Adsorption Dynamics of Copper Adsorption by Zn/Al-CO₃

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Abstract : Layered double hydroxide (Zn/Al-CO₃) was prepared by the co-precipitation method and characterized by SEM, XRD and FTIR. The batch adsorption experiments were carried out to study the effect of various parameters, such as the initial concentration, contact time and temperature on the adsorption of copper ion onto the layered double hydroxide (LDH). The Langmuir and Freundlich models were used to fit the experimental data of adsorption isotherms. The kinetic studies showed that the adsorption data followed the pseudo-second order model. Thermodynamic studies indicated that the adsorption of copper was a spontaneous process.

Key words: LDH, Co-precipitation, Langmuir and Freundlich isotherms, heavy metal.

I. INTRODUCTION

The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment [1].

The presence of heavy metals in the environment can be harmful to a variety of living species. Consequently, the removal of heavy metals from wastewater and water is important to protect public health [2]. The term heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous at low concentrations [3]. Heavy metals such as copper and lead can accumulate in living organisms and cause health disorders and various diseases.

Heavy metals in solution can be removed using several techniques such as precipitation [4], coagulation, chemical precipitation, adsorption [5] ozonation, membrane filtration and reverse osmosis [6]. Recently, adsorption has become a widely used technique due to its simplicity, potential regeneration and sludge-free operation [7]. Moreover, it can be an attractive technique if the adsorbent used can be synthesized cheaply and readily.

Layered double hydroxide (LDH) is a class of anionic clay with high anion exchange capacities. Layered double hydroxides are effective adsorbents for the removal of a variety of pollutants. LDHs have positively charged layers of metal hydroxides and the anions and water molecules are located between the layers. The positive charges that are produced from the isomorphous substitution of divalent cations and trivalent cations, are counter balanced by anions located between the layers (8). LDHs have a general formula of [M²⁺ 1-x M³⁺ x (OH)₂] [An- x/n. m H₂O], where M²⁺ and M³⁺ are divalent and trivalent metal cations, respectively, and A is the anion [9]. The anions between the layers can be polymers, organic dyes, surfactants and organic acids [10].

Wastewater effluents normally contain pollutants which carry positive and negative charges. The LDH anion exchange ability, large surface area and regeneration ability ensure that this adsorbent can be excellently utilized in wastewater purification [6]. Therefore, layered double hydroxide was selected in our work to optimize the removal of copper from aqueous solution.

II. MATERIALS AND METHODS

Synthesis of LDH

Carbonate form of Zn-Al LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3 M Zn (NO₃)₂.6H₂O and 0.1 M Al (NO₃)₃.9H₂O with Zn/Al ratios 4:1, was added drop wise into a 50 ml mixed solution of (NaOH (2M) + Na₂CO₃ (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.

Characterization of LDH

The powdered layered double hydroxide was characterized by Powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and EDX/TEM analysis.
Preparation of Metal Solution

All reagents used for this study were of analytical reagent grade and were procured from Zayo-Sigma Chemical Ltd. Jos, Nigeria. 1000 mg/l aqueous solutions of the metal ion was prepared as stock from their salt (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).

Experimental procedure

Batch adsorption experiments were carried out to study the effect of initial metal ion concentration, contact time and temperature on the adsorption of Cu2+ on layered double hydroxide. Adsorption studies were carried out using 10 ml of the metal ion solution and 0.2 g of the adsorbent. At the end of each experiment, the content of each tube was filtered using a Whatman No 14 filter paper after which the concentration of residual metal ions in each filtrate was determined.

Variation of initial metal ion concentration

Batch adsorption was carried out using initial metal ion concentrations of 0.08g/L, 0.12g/L and 0.16g/L of aqueous solution of Cu ions. 0.2g adsorbent (layered double hydroxide) was weighed into each of the three (100 ml) beakers and 10 ml of metal solution poured into each beaker. The adsorption mixtures were uniformly and continuously agitated with the use of a platform shaker at a fixed temperature of 30°C for 30 minutes after which the content of each beaker was filtered into clean sample bottles. A thermostated water-bath was used to maintain the temperature. The concentration of residual metal ions in the filtrates was determined using AAS. The amount of metal ions adsorbed from the solution was determined by difference.

Variation of contact time

The adsorption of the metal ion on layered double hydroxide was studied at various time intervals (0-30 min). Kinetic sorption studies were carried out using 10 ml of each metal ion solution with initial metal ion concentration of 0.16 mg/l. The metal ion solution was added into three labeled beakers each containing 0.2 g of the adsorbent. The mixtures were uniformly agitated at 30°C for 30 minutes. The experimental procedure was thereafter repeated at various time intervals of 10, 20 and 30 minutes. At the end of each contact time, the content of each tube was centrifuged and filtered. The concentration of metal ions in the filtrates was determined using AAS and the amount of metal ions adsorbed was calculated.

Variation of temperature

The adsorption of the metal ion on layered double hydroxide was studied at various temperatures (40-80°C) with the use of a thermostated water bath. Kinetic sorption studies were carried out using 10 ml of each metal ion solution of initial concentration 0.16 mg/l. The metal ion solutions were added into 3 labeled beakers each containing 0.5g of the adsorbent. The mixtures were uniformly agitated at 40°C for 30 minutes. The experimental procedure was repeated in the temperature range 60-80°C. At the end of each contact time, the content of each beaker was filtered and the residual concentration of metal ions in the filtrates were determined using AAS and the amount of metal ions adsorbed was calculated.

Data Analysis

The uptake of heavy metal ions was calculated from the mass balance, which was stated as the amount of solute adsorbed onto the solid. It is equal to the amount of solute removed from the solution. Mathematically it can be expressed by equation 1 [11]:

\[ q_e = \frac{(C_0 - C_e)}{s} \] .......................... 1

\( q_e \): Heavy metal ions concentration adsorbed on adsorbent at equilibrium (mg of metal ion/g of adsorbent).
\( C_0 \): Initial concentration of metal ions in the solution (mg/l).
\( C_e \): Equilibrium concentration or final concentration of metal ions in the solution (mg/l).
\( S \): Dosage concentration and it is expressed by equation 2:

\[ S = \frac{m}{v} \] .......................... 2

Where v is the initial volume of metal ions solution used and m is the mass of adsorbent. The percent adsorption (%) was also calculated using equation 3:

\[ \% \text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100\% \] .......................... 3

Equilibrium Studies

Langmuir plots were carried out using the linearized equation 4 below :

\[ \frac{M}{x} = \frac{1}{abC_e} + \frac{1}{b} \] .......................... 4

Where X is the amount of Cu2+ 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 essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter \( S_f \) [12].

\[ S_f = \frac{1}{1+aC_0} \] .......................... 5
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 carbon nanotube was assessed from the Freundlich plots using the linearized equation 6 below:

\[
\ln \frac{X}{M} = \frac{1}{n} \ln(C_e) + \ln K \tag{6}
\]

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

The fraction of layered double hydroxide surface covered by the \( Cu^{2+} \) was computed using equation 7.

\[
\theta = 1 - \frac{C_e}{C_o} \tag{7}
\]

With \( \theta \) as degree of surface coverage

**Thermodynamics Studies**

The effectiveness of the adsorbent (LDH) 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 6.

\[
K_d = \frac{C_{aq}}{C_{ads}} \tag{8}
\]

Where \( C_{aq} \) is concentration of \( Cu^{2+} \) (mg/g) in solution; \( C_{ads} \) is concentration of \( Cu^{2+} \) (mg/l) in LDHs.

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

\[
d\ln(C_e) = \frac{\Delta H^*}{RT^2} \tag{9}
\]

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

\[
\ln(C_e) = -\left(\frac{\Delta H^*}{R}\right)\frac{1}{T} + K \tag{10}
\]

where \( K \) is a constant.

The isosteric heat of adsorption is calculated from the slope of the plot of \( \ln C_e \) 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 8.

\[
\ln (1 - \theta) = S^* + \frac{E_a}{RT} \tag{11}
\]

The apparent Gibbs free energy of sorption \( \Delta G_o \) which is a fundamental criterion for spontaneity, was evaluated using the following equation:

\[
\Delta G^o = RT \ln K_d \tag{12}
\]

\( K_d \) is obtained from equation (Eq. 10).

The experimental data was further subjected to thermodynamic treatment in order to evaluate the apparent enthalpy \( (\Delta H^o) \) and entropy \( (\Delta S^o) \) of sorption using equation 13.

\[
\Delta G^o = \Delta H^o - T \Delta S^o \tag{13}
\]

The expression relating the number of hopping (n) and that of the surface coverage (\( \theta \)) as shown in equation 16 was applied to the experimental data.

\[
n = \frac{1}{(1-\theta) \varepsilon} \tag{14}
\]

**Kinetic Studies**

To determine the kinetic compliance of the experimental data, the results are subjected to the following kinetic models:

First-order kinetic model,

\[
\ln q_t = \ln q_e + K_1 t \tag{15}
\]

Second-order kinetic model

\[
\frac{1}{q_t} = \frac{1}{q_e} + K_2 t \tag{16}
\]

Pseudo-second order

\[
\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e t} \tag{17}
\]

**III. RESULTS AND DISCUSSION**

**Characterization**

**SEM/EDX**

Figures 1 & 2 clearly show the pre & post adsorption photographs and graph of SEM images and EDX respectively. The EDX graphs show 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.

**XRD**

The XRD patterns of Zn-Al/CO\(_3\) is shown in Figure 3. The strong peaks at 12.4°, 35.2°, 39.8° are characteristic of a layered structure. The peaks are sharp and symmetrical. According to \( a = 2d110 \), the crystal structure of Zn-Al-LDHs with different molar ratios are the same. The charge number of Al\(^{3+}\) is greater than that...
of Zn\textsuperscript{2+}. Hence, the distance of the layers increases and the coulomb repulsion between metal ions in the adjacent hexagonal unit cells decreases with increasing the Zn/Al ratio, making the lattice parameter a and c (=3d003) increase, especially c. This is based on the fact that parameter a is a function of the average radius of the metal cations while parameter c is a function of the average charge of the metal cations [13].

**FT-IR**

FT-IR spectra of the LDH sample is shown in Figure 4. As shown in Figure 4, a band near 3338 cm\(^{-1}\) corresponds to the vibration bands of hydroxyls (vOH). The bending mode of water molecules appears at 1639 cm\(^{-1}\) and the intensity increases slightly with increasing Zn/Al ratio. The sharp intense band at 1347 cm\(^{-1}\) is the antisymmetric stretching of interlayer carbonate. Compared with the peak of CO\textsubscript{3}\textsuperscript{2−} in CaCO\textsubscript{3} (1,430 cm\(^{-1}\)), a large shift toward a lower wavenumber indicates that the CO\textsubscript{3}\textsuperscript{2−} intercalating into the interlayer is not free, and is interlayered with water molecules between with hydrogen bonds are formed [14]. The peak picture is consistent with layered double hydroxide in the interlayer region.

**Effect of Temperature**

Figure 8 shows the effect of different temperatures (30, 60 and 80 °C ) and the percentage of metal removed from solution. It shows that there was a rapid adsorption from 0 - 30°C after which there was a decrease in amount adsorbed. Since adsorption is a physical process, effect of temperature is negligible.

**Thermodynamics**

Isosteric heat of adsorption \(\Delta H_c\) 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 \(\ln C\) against \(1/T\) in figure 6 gives a slope equal to \(\Delta H_c\). The value of \(\Delta H_c\) derived from equation 10 was 18.9 KJ/mol which indicates that adsorption mechanism was physical adsorption and in an heterogeneous surface.

The activation energy \(E_a\) and the sticking probability \(S^*\) were calculated from equation 11, the value shown in table 1 for \(E_a\) and \(S^*\) are 1.869 KJ/mol and 0.4 respectively as shown in figure 7. The value of activation energy shows that the sorption process was a physical one since it is less than 4.2 KJ/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 physi-sorption and chemisorption), \(S^*= 0\) (indefinite sticking – chemisorption), \(0<S^*<1\) (favourable sticking – physi- sorption).

The probability of Cu\textsuperscript{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\textsuperscript{2+} is calculated from equation 14. The hopping number presented in table 1 is 4. The lower the hopping number, the faster the adsorption. The low value of n obtained in this study suggests that the adsorption of Cu\textsuperscript{2+} on the layered double hydroxide was very fast.

Table 1 also presents the Gibbs free energy \(\Delta G^o\) for the sorption of Cu\textsuperscript{2+} by the layered double hydroxide which was calculated from equation 12. Gibbs free energy is the fundamental criterion of spontaneity. The \(\Delta G^o\) value of -0.3 KJ/mol was negative indicating that the sorption process was spontaneous. The value obtained for \(\Delta G^o\) was also less than -20 KJ/mol suggesting electrostatic interaction between the Cu\textsuperscript{2+} and the layered double hydroxide which supported physi-sorption mechanism. The values of the enthalpy change (\(\Delta H^o\)) and entropy change (\(\Delta S^o\)) were calculated from equation 13 to be -7.135 KJ/mol and 0.022 KJ/mol respectively as shown in figure 8. A plot of \(\Delta G^o\) against \(T\) gives a straight line graph with slope and intercept defining the \(\Delta H^o\) and \(\Delta S^o\). A negative \(\Delta H^o\) suggests that sorption proceeded favourably at a lower temperature and the sorption mechanism was exothermic. A positive \(\Delta S^o\) suggests that the freedom of the adsorbed Cu\textsuperscript{2+} was not restricted in the layered double hydroxide, indicating that physi-sorption mechanism predominates.

**Kinetic Studies**

**Effect of Time**

Maximum adsorption was observed at 10 minutes, this implies that the process was rapid and requires minimal contact time to reach equilibrium as shown in figure 9. The experimental data fitted pseudo-second order kinetic model with \(R^2 = 0.9876\) as shown in figure 10.

**Effect of Concentration**

The percentage sorption of Cu\textsuperscript{2+} by the LDH at different concentrations of the Cu\textsuperscript{2+} is presented in figure 11. The maximum adsorption of 60% took place at equilibrium concentration of 0.08g/l Cu\textsuperscript{2+}This is because at lower concentration more LDH pore spaces were available for the Cu\textsuperscript{2+} but as the concentration of Cu\textsuperscript{2+} increased, the adsorption capacity of the LDH decreased due to reduced availability of free pore spaces. The results indicated that the sorption of Cu\textsuperscript{2+} were very much dependent on the concentration of the Cu\textsuperscript{2+}.

**Isotherm Studies**

Figure 12 shows the Langmuir isotherm plot of adsorption of copper ions by layered double hydroxide. The result shows \((R^2 = 0.9996)\) a straight line and therefore, the experimental data fitted the isotherm model.

In determining the nature of the adsorption process, whether favourable or unfavourable, the dimensionless
constant separation term $S_f$ was investigated (equation 3). The result ($S_f=0.928$) in Table 1 was less than one and greater than zero which showed that the sorption of Cu$^{2+}$ onto the layered double hydroxide was favourable. The experimental data was further fitted in to confirm its applicability to the Freundlich model, the result as shown in figure 13 fitted perfectly ($R^2 = 1$). The adsorption capacity which is calculated from the slope of the graph is 0.908, less than one.

IV. CONCLUSION

From the present study, it can be concluded that layered double hydroxides can be used as potential adsorbent for the removal of copper ions from aqueous solution.

In particular, it displayed a high affinity to the copper ion probably due to the presence of the carbonate ion and water molecules in the interlayer region. The experimental data fitted both Langmuir and Freundlich isotherms. The overall adsorption process was rapid and spontaneous.

V. REFERENCES


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<th>Isotherm of adsorption</th>
<th>Sticking Probability</th>
<th>Activating energy</th>
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<th>Apparent entropy</th>
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<th>Surface coverage</th>
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Table 1: Equilibrium and Thermodynamic Parameters
Figure 1: Scanning Electron Microscope (SEM) micrograph of Zn/Al-CO$_3$ before (a) and after (b) adsorption studies.

Figure 2: Energy Dispersive Spectroscopy patterns of Zn/Al-CO$_3$ pre & post adsorption.

Figure 3: Zn/Al-CO$_3$ X-ray powder diffraction

Figure 4: Zn/Al-CO$_3$ Fourier transform infrared spectroscopy


Figure 5: Effect of Temperature on adsorption of Cu$^{2+}$ onto layered double hydroxide

Figure 6: Plot of In Ce vs. 1/T for the adsorption of Cu$^{2+}$ onto layered double hydroxide

Figure 7: Plot of In (1-θ) vs. 1/T(K$^{-1}$) for the adsorption of Cu$^{2+}$ onto layered double hydroxide

Figure 8: Plot of $\Delta G^\circ$ vs. Temperature for the adsorption of Cu$^{2+}$ onto layered double hydroxide

Figure 9: Effect of Time on adsorption of Cu$^{2+}$ onto layered double hydroxide

Figure 10: Plot of t/qt vs. t for the adsorption of Cu$^{2+}$ onto layered double hydroxide

Figure 11: Effect of Concentration on adsorption of Cu$^{2+}$ onto layered double hydroxide
Figure 12: Langmuir isotherm plot for Cu$^{2+}$ onto layered double hydroxide

Figure 13: Freundlich isotherm plot for the adsorption of Cu$^{2+}$ onto layered double hydroxide