Synthesis, Characterization and Application of Zn/Al-CO$_3$ for the Removal of Lead Ions

N. Ayawei[1*], A. K. Inengite[1], D. Wankasi[1,2] and E. D. Dikio[1,2]

[1]*Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria.*
[2]*Applied Chemistry and Nanoscience Laboratory, Department of Chemistry, Vaal University of Technology, P.O.Box X021, Vanderbijlpark, South Africa.*

Authors' contributions

This work was carried out in collaboration between all authors. Author NA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors DW and EDD managed the analysis of the study. Author AKI managed the literature searches. All authors read and approved the final manuscript.

Article Information

Original Research Article

ABSTRACT

In the present work, Zn/Al layered double hydroxide of ratio 2:1 was synthesis by co-precipitation method from their nitrate salts and utilized as adsorbent for the removal of lead ions from aqueous solution. The synthesized Zn/Al-CO$_3$ was characterized by SEM, XRD and FTIR. The effect of various parameters such as contact time, initial concentration and variable temperature were investigated. The results show that the adsorption process was depended on contact time rather than temperature and concentration. Studies of the essential thermodynamic parameters shows that the adsorption process was rapid, exothermic and spontaneous and also fitted both Langmuir and Freundlich isotherm. The results of various kinetic models are zero-order kinetics model R^2 =1, second-order kinetic model R^2 = 0.998 and pseudo-second order kinetics model R^2 = 0.999.

Keywords: Lead adsorption; isosteric heat of adsorption; activation energy; layered double hydroxide; kinetics; adsorption isotherms.

_____

*Corresponding author: E-mail: ayawei4acad@gmail.com;

1. INTRODUCTION

The treatment of waste water containing metals is a challenging problem [1]. Due to the rapid increase in metal concentration as well as increase in awareness of the toxicological effects of metals released into environment, a number of studies for metal recovery and removal for solutions have been done. Several conventional treatment methods such as ion-exchange, reverse osmosis, precipitation, flocculation, electrochemical treatment, solvent extraction, adsorption on activated carbon and membrane related processes are usually applied. These methods are often expensive and inefficient, complicated, or have production of toxic chemical sludge and its disposal problems [2,3]. Among these advanced treatments, at this moment, adsorption is considered more effective and less expensive than other technologies. Clay materials like layered double hydroxides are been considered as useful adsorbent in recent times because of their multiple applications.

Layered double hydroxide (LDH) compounds belong to a class of anionic clay having a hydrotalcite-like structure, consist of positively charged metal hydroxide layers separated from each other by anions and water molecules, as represented by the formal formula [M $II_{1-x}MIII_x(OH)_2]_{x+}[X$ m−x/mnH$_2$O] [4], where MII and MIII are divalent and trivalent metal ions, A n− is a compensate n-valent anion, and x can have values between 0.1 and 0.5. Various inorganic or organic anions have been introduced between the hydroxide layers by simple ion-exchange reactions or coprecipitation. LDHs are now well established as excellent anion-exchange materials and their extensive intercalation chemistry has widespread applications in areas such as heterogeneous catalysis [5,6], optical materials [7], biomimetic catalysis [8,9], separation science [10] and medical science [11]. Recently, LDH has received much scientific attention on their properties as an adsorbent [12,13]. This paper evaluated the feasibility of using Zn/Al-CO$_3$ synthesized by co-precipitation method for adsorption of Pb^{2+} without further calcination.

2. MATERIALS AND METHODS

2.1 Synthesis of LDH

Carbonate form of Mg-Al LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3 M Zn (NO$_3$)$_2$.6H$_2$O and 0.1 M Al (NO$_3$)$_3$.9H$_2$O with Zn/Al ratios 2:1, was added drop wise into a 50 ml mixed solution of (NaOH (2M) + Na$_2$CO$_3$ (1M) with vigorous stirring and maintaining a pH of greater than 10 at room temperature. After complete addition which last between 2 hours 30 minutes to 3 hours, the slurry formed was aged at 60°C for 18 hours. The products were centrifuged at 5000 rpm for 5 minutes, with distilled water 3-4 times and dried by freeze drying.

2.2 Zn/Al-CO$_3$ Characterization

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

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

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

2.3 Preparation of 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 (lead (II) sulfate, PbSO$_4$,). From the stock, working solutions of 0.13g/LPb, 0.25g/LPb and 0.38g/LPb were prepared from appropriate aliquots diluted to the appropriate concentration. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using (Unicam thermo/solar system 2009 model) Atomic Adsorption Spectrometer (AAS).

2.4 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 lead initial concentration have been studied in detail for batch technique.

2.5 Adsorption Isotherms

Batch adsorption studies of lead were performed at room temperature (25±2°C) to obtain the equilibrium isotherms. For isotherm studies, a series of 50 ml test tubes were used. Each test tube was filled with 10 ml of lead solution of varying concentrations (0.13 g/l – 0.38 g/l) and a known amount of sorbent (0.2 g) was added into each test tube and agitated for various time periods. The lead concentration retained in the sorbent phase (mg/g) was calculated by:

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of uranium (mg/L), respectively, V is the volume of the aqueous solutions (L), and m is the weight of the sorbent used (g). The distribution of lead between the solid liquid interfaces at equilibrium has been studied by the Langmuir and Freundlich isotherm models.

The Langmuir isotherm equation may be written as:

$$\frac{M}{x}\frac{1}{abC_e}\frac{1}{b} \qquad (2)$$

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

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

$$S_f = \frac{1}{(1+aC_o)} \qquad (3)$$

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 the Pb^{2+} onto the layered double hydroxide was assessed from the Freundlich plots using the linearized equation 4 below

$$In\frac{x}{M} = \frac{1}{n}(InC_e) + InK \qquad (4)$$

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

The fraction of copper surface covered by the Pb^{2+} was computed using equation 5

$$\theta = 1 - \frac{C_e}{C_o} \qquad (5)$$

With θ as degree of surface coverage

The Freundlich equation may be written as:

$$Inq_e = In\,K_f + \frac{1}{n}\,In\,C_e \qquad (6)$$

where K_f is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and 1/n is the constant indicative of the intensity of the adsorption.

2.6 Kinetic Studies

Four kinetic models were used in this work to explain the adsorption process which are; the zero-order, pseudo second-order, first-order kinetic and third-order kinetic models.

2.7 Zero-Order Kinetic Model

The solute adsorption rate on the adsorbent is based on the adsorption capacity and follows the pseudo first-order equation:

$$q_t = q_o + K_o t \qquad (7)$$

where; q_e and q_t are the amounts of the adsorbed metal ion (mg/g) at the equilibrium time and at any instant of time "t", respectively, and k_o is the rate constant of the zero-order adsorption operation (l/min). Plotting of q_t versus t gives a straight line for the zero-order kinetics [14,15].

2.8 Pseudo Second-Order Kinetic Model

The applicability of the pseudo second-order kinetics has to be tested for q_e estimation with equation given by:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \qquad (8)$$

Where; $h = k_2 q_e^2$ that can be regarded as the initial sorption rate as $t\rightarrow0$. Under such circumstances, the plot of t/qt versus t should give a linear relationship which allows the computation of q_e and k_2.

2.9 First-order Kinetic Model

The first-order kinetic model is given as:

$$Inq_t = Inq_o + K_1 t \tag{9}$$

A plot of Inq_t against t should give a straight line to confirm the model. K_1 and Inq_o are obtained from the slope and intercept respectively.

2.10 Third-order Kinetic Model

If the rate of sorption is dependent on the third-order-kinetic mechanism, then the third order kinetic model may be expressed as in the equation below:

$$\frac{1}{q_t^2} = \frac{1}{q_o^2} + K_3 t \tag{10}$$

K_3 is the third order rate constant. A plot $1/q_t^2$ against t, should give a linear relationship if the third-order kinetic model is applicable to the sorption system.

3. 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 Pb^{2+} in solution according to the value of the distribution (partition coefficient (K_d) [16] in equation 11.

$$K_d = \frac{C_{aq}}{C_{ads}} \tag{11}$$

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

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

$$\frac{d(InC_e)}{dT} = \frac{\Delta H^*}{RT^2} \tag{12}$$

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^{-1}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:

$$Inc_e = - \left[\frac{\Delta H_x}{R}\right]\frac{1}{T} + K \tag{13}$$

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 14.

$$In(1-\theta) = S^* + \frac{E_a}{RT} \tag{14}$$

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

$$\Delta G^o = RTInK_d \tag{15}$$

K_d is obtained from equation (Eq. 11).

The experimental data was further subjected to thermodynamic treatment in order to evaluate the apparent enthalpy (ΔH°) and entropy (ΔS°) of sorption using equation 16.

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{16}$$

The expression relating the number of hopping (n) and that of the surface coverage (θ) as shown in equation 17 was applied to the experimental data.

$$n = \frac{1}{(1-\theta)\theta} \tag{17}$$

4. RESULTS AND DISCUSSION

4.1 FT-IR

FT-IR spectra of the LDH sample is shown in Fig. 1. As shown in Fig. 1, 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_3^{2-} in $CaCO_3$ (1,430 cm^{-1}), a large

shift toward a lower wavenumber indicates that the CO_3^{2-} intercalating into the interlayer is not free, and is interlayered with water molecules between with hydrogen bonds are formed [17]. The peak picture is consistent with layered double hydroxide in the interlayer region.

4.2 XRD

The XRD patterns of Zn-Al/CO_3 is shown in Fig. 2. The strong peaks at 12.4°, 35.2°, 39.8° are characteristic of a layered structure. The sharp and symmetrical diffraction peaks. 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^{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 (=$3d_{003}$) 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 [18].

4.3 SEM/EDX

Figs. 3 & 4 clearly shows the pre & post adsorption photographs and graph of SEM images and EDX respectively. The EDX graphs shows the binding on the surface of the layered double hydroxide by the copper ion, while the SEM image of post adsorption shows coverage of available pores in relation to pre-adsorption image.

5. BATCH ADSORPTION STUDIES

5.1 Effect of Contact Time

The contact time between the pollutant (Pb^{2+}) and adsorbent (LDH) is an important parameter. Fig. 5 show the effect of contact time in minutes (10, 20, 30) between the layered double hydroxide and metal solution. The rapid adsorption and equilibrium in a short time is related to the efficiency of the layered double hydroxide. Adsorption of lead was highest at 30 minutes of contact.

The adsorption kinetics of the experimental data was analyzed by three kinetic models namely; the zero-order, pseudo second-order, first-order kinetic and third-order kinetic models. The results (zero-order kinetics model R^2 =1, second-order kinetic model R^2 = 0.998, pseudo-second order kinetics model R^2 = 0.999) shows very high compliance with all models as shown in Figs. 6 - 8.
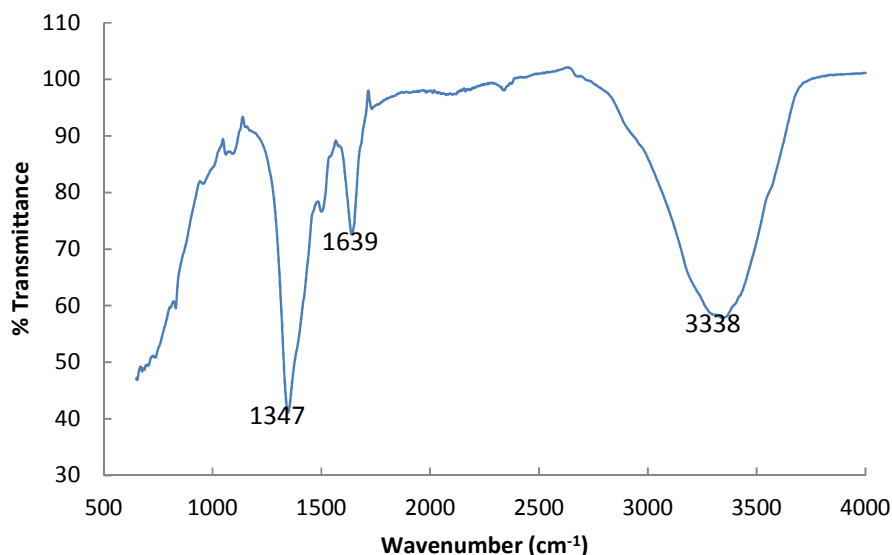

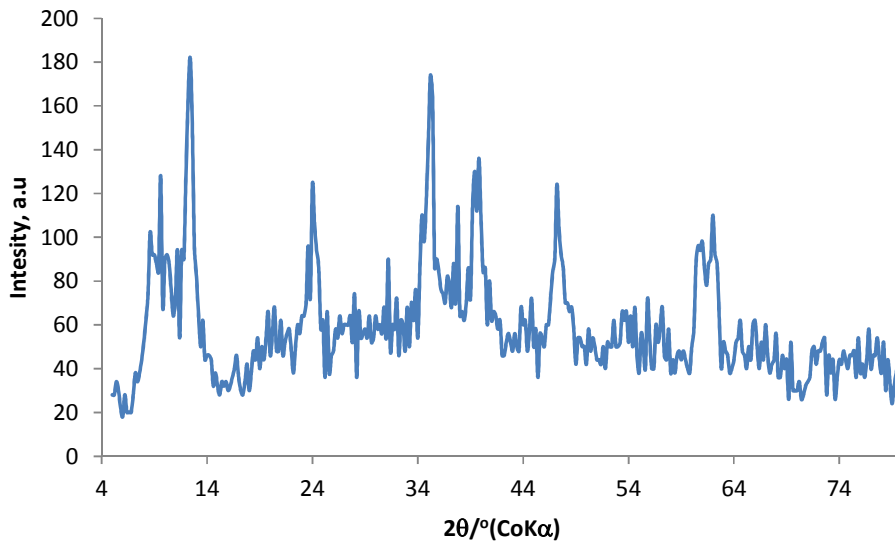**Fig. 1. Zn/Al-C0$_3$ Fourier transform infrared spectroscopy**

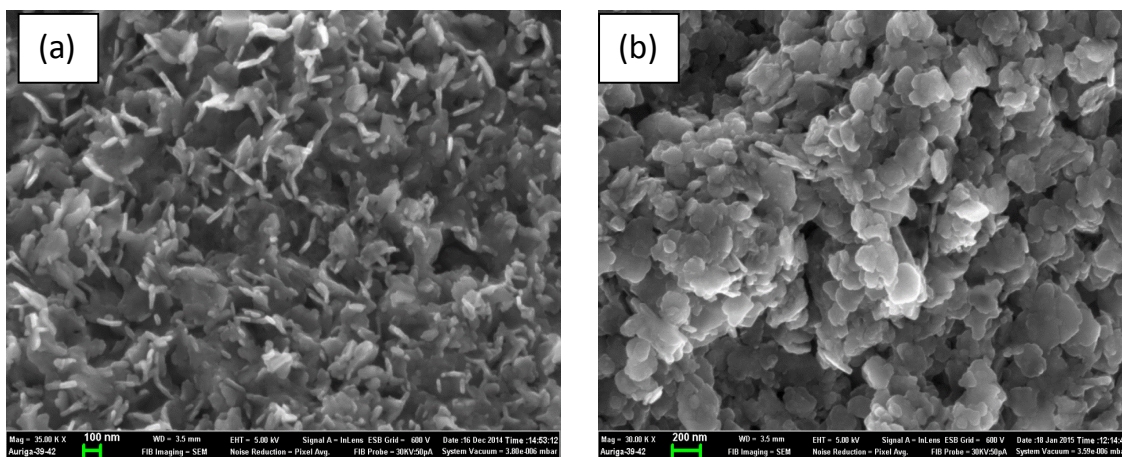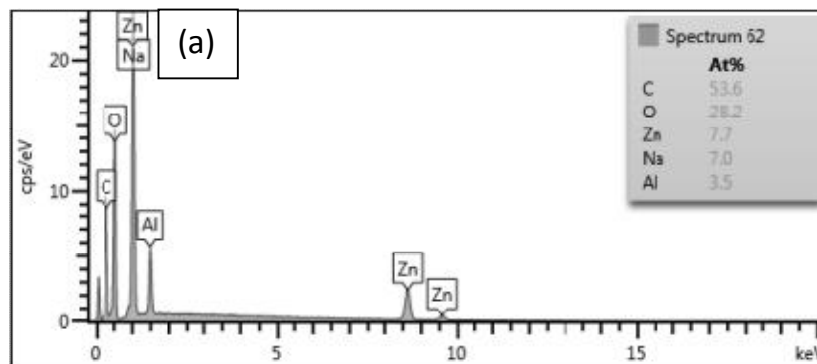**Fig. 2. Zn/Al-C0$_3$ X-ray powder diffraction**

Fig. 3. Scanning Electron Microscope (SEM) micrograph of Zn/Al-CO$_3$ before (a) and after (b) adsorption studies
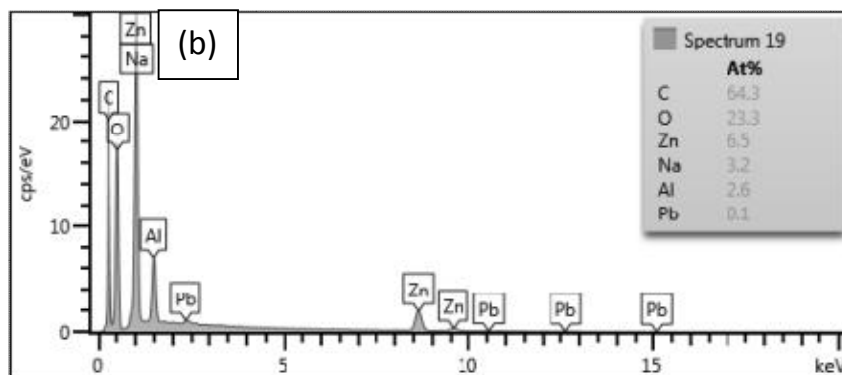
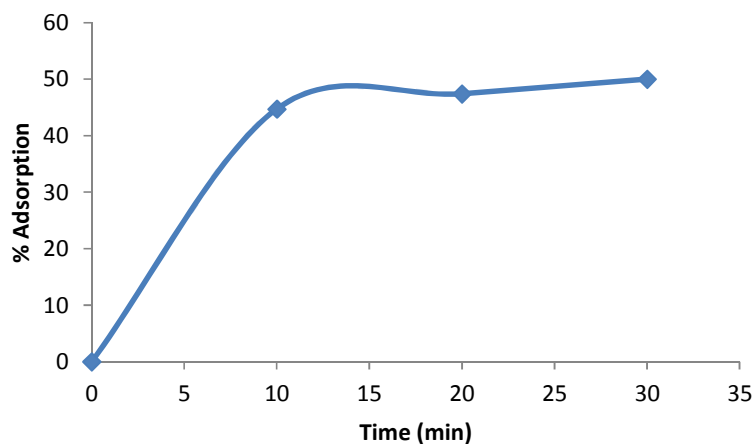**Fig. 4. Energy dispersive spectroscopy patterns of Zn/Al-CO$_3$ pre & post adsorption energy dispersive spectroscopy**

Fig. 5. Effect of time on adsorption of Pb^{2+} onto layered double hydroxide
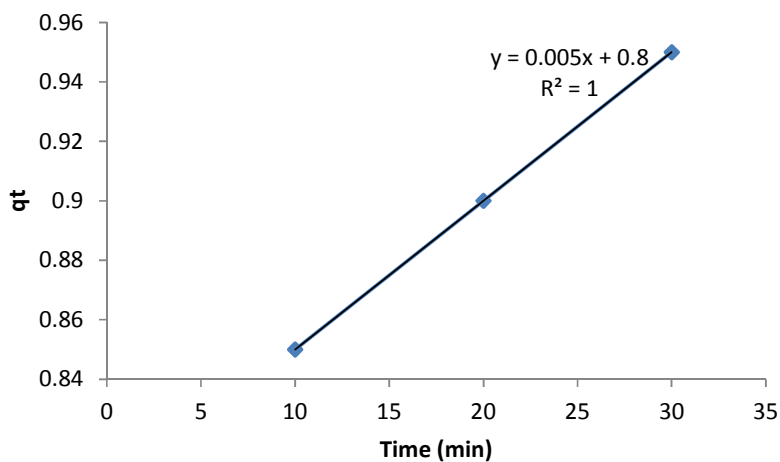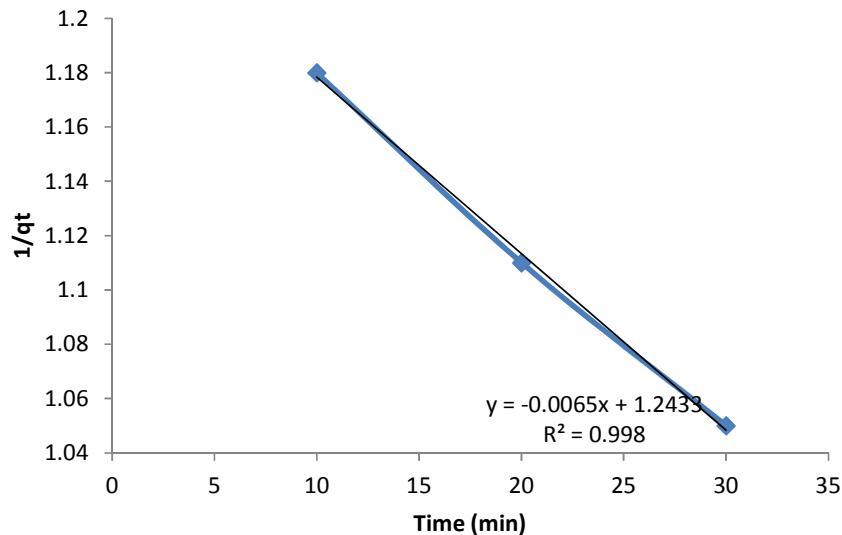

Fig. 6. Plot of qt vs. t for the adsorption of Pb^{2+} onto layered double hydroxide

Fig. 7. Plot of 1/qt vs. t for the adsorption of Pb²⁺ onto layered double hydroxide

$y = -0.0065x + 1.2433$
$R^2 = 0.998$

Fig. 7. Plot of 1/qt vs. t for the adsorption of Pb^{2+} onto layered double hydroxide
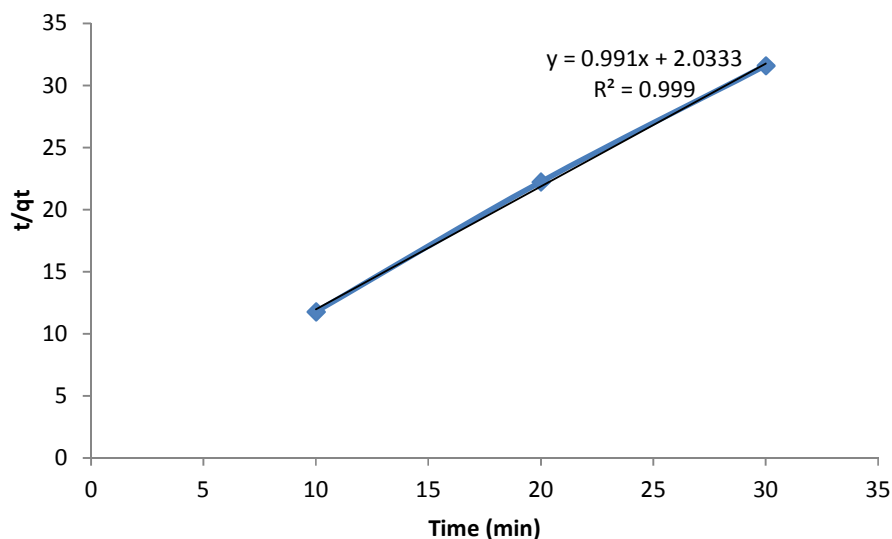
$y = 0.991x + 2.0333$
$R^2 = 0.999$

Fig. 8. Plot of t/qt vs. t for the adsorption of Pb^{2+} onto layered double hydroxide

5.2 Effect of Concentration

The dependence of the of the adsorption process of lead adsorption from different initial concentration (0.13, 0.25 and 0.38 g/L) by the adsorbent is shown in Fig. 9. Analysis of percentage adsorption versus initial varying concentration of Pb^{2+} ions showed that the percentage adsorption decreased with increase in initial concentration of the adsorbate, but the uptake capacity increase with increase in initial concentration. At lower concentrations of lead ions, the number of lead ions which are available in the solution is less as compare to the available sites on the adsorbent. However, at higher concentrations, the available sites for adsorption become fewer, and the percentage removal of lead ions depends on the initial concentration.
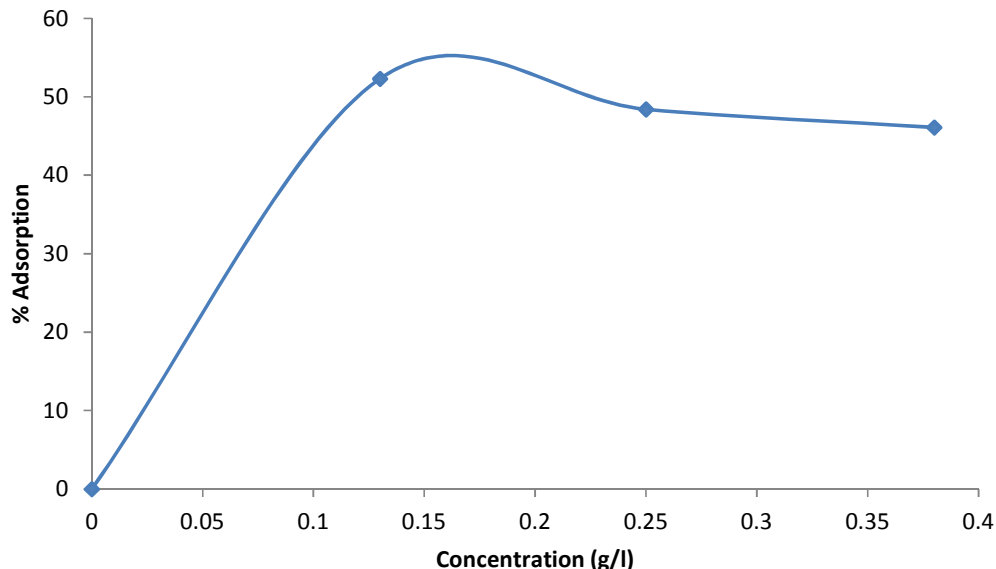
Fig. 9. Effect of concentration on adsorption of Pb^{2+} onto layered double hydroxide

The maximum removal of Pb^{2+} was achieved at 0.13 g/L (52.3%) on the layered double hydroxide.

5.3 Adsorption Isotherm Studies

Two types of adsorption model isotherms namely Langmuir isotherm and Freundlich isotherm were tested. The Langmuir isotherm model is given as follows: Fig.s 10 and 11 are the plots of Langmuir and Freundlich isotherms. The straight line graphs shows that the adsorption follows both isotherms as reported in Table 1.

In order to determine 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 =0.866) in Table 1 was less than one and greater than zero which showed that the sorption of Pb^{2+} onto the carbon layered double hydroxide was favourable.

Adsorption capacity which is from the extrapolation of Freundlich slope is equal to 0.887. The value of 1/n, which is related to the distribution of bonded ions on the adsorbent surface, represents beneficial adsorption if it is between 0.1 and 1. The 1/n values for the lead adsorbents are indicating that adsorption of Pb^{2+} are favourable.

The fraction of the layered double hydroxide surface covered by the Pb^{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 Pb^{2+}, which means high degree of adsorption.

5.4 Effect of Temperature

Increasing temperature can affect the adsorption processes mainly from two aspects. Firstly, it decreases solution viscosity and correspondingly increases the diffusion rate of the adsorbate within the pores of the adsorbents [19], it can increase the number of the adsorption sites through breaking of some internal bonds near the edge of active surface sites of the adsorbents [19]. Thus, rising temperature benefits for the enhancement of the adsorption capacity of lead ion onto the layered double hydroxide. Adsorption efficiency relative to time was identified at the lowest temperature {313K (52.6%), 333K (50%) and 353K (47.4%)} as shown in Fig. 12.

5.5 Thermodynamic Studies

Table 1 also presents the Gibbs free energy ΔG^o for the sorption of Pb^{2+} by the layered double hydroxide which was calculated from equation 15. Gibbs free energy is the fundamental criterion of spontaneity. The ΔG^o value of -0.26

KJ/mol was negative indicating that the sorption process was spontaneous. The value obtained for ΔG^o was also less than -20 KJ/mol suggesting electrostatic interaction between the Pb^{2+} and the layered double hydroxide which supported physic-sorption mechanism. The values of the enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated from equation 16 to be -4.8245KJ/mol and 0.0146KJ/molK respectively. A plot of ΔG^o against T gives a straight line graph (Fig. 13) with slope and intercept defining the ΔH^o and ΔG^o. A negative ΔH^o suggests that sorption proceeded favourably at a lower temperature and the sorption mechanism was exothermic. A positive ΔS^o suggests that the freedom of the adsorbed Pb^{2+} was not restricted in the layered double hydroxide, indicating that physic-sorption mechanism predominates.
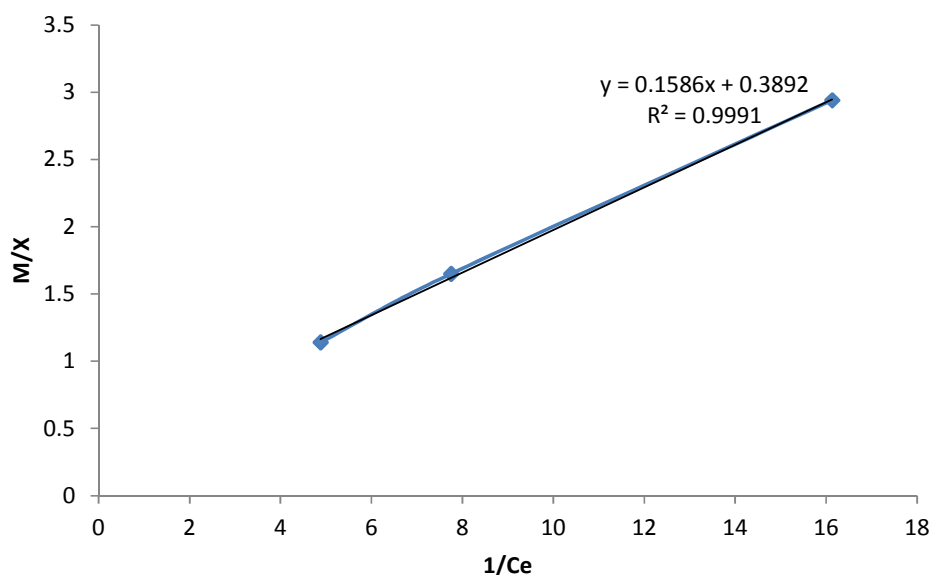

y = 0.1586x + 0.3892
R² = 0.9991

Fig. 10. Langmuir isotherm plot for Pb²⁺ onto layered double hydroxide
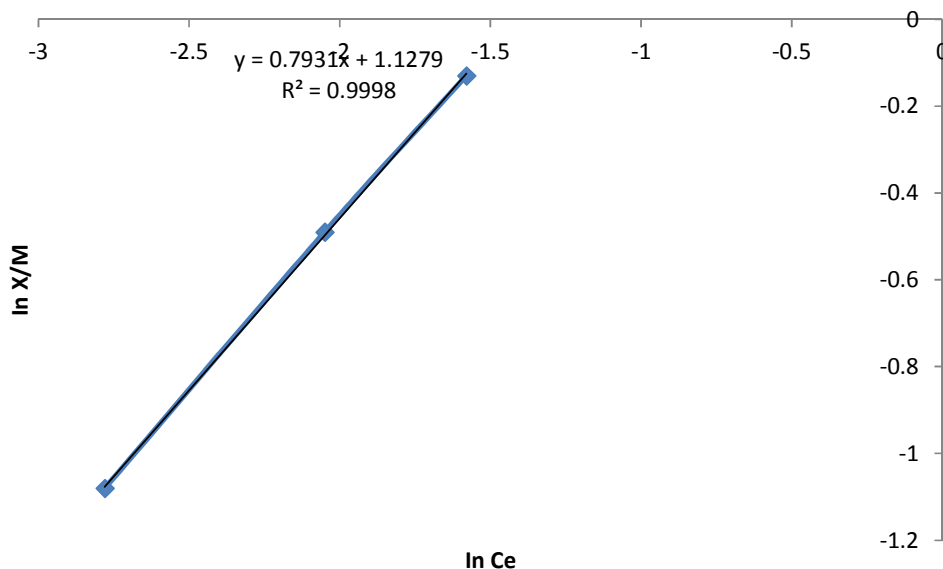

y = 0.7931x + 1.1279
R² = 0.9998

Fig. 11. Freundlich isotherm plot for the adsorption of Pb²⁺ onto layered double hydroxide
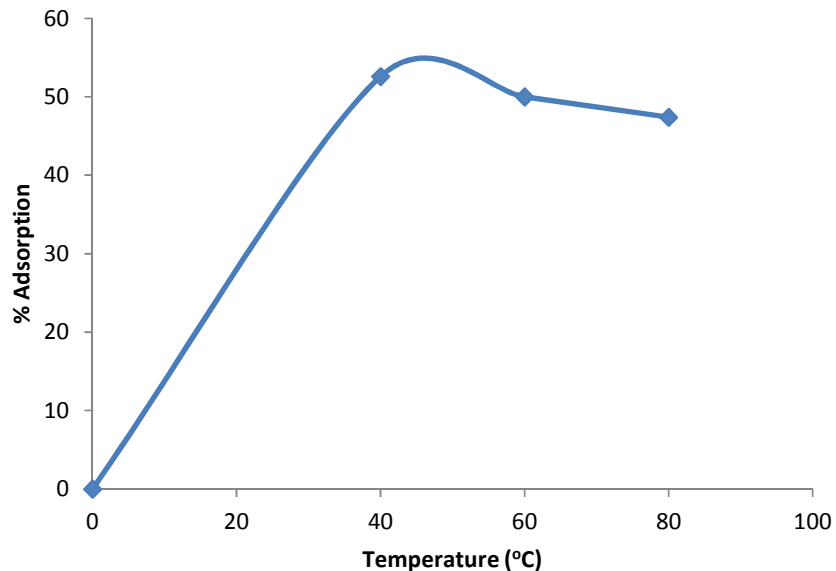
Fig. 12. Effect of temperature on adsorption of Pb^{2+} onto layered double hydroxide

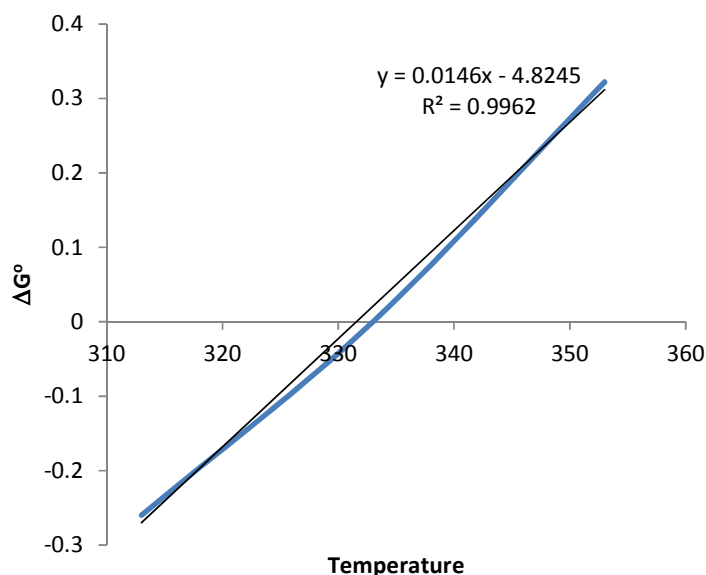$$y = 0.0146x - 4.8245$$
$$R^2 = 0.9962$$

Fig. 13. Plot of ΔG^o vs. T for the adsorption of Pb^{2+} onto layered double hydroxide

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. The low value of n obtained in this study suggests that the adsorption of Pb^{2+} on the layered double hydroxide was very fast.

Isosteric 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 Fig. 14 gives a slope equal to ΔH_x.

The value of ΔH_x derived from equation 12 was 12.6KJ/mol which indicates that adsorption mechanism was physical adsorption and in an heterogeneous surface.

The activation energy E_a and the sticking probability S^* (Fig. 15) were calculated from equation 14, the value shown in Table 1 for E_a and S^* are 0.283KJ/mol and 0.47 respectively.

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).
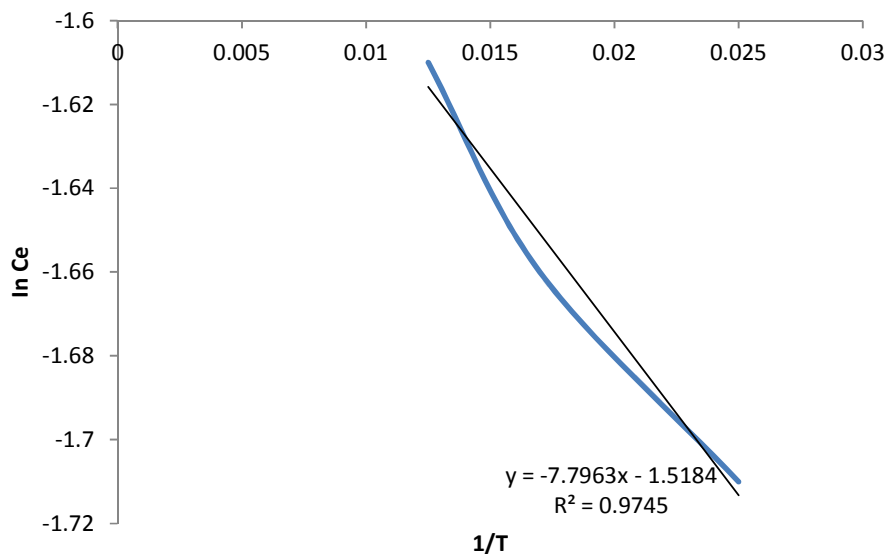

Fig. 14. Plot of lnC_e vs. $1/T$ for the adsorption of Pb^{2+} onto layered double hydroxide
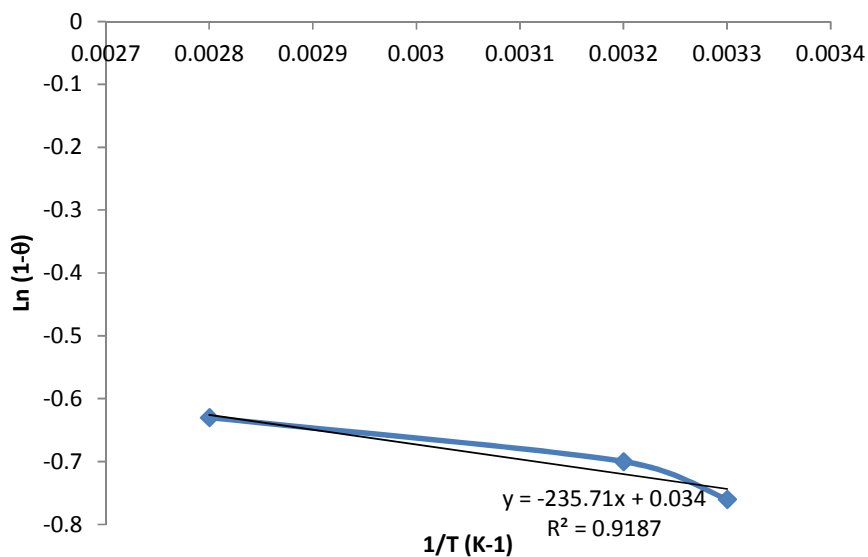

Fig. 15. Plot of $ln(1-\theta)$ vs. $1/T(K^{-1})$ for the adsorption of Pb^{2+} onto layered double hydroxide

Table 1. Equilibrium and thermodynamic parameters

Isosteric heat of adsorption ΔH_x KJ/mol	Sticking probability S*	Activation energy E_a KJ/mol	Gibbs free energy of adsorption ΔG^o KJ/mol	Apparent entropy ΔS^o KJ/molK	Apparent enthalpy ΔH^o KJ/mol	Surface coverage θ	Separation factor S_f	Hoping number n	Adsorption capacity Mol/g
12.6	0.47	0.283	-0.26	0.0146	-4.8245	0.53	0.866	4	0.887

6. CONCLUSION

In this study layered double hydroxide (Zn/Al-CO_3) was used to recover lead ions from aqueous solutions. The equilibrium data were described well by a Langmuir isotherm, indicating that the adsorption of lead on the Zn/Al-CO_3 was a monolayer process. The adsorption of lead ions on the Zn/Al followed zero-order kinetics model R^2 =1, second-order kinetic model R^2 = 0.998 and pseudo-second order kinetics model R^2 = 0.999. The spontaneous nature of the reaction process was highlighted from the values of ΔS^o, ΔH^o and ΔG^o. From the foregoing, it is clear that layered double hydroxides could be used effectively as adsorbents for the removal of heavy metals. They efficiency of the adsorbent (LDH) could be enhanced by increasing its amount.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Manoj K, Abhradip P, Joginder S, Shashank G, Madhu B, Ashish V, Yogender PK, Umesh CP. Removal of chromium from water effluent by adsorption onto Vetiveria zizanioides and anabaena species. 2013;5:341-348.
2. Dursun AY. A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger.* Biochem. Eng. J. 2006;28:187-195.
3. Satapathy D, Natarajan GS. Pottasium bromate modification of the granular activated carbon and its effect on nickel adsorption. Adsorption. 2006;12:147-154.
4. Meyn MK. Beneke G. Lagaly. Anion-exchange reactions of layered double hydroxides. Inorganic Chemistry. 1990; 29(26):5201-5207.
5. Kim MJ, Kim H, Jeong KE, Jeong SY, Park YK, Jeon JK. Catalytic decomposition of Dibenzothiophene sulfones over layered double hydroxide catalysts. Journal of Industrial and Engineering Chemistry. 2010;16(4):539-545.
6. Li P, Takahashi M, Chiba K. Enhanced free-radical generation by shrinking microbubbles using a copper catalyst. Chemosphere. 2009;77(8):1157-1160.
7. Sarakha L, Forano C, Boutinaud P. Intercalation of Luminescent Europium (III) complexes in layered double hydroxides. Optical Materials. 2009;31(3):562-566.
8. Sels B, De Vos D, Buntinx M, Pierard F, Kirsch-De Mesmaeker A, Jacobs P. Layered double hydroxides exchanged with Tungstate as Biomimetic catalysts for mild oxidative bromination. Nature, 1999;400(6747):855-857.
9. Ukrainczyk L, Chibwe M, Pinnavaia TJ, Boyd SA. Reductive dechlorination of carbon tetrachloride in water catalyzed by mineral-supported biomimetic cobalt macrocycles. Environmental Science and Technology. 1995;29(2):439-445.
10. Fogg AM, Green VM, Harvey HG, O'Hare D. New separation science using shape-selective ion exchange intercalation chemistry. Advanced Materials. 1999; 11(17):1466-1469.
11. Ryu SJ, Jung H, Oh JM, Lee JK, Choy JH. Layered double hydroxide as novel antibacterial drug delivery system. Journal of Physics and Chemistry of Solids. 2010;71(4):685-688.
12. Cornejo J, Celis R, Pavlovic I, Ulibarri MA. Interactions of pesticides with clays and layered double hydroxides: A review. Clay Minerals. 2008;43(2):155-175.
13. Srivastava B, Jhelum V, Basu DD, Patanjali PK. Adsorbents for pesticide uptake from contaminated water: A review. Journal of Scientific & Industrial Research. 2009;68:839-850.
14. Glasston S, Laidler KJ, Eyring H. The theory of rate processes: The kinetics of chemical reactions, viscosity, diffusion and

electrochemical phenomena. McGraw-Hill, New York; 1941.

15. Ruthven DM. Principles of adsorption and adsorption processes. John Wiley & Sons Ltd. New York; 1984.

16. Hernandez-Moreno MJ, Ulibarri MA, Rendon JL, Serna CJ. IR characteristics of hydrotalcite-like compounds. Phys. Chem. Miner. 1985;12:34–38.

17. Lin YJ, Li DQ, Evans DG, Duan X. Modulating effect of Mg-Al-CO3 layered double hydroxides on the thermal stability of PVC resin. Polym. Degrad. Stab. 2005; 88:286–293.

18. Boudrahem F, Aissani-Benissad F, Aït-Amar H. Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. Journal of Environment Management. 2009;90:3031–3039.

19. Acharya J, Sahu JN, Mohanty CR, Meikap BC. Removal of lead (II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation. Chemical Engineering Journal. 2009;149: 249–262.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=1048&id=16&aid=9245