty millilitres of 0.1 M HCl was added to 0.2 g of the NTB-modified and unmodified kaolinite clay samples fully loaded with 60 mg/L of Pb (II) and Cd (II). This was agitated for 30 mins. Thereafter, the supernatants were collected for Pb (II) and Cd (II) analysis. The amount of metal ion desorbed was obtained from the difference between the amount of metal ion fully loaded on the adsorbents and the amount of same in solution. The regenerated adsorbents were reused in the adsorption of 60 mg/L of Pb (II) and Cd (II) from aqueous solution to ascertain their adsorption efficiencies for both metal ions after regeneration.

The thermodynamic parameters, ΔH, ΔS and ΔG, for the adsorption process are calculated using the relation

$$\ln b = \Delta S/R - \Delta H/RT \tag{7}$$

where b is the Langmuir constant related to energy. The plot of $\ln b$ vs $1/T$ yields straight lines with the slope and the intercept giving values of ΔH and ΔS. These values could be used to compute ΔG from the Gibbs relation, $\Delta G = \Delta H - T\Delta S$ at constant temperature. In deriving the values of the thermodynamic parameters, it is assumed that the enthalpy does not change with temperature.

3. Results and discussions

3.1. Physicochemical properties

Some of the physicochemical characteristics of the unmodified kaolinite clay adsorbent used in this study have been described in Adebowale et al., (2005). The values of the PZC of modified and unmodified kaolinite clay samples were measured to be at pH 3.70 and 4.41 respectively. This suggests that modification of kaolinite clay with Sodium Tetraborate decreased the PZC of kaolinite clay.

The PZC value obtained above for NTB-modified kaolinite clay adsorbent indicates that it could be used to efficiently adsorb metal ions at pH values as low as 3.70 as the adsorbent becomes more negative at values above the PZC. The unmodified kaolinite clay adsorbent gave Cation Exchange Capacity (CEC) of 7.81 meq/100 g of kaolinite clay (Adebowale et al., 2005). However, the Cation Exchange Capacity of NTB-modified adsorbent was determined to be 32.18 meq/100 g of NTB-modified kaolinite clay.

The prominent peaks found in the unmodified adsorbent (Fig. 1a) were 7.17 Å (001), 4.25 Å, 3.57 Å (002), 3.34 Å, 2.56 Å, 2.49 Å, 2.33 Å, 2.12 Å and 1.98 Å which correspond to Kaolinite, Quartz, Kaolinite, Illite+Quartz, Goethite, Goethite, Gibbsite, Gibbsite and Dickite respectively (Moore and Reynolds, 1997). Fig. 1a and b represents the X-ray diffraction spectra for both
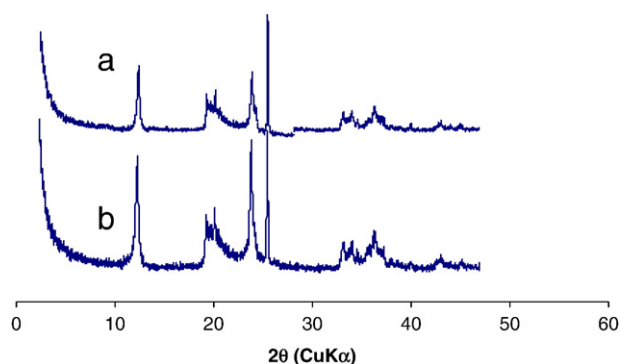

Fig. 1. X-ray crystallographic diffraction Pattern of unmodified kaolinite clay (a) and NTB-modified kaolinite clay (b).
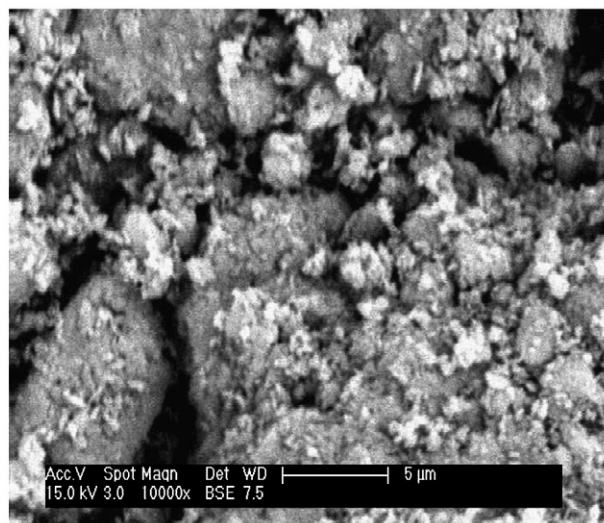

Fig. 2. Scanning Electron Microscope scan for unmodified kaolinite clay.

adsorbents. The above data suggests 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).

X-ray diffraction results obtained for NTB-modified adsorbent (Fig. 1b) showed that modification of kaolinite clay with sodium tetraborate reagent did not change the d-spacing on the lattice structure of the clay mineral to any significant degree, as similar peaks with those for the unmodified adsorbent were obtained. 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 NTB-modified kaolinite clay adsorbent showed peak intensities different from that of the unmodified adsorbent (Fig. 1a), which could be an indication of the modification of the kaolinite clay sample.

When viewed under a Scanning Electron Microscope (SEM), the shapes of NTB-modified adsorbent particles were quite similar to those of the unmodified adsorbent. NTB-modified and the unmodified kaolinite clay adsorbents gave particles with irregular structures. The unmodified adsorbent showed some white particles on the surface of the mineral particles (Figs. 2 and 3). These are likely to be non-clay minerals like Sodium, Potassium, Calcium, Iron and Magnesium (Galan et al., 1996).
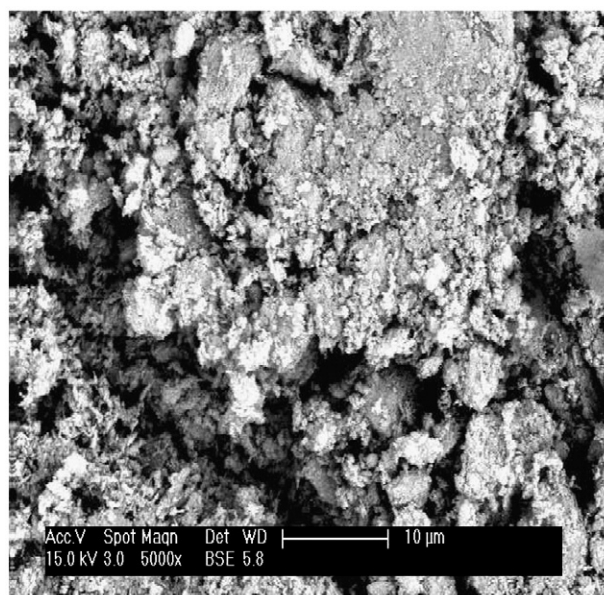

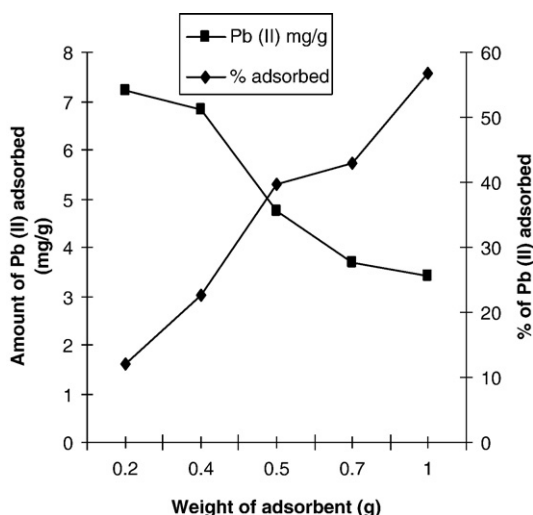Fig. 3. Scanning Electron Microscope scan for NTB-modified kaolinite clay.

Fig. 4. Effect of dosage on the adsorptive capacity of unmodified kaolinite for the adsorption of Pb.

Fig. 6. Effect of dosage on the adsorptive capacity of NTB-Modified kaolinite clay for the adsorption of Pb.

The specific surface area for NTB-modified kaolinite clay adsorbent was observed to be 15.84 m^2 g^{-1} while that of the unmodified adsorbent was 10.56 m^2 g^{-1}.

The Fourier Transformed Infrared Spectrograph of both NTB-modified and Unmodified Kaolinite clay absorbents have been described in our previous work (Unuabonah et al., in press).

In the NTB-modified kaolinite clay adsorbent the Si–O and Al–O peaks were found to shift from 1034.4 cm^{-1} and 918.7 cm^{-1} (Fig. 4) to 1027.86 cm^{-1} and 912.90 cm^{-1} respectively. These peaks were also broader and more prominent when they were compared with those of the unmodified kaolinite clay sample (Unuabonah et al., 2007a).

However, because of the structure of sodium tetraborate, it is possible to say that the –OH site may not be the only site available for the adsorption of Pb (II) and Cd (II) as lone pairs of electrons present on the boron atoms could also have participated in the adsorption of the metal ions. However, there was the absence of the outer –OH peak which rules out the possibility for the adsorption of Pb (II) and Cd (II) onto this site on this adsorbent.

3.2. Effect of adsorbent dose

Figs. 4–7 shows the effect of adsorbent dose on the adsorption capacity of the NTB-modified kaolinite clay. Increase in the dosage of both adsorbents from a range of 0.2–1.0 g resulted in a decrease in equilibrium adsorption capacity, qe, of the adsorbents (Figs. 4–7). However it was observed that the percentage of adsorbate adsorbed increased with
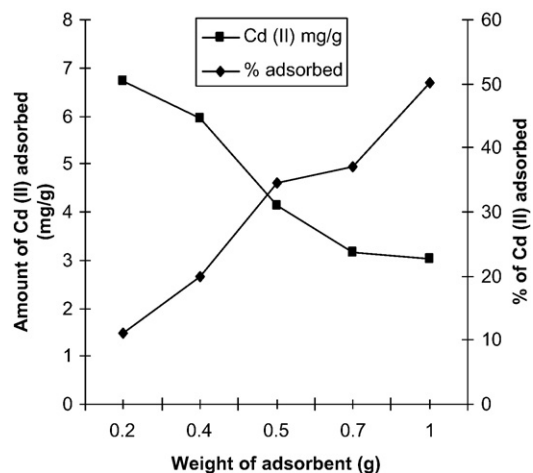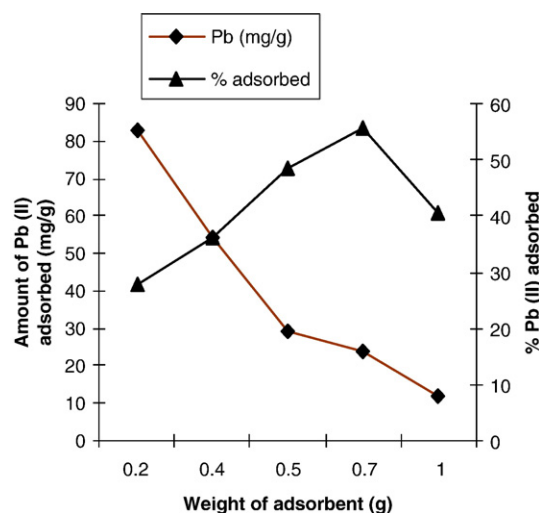
increase in adsorbent dose. A similar trend has been reported in our previous study of the unmodified sample (Unuabonah et al., 2007b) as well as by Ho and Ofomaja (2005) in the adsorption of Pb (II) by palm kernel fiber and Gupta and Bhattacharyya (2006) in the adsorption of Ni (II) on kaolinite clay. The increased percentage adsorption of these metal ions with increasing adsorbent dose is possibly due to increased surface negative charge and decrease in the electrostatic potential near the solid surface that favors sorbent–solute interaction.

However, the decreased equilibrium adsorption capacity, q_e, of the modified clay sample for the metal ions, as its dosages were increased, can be attributed to two reasons. There is decreasing total surface area of the adsorbent and an increase in diffusion path length, which is the result of aggregation of adsorbent particles (Shukla et al., 2002). This aggregation becomes increasingly significant as the weight of the adsorbent is increased (Bordas and Bourg, 2001).

The relationship between the adsorbent dose and equilibrium adsorption capacity, q_e, was found by linear regulation and obtained by coefficient of determination (r^2). It can be expressed as:

$$q_e = Sm_s + Y \tag{8}$$

Where the constant, Y, is the maximum adsorption capacity of the adsorbents, and m_s is the adsorbent dose and S is related to the adsorption potential of the adsorbents. The negative values of S show
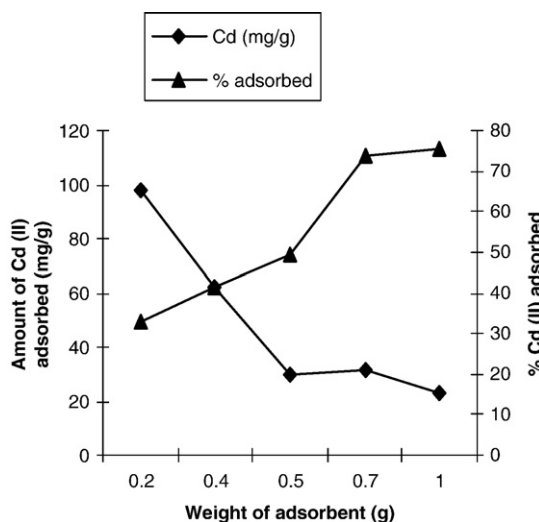

Fig. 5. Effect of dosage on the adsorptive capacity of unmodified kaolinite for the adsorption of Cd.

Fig. 7. Effect of dosage on the adsorptive capacity of NTB-Modified kaolinite clay for the adsorption of Cd.
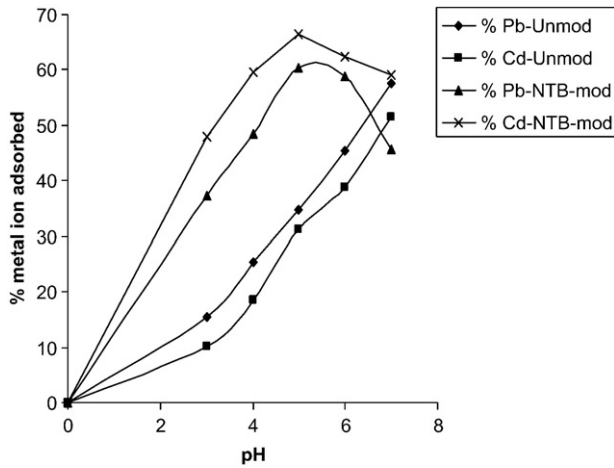
Fig. 8. Effect of pH on the adsorption of Pb (II) and Cd (II) onto unmodiified and NTB-modified kaolinite clay samples.

that with the increase in adsorbent dose, the equilibrium adsorption capacity, q_e, was decreased. Eq. (8) can be used to predict the amount of metal ion that will be adsorbed by a particular weight of both adsorbents used in this study.

The values of Y and S for the adsorption of Pb (II) onto the modified kaolinite clay sample were calculated from plots using Eq. (8), to be, 52.96 mg/g and −39.07 for and 7.49 and −4.62 for the unmodified kaolinite clay sample. For the adsorption of Cd (II), Y and S gave values of 57.20 mg/g and −41.10 for NTB-modified sample and 6.75 and −4.32 for the unmodified sample. This suggests the NTB-modified kaolinite clay has a better potential for the adsorption of both metals from aqueous solutions than the unmodified kaolinite clay.

3.3. Effect of pH

The unmodified kaolinite clay adsorbent showed an observed increase in the adsorption of both Pb (II) and Cd (II) as the pH of both metal ion solutions were increased (Fig. 8). This enhanced metal ion uptake of the adsorbents has also been reported by Orumwense (1996) and Coston et al. (1995) for Pb (II) and Spark et al. (1995). NTB-modified kaolinite clay showed a reverse trend for the adsorption of both metal ions after pH 5.5 (Fig. 8). This behavior shown by the NTB-modified kaolinite clay sample may be connected with the surface modified by sodium tetraborate which perhaps has lone pairs of electrons.

The variation of the adsorption of the divalent cation with the change in pH at constant weight of adsorbent and metal ion concentration may be given by Sposito (1984)

$$\ln\ D = a + b(\text{pH}) \tag{9}$$

where $D = f_{\text{adsorb}}/f_{\text{soln}}$, and a and b are empirical constants. D, the distribution ratio, is defined as the ratio of the fraction of metal ion that is adsorbed to the fraction of the metal ion in solution. A plot of $\ln D$ vs pH is called a Kurbatov plot. The pH at which $D = 1$, where 50% of the added metal is adsorbed and 50% is in solution, is designated pH_{50}.

From Eq. (9) the pH_{50} for the adsorption of Pb (II) and Cd (II) onto unmodified and NTB-modified samples were calculated. For Pb, the pH_{50} was 4 and 6 for NTB-modified and unmodified samples respectively. For the adsorption of Cd (II), pH_{50} were 3 and 7 for NTB-modified and unmodified kaolinite clay samples respectively.

Several reasons may be attributed to the increased adsorption of metal ions by unmodified adsorbent relative to adsorbate solution pH. The surface of the kaolinite clay sample contains a large number of active sites and may become positively charged at very low pH, thus increasing the competition between H+ and the metal ions for available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction.

Table 1
Data for adsorption capacity (q_e) of Pb (II) and Cd (II) for the Unmodified and NTB-modified Kaolinite clay sample and their corresponding Langmuir constants b

	q_e (mg/g)			b (L/g)		
Lead ions						
Adsorbents	298 K	313 K	323 K	298 K	313 K	323 K
Unmodified	16.16*	19.96	22.68	9.00×10^{-3}*	8.77×10^{-3}	8.53×10^{-3}
NTB-modified	42.92	46.95	56.18	1.26×10^{-2}	1.39×10^{-2}	1.44×10^{-2}
Cadmium ions						
Unmodified	10.75*	12.58	13.95	3.00×10^{-3}*	3.61×10^{-3}	4.73×10^{-3}
NTB-modified	44.05	51.81	55.87	2.40×10^{-2}	2.59×10^{-2}	2.70×10^{-2}

*Data obtained from Adebowale et al., 2006. Unmod = Unmodified kaolinite clay sample. NTB-mod = Sodium tetraborate modified kaolinite clay sample.

It was observed during the adsorption of metal ions onto NTB-modified kaolinite clay increasing metal ion concentration increased the pH of equilibrium solution of the metal ions from 5.5 to 6.21 and 6.68 for Pb (II) and Cd (II) respectively. Our Previous studies on the unmodified Kaolinite clay reported an observed decrease from the initial pH value of metal ions from 6.0 to pH 4.08 and 4.45 for Pb (II) and Cd (II) adsorption onto the unmodified kaolinite clay (Adebowale et al., 2006). The observed decrease of pH of the unmodified kaolinite clay was in the range of 1–1.82 units as the concentration of adsorbed metal ions increased from 60–1000 mg/L. This was found to support findings by Singh et al. (2001). No plausible reason can be given yet for the increase in pH of equilibrium metal ion solution for NTB-modified sample, although it is believed that NTB-modified kaolinite clay sample behaves as a soft acid which will definitely have strong affinity for a soft base like Cd (II) as against a hard base like Pb (II). Thus, it is also possible to suggest that the lone pairs of electrons introduced on the adsorbent's surface by sodium tetraborate reagent could possibly be involved in coordinate covalent reactions with the metal ions in the form of Pb (II) and Cd (II). This simply implies that there would be no release of H+ in the process and no monovalent specie of both metal ions will be adsorbed. This may have led to an observed increase in the pH of the adsorbate solution.

The decrease in pH for the unmodified kaolinite clay adsorbent became fairly constant with increase in metal ion concentrations (Adebowale et al., 2006).

3.4. Selectivity studies

Table 1 show the data obtained for the equilibrium studies for unmodified and NTB-modified samples, using the Langmuir isotherm model. It is observed that the Unmodified Kaolinite clay sample showed stronger preference for Pb (II) than Cd (II) while NTB-modified sample gave a reverse preference. Although Saha et al. (2001) and Sullivan, (1977) had proposed that soil surfaces act like soft bases that will attract soft nontransition metal like Pb (II) more than hard nontransition like Cd (II), yet this may not hold with true with our adsorbents. The higher adsorption
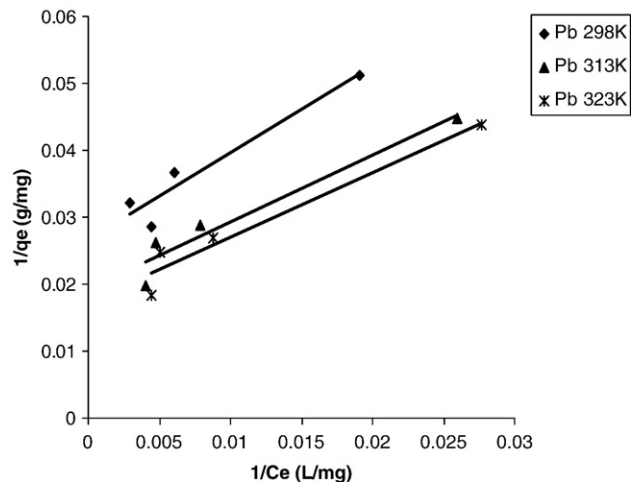

Fig. 9. Langmuir plots for the adsorption of Pb (II) onto unmodified kaolinite clay at various temperatures.
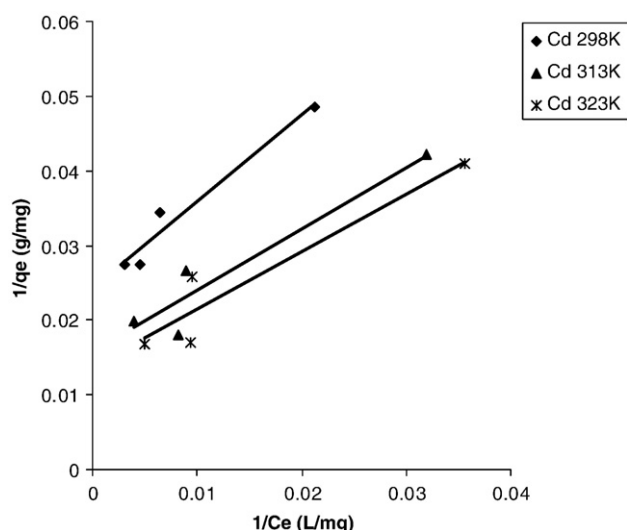
Fig. 10. Langmuir plots for the adsorption of Cd (II) onto NTB-modified kaolinite clay at various temperatures.

of Pb (II) as compared to Cd (II) could be that the unmodified adsorbent acts as a hard base that invariably have stronger affinity for *borderline [Lewis]* acids like Pb (II) than for soft acids like Cd (II). This is in accordance with the *Pearson's Hard and Soft Acids and Bases principle-HSAB principle* (Puls and Bohn, 1988; Pearson, 1963). From the *Frontier Molecular Orbital* (FMO) theory proposed by Klopman, (1968) *border line* [Lewis] acids such as Pb (II) have intermediate properties. Thus, it will bind to both *hard and soft [Lewis] bases* such as to give charge-controlled (ionic) complexes. Such interactions are dominated by the +/− charges on the Lewis acid and Lewis base species. However, the presence of lone pairs of electrons in NTB-modified adsorbent suggest that it will act as a *Pearson's Soft [Lewis] base* (Pearson, 1963) binding more effectively with *soft* [Lewis] acids like Cd (II) rather than to Pb (II) to give FMO-controlled (covalent) complexes. These interactions are dominated by the energies of the participating *Frontier Molecular Orbital* (FMO), the *Highest Occupied Molecular Orbital (HOMO)* and the *Lowest Unoccupied Molecular Orbital (LUMO)*. This is possibly true because it is believed that the free lone pairs of electron on *Boron* atoms on NTB-modified kaolinite clay surface may be interacting with the metals using its molecular orbitals.

However, both metal ions showed stronger affinity for the NTB-modified kaolinite clay than for the unmodified adsorbent because of the increased adsorption capacity of unmodified adsorbent occasioned by the modification with sodium tetraborate reagent. This explains the linear relationship obtained from Langmuir isotherm plots (Figs. 9 and 10).

The adsorption capacity of unmodified kaolinite clay adsorbent was raised from 16.16 mg/g and 10.75 mg/g for Pb (II) and Cd (II) adsorption respectively to 42.92 mg/g and 44.05 mg/g (Table 1). This is regarded as a ≈three fold increase for the adsorption of Pb (II) and over four fold increase for the adsorption of Cd (II). Even with the higher initial metal ion loadings and adsorbent dose used for the unmodified Kaolinite clay adsorbent as shown in Adebowale et al. (2006), its adsorption capacity was still far less than that of the NTB-modified Kaolinite clay adsorbent. This clearly suggests

that modification of kaolinite clay with sodium tetraborate increased its adsorption capacity for Pb (II) and Cd (II) over three fold.

With increasing temperature, it is observed that the adsorption capacity of the adsorbents for both metal ions was increased (Table 1). This suggests that the adsorption of Pb (II) and Cd (II) onto both unmodified and NTB-modified kaolinite adsorbent is endothermic in nature.

The Langmuir binding energy, *b*, for the adsorption of Pb (II) onto the unmodified sample was ten fold smaller than for the NTB-modified sample at all temperatures applied to the adsorbate and it decreased, with increasing temperature. For NTB-modified sample, the Langmuir binding energy parameter, *b*, increased with increasing temperature. This indicates that the adsorbent-adsorbate complexes formed during the adsorption process may be more stable on the NTB-modified kaolinite clay sample than on the unmodified Kaolinite clay sample.

A further confirmation on the mechanism of adsorption may be obtained from the change in entropy of the adsorption reaction, ΔS_{mean}, which suggests the relative stability of the adsorbent-adsorbate complexes formed. In the case of Pb (II), both samples gave similar results of $-21.32 \; J \; mol^{-1} \; K^{-1}$ and $-21.73 \; J \; mol^{-1} \; K^{-1}$ for unmodified and NTB-modified kaolinite clay samples respectively (Table 3). This may be attributed to Pb (II) being a borderline Pearson's [Lewis] acid, and will form adsorbent-adsorbate complexes that are equally stable on either a hard [Lewis] base (unmodified kaolinite clay) or a soft [Lewis] base (NTB-modified kaolinite clay). However, for the adsorption of Cd (II) onto unmodified and NTB-modified samples, ΔS_{mean}, was found to be $-1.21 \; J \; mol^{-1} \; K^{-1}$ and $-18.30 \; J \; mol^{-1} \; K^{-1}$ respectively (Table 3). This clearly confirms the relatively stronger adsorbent-adsorbate complex formed by Cd (II) with NTB-modified kaolinite clay than with the unmodified Kaolinite clay. The higher ΔS_{mean} values for the adsorption of Pb (II) onto both adsorbents relative to the adsorption of Cd (II) on both adsorbents may be because the adsorption of Pb (II) on to both adsorbent is less pH-dependent.

The selectivity of metal ions by adsorbents can also be described by pH_{50} values. The pH_{50} values are a relative measure of the selectivity of an adsorbent for a particular series of bivalent metal cations; the smaller the pH_{50} value the more selective the adsorbent for the metal cation (Sposito, 1984). From results of pH_{50} previously discussed it will be plausible to say that the NTB-modified kaolinite clay is more selective towards both Pb (II) and Cd (II) than unmodified kaolinite clay.

Another factor that influences the relative selectivity of cations in solution is the charge-ionic radius ratio. While selectivity behavior for Group IA and IIA elements of the periodic table can generally be explained using these factors, no such generalization can be made for the heavy metals (Puls and Bohn, 1988). The ionic potentials (Z^2/r) of both metals estimated based upon the charge (Z) and radius of the ion (r) follow the order: Cd (II) > Pb (II). According to Saha et al., 2001, if the metal adsorption on the clays were entirely electrostatic, ions of higher ionic potentials should adsorbed more strongly. Using the ionic radius the order is Pb (II) > Cd (II). The selectivity sequence observed in this study follows the ionic radius order above rather than the ionic potential order.

3.5. Effect of ionic strength of electrolyte

The effect of electrolyte on the adsorption of Pb (II) and Cd (II) onto NTB-modified and unmodified kaolinite clay adsorbents is shown in Table 2. It is observed that the simultaneous presence of electrolytes with

Table 2
Effect of Electrolyte on metal ion adsorption onto NTB-modified kaolinite clay

Parameters	NaNO$_3$			NaCl			Ca(NO$_3$)$_2$			CaCl$_2$			*
	0.1 M	0.01 M	0.001 M	0.1 M	0.01 M	0.001 M	0.1 M	0.01 M	0.001 M	0.1 M	0.01 M	0.001 M	0
Lead ions													
Q^o (mg/g)	33.78	40.98	43.86	32.68	37.04	43.10	26.11	34.01	39.68	24.21	27.78	37.74	42.92
b L/g	0.0094	0.0074	0.0072	0.0077	0.0073	0.0066	0.0011	0.0074	0.0064	0.011	0.0099	0.0053	0.024
R^2	0.9988	0.9903	0.9875	0.9981	0.9747	0.9875	0.9344	0.9685	0.9911	0.9113	0.9318	0.9391	0.9726
Cadmium ions													
Q° (mg/g)	36.63	39.68	40.49	32.79	36.10	38.02	25.19	28.74	29.50	17.99	23.53	26.46	44.05
b L/g	0.0094	0.0088	0.0094	0.0098	0.0095	0.0095	0.0094	0.0084	0.012	0.021	0.014	0.012	0.0126
R^2	0.9644	0.9957	0.9975	0.9127	0.9308	0.9823	0.9786	0.9689	0.9420	0.9589	0.9673	0.9708	0.9221

Q^o = Maximum adsorption capacity; b = Binding energy constant; R^2 = Correlation coefficient; * without electrolyte.

both Pb (II) and Cd (II) in aqueous solutions reduced the equilibrium adsorption capacity of both adsorbents for either metal ion.

For the adsorption of Pb (II) and Cd (II) onto unmodified adsorbent, there was a decrease of 0.19 – 18.38% and 33.7 – 52.76% respectively for Na-electrolyte. In the presence of Ca-electrolyte the adsorption of Pb (II) gave a decrease of adsorption capacity in the range of 5.05–36.51% while Cd (II) adsorption gave a decrease of 10.51–35.53%. Ca-electrolyte has a more negative impact on the adsorption capacity of unmodified kaolinite clay adsorbent. This is due to the divalent nature of cation in the Ca-electrolyte which is preferred to the monovalent cation of the Na-electrolyte (Adebowale et al., 2006).

NTB-modified kaolinite clay sample gave a decrease in the range of 4.31–25.88% for the adsorption of Pb (II) and 5.66–23.60% for the adsorption of Cd (II) when Na-electrolyte was used. With Ca-electrolyte, the decrease was in the range of 9.92–45.04% for Pb (II) and 31.27–58.08% for Cd (II). Similar trends mentioned above have been observed by Naidu et al. (1994) for adsorption of Cd (II) on soils, Adebowale et al. (2006) for adsorption of Pb (II) and Cd (II) on orthophosphate-modified and unmodified kaolinite, and Spark et al. (1995) for the adsorption Cu^{2+}, Zn^{2+}, Co^{2+} and Cd $(II)^{2+}$ on kaolinite.

This effect of ionic strength on metal ion adsorption is often attributed to changes in adsorbent-suspension pH through its effect on the diffuse double layer. The electrolytes are thought to operate by positively increasing the potential of plane of adsorption. Naidu et al. (1994) found out that pH of soil suspensions decreased by 0.4 to 1 unit on the average, with increase in ionic strength of electrolyte. However, the negative effect of increasing ionic strength of electrolytes on the adsorption of metal ions is found to be a direct effect on the electrolyte on the electrostatic potential in the plane of adsorption, rather than through its effect on surface charge. Therefore, a decrease in adsorption of metal ion with increasing ionic strength of electrolytes implies that increasing ionic strength is making the potential of the adsorbent surface less negative (i.e. the potential in the plane of adsorption is getting increasingly positive) and this would decrease metal ion adsorption.

3.6. Thermodynamics of adsorption

Thermodynamic parameters for the adsorption of Pb (II) and Cd (II) are shown in Tables 3 and 4. The plots used to obtain data for the various thermodynamic parameters are shown in Fig. 11.

The enthalpy of the adsorption ΔH_{mean} is a measure of the energy barrier that must be overcome by reacting molecules (Jencks, 1969). The values for ΔH_{mean} were found to be in the range of 4.35–10.84 J K^{-1} mol^{-1} and were all positive. This suggests that the adsorption reactions of Pb (II) and Cd (II) onto Unmodified and NTB-modified adsorbents are endothermic in nature meaning that increasing temperature will favour the adsorption both metals onto both adsorbents (Scheckel and Donald, 2001).

The value of ΔS_{mean} is an indication of whether or not the adsorption reaction is by associative or dissociative mechanism. The entropy measures the width of the saddle point of the potential energy surface over which reactant molecule must pass as activated complexes (Jencks, 1969). Entropy change >-10 J K^{-1} mol^{-1} generally implies dissociative mechanism (Scheckel and Donald, 2001). Entropy values obtained in this study (Table 3) are below this value except that for the adsorption of Cd (II) onto unmodified clay sample. This could suggest associative mechanism

Table 3
Thermodynamic parameters obtained from plots of ln b vs 1/T for the various adsorbents

Adsorbents	Lead ions			Cadmium ions		
	ΔH_{mean} (kJ mol^{-1})	ΔS_{mean} (J mol^{-1} K^{-1})	r^2	ΔH_{mean} (kJ mol^{-1})	ΔS_{mean} (J mol^{-1} K^{-1})	r^2
Unmodified	+5.31	−21.32	0.9909	+14.09	−1.21	0.9415
NTB-modified	+4.35	−21.73	0.9836	+3.79	−18.30	0.9990

Unmod = Unmodified kaolinite clay sample.
NTB-mod = Sodium tetraborate modified kaolinite clay sample.

Table 4
ΔG (kJ mol^{-1} K^{-1}) obtained from $\Delta G = -RT ln b$ for the various adsorbents

Adsorbents	Lead ions			Cadmium ions		
	298 K	313 K	323 K	298 K	313 K	323 K
Unmodified	+11.63	+11.96	+12.21	+14.39	+14.64	+14.38
NTB-modified	+10.84	+11.13	+11.39	+9.24	+9.51	+9.70

Unmod = Unmodified kaolinite clay sample. NTB-mod = Sodium tetraborate modified kaolinite clay sample.

of adsorption of both metal ions onto the adsorbents except for the adsorption of Cd (II) onto unmodified clay sample. This abnormality may not necessarily mean that the adsorption of Cd (II) onto unmodified kaolinite clay adsorbent is dissociative in nature but that there could be some structural changes in the adsorbate and adsorbent during the adsorption reaction (Yavuz et al., 2003).

ΔG_{mean}, values obtained were all small and positive which suggests that the adsorption of Pb (II) and Cd (II) onto unmodified and NTB-modified kaolinite clay samples require some small amount of energy to convert reactants into products (Scheckel and Donald, 2001). This is further supported by the positive ΔH_{mean} values obtained for the adsorption of Pb (II) and Cd (II) onto both adsorbents (Table 4). This may not suggest that the adsorption of Pb (II) and Cd (II) onto both adsorbents is non spontaneous, rather it could indicate that both adsorbents may show better performance in the adsorption of Pb (II) and Cd (II) from aqueous solutions when such solutions have temperature up to 323 K. This indicates the presence of an energy barrier in the adsorption process.

Ozcan and Ozcan, (2004) have suggested that positive values for ΔG are quite common with ion-exchange mechanism of adsorption of metal ions because of the activated complex of the metal ion formed with the adsorbent in the excited state. Besides, estimation of thermodynamic parameters using linear plots of thermodynamic models could introduce some errors that could shift values from the border of one extreme to another. When this occurs, adsorption reactions that have small but negative ΔG could shift to small but positive ΔG. This is case with the unmodified clay sample which indicates a small negative ΔG when the rate constants of the adsorption of Pb (II) and Cd (II) onto the adsorbent were used in the estimation of ΔG (Unuabonah et al., 2007b).

3.7. Data fitting

An error is required to evaluate the fit of an equation to the experimental data obtained from the optimization process employed. In this study, a non-linear Chi-square test was used (Ho and Ofomaja, 2005). The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from the models, with each squared difference divided by
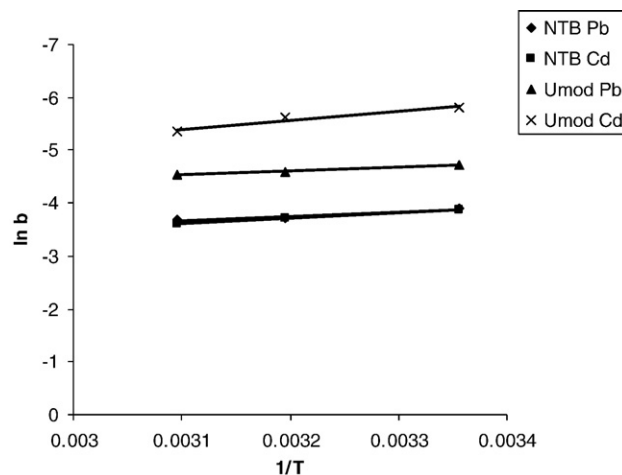
Fig. 11. Thermodynamic plots of ln b against 1/T for the adsorption of Pb (II) and Cd (II) onto unmodified and NTB-modified kaolinite clay samples.

the corresponding data obtained by calculating from the models. The equivalent mathematical statement is:

$$X^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{10}$$

Where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). If data from model are similar to the experimental data, χ^2 will be small in number, while if they differ, χ^2 will be a bigger number. Therefore, it is necessary to also analyze the data set using the non-linear Chi-square test to confirm the best fit isotherm for the sorption system.

The results of the application of the non-linear Chi-square test on experimental data, q_e, for four adsorption isotherms [Langmuir Model (**LM**), Freundlich Model (**FM**), Langmuir–Freundlich Model (**LF**), Toth Model (**TM**)] at ≤500 mg/L initial metal concentration are shown in Table 5.

At concentrations ≤500 mg/L of metal ions in aqueous solution, equilibrium data for the adsorption of Pb (II) onto the unmodified kaolinite clay adsorbent gave better fit to Freundlich model than other models while data for the adsorption of Cd (II) onto same adsorbent gave better fit to the Langmuir–Freundlich model than the other models (Adebowale et al., 2006). This is an implication of the fact that the adsorption sites on the unmodified kaolinite clay sample are heterogeneous in nature as suggested by the Freundlich model.

However, adsorption data for both metal ions onto NTB-modified kaolinite clay sample gave a more robust fit to the Langmuir isotherm model. These results indicate that the adsorption sites on the NTB-modified adsorbent are homogeneous in nature as implied by the Langmuir isotherm model.

Increasing the metal ion concentration to concentrations above 500 mg/L up to 1000 mg/L for the Unmodified adsorbents, from the χ^2 values for the adsorption data for both metal ions were found to fit less with the four equilibrium isotherm models [Pb (II) LM 7.93 FM 1.79 LF 13.65 TM 11.72 and Cd (II) LM 8.76 FM 2.04 LF 9.40 TM 17.26] (Unuabonah et al., 2007b). with Freundlich model giving the better fit of them all. This further strengthens the argument that the adsorption sites on the surface of the unmodified kaolinite clay sample are heterogeneous in nature (Adebowale et al., 2006). Adsorption of ≥500 mg/L Pb (II) and Cd (II) onto NTB-modified kaolinite clay sample gave no better adsorption results as it appears that a plateau have been reached on this adsorbent.

In both adsorbents, the adsorption data for Cd (II) seems to best fit the Freundlich isotherm model for the unmodified kaolinite clay sample and Langmuir isotherm model for NTB-modified kaolinite clay sample. This same trend was observed for data obtained for Pb (II) adsorption (Table 5).

3.8. Desorption

Desorption of fully adsorbed 60 mg/L Pb (II) and Cd (II) from the adsorption sites on the surface of the Unmodified and NTB-modified kaolinite clay sample showed that 95% and 87% of Pb (II) adsorbed onto

unmodified and NTB-modified kaolinite clay samples respectively were released from these surfaces. However, 99% desorption of Cd (II) was obtained for the Unmodified adsorbent while NTB-modified kaolinite clay sample released 91% of its adsorbed Cd (II). This suggests that the unmodified sample bind both metal ions less strongly than NTB-modified sample. This strongly correlates with the earlier suggestion from the binding energy constant, b.

Reusing both adsorbent in repeated cycles of adsorption of metal ions, it was found that of both metal ions were adsorbed onto both adsorbents. This may be attributed to nitric acid used for regeneration. Further studies are required to substantiate this claim.

4. Conclusion

Modification of kaolinite clay with sodium tetraborate reagent decreased its PZC from 4.40 to 3.70. The kaolinite clay sample was observed to be a surface modified as the XRD diffractogram did not suggest any crystallographic change in the d-spacing of the crystals in the crystal lattice of the Kaolinite clay adsorbent.

Modification of kaolinite clay with sodium tetraborate increased the Specific Surface Area (SSA) of Kaolinite clay from 10.56 m² g⁻¹ to 15.84 m² g⁻¹. There was an observed increase in the adsorption capacity of the kaolinite after modification with sodium tetraborate which corresponds to its increase in cation exchange capacity.

Adsorption of Pb and Cd on modified and unmodified clay was endothermic and accompanied by a decrease in entropy.

Modeling equilibrium adsorption data obtained suggest NTB-modified kaolinite clay adsorbent has homogeneous adsorption sites unmodified kaolinite clay has heterogeneous adsorption sites.

Desorption studies suggest that ≈85% of the metals were desorbed from both adsorbents. On reuse of the adsorbents only ≈80% of metals were adsorbed on the adsorbents.

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Table 5
Error Analysis for five adsorption isotherms using Linear Regression coefficient and Non-linear Chi-square test for the concentration of metal ions ≤500 mg/L

	Lead ions			
	F Model	LF Model	T Model	L Model
	χ^2	χ^2	χ^2	χ^2
Unmod	1.15	1.02	1.99	1.78
NTB-mod	0.89	1.58	2.53	8.05
	Cadmium ions			
	L Model	F Model	LF Model	T Model
	χ^2	χ^2	χ^2	χ^2
Unmod	0.50	0.41	0.36	10.06
NTB-mod	0.79	1.02	3.89	6.48

L = Langmuir. F = Freundlich. LF = Langmuir–Freundlich. T = Toth. Unmod = Unmodified kaolinite clay sample. NTB-mod = Sodium tetraborate modified kaolinite clay sample.

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