Synthesis and Application of Layered Double Hydroxide for the removal of Copper in Wastewater

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Abstract

Ni-Al Layered double hydroxide (Ni-Al LDHs) with M^{2+}: M^{3+} (4:1) ratio was synthesized by co-precipitation method from nitrate salt solutions. The layered double hydroxide was characterized by Fourier transform infrared spectroscopy, X-Ray Diffraction, Energy Dispersive Spectroscopy/Scanning Electronic Microscopy. The influences of phase contact time, temperature and initial concentrations were investigated to optimize the conditions for maximum adsorption. The experimental data were analyzed by Langmuir and Freundlich isotherm models and fitted well with correlation coefficient values of 0.9996 and 0.9995 respectively. The thermodynamic parameters of Isosteric heat of adsorption (ΔH_x), Activation energy (E_a), Enthalpy change (ΔH^o) and Entropy change (ΔS^o) were calculated to be 18.1KJ/mol, 1.447KJ/mol, -7.135J/mol and 24J/molK respectively. The results shows that the adsorption process was spontaneous and exothermic.

Keywords: synthesis, characterization, adsorption isotherms, thermodynamics

1. Introduction

Layered double hydroxide (LDH) is a class of anionic clays with high anion exchange capacities which can be used as an effective adsorbent for the removal of variety of anionic pollutants. The chemical composition of LDHs can be described by the general formula $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+} [(A^{n-})_{x/n} . mH_2O]^{x-}$ where M^{2+} = divalent metals, M^{3+} is trivalent metals, and A^{n-} is an anion with charge n. Molar fraction number mol of water in LDH interlayer per formula weight of compounds and $x = M^{3+}/(M^{3+} + M^{2+})$ molar fraction (normally, it is between 0.2 and 0.33) (F. Cavani, et al, 1991). The most common method for the synthesis of LDHs is co-precipitation. However, other synthesis methods such as rehydration, hydrothermal reaction, pre-pillaring and intercalation have been reported (Hetterley, R. D. et al, 2008, Richardson, M. C. et al, 2009). The flexibility of layered double hydroxides has place premium on their applications in various fields including catalysis, photochemistry, pharmacy, adsorption etc. The use of layered double hydroxide for the removal of heavy metals in aqueous media has been studied and the results shows the adsorption capacities of LDHs (G. N. Pshinko, 2013, Gong, J. et al 2001, M. R. Perez, et al, 2006, Zaini, et al, 2011). However, in all these studies, calcination has been further done to the original LDH either to enhance the quality of crystals or increase the adsorption capacity which ultimately makes the process more expensive.

The presence of heavy metals in our environment is a cause of great concern to environmentalists and Governments all over the world because of their effects on humans, plants and animals. As reported by Mahvi, H. A., 2008, heavy metal ions in aqueous solutions creates many problems for humans, animals and plants. Copper is very essential to human life and health, but is also very dangerous at higher levels of concentration. Copper is extensively discharged from the electrical industry, pulp, paper mills and petroleum refineries (Igwe, J. C. et al 2006). A number of technologies for the removal of heavy metal ions from aqueous solutions have been developed over the years (Gupta, V. K. et al 2006, Lu, H. J. et al 2008). The most important of these techniques include chemical precipitation, filtration and reverse osmosis. However, all these techniques have their inherent advantages and limitations in application. Adsorption has become one of the preferred methods for removal of

toxic contaminants from water as it has been found to be very effective , economical , versatile and simple (King, P., et al, 2006, Chen, D. Z. et al, 2010). Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch processes, ease of operation, little sludge generation and low capital cost (Tran, H. H. et al, 1999, Mohanty, K., 2006). The main properties of the adsorbents are strong affinity and high loading capacity for the removal of heavy metals.

This paper takes a look at the direct application of the LDH produced by coprecipitation method for the adsorption of copper ions. The thermodynamic and equilibrium parameters were determined for optimization and design purpose.

2. Materials and Methods

2.1 Synthesis of LDH

Carbonate form of Ni-Al 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 Al $(NO_3)_3.9H_2O$ with Ni/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 ℃ for 18 hours. The product was centrifuged at 5000 rpm for 5 minutes with distilled water (3-4 times) and dried by freeze drying.

2.2 Characterization of Layered Double Hydroxide

The morphology and microstructure of the sample were characterized by a Scanning Electron Microscopy (SEM) (type FEI Quanta 200), X-ray diffraction (XRD, Bruker D8 diffractometer with Cu Kα radiation, λ =1.5418 Å, a scan rate of 0.02°2θ/s from 5 to 70°) and Fourier transformation infrared spectra (FT-IR, Perkin-Elmer-283B FT-IR spectrometer, the wave number range from 400 to 4000 cm^{-1}).

2.3 Aqueous Solution of Heavy Metal

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 (CuSO4,). From the stock, working solutions of 0.08g/LCu, 0.12g/LCu and 0.16g/LCu 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).

2.4 Adsorption Experiments

Batch adsorption experiments were carried out to investigate the quantitative uptake of copper 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 ± 0.5 ℃.

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of copper (0.08g/l, 0.12g/l and 0.16g/l). All other factors were kept constant.

2.5 Data Analysis

The metal adsorption (q_e) and the removal efficiency R of the layered double hydroxide were calculated by the following equations (Mohanty, K., 2006, Zhang, L. et al, 1998).

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

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

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:

$$\frac{M}{x} = \frac{1}{abC_e} + \frac{1}{b} \tag{3}$$

Where X is the amount of Cu^{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.

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

With C_o as initial concentration of Cu^{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 the Cu^{2+} in the Layered double hydroxide was assessed from the Freundlich plot using the linearized equation 5 below

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

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 Cu^{2+} was computed using equation 6:

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

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 Cu^{2+} in solution according to the value of the distribution (partition coefficient (K_d) in equation 7.

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

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

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

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

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:

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

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.

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

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

$$\Delta G^o = RT In K_d \tag{11}$$

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.

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{12}$$

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.

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

3. Results and Discussions

3.1 SEM/EDS

Scanning electron microscope (SEM) and Energy dispersive spectroscope (EDS) images of as-synthesized layered double hydroxides are presented in figure 1 & 2.

The images shows the surface morphology of the layered double hydroxides before and after adsorption studies were carried out. SEM image before adsorption studies, figure 1(a), show a 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.
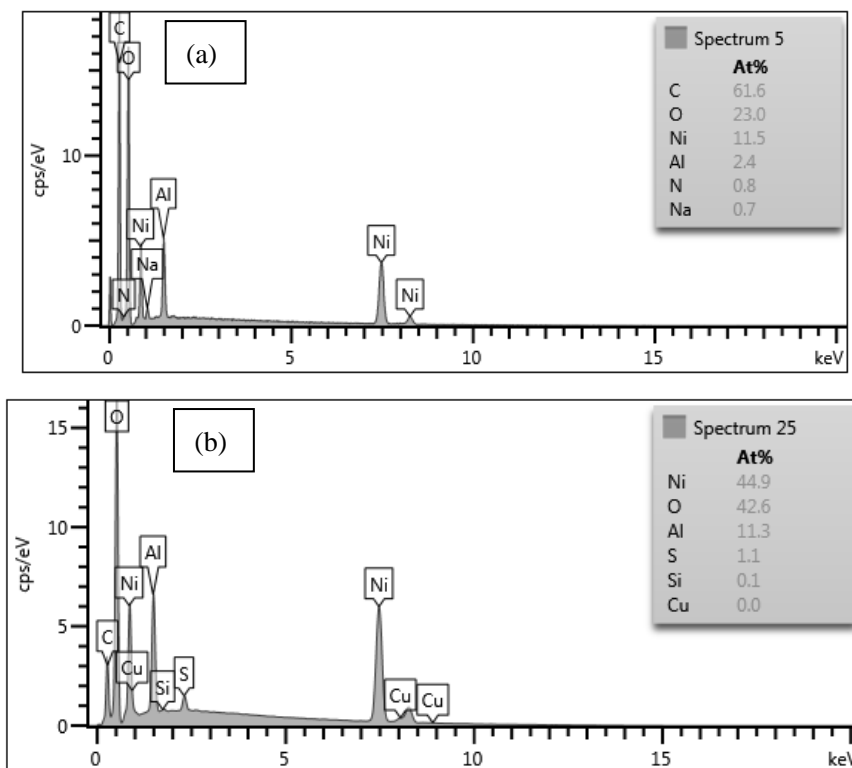

Figure 1. Energy Dispersive Spectroscopy patterns of Ni/Al-CO$_3$ pre & post adsorption Energy Dispersive Spectroscopy, before (a) and after (b) adsorption studies.
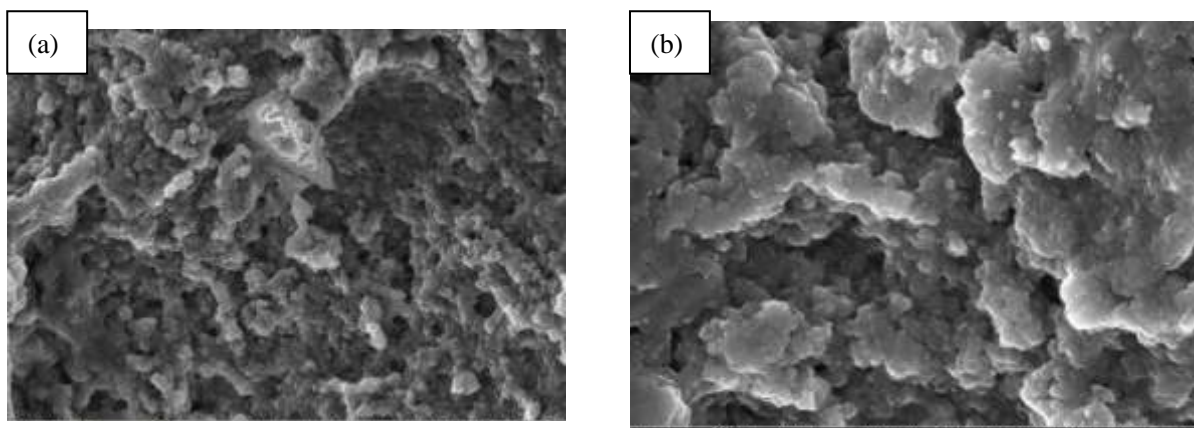
Figure 2. Scanning Electron Microscope (SEM) micrograph of Ni/Al-CO$_3$ before (a) and after (b) adsorption studies.

3.1 FT-IR

The functional groups, types of bonding and identify components in the samples were determined by a Perkin Elmer Spectrum 1000 series Spectrophotometer equipped with attenuated total reflectance (ATR). The infrared spectra of the samples were recorded in the range of frequency of 400–4,000 cm^{-1}.

Figure 3 shows the FT-IR spectra and peak numbers of the Ni/Al-LHD. The strong bond around 3400 cm^{-1} is associated with the stretching vibration of OH groups in the brucite like layer and interlayer inter molecules.

The broadening of the bond was attributed to the hydrogen-bond formation. Less intense absorption bond around 1650 – 1500 cm^{-1} was assigned to the bending vibration of the interlayer water molecules.

The carbonate ion peak is around 1400cm^{-1} which is consistent with layered double hydroxides.

The low wave number region of <1000cm^{-1}, the lattice vibration modes of the layered double hydroxides sheets such as M-O is assigned between 840 - 550 cm^{-1}.
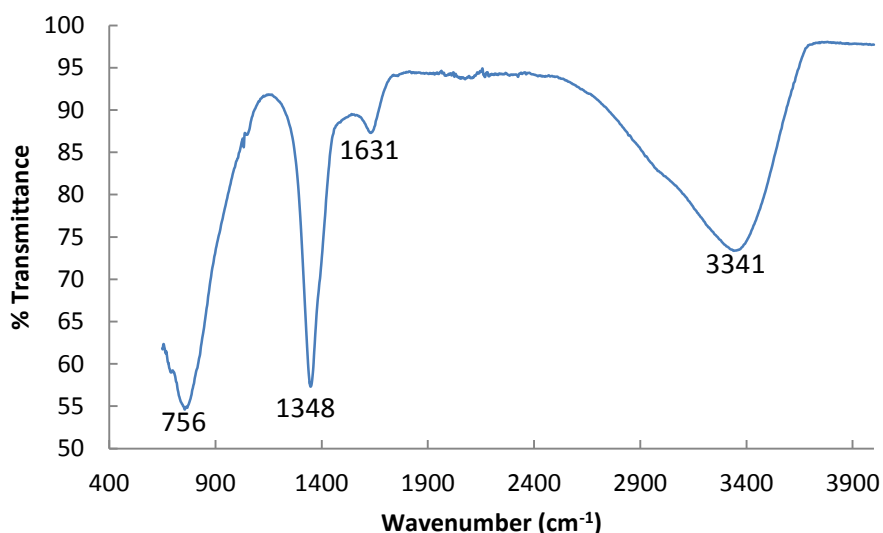

Figure 3. Ni/Al-C0$_3$ Fourier transform infrared spectroscopy

3.2 XRD

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-Al LDH, modified stearate Ni-Al LDH, blends and nanocomposites using Bragg's equation nλ= 2dsinθ. Data were recorded in 2θ range of 2 $^{\circ}$–30 $^{\circ}$using the scan rate of 2 $^{\circ}$/min.

Figure 4 shows the XRD patterns of the Ni/Al. The basal reflections are observed at low 2θ values and weaker non-basal reflections at higher 2θ. The reflections in the Ni-Al based layered double hydroxide is indexed to rhombohedral symmetry (space group R-3m). We observe two successive reflections at 7.58 Å and 3.8 Å respectively, which could be indexed to (003) and (006) planes. The lattice parameters (a = 3.06 Å, c = 7.58 Å) could be indexed to (00l) and (hk0) reflections. The reflection in the mid-2θ region of the PXRD pattern can be indexed to h0l/0kl reflections and are used to determine the specific stacking sequence of layers with respect to each other.
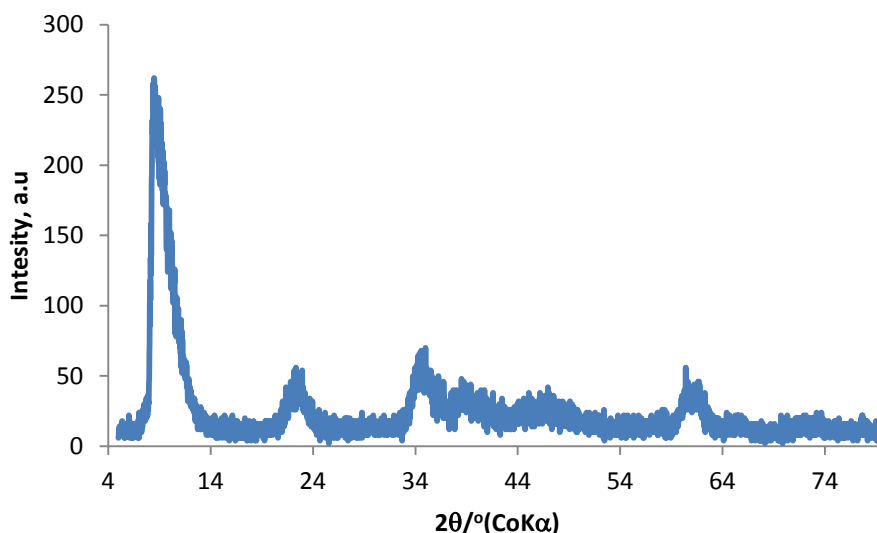

Figure 4. Ni/Al-C0$_3$ X-ray powder diffraction

3.3 Effect of Concentration

Removal efficiency of copper ions by the adsorbents is illustrated in Figure 5. It shows that removal efficiency decreased with increasing of initial concentrations (58.8%, 55.5% and 52.5%) 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.
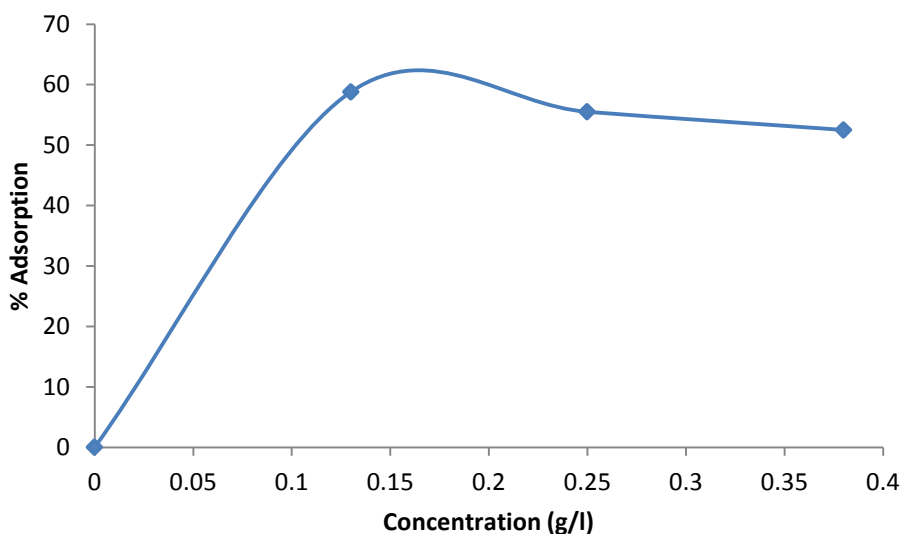

Figure 5. Effect of Concentration on adsorption of Cu^{2+} onto layered double hydroxide

3.4 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 LDH interaction in this study.

The Langmuir plot in figure 6 fitted the experimental data with $R^2 = 0.9996$ and therefore, confirm monolayer coverage.

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 0.981, 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).
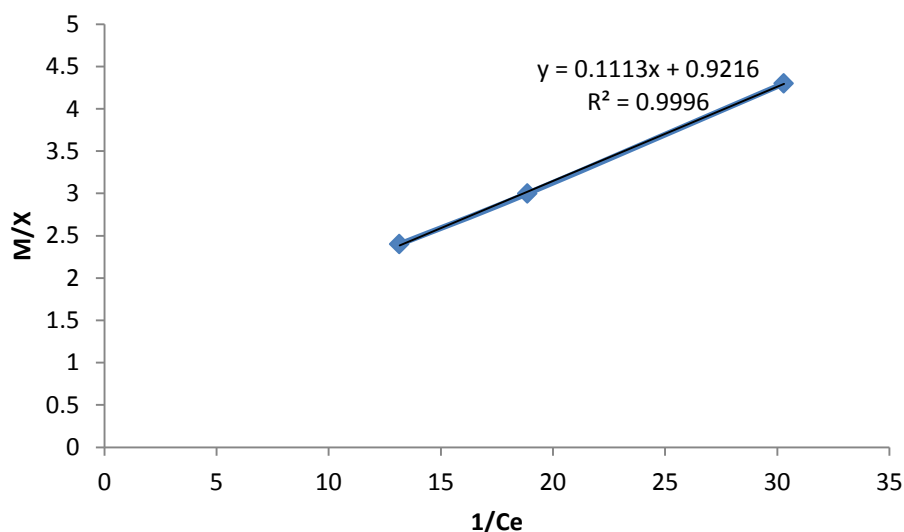

Figure 6. Langmuir Isotherm plot for adsorption of Cu^{2+} on layered double hydroxide

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

The fraction of the layered double hydroxide surface covered by the Cu^{2+} is given as 0.55 (table 1). This value indicates that 55% of the pore spaces of the Layered double hydroxide surface were covered by the Cu^{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 0.54.
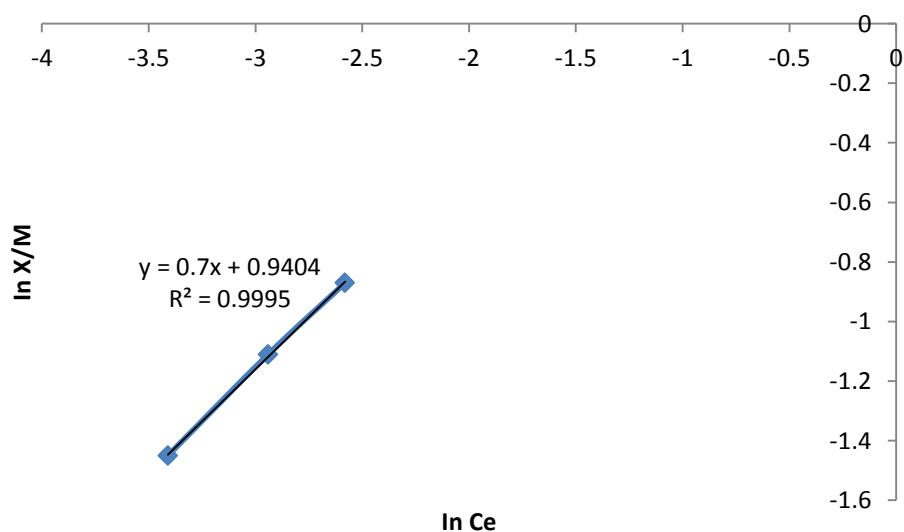

Figure 7. Freundlich Isotherm plot for adsorption of Cu^{2+} on layered double hydroxide

3.5 Effect of Temperature

As shown in figure 8 adsorption was highest at 313K (46.3%), and decreased slightly to 333K (42.5%) and 353K (38.8%). This implies rapid adsorption at the lowest temperature. This could be attributed to the amount of adsorbent used for the adsorption process.
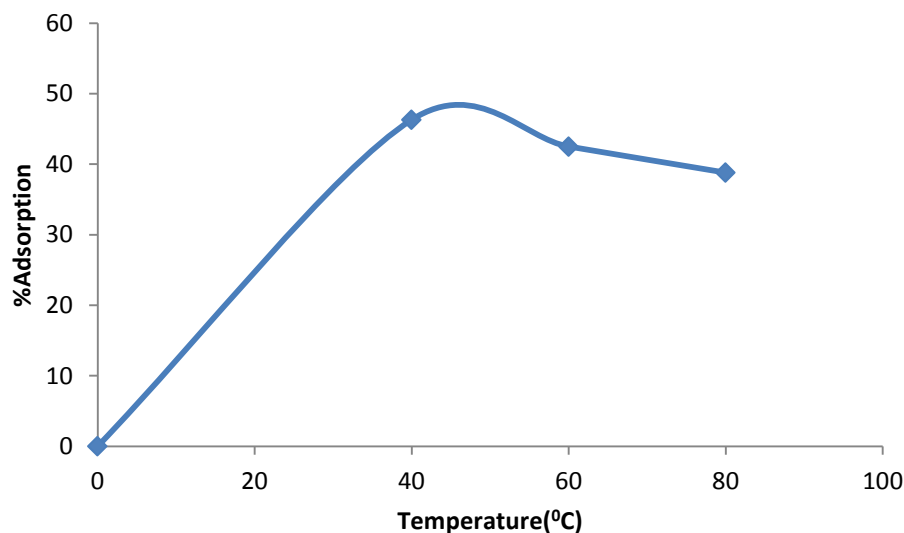

Figure 8. Effect of Temperature on adsorption of Cu^{2+} onto layered double hydroxide

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 18.1KJ/mol which indicates that adsorption mechanism was physical adsorption and in an heterogeneous surface.
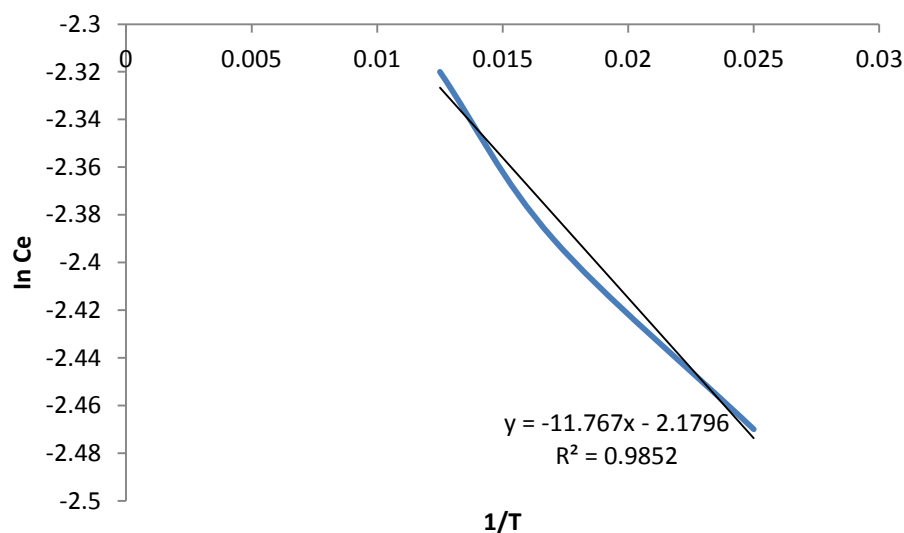

Figure 9. Plot of InC_e vs. $1/T$ for the adsorption of Cu^{2+} onto layered double hydroxide

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 1.447KJ/mol and 0.40 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).
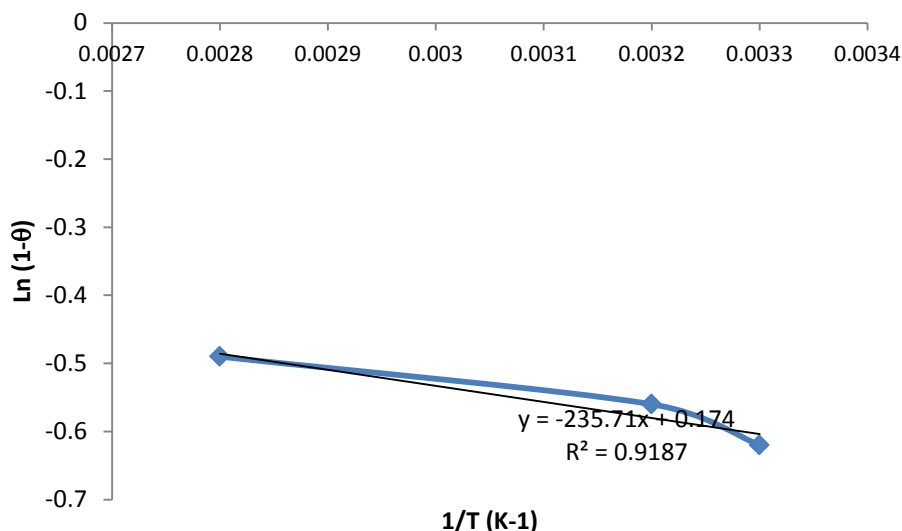
Figure 10. Plot of In(1-θ) vs. 1/T(K^{-1}) for the adsorption of Cu^{2+} onto layered double hydroxide

The values of the enthalpy change (ΔH^o) and entropy change ΔS^o were calculated from equation 10 to be -7.135J/mol and 24 J/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 (24J/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.
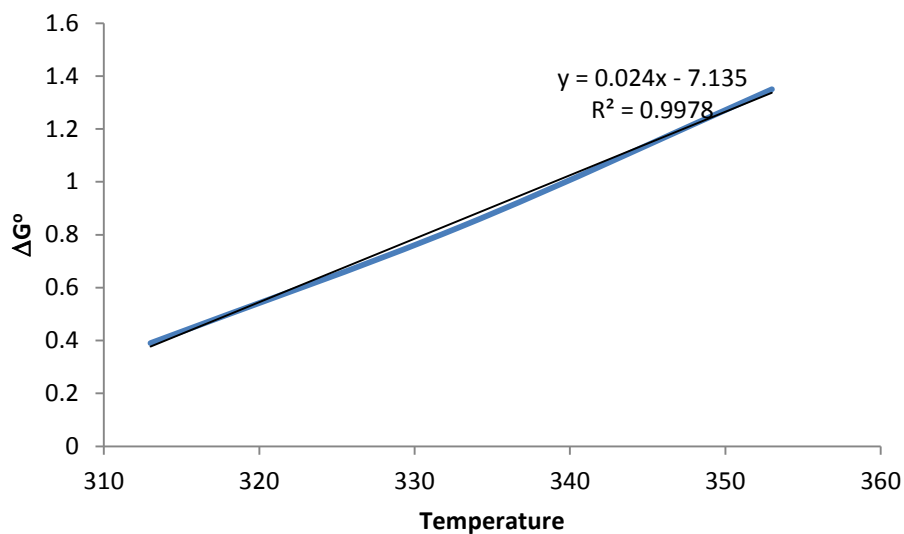

Figure 11. Plot of ΔG^o vs. Temperature for the adsorption of Cu^{2+} onto layered double hydroxide

The probability of Cu^{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 Cu^{2+}. The hopping number presented in table 1 is 4. The lower the hopping number, the faster the adsorption.

Table 1. Equilibrium and Thermodynamic Parameters

Isosteric heat of adsorption ΔH_x KJ/mol	Sticking Probability S*	Activation energy E_a KJ/mol	Apparent entropy ΔS^o J/molK	Apparent enthalpy ΔH^o J/mol	Surface coverage θ	Separation factor S_f	Hoping number N	Sorption coefficient K_d
18.1	0.4	1.447	24	-7.135	0.55	0.974	4	0.54

4. Conclusion

In this study layered double hydroxide was used to recover copper (Cu^{2+}) ions from aqueous solutions. The results indicate that removal of copper (Cu^{2+}) strongly dependent on contact time. Increasing temperature and concentration does not have favourable effect on the adsorption capacity of layered double hydroxide. The equilibrium data were described well by a Langmuir isotherm and Freundlich isotherm indicating that the adsorption of copper on layered double hydroxide was as a monolayer. The study of thermodynamic properties indicate a spontaneous adsorption process. The efficiency of the LDH could be enhanced by increasing its amount considerably.

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