Layered Double Hydroxide Adsorption of Lead: Equilibrium, Thermodynamic and Kinetic Studies

*Ayawei N[1], Abasi, C. Y[1], Wankasi D[1, 2], Dikio E. D[1, 2]

[1]Department of Chemical Sciences, Niger Delta University, Wilberforce Island,
Bayelsa State, Nigeria
[2]Applied Chemistry and Nanoscience Laboratory, Department of Chemistry,
Vaal University of Technology, Vanderbijlpark, South Africa
ayawei4acad@gmail.com

Abstract: *Layered double hydroxide (LDH) with Mg/Al ratio of 4:1 was synthesis by co-precipitation method and characterized for batch adsorption studies. Pre and post EDX analysis shows binding on the surface confirming adsorption. Kinetic modeling of the metal ion removal was done using First-Order and Pseudo second order models rate expressions respectively. Equilibrium isotherm data analysis for the metal ion was done with the Langmuir and Freundlich equations. Both the Langmuir adsorption isotherm (R^2=0.9993) and Freundlich adsorption isotherm ($R^2$0.9998) described the adsorption data very well. Thermodynamic parameters such as enthalpy (ΔH∘), entropy (ΔS∘), Gibbs free energy (ΔG∘), activation energy (Ea) and isosteric heat of adsorption were calculated and the results are discussed in detail.*

Keywords: *Layered double hydroxide, Heavy metal, Adsorption, Isotherms, Kinetics, Thermodynamics.*

1. BACKGROUND

The presence of heavy metals in the aquatic environmental has been a big deal to scientists and engineers due to their increased discharge, toxic nature and other adverse effects on receiving waters [1, 2]. They also can be absorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [3, 4, 5, 6, 7]. Lead is widely used in many important industrial applications, such as storage battery, manufacturing, printing pigments, fuels, photographic materials and explosive manufacturing [8]. Lead exposure causes weakness in fingers, wrists and ankles. The effects of lead toxicity are very wide ranging and include impaired blood synthesis, hypertension, severe stomach ache, brain, kidney damage and even can cause miscarriage in pregnant women [9]. The permissible level for lead in drinking water is 0.05 mg L−1 according to the US Environmental Protection Agency (EPA). Therefore, a very low concentration of lead in water is very toxic [10]. Several methods are commonly used for the treatment of heavy metals, such as adsorption, chemical precipitation, coagulation, flocculation, extraction and reverse osmosis [11, 12.13, 14, 15, 16].

Adsorption has been shown to be an economical alternative for removing trace of metals from water. Among the numerous materials applied in adsorption processes, activated carbons, primarily due to their low cost and high adsorption ability, are still the most widely used materials for adsorption of impurities [17, 18, 19].

Layered double hydroxide (LDH) or hydrotalcite (HT) type materials are widely used in catalysis, ion-exchange, adsorption, and pharmaceutics [20]. The general formula for the LDH materials is [MII1-x MIIIx (OH)2]x+ (Am-)x/m] •nH2O, where M are bivalent or trivalent cations with similar radii, and A are interlayer anions, mostly CO32-. Their structure is similar to that of brucite (Mg (OH) 2) type octahedral layers. The cations in the layer can be changed using a wide range of main group cations (e.g. Mg, Al) or transition metal cations (e.g. V, Cr, Mn, Fe, Co, Ni). These cations normally are in the divalent or trivalent state, although preparation of LDH with tetravalent cations has also been previously reported [21, 22]. All these materials having various compositions share typical common characteristics: layered structure and the formation of mixed-metal oxides after thermal treatment. Interest in these compounds has increased in recent years because of the possibilities for post-synthetic modifications [23, 24, 25, 26, 27]. The most common method applied for preparation of

LDH is co-precipitation, wherein precipitating agents such as NaOH or/and NaHCO3 are added to the solution of metal salts [23]. LDH possess a unique layered structure. On the other hand, during calcination at high temperatures the layered structure could easily be destroyed. However, the regeneration (or reconstitution) of the LDH layered structure is possible after soaking of mixed-metal oxides formed after thermal treatment in an aqueous solution containing anions to be intercalated. Such reverse reactions from mixed oxides to layered double hydroxides are referred in literature as "memory effect" with a topotactical character of the regeneration reaction [28, 29].

2. EXPERIMENTAL

2.1. Synthesis of LDH

Carbonate form of Mg-Al LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3 M Mg $(NO_3)_2.6H_2O$ and 0.1 M Al $(NO_3)_3.9H_2O$ with Mg/Al ratios 4:1, was added drop wise into a 50 ml mixed solution of (NaOH (2M) + Na_2CO_3 (1M)) with vigorous stirring and maintaining a pH of greater than 10 at room temperature. After complete addition which last between 2 hours 30 minutes to 3 hours, the slurry formed was aged at 60°C for 18 hours. The products were centrifuged at 5000 rpm for 5 minutes with distilled water 3-4 times and dried by freeze drying.

2.2. Characterizations

X-ray diffraction (XRD) pattern of the sample was characterized by using a Shimadzu XRD-6000 diffractometer, with Ni-filtered Cu-Kα radiation (λ= 1.54 A°) at 40 kV and 200 ma. Solid samples were mounted on alumina sample holder and basal spacing (d-spacing) was determined via powder technique. Samples scan were carried out at 10-60°, 2θ / min at 0.003° steps.

FTIR spectrum was obtained using a Perkin Elmer 1725X spectrometer where samples will be were finely ground and mixed with KBr and pressed into a disc. Spectrums of samples were scanned at 2 cm-1 resolution between 400 and 4000cm-1.

FESEM/EDX was obtained using Carl Zeiss SMT supra 40 VPFESEM Germany and inca penta FET x 3 EDX, Oxford. It was operated at extra high tension (HT) at 5.0 kV and magnification at 20000X. FESEM uses electron to produce images (morphology) of samples and was attached with EDX for qualitative elemental analysis.

2.2.1. Preparation of Metal Solution

All reagents used for this study were analytical reagent grade and were procured from Zayo-Sigma Chemical Ltd. Jos, Nigeria. 1000 mg/l aqueous solutions of the metals ion was prepared as stock from their salts (PbSO4,). From the stock, working solutions of 0.13g/LPb, 0.25g/LPb and 0.38g/LPb were prepared from appropriate aliquots diluted to the appropriate concentration. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using (Unicam thermo/solar system 2009 model) Atomic Adsorption Spectrometer (AAS).

2.3. Metal Ion Analysis

The adsorption of Pb (II) ions on to layered double hydroxide was studied by the mean of batch technique. The procedure used for this study is described as following: a known weight (0.2gm) of layered double hydroxide was equilibrated with 10ml of the lead solution of known concentration, in a stopped propylene flask, at a fixed temperature and in a thermostatic shaker for a known period time. After the equilibration using a constant stirring speed, the suspension was filtered out and analysed for its lead concentration, using atomic adsorption spectrometer (Analyst 100 Perkin Elmer).

The effect of several parameters such as contact time, initial concentration of lead solutions and temperature on the adsorption was studied following different sets of experiments:

3. RESULTS AND DISCUSSIONS

Characterization of adsorbent

3.1. FT-IR

The IR spectra of synthesized anion clays (Figure 1) resemble those of other hydrotalcite -like phases [27]: The band at 3451 cm^{-1} which could be attributed to the stretching vibration of hydroxyl group. The low intensity band at 1543 cm^{-1} is assigned to bending vibration of strongly adsorbed water (solvation water for compensating anion vibration). The band at 1385 cm^{-1} is assigned to carbonate vibration (CO_3^{2-}), the bands at 665 is due to M–O vibration.
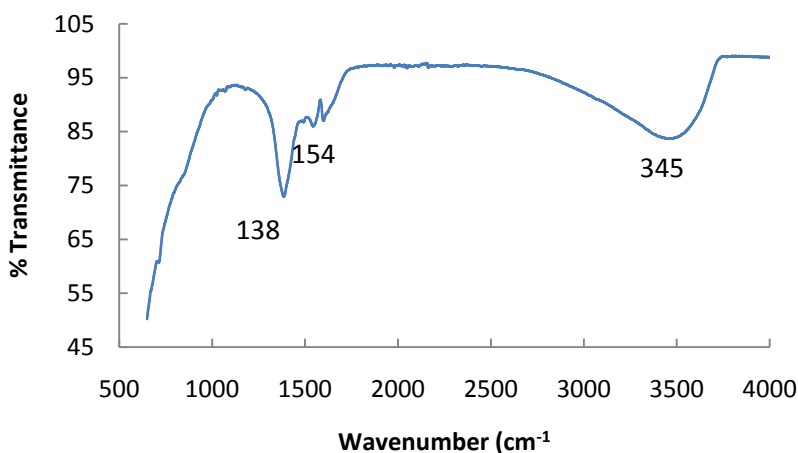
Fig1. Mg/Al-C0$_3$ *Fourier transform infrared spectroscopy*

3.2. XRD

The typical XRD pattern (Figure 2) shows a lamellar structure of LDH material. The XRD patterns were indexed in theR-3m space group, c the lattice parameter corresponding to three times the interlayer distances (c=3d$_{003}$).The peak (110) indicates the inter-metallic distance used to calculate a lattice parameter (a=2d110). The values of the parameters c and a are respectively 23.13 and 3.02Ă.These values are similar to those reported in literature [27-28].
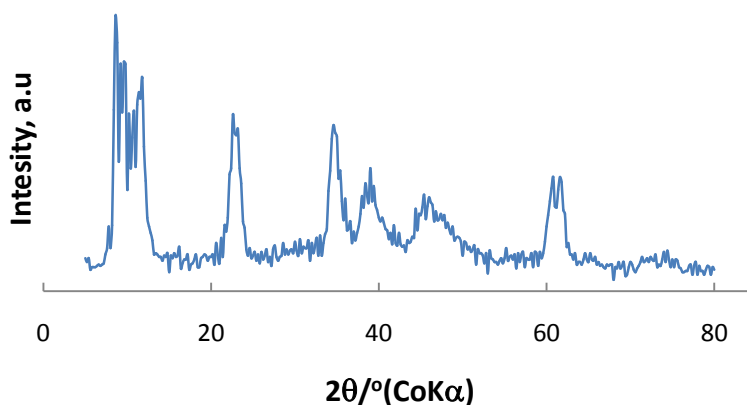

Fig2. Mg/Al-C0$_3$ X-ray powder diffraction
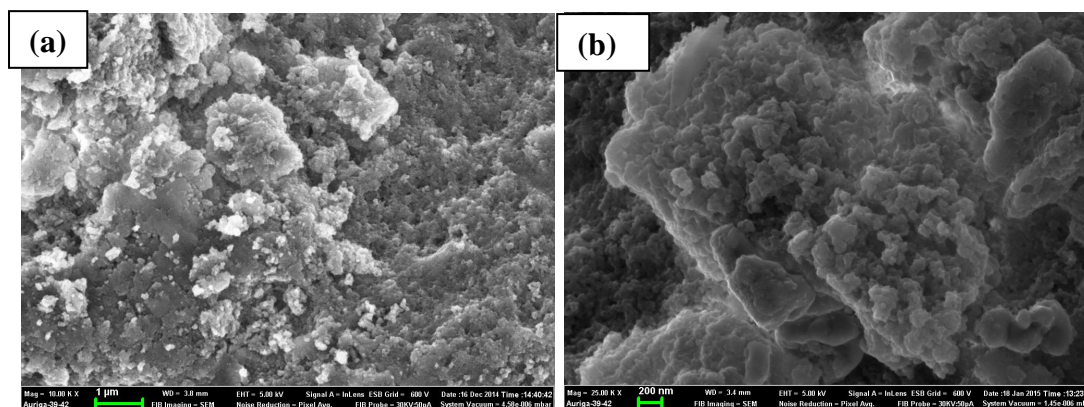
3.3. SEM/EDX

Fig3. *Scanning Electron Microscope (SEM) micrograph of Mg/Al-CO$_3$ before (a) and after (b) adsorption studies*

Figures 3 & 4 clearly shows the pre & post adsorption photographs and graph of SEM images and EDX respectively. The EDX graphs shows the binding on the surface of the layered double hydroxide

by the copper ion, while the SEM image of post adsorption shows coverage of available pores in relation to pre-adsorption image.
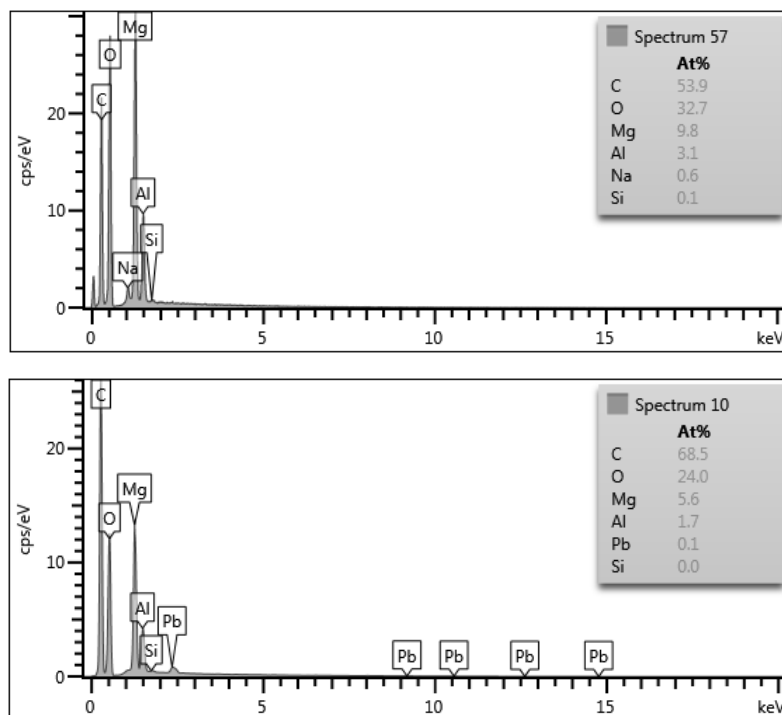
Fig4. *Energy Dispersive Spectroscopy patterns of Mg/Al-CO₃ pre & post adsorption Energy Dispersive Spectroscopy*

3.4. Data Analysis

For data analysis, various equilibrium, kinetic, and thermodynamic models (equations) were employed to interpret the data and establish the extent of adsorption. The amount of metal uptake was computed using the material balance equation for batch dynamic studies (equation) [30].

$$q_e = \frac{V}{M}(C_o - C_e) \tag{1}$$

with q_e is metal uptake capacity (mg/g LDH at equilibrium), Ce is metal ion concentration in solution (mg/g), V is the volume of solution in litres and M, the dry weight of LDH used in (g).

4. EFFECT OF CONCENTRATION
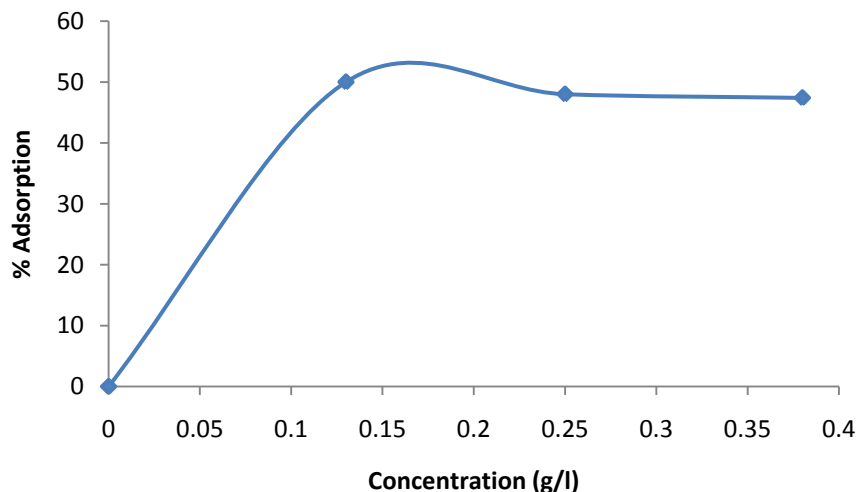
Fig5. *Effect of concentration on adsorption of Pb²⁺ onto layered double hydroxide*

0.2gram each of the powder sample was collected and weighed using an electronic weighing balance, the weighed sample was placed in three (3) pre-cleaned test tube. 10ml of each metal ion solution

with standard concentration of 0.13g/L, 0.25g/L and 0.38g/L which was made from spectroscopic grade standards of lead ion (Pb^{2+}) {from lead nitrate: $Pb(NO_3)_2$} were added to each test tube containing the weighed sample and equilibrated by rocking (agitation) for 30 minutes and then centrifuged at 2500rpm for 5 minutes and decanted. The supernatants were stored for lead ion (Pb^{2+}) analysis as stated in metal analysis. The result (figure 5) indicates that adsorption did not depend on increase in concentration of the metal ion solution.

5. EFFECT OF CONTACT TIME

0.2gram each of the powder sample was weighed using an electronic weighing balance and placed in three (3) pre-cleaned test tube. 10ml of the metal ion solution with standard concentration of 0.35g/L which was made from spectroscopic grade standard of lead ion (Pb^{2+}) {from lead nitrate: $Pb(NO_3)_2$} was added to each test tube containing the weighed sample and equilibrated rocking (agitation) for each time intervals of 10, 20 and 30 minutes respectively. The powered sample suspension were centrifuged for 5 minutes at 2500rpm and decanted. The supernatants were stored for lead ion (Pb^{2+}) analysis as stated in metal analysis. The result (figure 6) shows that increase in contact time significantly increases the adsorption capacity of the layered double hydroxide.
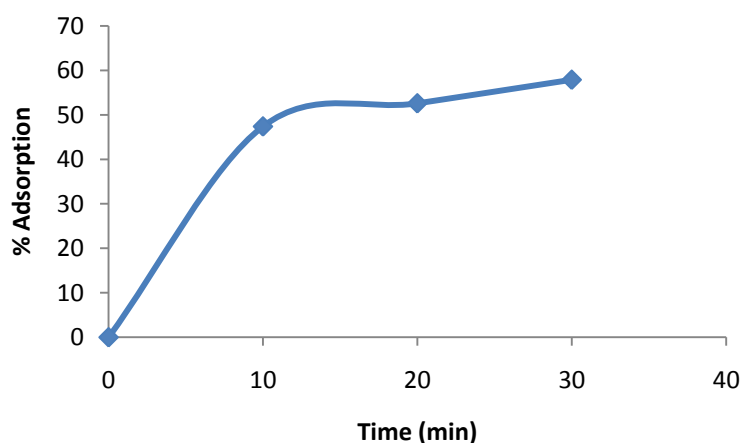

Fig6. *Effect of contact time on adsorption of Pb^{2+} onto layered double hydroxide*

6. EFFECT OF TEMPERATURE

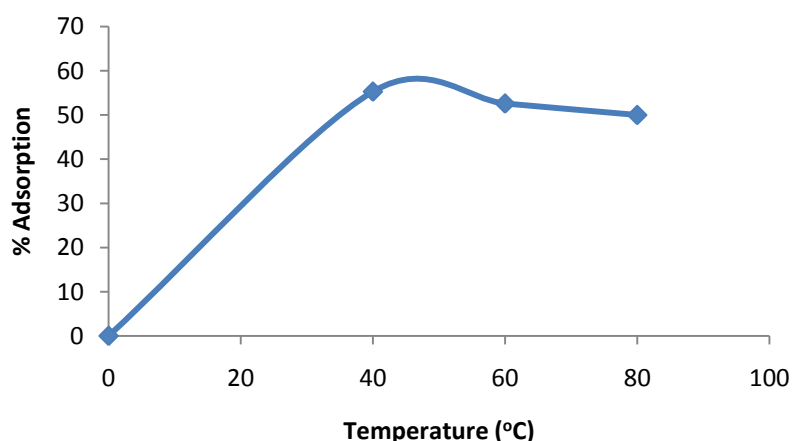**Fig7.** *Effect of temperature on adsorption of Pb^{2+} onto layered double hydroxide*

0.2gram each of the powder sample was collected and weighed using an electronic weighing balance; the weighed sample was placed in three (3) pre-cleaned tubes. 10ml of the metal ion solution with standard concentration of 0.38g/L which was made from spectroscopic grade standard of lead ion (Pb^{2+}) {from lead nitrate: $Pb(N0_3)_2$} was added to each test tube containing the weighed sample and equilibrated rocking (agitation) for 30 minutes at temperatures of 28^0C (room temperature), 40^0C, 60^0C and 80^0C respectively using Gallenhamp water bath. This was immediately centrifuged at 2500rpm for 5 minutes and then decanted. The supernatant were stored for lead ion (Pb^{2+}) analysis as

stated in metal analysis. The result as shown in figure 7 shows that the adsorption process is not dependent on temperature increase.

7. ADSORPTION ISOTHERM

In order to describe the adsorbate-adsorbent interaction, the isotherm data were analyzed by fitting them into Langmuir and Freundlich equations to find out the suitable model that may be used for design consideration.
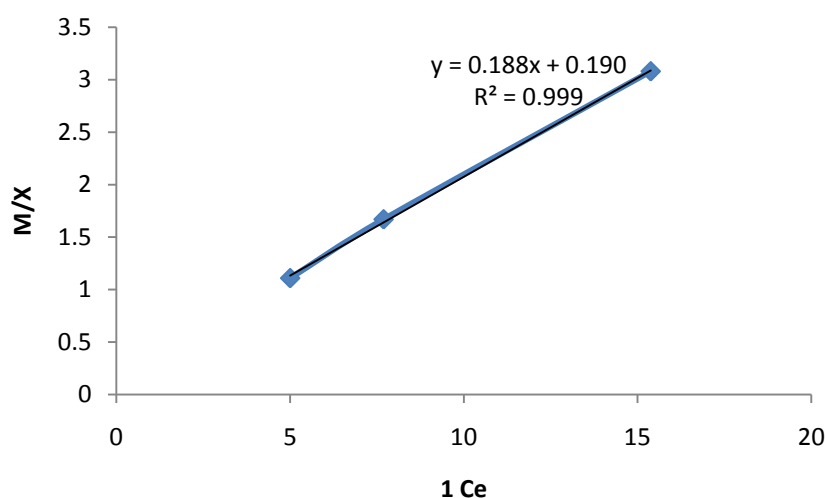
8. LANGMUIR ISOTHERM

The Langmuir adsorption mode [31] is based on the assumption that maximum adsorption corresponds to saturated monolayer of solute molecules on the adsorbent surface. The linear form of Langmuir equation is

$$\frac{M}{x} = \frac{1}{ab\,C_e} + \frac{1}{b} \tag{2}$$

Where X is the amount of Pb^{2+} adsorbed per mass M of layered double hydroxide, in mg/g a and b are the Langmuir constants obtained from the slope and intercepts of the plots.

The plot of M/X against 1/Ce (Figure 8) shows the adsorption obeys equation (2). The Langmuir constants a and b which are determined from the slope and intercept of the plot, are 0.1908 and intercept 0.1884 respectively. The R^2 value (0.9993) suggest that the adsorption follows Langmuir model.

Fig8. *Langmuir Isotherm plot for adsorption of Pb^{2+} on layered double hydroxide*

The essential characters of Langmuir isotherm can be expressed in term of dimensionless constant separation factor R_L [32] given by

$$R_L = \frac{1}{1+bC_o} \tag{3}$$

Where C_o (mg L^{-1}) is the highest initial concentration of Pb^{2+} and b(L mg^{-1}) is Langmuir constant.

The value of R_L in the present investigation is found to be 0.741 showing the adsorption is favoured ($0<R_L<1$) at the temperature studied.

9. FREUNDLICH ISOTHERM

The Freundlich isotherm considers multilayer adsorption with heterogeneous energetic distribution of active sites accompanied by interaction between adsorbed molecules. [12] The linear Freundlich isotherm is

$$In\frac{X}{M} = \frac{1}{n}(InC_e) + Ink \tag{4}$$

Where, K is Freundlich constant, which indicates the relative adsorption capacity of the adsorbent and n is a measure of the adsorption intensity or surface heterogeneity (a value closer to zero represents a more heterogeneous surface).

The linear plot of In X/M against In C_e, (Figure 9) shows that the adsorption of Pb^{2+} on layered double hydroxide also follows Freundlich isotherm model. Freundlich constant K and n were 1.3324 and 0.9001 respectively. The value of n>1 indicates favorable adsorption ($R^2 = 0.9998$).
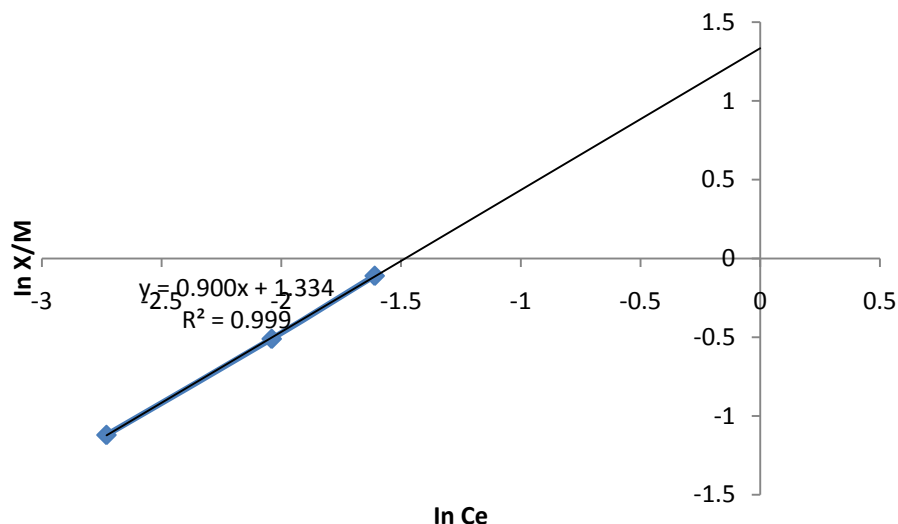

Fig9. *Freundlich Isotherm plot for adsorption of Pb^{2+} on layered double hydroxide*

10. ADSORPTION THERMODYNAMICS

Thermodynamic parameters such as change in free energy ΔG^o, enthalpy ΔH^o and entropy $\Delta S\circ$ were determined using the following equations [34, 35]

$$C_{solid} \underset{K_2}{\overset{K_1}{\rightleftarrows}} C_{liquid} \tag{5}$$

$$K_o = \frac{C_{Solid}}{C_{Liquid}} \tag{6}$$

$$\Delta G^o = -RT \, In \, K_o \tag{7}$$
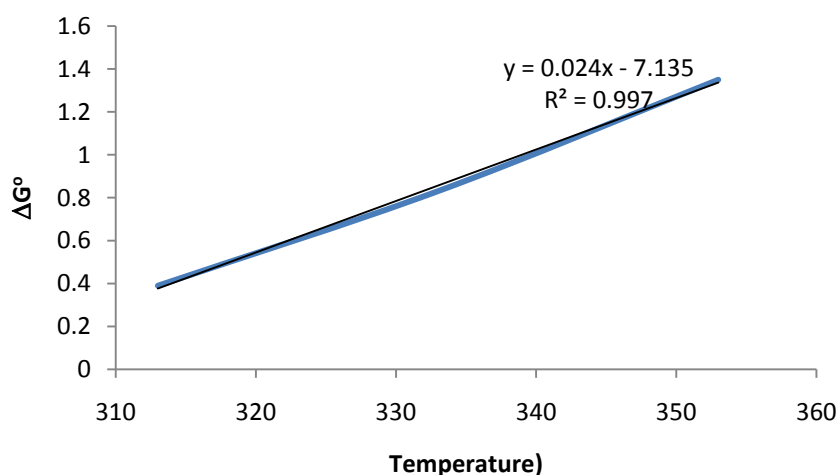
$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{8}$$

Fig10. *Plot of ΔG^o vs. Temperature for the adsorption of Pb^{2+} onto layered double hydroxide.*

A plot of Gibbs' free energy change, ΔG^o versus temperature, T as in figure 10 will be linear with the slope and intercept giving the values of ΔH^o and ΔS^o respectively. These values are presented in Table 1. The negative value of ΔH^o is (-7.135 kJmol^{-1}) implies that the adsorption phenomenon. In an exothermic process, the total energy absorbed in bond breaking is less than the total energy released in bond making between adsorbed and adsorbent, resulting in the release of extra energy in the form of heat. A positive value of ΔS^o (0.024KJ/molK) reflects the affinity of the adsorbent towards the

adsorbate species. In addition, positive value of ΔS^o suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of randomness in the system. The positive ΔS^o value also corresponds to an increase in the degree of freedom of the adsorbed species.

The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system [35].

The values of ΔG^o were obtained from the application of equation (7). The negative values of ΔG^o show that the adsorption is highly favorable and spontaneous. It was also observed that the negative values of ΔG^o increases with increase in temperature, which indicate that the adsorption is preferable at high temperature, which was observed from the experimental data.
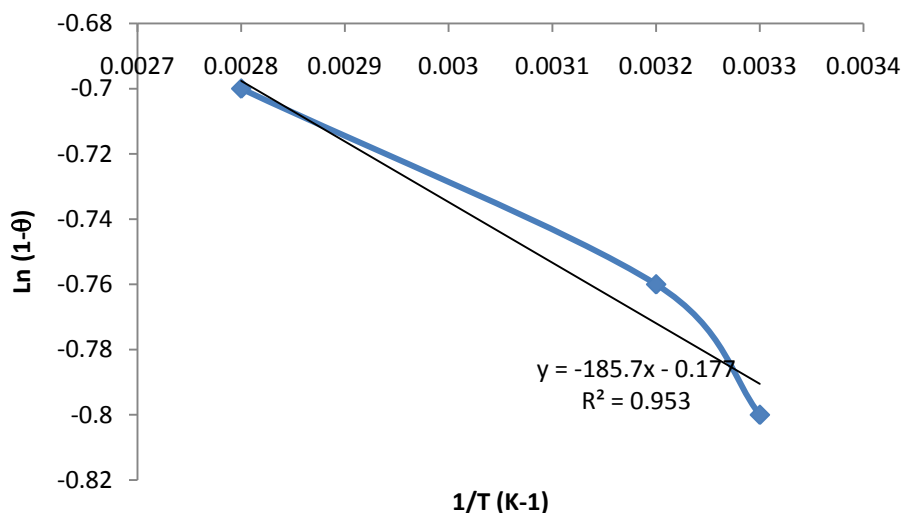
In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows [36]:

$$\theta = \left[1 - \frac{C_e}{C_1}\right] \ or \ \frac{C_e}{C_i} = 1 - \theta \tag{9}$$

$$S^* = (1 - \theta)e^{-\frac{E_a}{RT}} \tag{10}$$

$$In \ S^* = In(1 - \theta) - \frac{E_a}{RT} \tag{11}$$

$$In(1 - \theta) = In \ S^* + \frac{E_a}{RT} \tag{12}$$

Fig11. *Plot of In(1-θ) vs. reciprocal temperature for the adsorption of Pb^{2+} onto layered double hydroxide.*

The sticking probability S *, is a function of the adsorbate / adsorbent system under investigation, its value lies in the range 0<S *<1 for preferable process and is dependent on the temperature of the system [36]. The 'ɵ' is the surface coverage, which can be calculated from equation 9. The values of Ea and S * can be calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively (Figure 11 & Table 1). The values of E_a was found to be -1.472 kJ/mol -1 for the adsorption of Pb^{2+} onto the layered double hydroxide. The negative Ea value indicates that low temperature or energy favours the sorption and the process is exothermic. The sticking probability value was less than 1 (Table 1), which indicates that the probability of the Pb^{2+} ions to stick on surface of layered double hydroxide is very high as S*<< 1, this value confirm that, the sorption process is physisorption.

The isosteric heat of adsorption at constant surface coverage is calculated using the Clausius-Clapeyron equation:

$$\frac{d(In\,C_e)}{dT} = -\frac{\Delta H_x}{RT^2} \tag{13}$$

where, Ce is the equilibrium adsorbate concentration in the solution (mg.L-1), ΔH_x is the isosteric heat of adsorption (kJ mol-1), R is the ideal gas constant (8.314 J.mol-1K-1), and T is temperature (K). Integrating the above equation, assuming that the isosteric heat of adsorption is temperature independent, gives the following equation:

$$Inc_e = -\left[\frac{\Delta H_x}{R}\right]\frac{1}{T} + K \tag{14}$$

where K is a constant.

The isosteric heat of adsorption is calculated from the slope of the plot of ln Ce versus 1/T different amounts of adsorbate onto adsorbent.

The magnitude of ΔH_x (17.6 kJ mol^{-1}) as extrapolated from the slope in figure 12 gives information about the adsorption mechanism as chemical ion-exchange or physical sorption. For physical adsorption, ΔH_x should be below 80 kJ mol^{-1} and for chemical adsorption it ranges between 80 and 400 kJ.mol-1.
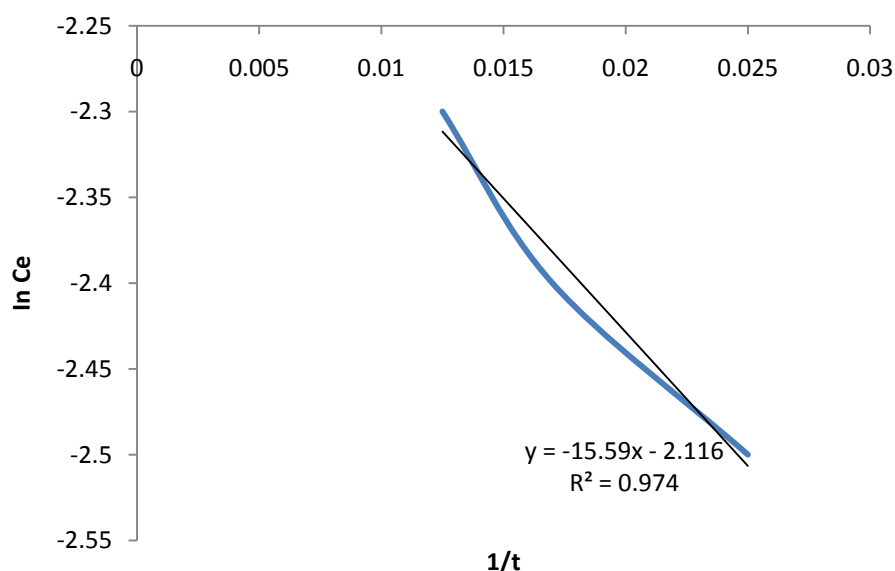
Fig12. *Plot of InCe vs. 1/t for the adsorption of Pb^{2+} onto layered double hydroxide.*

11. ADSORPTION KINETICS

First-Order and Pseudo second order models were applied to test the experimental data in order to explain the kinetics of lead ion adsorption process of the layered double hydroxide.

$$Inq_t = Inq_o + K_1 t \tag{15}$$

where, k_1 (min-1) is the rate constant,

q_o (mg g-1) is the amount of Pb^{2+} adsorbed on surface at equilibrium,

q_t (mg g-1) is the amount of Pb^{2+} adsorbed on surface at time t (min).

The adsorption rate constant, k_1 and q_o were calculated from the plot of In q_t vs. t, (Figure 13) and are listed in Table 2.

The pseudo second order kinetic model is given by equation 5.[37]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{16}$$

where, k2 (g mg-1 min-1) is pseudo second order rate constant. The plot of t/qt vs t is shown in Figure 14. The correlation coefficient of the chosen kinetic models namely: first-order-kinetic model and pseudo-second-order model are 0.9992 and 0.9967 respectively. This indicate that pseudo-second-order model best define adsorption process of lead ion on the layered double hydroxide.
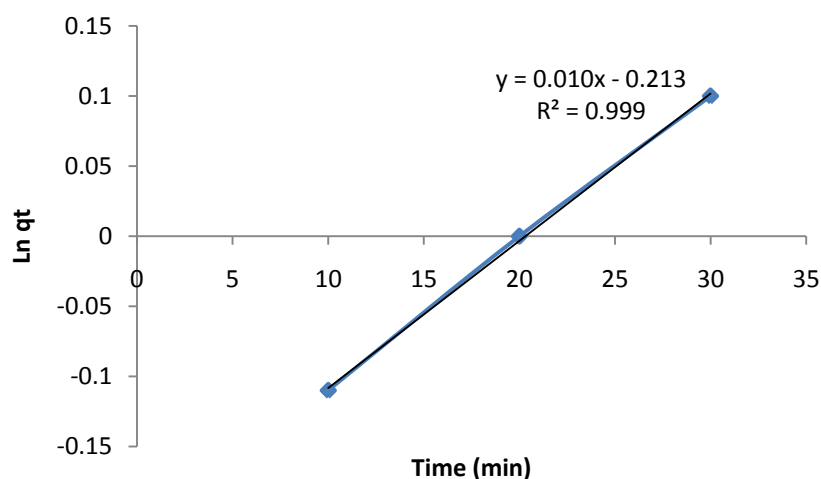
$$y = 0.010x - 0.213$$
$$R^2 = 0.999$$

Fig13. *Plot of In q_t vs. t for the adsorption of Pb^{2+} onto layered double hydroxide.*

$$y = -0.01x + 1.206$$
$$R^2 = 0.996$$
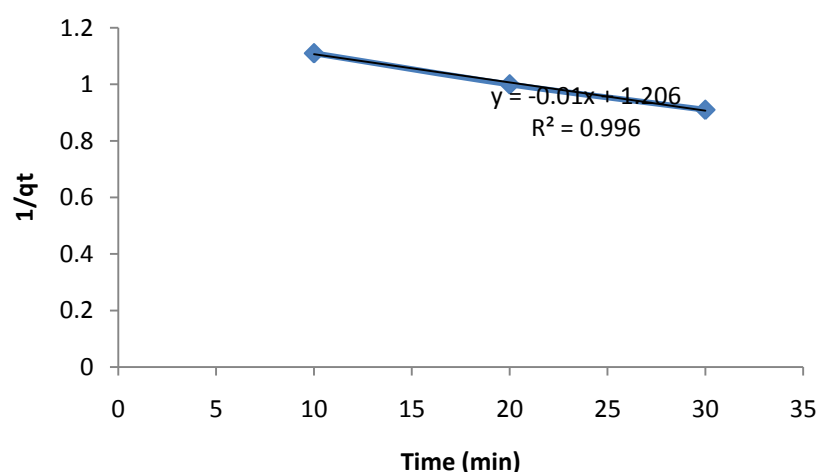
Fig14. *Plot of t/q_t vs. t for the adsorption of Pb^{2+} onto layered double hydroxide.*

Table1. *Equilibrium and Thermodynamic Parameters*

Isosteric heat of adsorption ΔH_x KJ/mol	Sticking Probability S*	Activation energy E_a KJ/mol	Gibbs free energy of adsorption ΔG^o KJ/mol	Apparent entropy ΔS^o J/mol	Apparent enthalpy ΔH^o J/mol	Surface coverage θ	Separation factor R_L	Hoping number n	Sorption coefficient K_d
17.6	0.5	-1.472	-0.546	0.024	-7.135	0.55	0.741	4	1.24

12. CONCLUSION

From this study it is very clear that layered double hydroxides could be very useful adsorbents in our long quest for environmental remediation. The efficient removal of the lead ion in aqueous solution could be enhanced by increasing the quantity of layered double hydroxide.

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