

Equilibrium, kinetic and thermodynamic studies of the uptake of copper by layered double hydroxide

Ayawei Nimibofa¹, Ekubo Allen Tobin¹, Shooto Ntaote David², Wankasi Donbebe¹, Dikio Ezekiel Dixon²

¹Niger Delta Universities, Wilberforce Island, Yenagoa Bayelsa State, Nigeria

²Applied Chemistry and Nano-Science Laboratory, Department of Chemistry, Vaal University of Technology Vanderbijlpark, South Africa

Abstract

This study explored the adsorption capacity of Mg/Al layered double hydroxide (LDH) for the removal of Cu²⁺ from aqueous solutions after synthesis and characterization. The effect of various operational parameters such as concentration, temperature and sorption time on the adsorption of Cu²⁺ was investigated using batch adsorption process experiments. It was found that layered double hydroxide (LDH) can be used as adsorbent for the removal of copper ions in aqueous solution containing low concentration of the metal salt. The average values of activation energy, isosteric heat of adsorption, entropy and enthalpy were 1.447, 12.9, 0.0137 and -4.8390 kJ/mol, respectively. This shows that the adsorption of the metal ion on the adsorbent follows a physical adsorption mechanism. The kinetic results conform to pseudo-second order model ($R^2 = 0.9959$) and second order kinetic model ($R^2 = 0.9952$) while the adsorption characteristics of the adsorbent followed both Langmuir and Freundlich adsorption isotherm models.

Keywords: layered double hydroxide, adsorption, Freundlich Isotherm, Langmuir Isotherm, isosteric heat of adsorption, Gibbs energy change.

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Heavy metal pollution in wastewater has always been a serious environmental problem, because heavy metals are not biodegradable and can be accumulated in living tissues [1]. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Elevated environmental levels of Cu(II) come from variety of sources. Mining, metal cleaning, plating baths, pulp, paper and paper board mills, refineries, fertilizer industries, etc., are the potential sources of Cu(II) in industrial effluents [2]. Copper, a widely used metal in industry, is an essential trace element for human health and plays an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity. According World Health Organization (WHO), the maximum acceptable concentration of Cu(II) in drinking water is 1.5 mg/L. The adult human body contains 100–150 mg of Cu(II), but excess amounts in the body can be toxic [3]. In aqueous environments, the speciation of the metal is dependent both on ligand concentration and pH. If the excessive amount of Cu(II) enters into the environment, they can cause serious health issues such as nausea, headache, dizziness, respiratory difficulties, hemolytic anemia, massive gastrointestinal bleeding,

liver and kidney failure, even death [4–7]. Removal of metal ions from wastewater in an effective manner has become an important issue. Efficient methods for the removal of metals have resulted in the development of new separation techniques. Precipitation, ion-exchange, flocculation, adsorption, electro-chemical processes, electro dialysis, nanofiltration and reverse osmosis are commonly applied for the treatment of wastewater [8]. However, these methods are either inefficient or expensive when heavy metals exist in low concentrations [9]. Additionally, these methods may also affect the generation of secondary wastes, which are difficult to treat. Adsorption is an alternative technology to which an increased amount of studies have been focused because of cost effectiveness, local availability and technical feasibility for the removal of heavy metal ions from the wastewater [10]. Different factors affecting the adsorption, such as the contact time, adsorbent dose, pH and temperature, were examined to optimize the adsorption equilibrium and the kinetic data are fitted using different models and parameters.

Layered nanomaterials are getting lots of attention due to their unique structural flexibility, which is useful for the development of new hybrid materials with controlled functionality [11]. The layered double hydroxide (LDH) is also known as hydrotalcite-like material or anionic clay, it is the large group of natural or synthetic materials that are layered, containing the hydroxide of two or more different kinds of metal cations and pos-

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Correspondence: A. Nimibofa, Niger Delta Universities, Wilberforce Island, P.M.B. 071 Yenagoa Bayelsa State, Nigeria.

E-mail: ayawei4acad@gmail.com

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sessing an overall positive charge, which neutralized by the incorporation of exchangeable anion [12]. The structure of LDH closely related to brucite-like layer, $\text{Mg}(\text{OH})_2$, where Mg^{2+} is octahedrally surrounded by six OH and share edges with to form infinite sheet [13]. Some of the divalent ions are replaced by trivalent ions, resulting in positively charge sheet and compensated by anions in the interlayer galleries along with the water molecules [14–16].

The general formula that represents this class of materials is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} is divalent cation (Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Mn^{2+}), M^{3+} is trivalent cation (Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} or Mn^{3+}) and A^{n-} is an interlayer anion (Cl^- , NO_3^- , ClO_4^- , CO_3^{2-} , SO_4^{2-} and other inorganic anions) [11,17,18]. The x value is the charge density for the mole ratio $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$ [19]. The monovalent anions such as NO_3^- and Cl^- within the interlayer gallery space can be easily replaced by desired anions [20]. The structure of LDH forms two-dimensional crystals consisting of thin crystalline layers stacked by van der Waals and/or weak electrostatic interaction; thus various guest anions can be inserted into the LDH interlayer galleries [17]. This material is two dimensional type layered structure consisting of thin crystalline layers with a thickness of a few nanometers [21]. LDHs have anionic exchange capacity and the ability to capture organic and inorganic anions make them almost unique as inorganic materials [22]. LDH has been used in diverse applications such as adsorbents [23], drug delivery [24], controlled release formulation [15], and sensors [25]. There are varied ways to intercalate anions into LDH interlayer gallery, such as co-precipitation method [26], hydrothermal method [24] and ion-exchange method [15].

This work investigated the direct application of the LDH for the removal of Cu^{2+} without further intercalation.

EXPERIMENTAL

Synthesis of LDH

Carbonate form of Mg–Al LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.4 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with Mg/Al 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 2.5 and 3 h, the slurry formed was aged at 60 °C for 18 h. The products were centrifuged at 5000 rpm for 5 min, with distilled water 3–4 times and dried by freeze drying.

Characterizations

The powdered layered double hydroxide was characterized by Powder X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR) and EDX/TEM analysis.

Aqueous solution of heavy metal

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 metals ion was prepared as stock from their salts (CuSO_4). From the stock, working solutions were diluted to the appropriate concentrations. 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).

Sorption studies

The adsorption of Cu(II) ions onto layered double hydroxide was studied by the mean of batch technique. The procedure used for this study is described as following: a known weight (0.2 g) of layered double hydroxide was equilibrated with 10 ml of the lead solution of known concentration, in a stoppered 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 copper solutions and temperature on the adsorption was studied following different sets of experiments:

A 0.2 g of the powder sample was weighed out using an electronic weighing balance and placed in three (3) pre-cleaned test tubes. 10 ml of metal ion solution with standard concentration of 0.08, 0.12 and 0.16 g/L which was made from spectroscopic grade standards of copper ion from copper sulphate was added to each test tube containing the weighed sample and equilibrated by rocking (agitation) for 30 min and then centrifuged at 2500 rpm for 5 min and decanted. The supernatants were stored for lead ion analysis as stated in metal analysis. For contact time 10, 20 and 30 min were used at standard concentration of 0.16 g/L of copper and for effect of temperature on the uptake of copper ions by the LDH, temperature range of 40–80 °C was applied at standard concentration of 0.16 g/L of copper solution.

Data analysis

For data analysis, various equilibrium, kinetic, and thermodynamic models (equations) were employed to interpret the data and establish the extent of adsorp-

tion. The amount of metal uptake was computed using the material balance equation for batch dynamic studies [23]:

$$q_e = \frac{V}{M}(c_0 - c_e) \quad (1)$$

where q_e is metal uptake capacity (mg/g LDH at equilibrium), c_e is metal ion concentration in solution (mg/g) at equilibrium, c_0 is the initial metal ion solution (mg/g), V is the volume of solution in litres and M the dry weight of LDH used in (g).

Langmuir plots were carried out using the linearized equation:

$$\frac{M}{X} = \frac{1}{abc_e} + \frac{1}{X} \quad (2)$$

where X is the amount of Cu^{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 essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter S_F [24]:

$$S_F = \frac{1}{1 + ac_0} \quad (3)$$

with c_0 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 [25] plots using the linearized equation:

$$\ln \frac{M}{X} = \frac{M}{n} \ln c_e + \ln k \quad (4)$$

where k and n are Freundlich constants and $1/n$ is approximately equal to the adsorption capacity. The fraction of double layered hydroxide covered [26] by the Cu^{2+} was computed:

$$\theta = 1 - \frac{c_e}{c_0} \quad (5)$$

with θ as degree of surface coverage.

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)):

$$K_d = \frac{c_{\text{aq}}}{c_{\text{ads}}} \quad (6)$$

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:

$$\frac{d(\ln c_e)}{dT} = \frac{\Delta H^*}{RT^2} \quad (7)$$

where c_e is the equilibrium adsorbate concentration in the solution (mg L^{-1}), ΔH^* is the isosteric heat of adsorption (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is temperature (K). Integrating the above equation, assuming that the isosteric heat of adsorption is temperature independent, gives the following equation:

$$\ln c_e = - \left[\frac{\Delta H^*}{R} \right] \frac{1}{T} + K \quad (8)$$

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:

$$\ln(1 - \theta) = S^* + \frac{E_a}{RT} \quad (9)$$

The apparent Gibbs energy change of sorption, ΔG° , which is a fundamental criterion for spontaneity, was evaluated using the following equation:

$$\Delta G^\circ = RT \ln K_d \quad (10)$$

K_d is obtained from equation (Eq. (6)).

The experimental data was further subjected to thermodynamic treatment in order to evaluate the apparent enthalpy (ΔH°) and entropy (ΔS°) change of sorption:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

The expression relating the number of hopping (n) and that of the surface coverage (θ) as shown in Eq. (11) was applied to the experimental data:

$$n = \frac{1}{(1 - \theta)\theta} \quad (12)$$

To determine the kinetic parameters of adsorption of the LDH, second-order and pseudo-second-order kinetic models were applied to test the experimental. The second-order kinetic model is as follows:

$$\frac{1}{q_t} = \frac{1}{q_0} + k_2 t \tag{13}$$

where k_2 (min^{-1}) is the rate constant, q_0 (mg g^{-1}) is the amount of Cu^{2+} adsorbed on surface at equilibrium, q_t (mg g^{-1}) is the amount of Cu^{2+} adsorbed on surface at time t (min).

The pseudo-second-order kinetic model is given by Eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{14}$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is pseudo-second-order rate constant.

RESULTS AND DISCUSSIONS

SEM/EDX

Figures 1 and 2 clearly show the pre and 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.

XRD

The typical XRD pattern (Fig. 3) shows a lamellar structure of LDH material. Peaks at 8.6, 23.4 and 34.6 correspond to d – spacing at 1.027, 0.3797 and 0.259

nm, respectively. This is consistent with layered materials. These values are similar to those reported in literature [27].

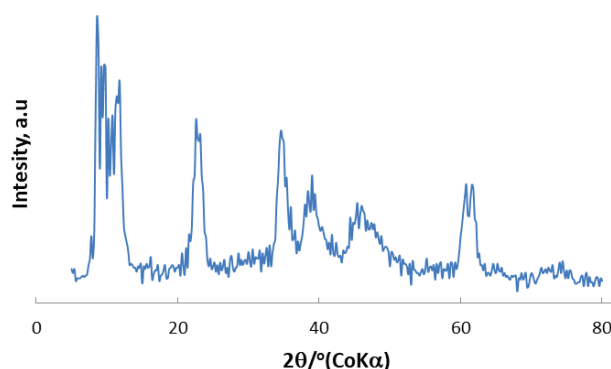


Figure 3. Mg/AlCO₃ X-ray powder diffraction.

FT-IR

The IR spectra of synthesized anion clays (Fig. 4) resemble those of other hydrotalcite-like phases [27]: The band at 3408 cm^{-1} which could be attributed to the stretching vibration of hydroxyl group. The low intensity band at 1632 cm^{-1} is assigned to bending vibration of strongly adsorbed water (solvation water for compensating anion vibration). The band at 1363 cm^{-1} is assigned to carbonate vibration (CO_3^{2-}), the bands at 672 is due to M–O vibration.

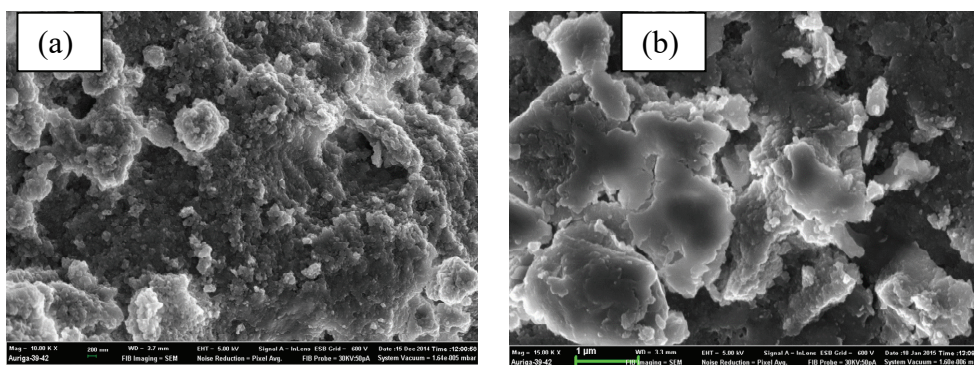


Figure 1. Scanning electron microscope (SEM) micrograph of Mg/AlCO₃ before (a) and after (b) adsorption studies.

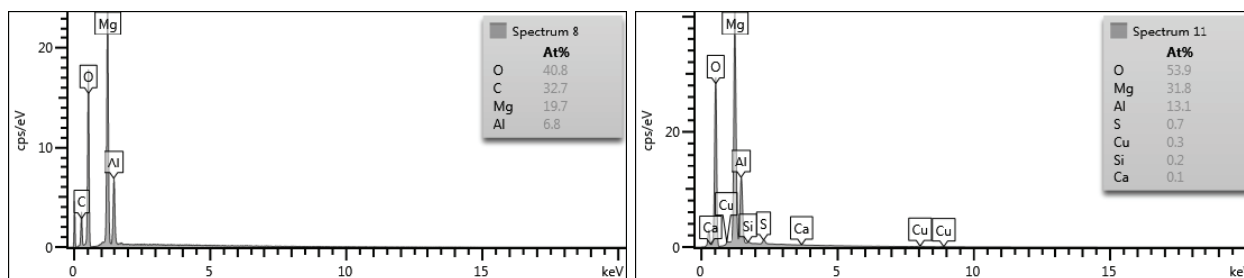


Figure 2. Energy dispersive spectroscopy patterns of Mg/AlCO₃ pre- and post-adsorption Energy dispersive spectroscopy.

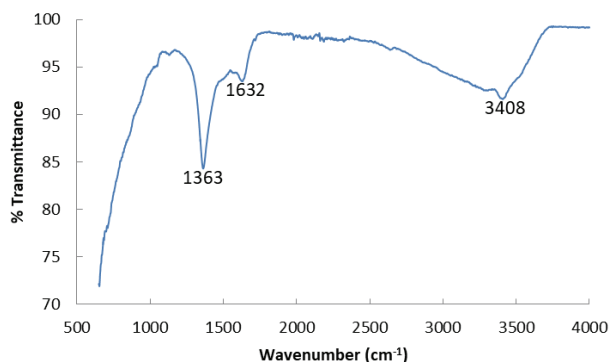


Figure 4. Mg/AlCO₃ Fourier transform infrared spectroscopy.

Adsorption study

Effect of concentration. The percentage sorption of Cu²⁺ by the LDH at different concentrations of the Cu²⁺ is presented in Figure 5. The maximum adsorption of 60% took place at equilibrium concentration of 2.0 mg/l Cu²⁺. This is because at lower concentration more LDH pore spaces were available for the Cu²⁺ but as the concentration of Cu²⁺ increased, the adsorption capacity of the LDH decreased due to reduced availability of free pore spaces. The results indicated that the sorption of Cu²⁺ was very much dependent on the concentration of the Cu²⁺.

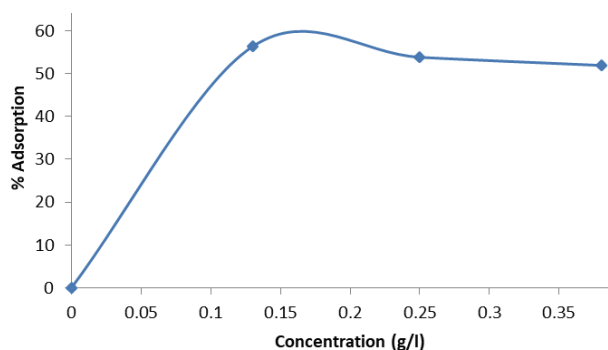


Figure 5. Effect of concentration on adsorption of Cu²⁺ onto layered double hydroxide.

Effect of temperature. Figure 6 also presents the plot of percentage adsorption of Cu²⁺ by the LDH at varying temperatures with optimum sorption of 50% occurring at 28 °C. The plot showed that further increase in temperature resulted in a slight decrease in adsorption. This is in agreement with the general principle that physical adsorption decreases with increase in temperature. This behaviour could be attributed to the weakening of the attractive forces between the LDH and Cu²⁺, the increased kinetic energy of the Cu²⁺ and the decrease in the thickness of the boundary layers of the LDH due to the higher tendency of the Cu²⁺ to escape from the pores.

Time dependency. Time dependency studies show the amount of time needed for maximum adsorption to

occur. The variation in percentage removal of Cu²⁺ with time has been presented in Figure 7. It indicates that a maximum of 65% removal of Cu²⁺ was observed in 20 min and remained constant afterwards. The relatively short contact time required to attain equilibrium suggests that a rapid uptake of Cu²⁺ by the LDH occurred to fill some of the vacant pores in the LDH and after which the remaining spaces were difficult to be occupied due to repulsive forces between the Cu²⁺.

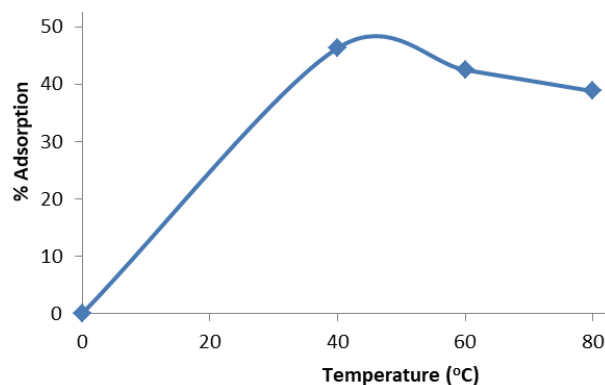


Figure 6. Effect of temperature on adsorption of Cu²⁺ onto layered double hydroxide.

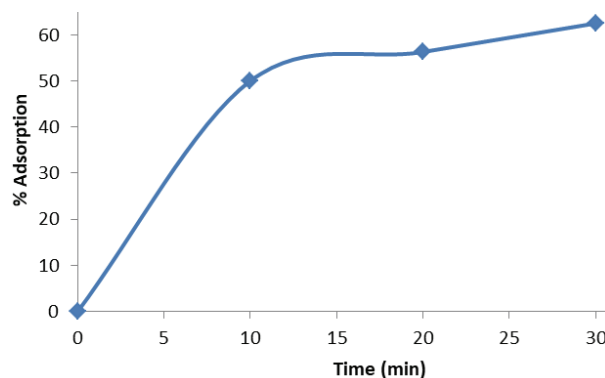


Figure 7. Effect of contact time on adsorption of Cu²⁺ onto layered double hydroxide.

Adsorption isotherms. The extent of adsorption can be correlated by means of an isotherm. Attempts were made to fit the data obtained from the adsorption experiments into various adsorption isotherms. The linear plots of the Langmuir and Freundlich isotherm models for the sorption of Cu²⁺ by the LDH are presented in Figures 8 and 9. These straight line plots confirmed the application of the Langmuir and Freundlich isotherm models to the adsorption of Cu²⁺ by the LDH. The slopes and intercepts were used to compute the Langmuir constants and adsorption capacity.

In order to determine the nature of the adsorption process, whether favourable or unfavourable, the dimensionless constant separation term S_F was investigated (Eq. (3)). The result ($S_F = 0.974$) 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.

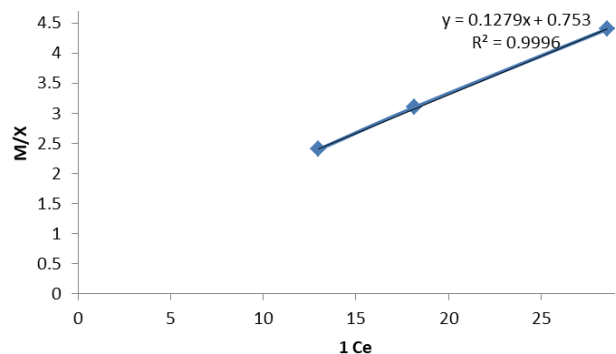


Figure 8. Langmuir Isotherm plot for adsorption of Cu^{2+} on layered double hydroxide.

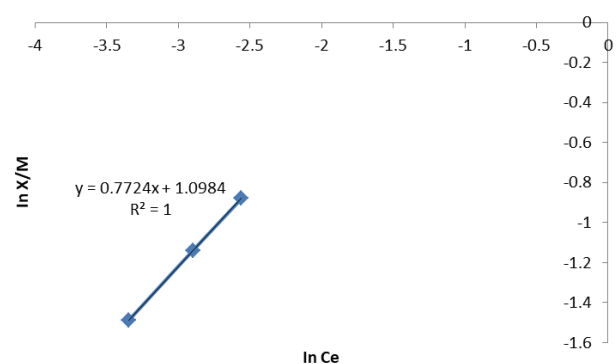


Figure 9. Freundlich Isotherm plot for adsorption of Cu^{2+} on layered double hydroxide.

The fraction of the LDH surface covered by the Cu^{2+} is given as 0.46 (Table 1). This value indicates that 46% of the pore spaces of the LDH surface were covered by the Cu^{2+} which means average degree of adsorption.

The effectiveness of the LDHs as adsorbent for Cu^{2+} from solution was assessed through the sorption distribution or partition coefficient K_d presented in Table 1. The value of K_d (0.86) suggests that LDHs are an effective adsorbent and that a very few number of cycles of equilibrium sorption process will be required to reduce the levels of Cu^{2+} in solution.

In order to calculate the isosteric heat of adsorption (ΔH_x , Figure 10) for the sorption of Cu^{2+} onto the LDH, Eq. (8) was used. The value of ΔH_x ($12.9 \text{ kJ mol}^{-1} \text{ K}^{-1}$) is positive as presented in Table 1. The magnitude of ΔH_x value gives information about the adsorption mech-

anism 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} .

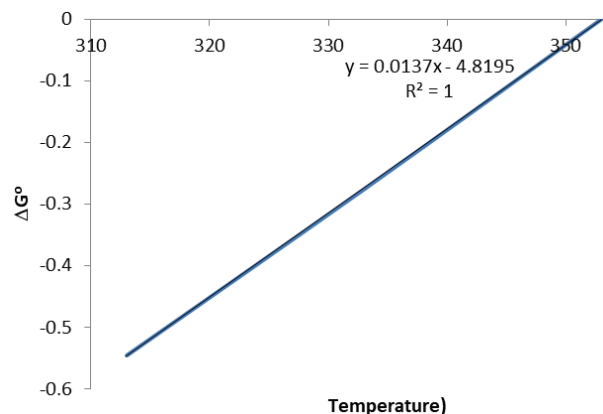


Figure 10. Plot of ΔG° vs. temperature for adsorption of Cu^{2+} onto layered double hydroxide.

The activation energy E_a and the sticking probability S^* (Figure 11) were calculated from Eq. (9). The value of E_a and S^* were shown in Table 1 as $1.447 \text{ kJ mol}^{-1}$ and 0.46, respectively. Two main types of adsorption may occur, physical and chemical. In physisorption, the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small. The activation energy for physisorption is usually no more than 4.2 kJ mol^{-1} since the forces involved in physisorption are weak. Chemisorption is specific and involves forces much stronger than in physisorption on. Therefore, the activation energy for chemisorption is of the same magnitude as the heat of chemical reactions. Two kinds of chemisorptions are encountered, activated and, less frequently, nonactivated. Activated chemisorption means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation (high E_a). However, in some systems the chemisorption occurs very rapidly, suggesting the activation energy is near zero. This is termed as a non-activated chemisorption. Relatively low value of E_a also suggests that the sorption process is diffusion controlled. 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

Table 1. Equilibrium and thermodynamic parameters

Isosteric heat of adsorption change, ΔH_x kJ/mol	Sticking probability S^*	Activation energy, E_a kJ/mol	Gibbs energy change of adsorption, ΔG° kJ/mol	Apparent entropy change, ΔS° J/(mol K)	Apparent enthalpy change, ΔH° J/mol	Surface coverage, θ	Separation factor, S_F	Hoping number, N	Sorption coefficient, K_d
12.9	0.46	1.447	-0.546	13.7	-4.839	0.55	0.974	4	0.86

physic-sorption and chemisorption), $S^* = 0$ (indefinite sticking – chemisorption), $0 < S^* < 1$ (favourable sticking – physic-sorption). The value of S^* obtained for the sorption of Cu^{2+} by the LDHs was between zero and one which indicates that the adsorption was favourable and followed physic-sorption mechanism.

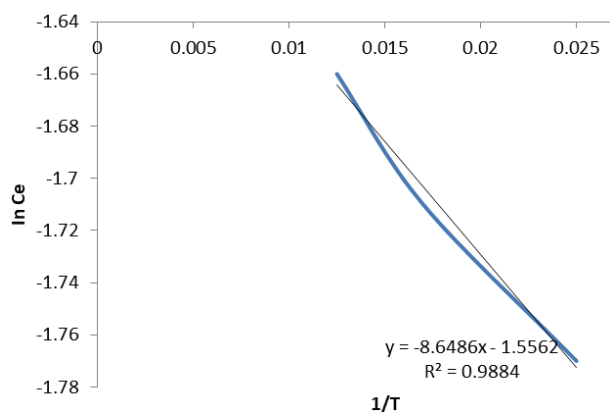


Figure 11. Plot of $\ln C_e$ vs. $1/T$ for adsorption of Cu^{2+} onto layered double hydroxide.

The values of the enthalpy change (ΔH^0 , Figure 10) and entropy change ΔS were calculated from equation 10 to be -4.839 J/mol and 13.7 J/(mol K), respectively. A negative ΔH^0 suggests that sorption proceeded favourably at a lower temperature and the sorption mechanism was exothermic. A positive value of ΔS^0 (13.7 J/(mol K)) 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. This is further confirmed by the value of ΔG^0 which is -8.8 kJ/mol.

The probability of Cu^{2+} finding vacant site on the surface of the carbon 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). The low value of n obtained in this study suggests that the adsorption of Cu^{2+} on the layered double hydroxide was very fast.

The experimental data was further subjected to certain kinetic parameters as shown in Figures 12 and 13. The results conform to pseudo-second order model ($R^2 = 0.9959$) and second order kinetic model ($R^2 = 0.9952$).

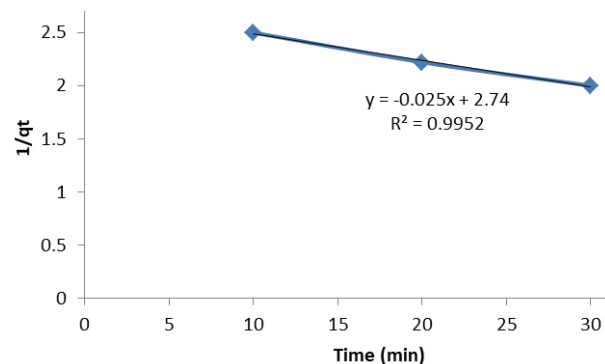


Figure 12. Plot of $1/q_t$ vs. t for the adsorption of Cu^{2+} on layered double hydroxide.

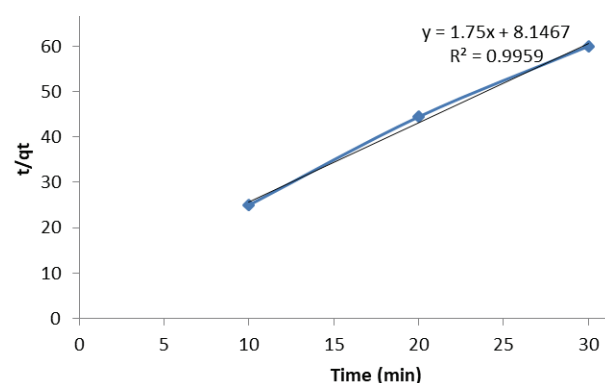


Figure 13. Plot of t/q_t vs. t for the adsorption of Cu^{2+} on layered double hydroxide.

CONCLUSION

The successful synthesis and initial characterization created a unique fingerprint for the layered double hydroxide whose binding capacity was further confirmed by the post-adsorption characterization studies. The equilibrium, kinetic and thermodynamic batch adsorption studies recorded a significant uptake of the Cu^{2+} by the LDH which was diffusion controlled. The adsorption was favored by low temperature and energy which was exothermic with a physisorption mechanism. Therefore, Mg/Al layered double hydroxide is a viable option for the removal of Cu^{2+} in aqueous medium.

REFERENCES

- [1] L. Deng, Y. Y. Su, H. Su, X. Wang, X. Zhu, Biosorption of copper (II) and lead (II) from aqueous solutions by nonliving green algae *Cladophora fascicularis*: Equilibrium, kinetics and environmental effects, *Adsorption* **12** (2006) 267–277.
- [2] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, *Chem. Eng. J.* **32** (2007) 299–309.
- [3] V.K. Gupta, A. Rastogi, V.K. Saini, N. Jain, Biosorption of copper(II) from aqueous solutions by *Spirogyra* species, *J. Colloid Interface Sci.* **296** (2006) 59–63.

- [4] R. Gong, R. Guan, J. Zhao, X. Liu, S. Ni, Citric acid functionalizing wheat straw as sorbent for copper removal from aqueous solution, *Journal of Health Science* **54** (2008) 174–178.
- [5] I.S. Ayhan, M. Ozacar, Biosorption of Cu(II) from aqueous solutions by mimosa tannin gel, *J. Hazard. Mater.* **157** (2008) 277–285.
- [6] P.C. Siao, G.C. Li, H.L. Engle, L.V. Hao, Biosorption of Cu(II) ions from synthetic and actual wastewater using three algal species, *Trinidad, J. Appl. Phycol.* **19** (2007) 733–743.
- [7] H. Yazici, M. Kilic, M. Solak, Biosorption of copper (II) by *Marrubium globosum* subsp. *globosum* leaves powder: Effect of chemical pretreatment, *J. Hazard. Mater.* **151** (2008) 669–675.
- [8] T.S. Anirudhan, P.G. Radhakrishnan, Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell, *J. Chem. Therm.* **40** (2008) 702–709.
- [9] H. Duygu, H. Kumbur, B. Saha, J. Hans van Leeuwen, Use of *Rhizopus oligosporus* produced from food processing wastewater as a biosorbent for Cu(II) ions removal from the aqueous solutions, *Biores. Technol.* **99** (2008) 4943–4948.
- [10] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, *Colloids Surfaces* **317** (2008) 512–521.
- [11] J.M. Oh, T.T. Biswick, J.H. Choy, Layered material for green materials, *J. Mater. Chem.* **19** (2009) 2553–2563.
- [12] P.S. Braterman, Z.P. Xu, F. Yarberr, Layered Double Hydroxide, in: S.M. Aubach, K.A. Carrado, P.K. Dutta (Eds.), *Handbook of layered materials*, Marcel Dekker, New York, 2004, pp. 373–450.
- [13] F. Cavani, F. Trifiro, A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, *Catal. Today* **11** (1991) 173–301.
- [14] J. Tronto, K.C. Sanchez, E.L. Crepaldi, Z. Naal, I.K. Stanley, J.B. Valim, Synthesis, characterization and electrochemical study of layered double hydroxide intercalated with 2-thiophenecarboxylate anions, *J. Phys. Chem. Solids* **65** (2004) 493–498.
- [15] M. Sillion, D. Hritcu, G. Lisa, M.I. Popa, New hybrid materials based in layered double hydroxides and antioxidant compounds. Preparation, characterization and release kinetic studies, *J. Porous Mater.* **19** (2012) 267–276.
- [16] S.H. Sarijo, S.A.I.S.M. Ghazali, M.Z. Hussien, N.J. Sidek, Synthesis of nanocomposite 2-methyl-4-chlorophenoxyacetic acid with layered double hydroxide: physicochemical characterization and controlled release properties, *J. Nanopart. Res.* **15** (2013) 1356–1365.
- [17] S.H. Hwang, Y.S. Han, J.H. Choy, Intercalation of functional organic molecule with pharmaceutical, cosmetic and nutraceutical functions into layered double hydroxide and zinc basic salts, *Bull. Korean Chem. Soc.* **22** (2001) 1019–1022.
- [18] J.W. Lee, W.C. Choi, J.D. Kim, Size-controlled layered hydroxide intercalated with dodecyl sulphate: effect of alcohol type on dodecyl sulphate template, *Cryst. Eng. Comm.* **12** (2010) 3249–3254.
- [19] M.Z. Hussien, A.M. Jaafar, A. Yahaya, Z. Zainal, The effect of single, binary and ternary anion chloride, carbonate and phosphate on the release of 2,4-dichlorophenoxyacetate intercalated into the Zn-Al layered double hydroxide nanohybrid, *Nanoscale Res. Lett.* **4** (2009) 1351–1357.
- [20] W.G. Hou, Z.L. Jin, Synthesis and characterization of Naproxen intercalated Zn-Al layered double hydroxides, *Colloid. Polym. Sci.* **285** (2007) 1449–1454.
- [21] S. Sasaki, S. Aisawa, H. Hirahara, A. Sasaki, H. Nakayama, E. Narita, Synthesis of *p*-sulfonated calyx[4] arene-intercalated layered double hydroxide and their adsorption properties for organic molecules, *J. Eur. Ceram. Soc.* **26** (2006) 655–659.
- [22] F. Li, X. Duan, Applications of layered double hydroxide, *Struct. Bond.* **119** (2006) 193–223.
- [23] F. Bruna, R. Celis, I. Pavlovic, C. Barriga, C. Cornejo, M.A. Ulibarri, Layered double hydroxide as adsorbent and carriers of the herbicides (4-chloro-2-methylphenoxy)acetic acid (MCPA) system Mg–Al, Mg–Fe and Mg–Al–Fe, *J. Hazard. Mater.* **168** (2009) 1476–1481.
- [24] X. Kong, S. Shi, J. Han, F. Zhu, M. Wei, X. Duan, Preparation of Glycyl-Tyrosine intercalated layered double hydroxide film and its in vitro release behaviour, *Chem. Eng. J.* **157** (2010) 598–604.
- [25] I.M. Isa, N.M. Sohaimi, Hashim, N.A. Kamari, A. Mohamed, M. Ahmad, S.A. Ghani, Suyanta, Determination of salicylate ion by potentiometric membrane electrode base on zinc aluminium layered hydroxide-4-(2,4-dichlorophenoxy)butrate nanocomposite, *Int. J. Electrochem. Sci.* **8** (2013) 2112–2121.
- [26] M. Yadollahi, H. Namazi, Synthesis and characterization of carboxymethyl cellulose/layered double hydroxide nanocomposite, *J. Nanopart. Res.* **15** (2013) 1563–1572.
- [27] L. Lv, J. He, M. Wei, D.G. Evans, X. Duan, Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: equilibrium and kinetic studies, *Water Research* **40** (2006) 735–743.

IZVOD

RAVNOTEŽNA, KINETIČKA I TERMODINAMIČKA STUDIJA IZDVAJANJA BAKRA POMOĆU SLOJEVITOG DVOSTRUKOG HIDROKSIDA

Ayawei Nimibofa¹, Ekubo Allen Tobin¹, Shooto Ntaote David², Wankasi Donbebe¹, Dikio Ezekiel Dixon²¹*Niger Delta Universities, Wilberforce Island, Yenagoa Bayelsa State, Nigeria*²*Applied Chemistry and Nano-Science Laboratory, Department of Chemistry, Vaal University of Technology Vanderbijlpark, South Africa*

(Naučni rad)

U ovom radu ispitan je adsorpcioni kapacitet Mg/Al sintetisanog i okarakterisanog slojevitog dvostrukog hidroksida (LDH) za jon bakra Cu^{2+} iz vodenih rastvora. Uticaj različitih procesnih parametara kao što su koncentracija, temperatura i sorpciono vreme na adsorpciju Cu^{2+} ispitani su korišćenjem serije eksperimenata. Utvrđeno je da se slojeviti dvostruki hidroksid (LDH) može koristiti kao adsorbent za uklanjanje bakarnih jona u vodenom rastvoru koji sadrži nisku koncentraciju metalne soli. Prosečne vrednosti energije aktivacije, izosterne toplote adsorpcije, entropije i entalpije bile su 1,45, 12,9, 0,0137 i $-4,84$ kJ/mol, redom. Ovo pokazuje da je adsorpcija metalnog jona na adsorbentu fizički mehanizam adsorpcije. Kinetički rezultati su u skladu sa modelom pseudo-drugog reda ($R^2 = 0,9959$) i kinetičkim modelom drugog reda ($R^2 = 0.9952$) dok su adsorpcione karakteristike adsorbenta pratile izotermne modele Langmuir i Freundlich adsorpcije.

Ključne reči: • Dvostruki slojeviti hidroksidi • Adsorpcija • Lengmirova izoterma • Izosterna toplota adsorpcije • Gibsova energija