Equilibrium, Thermodynamic and Kinetic Studies of the Adsorption of Lead(II) on Ni/Fe Layered Double Hydroxide

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ABSTRACT--- *$Ni/Fe-CO_3$ layered double hydroxide of ratio 3:1 was synthesis by co-precipitation method for the adsorption of lead ions in aqueous solution. The synthesized layered double hydroxide ($Ni/Fe-CO_3$) was then characterized by Powder X-ray Diffraction (PXRD), Fourier Transform Infrared (FT-IR) and SEM/EDX analysis. The experimental data fitted both Langmuir and Freundlich isotherms with regression correlation coefficient values of 0.9993 and 0.9998 respectively. The essential thermodynamic parameters of ΔH^o, ΔS^o, ΔH_x and E_a were calculated to be -5.0496KJ/mol, 15.2J/molK, 12.6KJ/mol and -0.89KJ/mol respectively, thus showing the exothermic nature of the process and the randomness of the system. The low activation energy (E_a) value is consistent with physical adsorption. The isosteric heat of adsorption ΔH_x was calculated to be 12.6KJ/mol. The results also fitted pseudo-second order model ($R^2=1$).*

Keywords---- Thermodynamics, Kinetics Layered double hydroxide, Freundlich Isotherm, Langmuir Isotherm

1. INTRODUCTION

The presence of heavy metals in aqueous effluents is a major environmental problem owing to their toxicity to humans and to other life forms. Heavy metals, such as cadmium lead Pb(II) often present in industrial wastewaters, are hazardous to the aquatic ecosystem and pose possible human health risk. Cadmium is used in a wide variety of industries such as metal plating, metallurgical alloying, mining, ceramics and other industrial operations [1]. Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [2-4]. Therefore, cadmium level in wastewater, drinking water, and water used for agriculture should be reduced to the maximum permissible concentration (0.01 -1mg L) [5]. Lead can be traced to industrial discharges from a variety of sources, such as batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, and glass industry. The lead contamination is also due to emissions of vehicles and roadside runoffs. Lead has been reported the tolerance limit in drinking in water at 0.05 mg L^{-1} [6]. The presence of Pb(II) in drinkable water is known to cause various types of serious health problems such as anemia, encephalopathy, hepatitis and nephritic syndrome [6,7]. Although the inorganic form of lead is a general metabolic poison and enzyme inhibitor, organic forms are even more poisonous [6,8]. As the toxicity and persistence in environment of heavy metals, many technologies have been developed as conventional, biosorption and nanotechnology. Conventional physicochemical methods for removing heavy metals from waste streams include chemical reduction, electrochemical treatment, ion exchange, precipitation and evaporative recovery. These processes are generally expensive when the initial heavy -1metal concentrations are in the range of 10-100 mg L [9]. Biosorption is a technology for the removal heavy metals from industrial wastewater. The major advantages of the biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials such as naturally abundant algae or by prod- ucts of fermentation industries or waste material from another industry as biosorbents [10,11]

LDHs, also known as hydrotalcite-like materials or anionic clays, can be found in nature as minerals and readily synthesized in the laboratory. In nature, they are formed from the weathering of basalts or precipitation in saline water sources [12]. All LDH minerals found in nature and synthesized in the lab- oratory have a structure similar to that of hydrotalcite or its hexagonal analog, manasseite, and the ma- jority adheres to the general formula of $[M^{2+}_{1-x} M^{3+}_x (OH)_2] [A^{n-}_{x/n}. m H_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively, A is the anions, and x is ratio $M^{3+}/(M^{2+} + M^{3+})$. However, LDH materials are not limited to divalent M^{2+} and trivalent M^{3+}, but extended to monovalent M^+ (such as LiI) and tetravalent M^{4+} (such as TiIV, SiIV) cations [12–14]. Structurally, LDHs consist of

cationic brucite-like layers and interlayer anions as well as water molecules. In the brucite-like layer $[M^{2+}(OH)_2]$, the substitution of M^{2+} by M^{3+} leads to a positive charge ($[M^{2+}_{-x}M^{3+}_x(OH)_2]^{x+}$), which is neutralized by the interlayer exchangeable anion $[(A^{n-})_{x/n}]$. In general, the interlayer region also contains various amounts of water (mH_2O), hydrogen-bonded to the hydroxide layers and/or to the interlayer anions [12].

This paper studies the direct application of LDH synthesized by coprecipitation method for the adsorption of lead ion. The essential thermodynamic, kinetic and equilibrium parameters were determined for optimization and design purpose.

2. MATERIALS AND METHODS

Synthesis of LDH

Carbonate form of Ni-Fe LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3 M Ni $(NO_3)_2.6H_2O$ and 0.1 M Fe $(NO_3)_3.9H_2O$ with Ni/Fe ratios 3:1, 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 product was centrifuged at 5000 rpm for 5 minutes, with distilled water (3-4 times) and dried by freeze drying.

Characterization of layered double hydroxide

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.

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

A Shimadzu XRD 6000 Diffractometer with nickel filtered Cu-Kα (λ = 0.1542 nm) beam operated at 30 kV and 30 mA was used to determine the interlayer d-spacing of the clay layer in the original Ni-Fe LDH, modified stearate Ni-Fe LDH, blends and nanocomposites using Bragg's equation nλ= 2dsinθ. Data were recorded in 2θ range of 2º–30º using the scan rate of 2º/min.

Aqueous solution of heavy metal

The adsorbate Pb^{2+} was procured from Zayo-Sigma Chemical Ltd. Jos, Nigeria. The stock solution of Pb^{2+} was prepared by dissolving a required amount of $Pb(NO_3)_2$ in doubly distilled water at room temperature. The experimental solutions were obtained by diluting a stock solution of Pb^{2+} with double distilled water to the desired concentration.

3. ADSORPTION EXPERIMENTS

Batch adsorption experiments were carried out to investigate the quantitative uptake of lead by the layered double hydroxide. The analytical variables such as time, temperature, and copper initial concentration have been studied in detail for batch technique with 0.2g of the adsorbent.

The adsorption experiments were performed at three different temperatures viz. 40, 60 and 80˚C in a thermostat attached with a shaker, Remi make. The constancy of the temperature was maintained with an accuracy of ± 0.5º C.

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of lead (0.13g/l, 0.25g/l and 0.38g/l). All other factors were kept constant.

4. DATA ANALYSIS

The metal adsorption (q_e) and the removal efficiency R of the layered double hydroxide were calculated by the following equations [13,14]

$$q_e = \frac{v}{M}(C_o - C_e) \qquad\qquad 1$$

$$R(\%) = \frac{C_o - C_e}{C_o}x100 \qquad\qquad 2$$

with q_e as metal uptake capacity (mg/g double layered hydroxide at equilibrium), C_e is metal ion concentration in solution (mg/l) at equilibrium, C_o, the initial metal ion solution (mg/l), V, the volume of solution in litres and M, the dry weight of layered double hydroxide used in (g).

Langmuir plot was carried out using the linearized equation 3 below:

$$\frac{M}{x} = \frac{1}{ab\,C_e} + \frac{1}{b} \qquad\qquad\qquad 3$$

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

The essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter S_f .

$$S_f = \frac{1}{1 + aC_o} \qquad\qquad\qquad 4$$

With C_o as initial concentration of Pb^{2+} in solution, the magnitude of the parameter S_f provides a measure of the type of adsorption isotherm. If $S_f > 1.0$, the isotherm is unfavourable; $S_f = 1.0$ (linear); $0 < S_f < 1.0$ (favourable) and $S_f = 0$ (irreversible).

The adsorption intensity of Pb^{2+} in the Layered double hydroxide was assessed from the Freundlich plot using the linearized equation 5 below

$$In\frac{x}{m} = \frac{1}{n}(InC_e) + InK \qquad\qquad\qquad 5$$

where K and n are Freundlich constants and 1/n is approximately equal to the adsorption capacity.

The fraction of double layered hydroxide surface covered by the Pb^{2+} was computed using equation 6:

$$\theta = 1 - \frac{C_e}{C_o} \qquad\qquad\qquad 6$$

With θ as degree of surface coverage

The effectiveness of the adsorbent (double layered hydroxide) was assessed by the number of cycles of equilibrium sorption process required to reduce the levels of Pb^{2+} in solution according to the value of the distribution (partition coefficient (K_d) in equation 7.

$$K_d = \frac{C_{aq}}{C_{ads}} \qquad\qquad\qquad 7$$

Where C_{aq} is concentration of Pb^{2+} in solution, mg/l; C_{aq} is concentration of Pb^{2+} in Double layered hydroxide in mg/l.

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

$$\frac{d(Inc_e)}{dT} = -\frac{\Delta H_x}{RT^2} \qquad\qquad\qquad 8$$

where, Ce is the equilibrium adsorbate concentration in the solution (mg.L-1), ΔHx 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:

$$Inc_e = -\left[\frac{\Delta H_x}{R}\right]\frac{1}{T} + K \qquad\qquad\qquad 9$$

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 linear form of the modified Arrhenius expression was applied to the experimental data to evaluate the activation energy (E_a) and sticking probability S*
as shown in equation 10.

$$In(1 - \theta) = S^* + \frac{E_a}{RT} \qquad\qquad 10$$

The apparent Gibbs free energy of sorption ΔG^0 which is a fundamental criterion for spontaneity, was evaluated using the following equation

$$\Delta G^o = RTInK_d \qquad\qquad 11$$

K_d is obtained from equation (Eq. 7).

The experimental data was further subjected to thermodynamic treatment in order to evaluate the apparent enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of sorption using equation 12.

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad\qquad 12$$

The expression relating the number of hopping (n) and that of the surface coverage (θ) as shown in equation 13 was applied to the experimental data.

$$n = \frac{1}{(1-\theta)\theta} \qquad\qquad 13$$

The experimental data were further fitted into certain kinetic models to determine compliance.

The pseudo second order model is given by equation 5.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad\qquad 14$$

where, k2 (g mg-1 min-1) is pseudo second order rate constant. The plot of t/q_t vs t is shown in Figure 14.

5. RESULTS AND DISCUSSIONS

Characterization

Scanning electron microscope (SEM) and Energy dispersive spectroscope (EDS) images of as-synthesized layered double hydroxides are presented in figures 1 & 2. The images shows the surface morphology of the layered double hydroxides before and after adsorption studies. SEM image before adsorption studies, figure 1(a), shows a heterogeneous/rough surface with several pores while the image after adsorption studies, figure 1(b), show a smooth surface with several agglomeration of reacted hydroxide line. The smooth surface observed could be due to adsorbed metal ions filling the pores that existed before adsorption studies. The energy dispersive spectrograph before adsorption studies, figure 2(a), show the presence of metal ions used in the synthesis of the layered double hydroxides such as aluminium, sodium, and nickel and their percentage compositions. After adsorption studies, figure 2(b), the energy dispersive spectrograph, show the presence of lead ions adsorbed by the layered double hydroxide. The EDS also show that a chemical change has taken place during adsorption studies as observed
in the elemental composition presented.

EDX
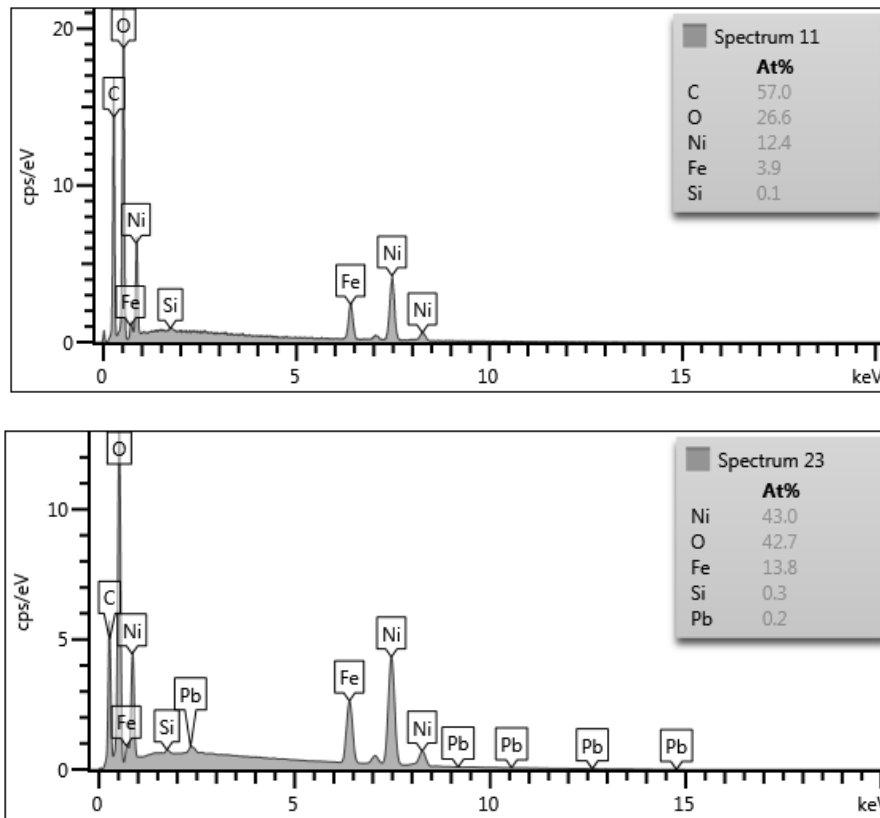
Figure 1: Energy Dispersive Spectroscopy patterns of Zn/Fe-CO$_3$ pre & post adsorption Energy Dispersive Spectroscopy

SEM
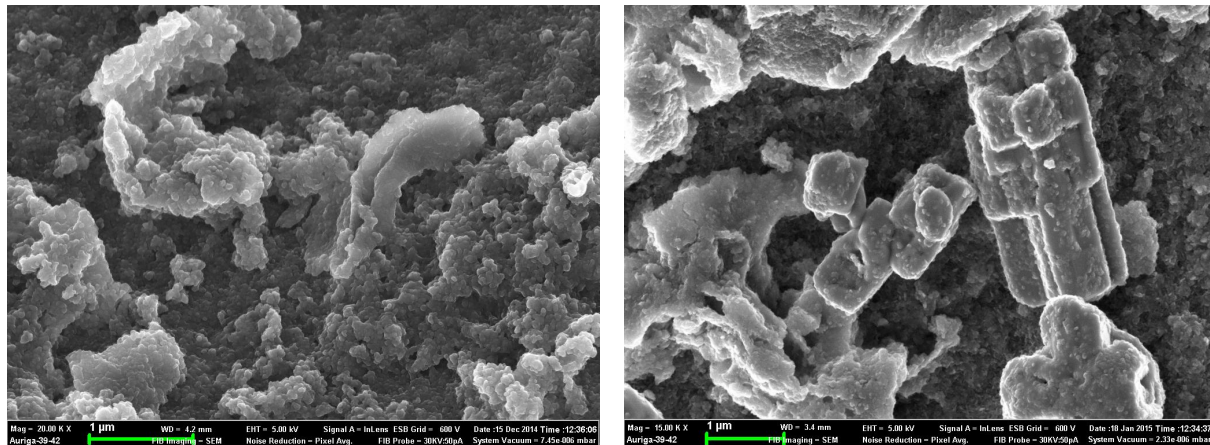
Figure 2: Scanning Electron Microscope (SEM) micrograph of Zn/Fe-CO$_3$ before (a) and after (b) adsorption studies.

FT-IR

As shown in Figure 3, the band near $3485 cm^{-1}$ corresponds to the vibration bands of hydroxyls (vOH). The bending mode of water molecules appears at 1733 cm^{-1}. The sharp intense band at 1352 cm^{-1} is the antisymmetric stretching of interlayer carbonate and the band at 719 cm^{-1} is due to M-O vibration. This confirms the presence of precursor functional groups.
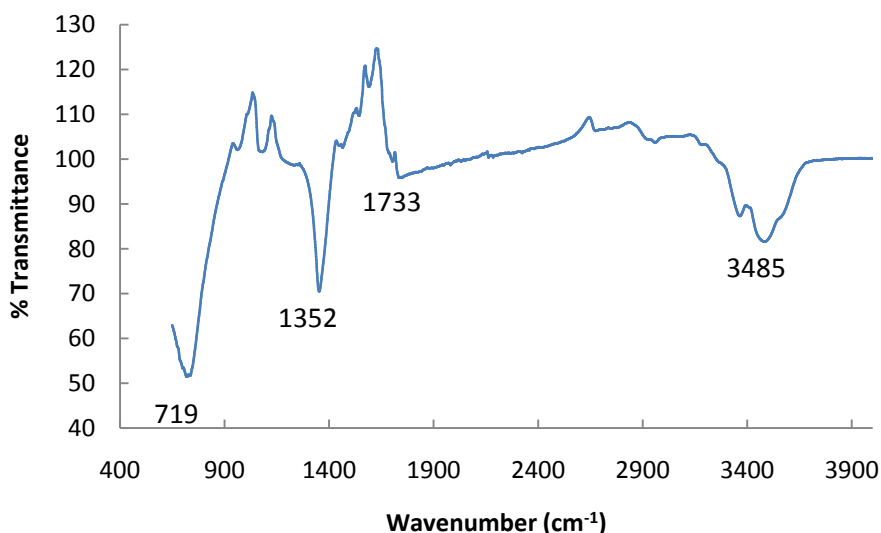
Figure 3: Mg/Fe-C0$_3$ Fourier transform infrared spectroscopy

XRD

Figure 4 shows the X-ray diffraction of Ni/Fe-CO$_3$. It exhibits the typical profile for LDH materials with sharp intense peaks at low theta values, whereas they become weaker and less defined at higher angular values. No residual peaks were observed thus confirming the absence of contaminant phases. Basal peaks were located near 2θ of 8.6º, 23º and 34.6º corresponding to diffraction by (003), (006) and (009) planes and d-spacing of 1.04, 0.772 and 0.259 respectively. These three peaks shows the presence of an ordered layered structure.
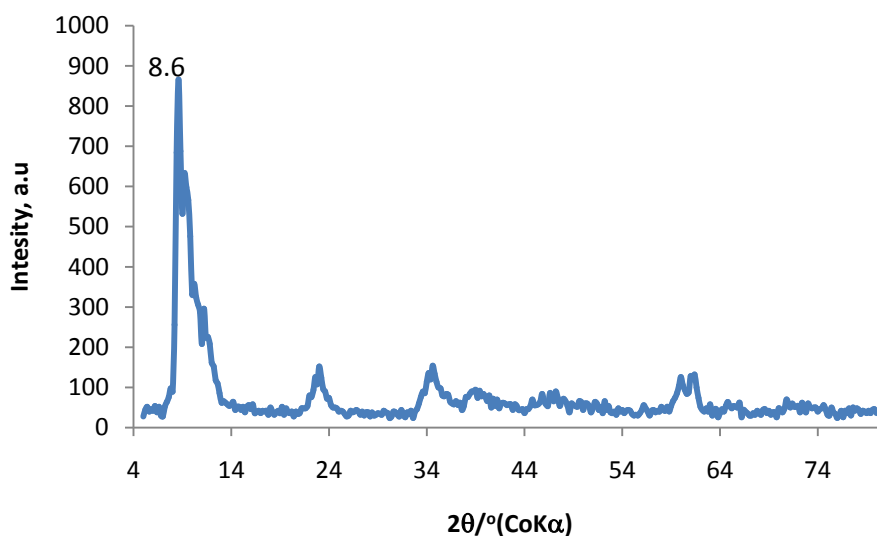

Figure 4: Mg/Fe-C0$_3$ X-ray powder diffraction

Effect of Concentration

Removal efficiency of lead ions by the adsorbents is illustrated in Figure 5. It shows that removal efficiency decreased with increasing of initial concentrations (50%, 48% and 47.4%) respectively, this is probably due to rapid adsorption at all available site and the relatively small amount of adsorbent that was used, an increase in the amount of adsorbent may therefore reverse adsorption trend.
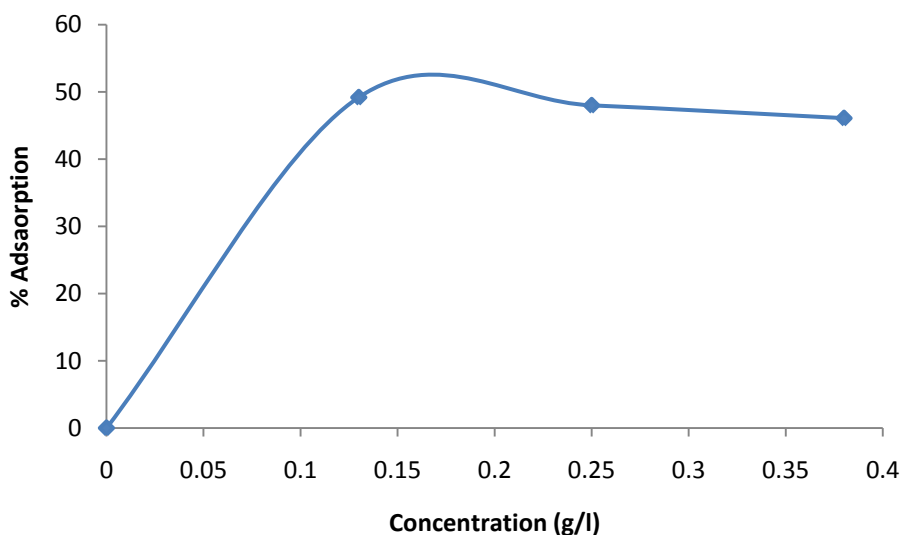
Figure 5: Effect of concentration on adsorption of Pb^{2+} onto layered double hydroxide

Isotherm Analysis

To investigate an interaction of adsorbate molecules and adsorbent surface, two well-known models, the Langmuir and Freundlich isotherms, were selected to explicate $Ni/Fe-CO_3$ LDH interaction in this study.

The Langmuir plot in figure 6 fitted the experimental data with $R^2 = 0.9999$ and therefore, confirm monolayer coverage.
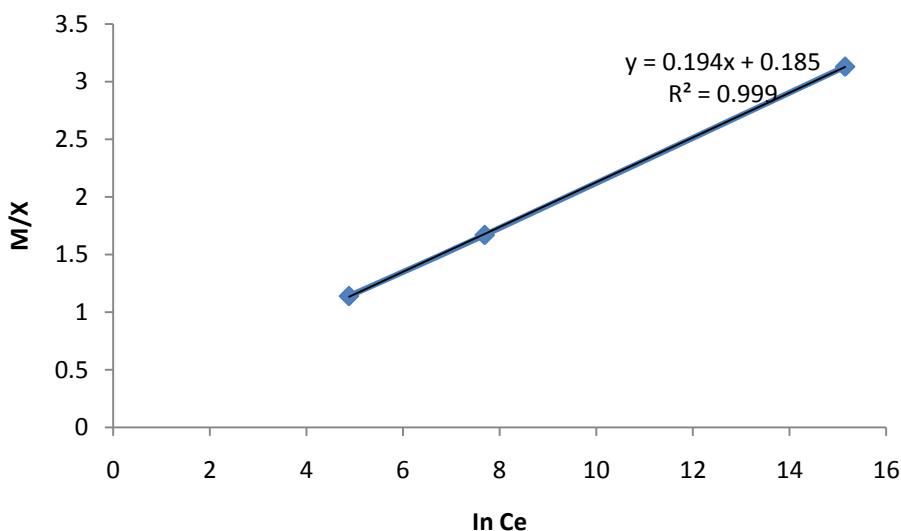
Figure 6: Langmuir Isotherm plot for adsorption of Pb^{2+} on layered double hydroxide

The influence of isotherm shape on whether adsorption is favourable or unfavourable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant separation factor (R_L), given by Eq. (4). The calculated value of R_L from figure 6 is 0.727, which is within the range of 0–1, thus confirms the favourable uptake of the layered double hydroxide adsorption process. The degree of favourability is generally related to the irreversibility of the system, giving a qualitative assessment of the layered double hydroxide interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

The adsorption capacity of the layered double hydroxide was extrapolated from the slope of the plot of Freundlich to be 1 in figure 7.
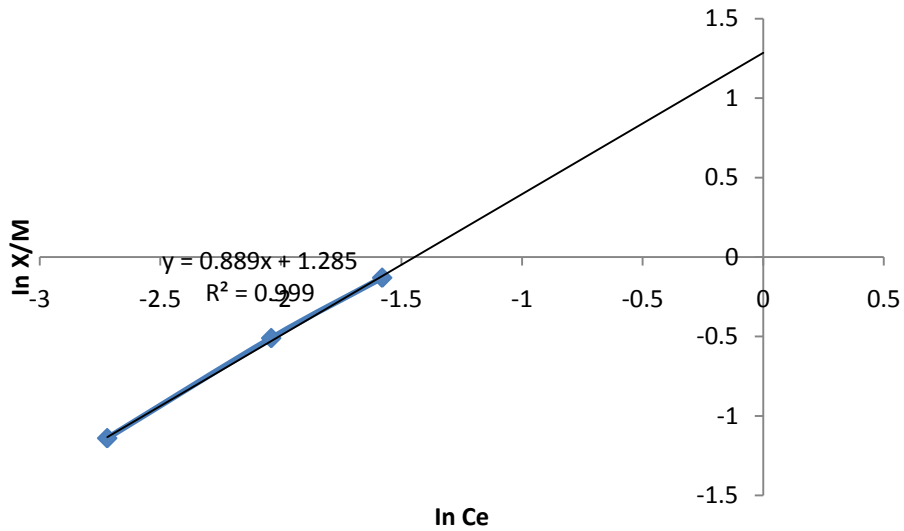

Figure 7: Freundlich Isotherm plot for adsorption of Pb^{2+} on layered double hydroxide

The fraction of the layered double hydroxide surface covered by the Pb^{2+} is given as 0.53 (table 1). This value indicates that 53% of the pore spaces of the Layered double hydroxide surface were covered by the Pb^{2+}, which means high degree of adsorption.

The effectiveness of layered double hydroxide which is the sorption coefficient of adsorbent was determined from equation 7 to be 0.42.

Effect of Temperature

As shown in figure 8 adsorption was highest at 313K (52.6%), and decreased slightly to 333K (50%) and 353K (47.4%). This implies rapid adsorption at the lowest temperature. This could be attributed to the amount of adsorbent used for the adsorption process.
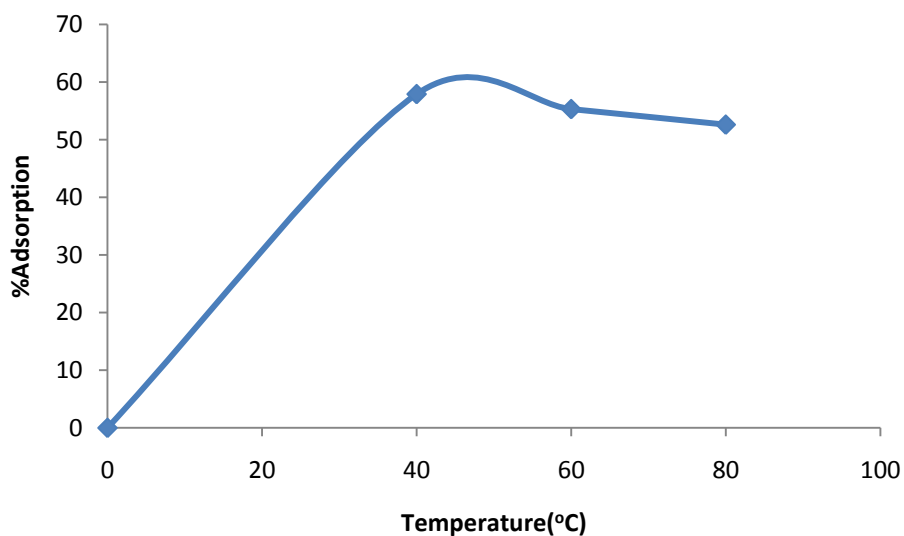
Figure 8: Effect of temperature on adsorption of Pb^{2+} onto layered double hydroxide

Isoteric heat of adsorption ΔH_x is one of the basic requirements for the characterization and optimization of an adsorption process and is a critical design variable in estimating the performance of an adsorptive separation process. It also gives some indication about the surface energetic heterogeneity. Knowledge of the heats of sorption is very important for equipment and process design. A plot of InC_e against $1/T$ in figure 9 gives a slope equal to ΔH_x. The value of ΔH_x derived from equation 11 was 12.6KJ/mol which indicates that adsorption mechanism was physical adsorption and in an heterogeneous surface.
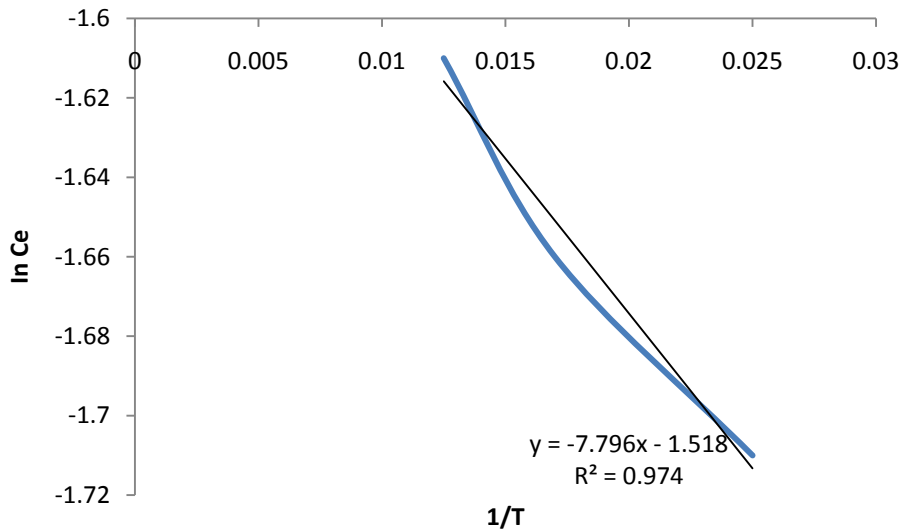
Figure 9: Plot of In Ce vs. 1/t for adsorption of Pb^{2+} onto layered double hydroxide

The activation energy E_a and the sticking probability S^* were calculated from equation 10, the value shown in table 1 for E_a and S^* are -0.89KJ/mol and 0.47 respectively, as shown in the plot in figure 10. The value of activation energy shows that the sorption process was a physical one less than 4.2KJ/mol. The sticking probability S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent. It is often interpreted as $S^*>1$ (no sorption), $S^*=1$ (mixture of physic-sorption and chemisorption), $S^* = 0$ (indefinite sticking – chemisorption), $0<S^*<1$ (favourable sticking – physic-sorption).
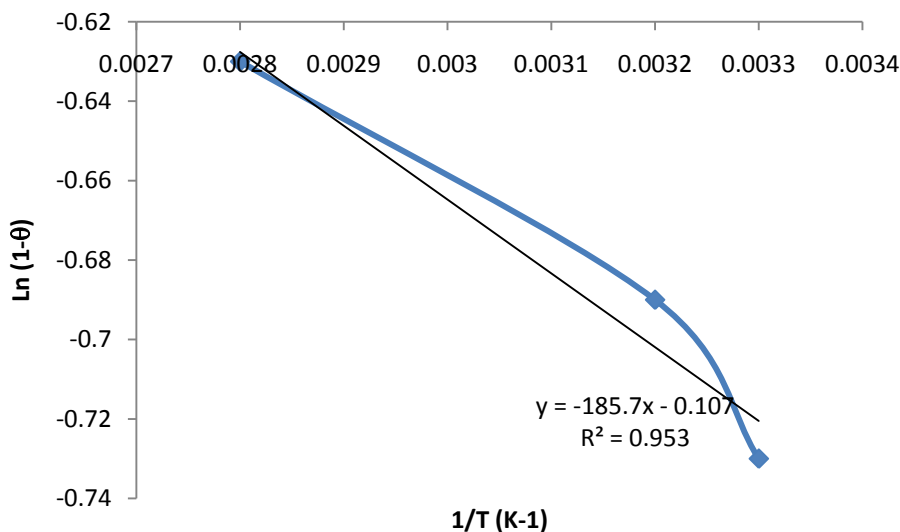
Figure 10: Plot of In(1-θ) vs. $1/T(K^{-1})$ for the adsorption of Pb^{2+} onto layered double hydroxide

The values of the enthalpy change (ΔH^o) and entropy change ΔS^o were calculated from equation 10 to be -5.0496J/mol and 15.2J/molK respectively, as shown in figure 11. A negative ΔH^o suggests that sorption proceeded favourably at a

lower temperature and the sorption mechanism was exothermic. A positive value of ΔS^0 (15.2J/molK) reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value of ΔS^0 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^0 value also corresponds to an increase in the degree of freedom of the adsorbed species.
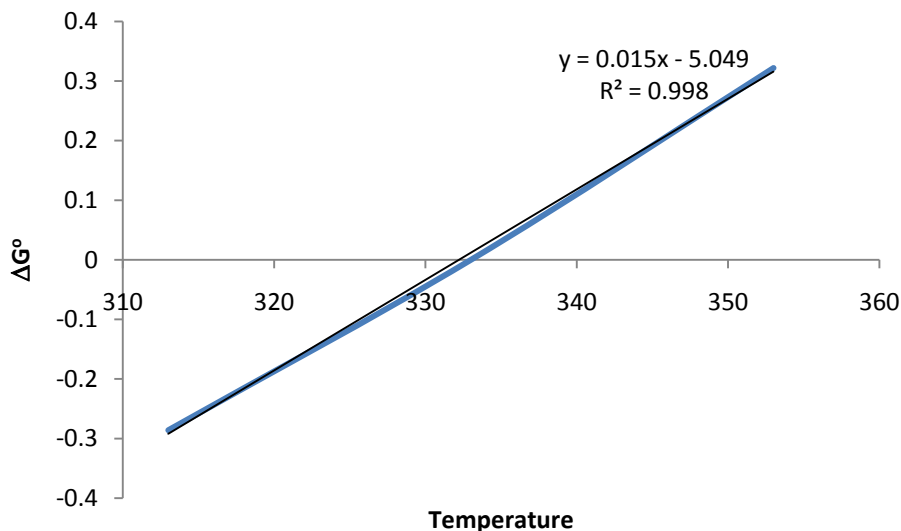
Figure 11: Plot of ΔG^o vs. Temperature for adsorption of Pb^{2+} onto layered double

The probability of Pb^{2+} finding vacant site on the surface of the layered double hydroxide during the sorption was correlated by the number of hopping (n) done by the Pb^{2+}. The hopping number presented in table 1 is 4. The lower the hopping number, the faster the adsorption.

T,K	ΔG^o, KJ/mol	ΔH^o, KJ/mol	ΔS^o, J/mol K	Ea, KJ/mol	ΔH_x, KJ/mol
313	-0.286				
333	0	-5.0496	15.2	-0.89	12.6
353	-0.322				

*Table 1: Thermodynamic Parameters of the Adsorption of Lead onto Layered Double Hydroxide*

Effect of Time

As shown in figure 8 adsorption was highest at 313K (52.6%), and decreased slightly to 333K (50%) and 353K (47.4%). This implies rapid adsorption at the lowest temperature. This could be attributed to the amount of adsorbent used for the adsorption process.
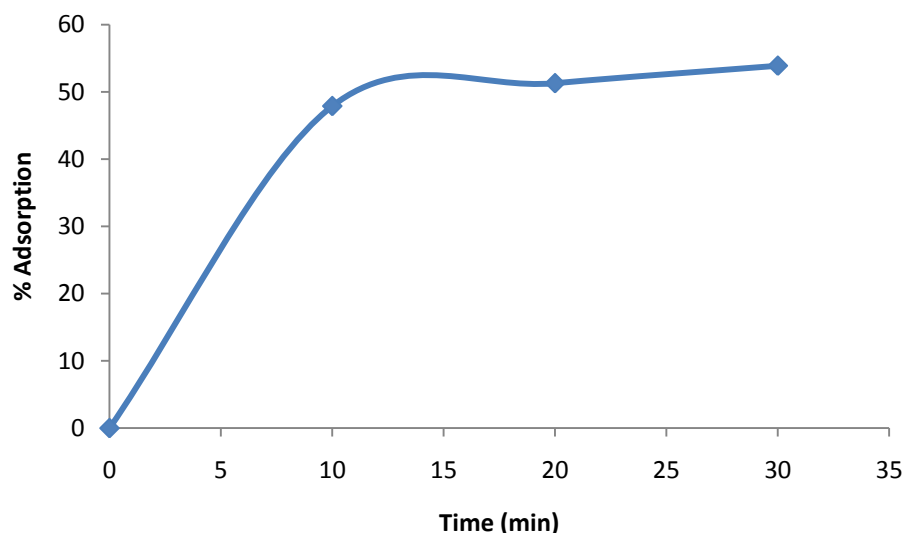
Figure 12: Effect of contact time on adsorption of Pb^{2+} onto layered double hydroxide

To explain the kinetics of the adsorption of Pb2+ ions by layered double hydroxide at $30^{o}C$, it is necessary to determine empirically which adsorption kinetic model fits best to the adsorption equilibrium date in order to determine the kinetic parameters pertaining to adsorption. Different adsorption kinetic models have been used to determine the adsorption parameters: Pseudo-first-order kinetic model [17, 18], pseudo-second-order kinetic model [15, 16], Elovich equation [17] and intraparticle diffusion model [17]. From the results, it was found that the experimental data fitted the pseudo-second-order kinetic model.
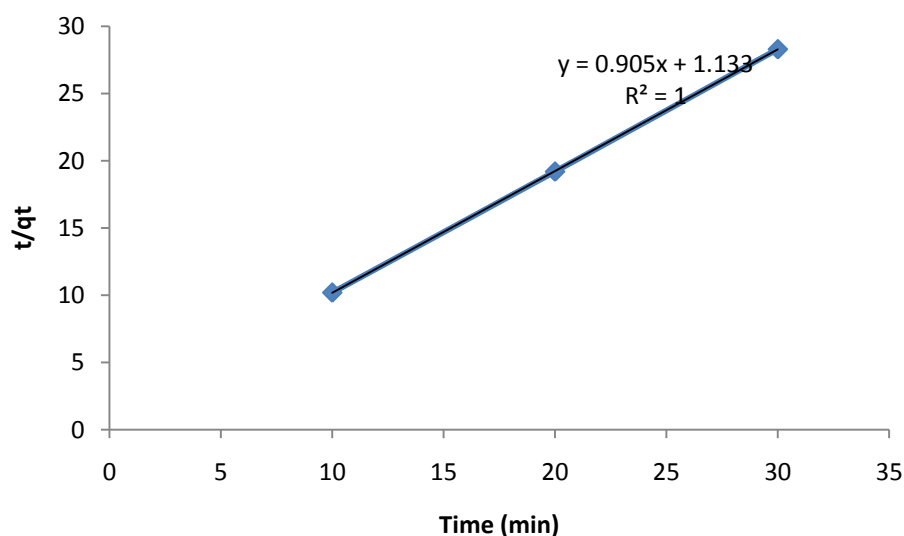
Figure 13: Plot of 1/qt vs. t for adsorption of Pb^{2+} onto layered double hydroxide

6. CONCLUSION

The adsorption of lead ions from aqueous solution using the agricultural by-product sesame leaf was investigated. Various impact factors such as contact time, initial lead ions concentration and temperature were optimized. From this study it is very clear that layered double hydroxide ($Ni/Fe-CO_3$) could be very useful adsorbents in our long quest for environmental remediation. The experimental data defines pseudo-second order model with regressin correlation coefficient value of 1. The data also complied with both Langmuir and Freundlich Isotherms. The thermodynamic parameters of ΔH^{o}, ΔS^{o}, ΔH_x and E_a were also calculated to be -5.0496KJ/mol, 15.2J/molK, 12.6 KJ/mol and -0.98KJ/mol respectively which confirms the spontaneity and exothermic nature of the process.

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