



## Adsorption of Congo Red by Ni/Al-CO<sub>3</sub>: Equilibrium, Thermodynamic and Kinetic Studies

N. AYAWEI<sup>1</sup>, A.T. EKUBO<sup>2</sup>, D.WANKASI<sup>1,3</sup> and E.D. DIKIO<sup>1,3</sup>

<sup>1</sup>Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria

<sup>2</sup>Department of Chemical Sciences, Federal University of Technology, Otuoke, Bayelsa State, Nigeria

<sup>3</sup>Applied Chemistry and Nanoscience Laboratory, Department of Chemistry, Vaal University of Technology, P. O. Box X021, Vanderbijlpark, South Africa

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

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### ABSTRACT

Experimental investigations were carried out using Ni/Al-CO<sub>3</sub> layered double hydroxide as adsorbent for removal of toxic anionic dye namely Congo red from aqueous solutions. The effect of contact time, initial dye concentration and temperature were experimentally studied in batch mode to evaluate the kinetic, equilibrium and thermodynamic parameters of the adsorption process. Experimental results revealed that the degradation of the dye is mostly dependent on temperature. The dye degradation process obeyed the zero-order kinetic model, first-order kinetic model, second-order kinetic model, pseudo second order kinetic and third order kinetic model with correlation coefficient values 1, 0.9998, 0.9999, 0.9999 and 0.9997 respectively. Langmuir, Freundlich, Temkin and Dubinin-Kaganer-Radushkevich isotherms were applied to the equilibrium data and was well described by all. Thermodynamic studies showed congo red adsorption on the layered double hydroxide was endothermic and spontaneous in nature. The results indicate that layered double hydroxide could be employed as alternative for removal of anionic dyes from industrial wastewater.

**Keyword:** Congo Red, Layered double hydroxides, Kinetic, Dye, Adsorption, isotherms, thermodynamics.

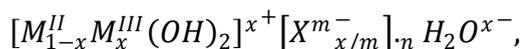
### INTRODUCTION

It was estimated that 10-20 % of dye was lost during the dyeing process and released as effluent<sup>1</sup>. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals and, therefore, are difficult to be

decolorized once released into the aquatic environment<sup>2</sup>. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms<sup>3</sup>. Therefore, it is very important to develop new systems that can be used for removing dyes from waters.

The treatment of dyes in industrial wastewater possesses several problems since dyes are generally difficult to biodegrade and photodegrade. Many different techniques including cloud point extraction, oxidation processes, nanofiltration, ozonation and coagulation have been used for the removal of colored dyes from wastewater<sup>4-7</sup>. However, adsorption is the most popular physicochemical treatment for the removal of dissolved organics from waters.

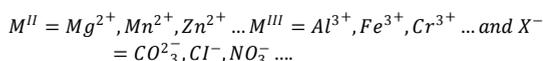
Layered double hydroxides (LDH) or anionic clays are lamellar ionic compounds, containing a positively charged layer and exchangeable anions in the interlayer<sup>8</sup>. They consist of brucite-like layers, with a partial M<sup>II</sup> for M<sup>III</sup> substitution, leading to an excess of positive charge compensated with anions situated in the interlayer together with water molecules. These materials can be represented by the general formula



abbreviated as



where



The flexibility of the structure of these materials as well as their high anionic exchange capacity make them suitable for many applications<sup>9,10</sup>, such as the sorption of many inorganic<sup>11-14</sup> and organic<sup>15-20</sup> anions, potential contaminants of waters. Some authors have reported about LDH containing chelating agents such as etilendiaminetetraacetate, edta<sup>21</sup> and nitrilotriacetate, NTA,<sup>22</sup> as well as the metal cations uptake by these materials<sup>23,24,25</sup>.

Materials and Methods

### Synthesis of Ni/Al-CO<sub>3</sub>

Carbonate form of Ni/Al LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3 M Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.1 M Al (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with Ni/Al ratios 2:1, was

added drop wise into a 50 ml mixed solution of (NaOH (2M) + Na<sub>2</sub>CO<sub>3</sub> (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 Layered Double Hydroxide

X-ray diffraction (XRD) pattern of the sample was characterized by using a Shimadzu XRD-6000 diffractometer, with Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) 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°, 2 $\theta$  / min at 0.003° steps.

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

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.

### Preparation of Congo Red Solution

Congo red (CI=22120) was supplied by Merck (Mumbai, India). A stock solution of CR dye was prepared (100mg/L) by dissolving a required amount of dye powder in deionized water. The stock solution was diluted with deionized water to obtain the desired concentration ranging from 20 to 40mg/L.

The concentration of CR in the experimental solution was determined from the calibration curve prepared by measuring the absorbance of different known concentrations of CR solutions at  $\lambda_{max} = 497 \text{ nm}$  using a UV-vis spectrophotometer (Shimadzu, Kyoto, Japan). The pH meter using a combined glass electrode (model HI 9025C, Hanna instruments, Singapore).

### Experimental Procedure

Batch adsorption experiments were carried out to study the effect of initial congo red concentration, contact time and temperature on the adsorption of Congo red on the layered double hydroxide. Adsorption studies were carried out using 25 ml of each dye solution and 0.2g 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 congo red was determined by UV-Vis spectrophotometer analysis. All experiments were carefully conducted to acquire good result.

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 20 to 40 mg/L. All other factors are kept constant.

The effect of period of contact on the removal of the dye on adsorbent in a single cycle was determined by time intervals of 10, 20 and 30 minutes.

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  $\pm 0.5^\circ\text{C}$ .

The equilibrium adsorption capacity and the yield of adsorption were calculated respectively by equations 1 and 2 below:

$$q_{eq} = \frac{C_{init} - C_{eq}}{m} \quad \dots(1)$$

$$R\% = \frac{C_{init} - C_{eq}}{C_{eq}} \times 100 \quad \dots(2)$$

where  $C_{init}$  and  $C_{eq}$  are, respectively, the initial and equilibrium concentrations of metal ions in solution (mmol/l) and  $m$  is the layered double hydroxide dosage (g/l).

### Isotherms analysis

To determine the equilibrium parameters

of the adsorption process four isotherms namely, Freundlich, Langmuir, Temkin and Dubinin–Kaganer–Radushkevich (DKR) were applied to test the experimental data.

For the Freundlich isotherm the ln-ln version was used:

$$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq}$$

The Langmuir model linearization (a plot of  $1/q_{eq}$  vs  $1/C_{eq}$ ) was expected to give a straight line with intercept of  $1/q_{max}$ :

$$\frac{1}{q_{eq}} = \frac{1}{K_l q_{max} C_{eq}} + \frac{1}{q_{eq}}$$

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

$$S_f = \frac{1}{1 + aC_0}$$

With  $C_0$  as initial concentration of Congo Red 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 DKR isotherm is reported to be more general than the Langmuir and Freundlich isotherms. It helps to determine the apparent energy of adsorption. The characteristic porosity of adsorbent toward the adsorbate and does not assume a homogenous surface or constant sorption potential<sup>26</sup>.

The Dubinin–Kaganer–Radushkevich (DKR) model has the linear form

$$\ln q_e = \ln X_m - \beta \quad \dots(6)$$

where  $X_m$  is the maximum sorption

capacity,  $\beta$  is the activity coefficient related to mean sorption energy, and  $\hat{a}$  is the Polanyi potential, which is equal to

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad \dots(7)$$

where R is the gas constant (kJ/kmol). The slope of the plot of  $\ln e q$  versus  $\varepsilon$  gives  $\beta$  ( $\text{mol}^2/\text{J}^2$ ) and the intercept yields the sorption capacity,  $X_m$  (mg/g). The values of  $\hat{a}$  and  $X_m$ , as a function of temperature are listed in table 1 with their corresponding value of the correlation coefficient,  $R^2$ . It can be observed that the values of  $\hat{a}$  increase as temperature increases while the values of  $X_m$  decrease with increasing temperature.

The values of the adsorption energy, E, was obtained from the relationship [27]

$$E = (2\beta)^{-1/2} \quad \dots(8)$$

The Temkins isotherm model was also applied to the experimental data, unlike the Langmuir and Freundlich isotherm models, this isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the adsorption that the free energy of adsorption is simply a function of surface coverage [28]. The linear form of the Temkins isotherm model equation is given in (9).

$$qe = B \ln A + B \ln Ce \quad \dots(9)$$

Where  $B = [RT/b_T]$  in (J/mol) corresponding to the heat of adsorption, R is the ideal gas constant, T(K) is the absolute temperature,  $b_T$  is the Temkins isotherm constant and A (L/g) is the equilibrium binding constant corresponding to the maximum binding energy.

$$q_t = q_o + K_o t \quad 10$$

First-Order Kinetic model,

$$\ln q_t = \ln q_o + K_t t \quad 11$$

Second-Order Kinetic model,

$$\frac{t}{q_t} = \frac{t}{q_o} + K_2 t \quad 12$$

Third-order kinetic model

$$\frac{1}{q_t^2} = \frac{1}{q_o^2} + K_3 t \quad 13$$

Pseudo-second order model

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e t} \quad 14$$

where  $q_o$  (mg/g) and  $q_t$  (mg/g) are the adsorbed amounts of CR at equilibrium and time  $t$  (min);  $K_o$ ,  $K_1$ ,  $K_2$  and  $K_3$  are the adsorption rate constants for the kinetic models.

**Table 1: Characteristic Parameters of the Adsorption Isotherm Models for Congo Red adsorption by Layered Double Hydroxide**

Isotherm Model	Isotherm Parameter	Results
Freundlich	1/n	0.872
	$K_f$	2.1306
	$R^2$	1
Langmuir	$S_f$	0.7
	$R^2$	0.9924
Dubinin- kaganer-Radushkevich	E, KJ/mol	0.6859
	$b_D$ , $\text{mol}^2/\text{KJ}^2$	1.0635
	$q_D$ , mg/g	0.9589
	$R^2$	0.9972
Temkin	A	1.377
	b	$1.107 \times 10^3$
	B	2.0498
	$R^2$	0.9689

### Thermodynamic parameters

Thermodynamic parameters such as change in Gibb's free energy  $\Delta G^\circ$ , enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  were determined using the following equation [9]:

where  $K_d$  is the apparent equilibrium constant,  $q_{eq}$  (or  $[\text{Congo Red}]_{\text{uptake}}$ ); is the amount of metal adsorbed on the unitary sorbent mass (mmol/g) at equilibrium and  $C_{eq}$  (or  $[\text{Congo Red}]_{eq}$ ) equilibrium concentrations of metal ions in solution ( $q_{eq}/C_{eq}$ ), when amount adsorbed is equals  $q_{eq}$ ; -  $\frac{q_{eq}}{C_{eq}}$  relationship depends on the type of the adsorption that occurs, i.e. multi-layer, chemical, physical adsorption, etc.

The thermodynamic equilibrium constants ( $K_d$ ) of the Congo Red adsorption on studied layered double hydroxide were calculated from the intercept of the plots of  $\ln(q_{eq}/C_{eq})$  vs.  $q_{eq}$ .

Then, the standard free energy change  $\Delta G^\circ$ , enthalpy change  $\Delta H^\circ$  and entropy change  $\Delta S^\circ$  were calculated from the Van't-Hoff equation [9].

$$\Delta G^\circ = -RT \ln K_d \quad \dots(16)$$

where  $K_d$  is the apparent equilibrium constant; T is the temperature in Kelvin and R is the gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>):

The slope and intercept of the Van't-Hoff plot [8] of  $\ln K_d$  vs.  $1/T$  were used to determine the values of  $\Delta H^\circ$  and  $\Delta S^\circ$ ,

$$\ln K_d = \left[ -\frac{\Delta H^\circ}{R} \right] \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad \dots(17)$$

Then, the influence of the temperature on the system entropy was evaluated using the

equations [11]. The plot of  $\Delta G^\circ$  vs. t also give the result of  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots(18)$$

The thermodynamic parameters of the adsorption were also calculated by using the Langmuir constant ( $K_L$ ), Freundlich constants ( $K_F$ ) for the equations [12–14] instead of ( $K_d$ ). The obtained data on thermodynamic parameters were compared, when it was possible.

The differential isosteric heat of adsorption ( $\Delta H_x$ ) at constant surface coverage was calculated using the Clausius-Clapeyron equation [12]:

$$\frac{d \ln(C_{eq})}{dT} = -\frac{\Delta H_x}{RT^2} \quad \dots(19)$$

Integration gives the following equation [10]:

$$\ln(C_{eq}) = \frac{\Delta H_x}{R} \frac{1}{T} + k \quad \dots(20)$$

where K is a constant. The differential isosteric heat of adsorption was calculated from the slope of the plot of  $\ln(C_{eq})$  vs  $1/T$  and was used for an indication of the adsorbent surface heterogeneity. For this purpose, the equilibrium concentration ( $C_{eq}$ ) at constant amount of adsorbate adsorbed was obtained from the adsorption isotherm data at different temperatures.

## RESULTS AND DISCUSSION

### Characterization of LDH FT-IR

Figure 2 shows the pre and post adsorption spectra of congo red on Ni/Al-LHD. The strong bond around 3400cm<sup>-1</sup> as shown in 4(a) is

**Table 2: Thermodynamic Parameters of the Adsorption of Congo Red onto Layered Double Hydroxide**

T, K	$\Delta G^\circ$ , KJ/mol	$\Delta H^\circ$ , KJ/mol	$\Delta S^\circ$ , J/molK	$E_a$ KJ/mol	$\Delta H_x$ KJ/mol
313	-0.109	4.152	13.5	-9.34	39.9
333	-0.332				
353	-0.646				

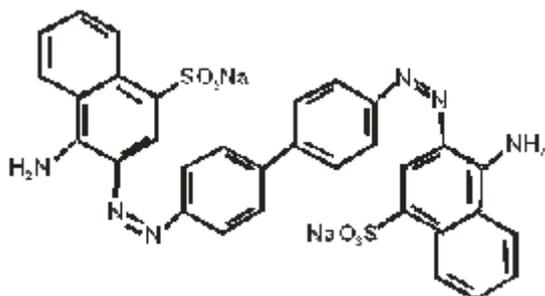


Fig. 1: Molecular Formula of Congo Red

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  $1650 - 1500 \text{ cm}^{-1}$  was assigned to the bending vibration of the interlayer water molecules. The carbonate ion peak is around  $1400 \text{ cm}^{-1}$  which is consistent with layered double hydroxides. Figure 4(b) shows sharp peak around

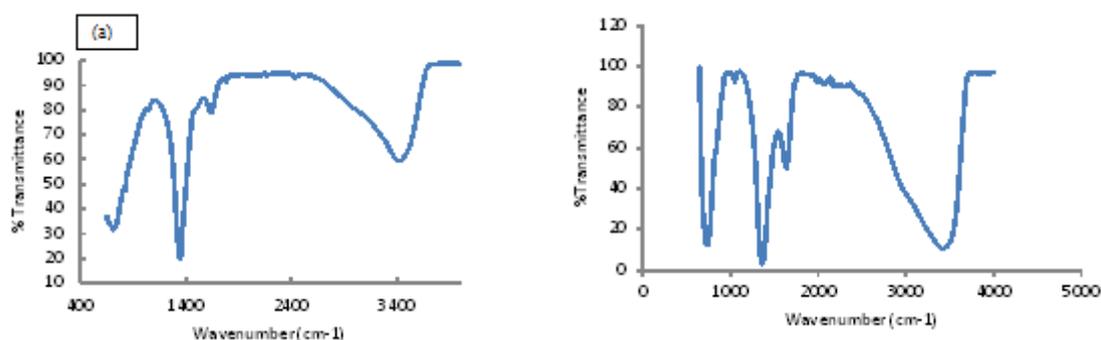


Fig. 2: Ni/Al- $\text{CO}_3$  Fourier transform infrared spectroscopy, before (a) and after (b) adsorption studies

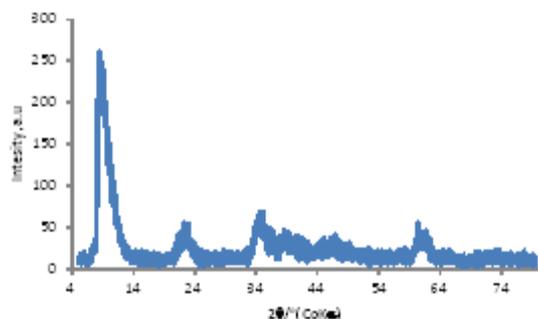


Fig. 3: X-ray powder diffraction diffractogram of Ni/Al<sub>2</sub>-CO<sub>3</sub>

$733 \text{ cm}^{-1}$  which is characteristic of bending vibration of primary amine and phosphate bond stressing between  $1100 \text{ cm}^{-1} - 1200 \text{ cm}^{-1}$ . This shows adsorption actually occurs via formation of complex between the congo red and the layered double hydroxides [29].

#### XRD

Figure 3 shows the XRD patterns of the Ni/Al. The basal reflections are observed at low  $2\theta$  values and weaker non-basal reflections at higher

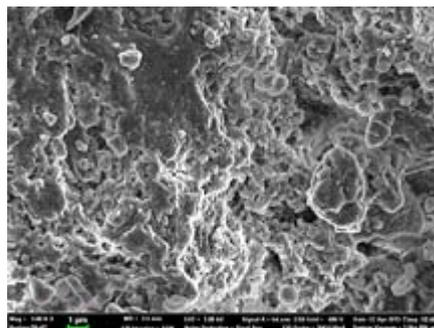
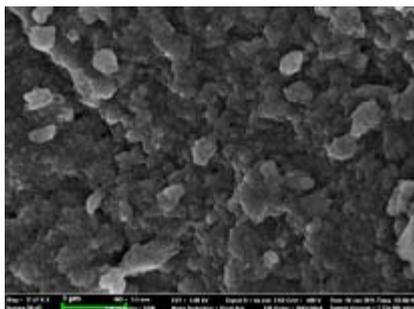


Fig. 4: Scanning Electron Microscope (SEM) micrograph of Ni/Al- $\text{CO}_3$  before (a) and after (b) adsorption studies

2*q*. The reflections in the Ni-Al based layered double hydroxide is indexed to rhombohedral symmetry (space group R-3m). Three successive reflections at 8.5Å, 22.34Å and 34.98Å respectively, which could be indexed to (003) and (006) and (009) planes corresponding to d-spacing of 1.039nm, 0.3975nm and 0.2562nm respectively.

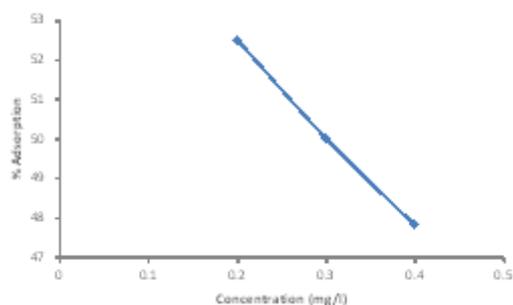
**SEM**

Figures 4 clearly shows the pre & post adsorption SEM images. The SEM image of post

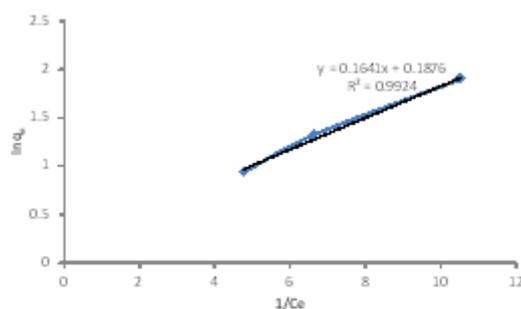
adsorption shows coverage of available pores in relation to pre-adsorption image.

**Effect of Concentration**

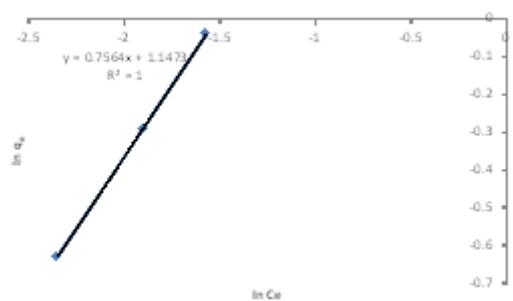
Removal efficiency of Congo Red by adsorbents is illustrated in figure 5. It shows that removal efficiency decreased with increasing of initial concentration (52.5%, 50% and 47.8%) respectively, this is probably due to rapid adsorption at all available site and relatively small amount of adsorbent that was used, an increase in the amount



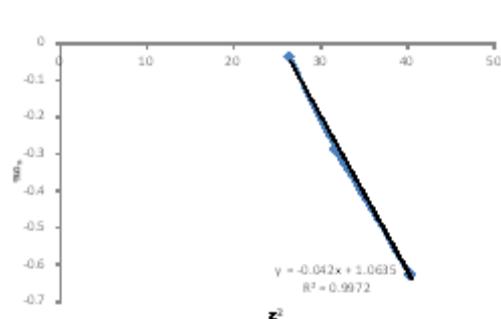
**Fig. 5: Effect of Concentration on adsorption of Congo Red onto layered double hydroxide**



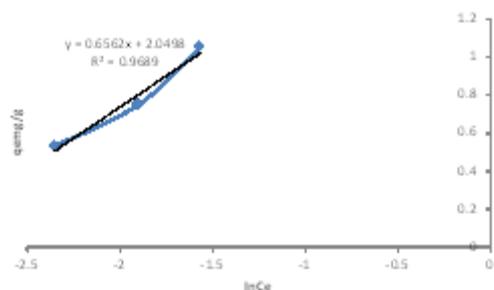
**Fig. 6: Langmuir Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide**



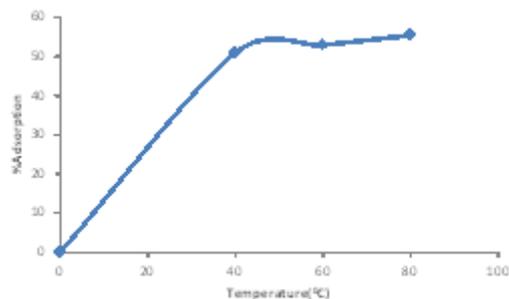
**Fig. 7: Freundlich Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide**



**Fig. 8: Dubinin-kaganer-radushkevich (DKR) Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide**



**Fig. 9: Temkin Isotherm Model plot for adsorption of Congo Red onto Layered Double Hydroxide**

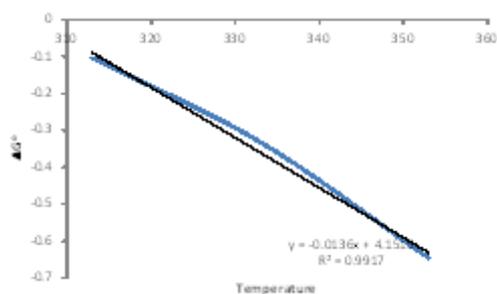


**Fig. 10: Effect of Temperature on adsorption of Congo Red onto layered double hydroxide**

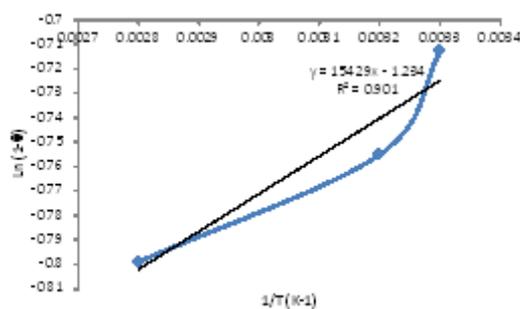
of adsorbent may therefore reverse adsorption trend.

### Isotherm Analysis

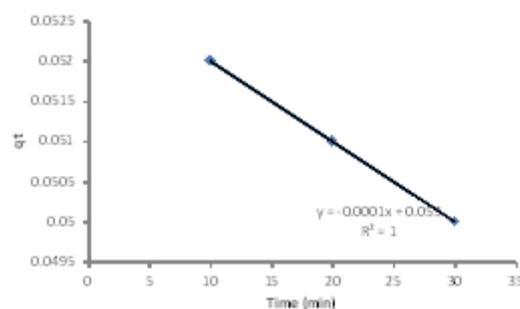
To investigate an interaction of adsorbate molecules and adsorbent surface, four well-known models, the Langmuir, Freundlich, Dubinin-kaganer-radushkevich and Temkin isotherms, were selected to explicate LDH interaction in this study.



**Fig. 11:** Plot of  $\Delta G^\circ$  vs. Temperature for the adsorption of Congo Red onto layered double hydroxide



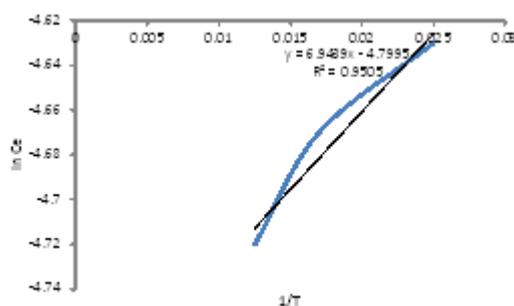
**Fig. 13:** Plot of  $\ln(1-q)$  vs.  $1/T(K^{-1})$  for the adsorption of Congo Red onto layered double hydroxide



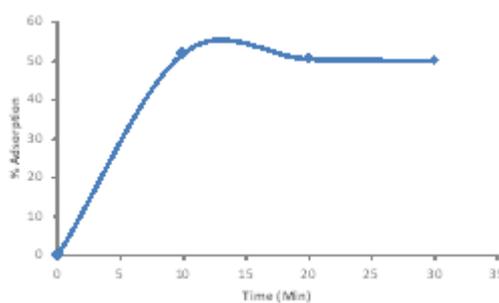
**Fig. 15:** Plot of  $qt$  vs.  $t$  for the adsorption of Congo Red onto layered double hydroxide

The Langmuir plot in figure 6 fitted the experimental data with  $R^2 = 0.9924$  and therefore, confirm monolayer coverage.

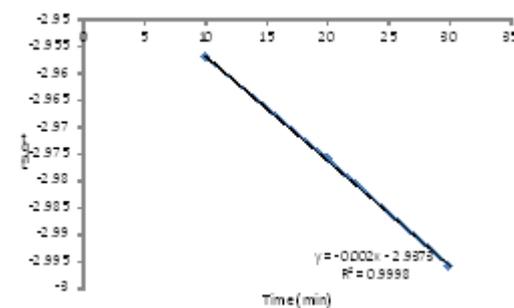
The influence of isotherm shape on whether adsorption is favourable or unfavourable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant separation



**Fig. 12:** Plot of  $\ln C_e$  vs.  $1/T$  for the adsorption of Congo Red onto layered double hydroxide



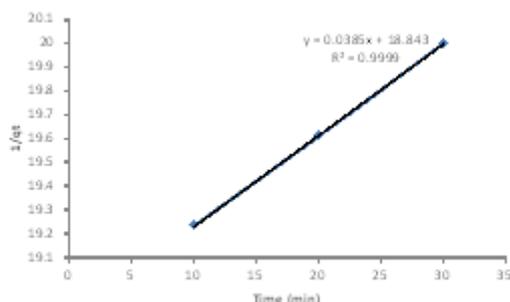
**Figure 14:** Effect of Contact Time on adsorption of Congo Red onto layered double hydroxide



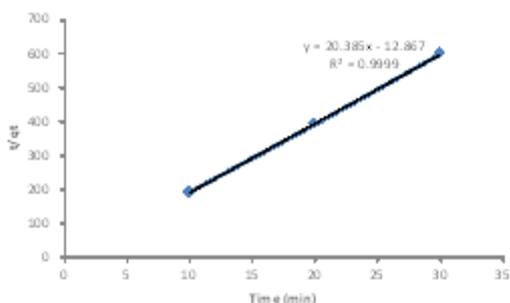
**Fig. 16:** Plot of  $\ln qt$  vs.  $t$  for the adsorption of Congo Red onto layered double hydroxide

factor ( $R_L$ ), given by Eq. (4). The calculated value of  $R_L$  from figure 5 is 0.7, which is within the range of 0–1, thus confirms the favourable uptake of the layered double hydroxide adsorption process.

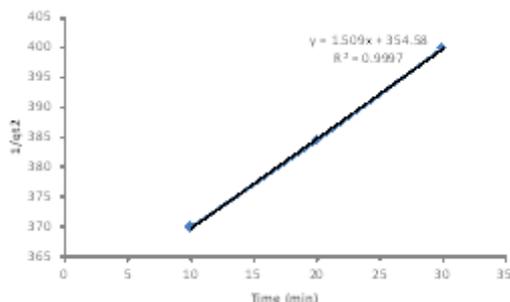
From the plot of  $\ln q_e$  against  $\ln C_e$  the Freundlich constants  $K_f$  and  $n$  which respectively indicating the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope as shown in figure 6 and table 1.



**Fig. 17:** Plot of  $1/qt$  vs.  $t$  for the adsorption of Congo Red onto layered double hydroxide



**Fig. 18:** Plot of  $1/qt$  vs.  $t$  for the adsorption of Congo Red onto layered double hydroxide



**Fig. 19:** Plot of  $1/qt^2$  vs.  $t$  for the adsorption of Congo Red onto layered double hydroxide

The fraction of the layered double hydroxide surface covered by the Congo Red is given as 0.47 (table 1). This value indicates that 47% of the pore spaces of the Layered double hydroxide surface were covered by the Congo Red which means high degree of adsorption.

The plot of  $\ln q_e$  against  $e^2$  is shown in Figure 8 and the constants  $q_D$  and  $B_D$  were calculated from the intercept and slope respectively. The DKR constants such as  $q_D$ ,  $B_D$ , and the apparent energy  $E$  were calculated to be 0.9589, 1.0635 and 0.6859 kJ/mol respectively. If the value of  $E$  lies between 8 and 16 kJ/mol the sorption process is a chemisorptions one, while values of below 8 kJ/mol indicates a physical adsorption process. The value of the apparent energy of adsorption (0.6859 kJ/mol) obtained indicated physisorptions between layered double hydroxide and Congo Red dye.

Temkin adsorption isotherm model is usually chosen to evaluate the adsorption potentials of an adsorbent for the adsorbate from an experimental data. This model gives the mechanism and adsorption capacity of an adsorbate in a sorption process. By plotting  $q_e$  against  $\ln C_e$ , the Temkin constants  $A$  and  $B$  were calculated from the slope and intercept. The constants  $A$  and  $B$  are 1.377 and 2.0498 respectively while the correlation coefficient value was 0.9689, indicating that the adsorption process is physical.

#### Effect of Temperature

As shown in figure 10 adsorption was lowest at 313K (51%), and increased slightly to 333K (53%) and 353K (55.5%). This means that adsorption capacity increase with higher temperature.

The values of the enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated from equation 10 to be 4.152 kJ/mol and 13.5 J/molK respectively, as shown in figure 11. A positive  $\Delta H^\circ$  suggests that sorption proceeded favourably at higher temperature and the sorption mechanism was endothermic. A positive value of  $\Delta S^\circ$  (13.5 J/molK) reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value

of  $\Delta S^\circ$  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<sup>23, 24, 25</sup>. The positive  $\Delta S^\circ$  value also corresponds to an increase in the degree of freedom of the adsorbed species.

Isothermic heat of adsorption  $DH_x$  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  $\ln C_e$  against  $1/T$  in figure 12 gives a slope equal to  $DH_x$ . The value of  $DH_x$  derived from equation 11 was 39.9KJ/mol which indicates that adsorption mechanism was physical adsorption and in an heterogeneous surface<sup>24, 25</sup>.

The activation energy  $E_a$  and the sticking probability  $S^*$  were calculated from equation 12, the value shown in table 1 for  $E_a$  and  $S^*$  are -9.34KJ/mol and 0.49 respectively, as shown in the plot in figure 13. 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 physisorption and chemisorption),  $S^* = 0$  (indefinite sticking – chemisorption),  $0 < S^* < 1$  (favourable sticking – physisorption) [25].

#### Effect of Time

The adsorption kinetic study is important in predicting the mechanisms (chemical reaction or mass-transport process) that control the rate of the

pollutant removal and retention time of adsorbed species at the solid-liquid interface. That information is important in the design of appropriate sorption treatment plants.

The effect of contact time of the phases on removal of Congo Red by the Layered double hydroxide from solutions of initial concentration equal to 400mg CR/L at three different times (10, 20 and 30 minutes) is presented in Figure 14.

The result shows that adsorption was highest at 10 minutes, thereafter, a gradual decrease occurred (10=52%, 20=50.5% and 30=50%).

The experimental data were fitted into different kinetic models including (Figures 15 - 19) zero-order-kinetic model, first-order-kinetic model, second-order-kinetic model, pseudo-second-order-kinetic model and third-order-kinetic model to ascertain the suitability of the models. The correlation coefficient values of 1, 0.9998, 0.999, 0.9999 and 0.9997 respectively confirms the applicability of the chosen kinetic models.

#### CONCLUSION

The present investigation shows that Ni/Al-CO<sub>3</sub> synthesized by coprecipitation method can be employed as a potentially viable sorbent for the removal of Congo Red dye from industrial wastewaters. The Congo Red adsorption was found to be greatly dependent on temperature. The experimental data were well defined by Langmuir, Freundlich, Temkin and Dubinin-Kaganer-Radushkevich isotherms. The experimental data also fitted all the kinetic models applied in this paper. The values of  $DH^\circ$  and  $DS^\circ$  indicated that the adsorption process was endothermic and process is dependent on increase in temperature, thereby increasing the randomness of the solid/liquid phase of the reaction system.

#### REFERENCES

- Zhiqiao, H. Shuang, S. Huamin, Z. Haiping, Y. and Jianmeng, C., C.I.Reactive Black 5 decolorization by combined sonolysis and ozonation., *Ultrasonics Sonochem.*, **2007.**, *14* (3), 298- 304
- Sharma, J. and Janveja, B. A study on

- removal of congo red dye from the effluents of textile industry using rice husk carbon activated by steam, *Rasayan J. Chem.*, **2008**, 7(4), 936-942.
3. Shen, D., Fan, J., Zhou, W., Gao, B., Yue, Q. & Kang, Q.. Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems. *J. Hazard. Mater.* **2009.**, 172, 99-107.
  4. Kyzio<sup>3</sup>-Komošniška, J., Rosik-Dulewska, C., Paj<sup>3</sup>k, M. & Jarzyna, M.. Removal of direct dyes from wastewater by sorption onto smectite clay. *Arch. Environ. Prot.* **2010.**, 3, 3–14.
  6. Bhattacharyya K.G. and Sharma, A. "Kinetics and Thermodynamics of Methylene Blue Adsorption on Neem Leaf Powder" *Dyes and Pigments*, **(2005)**, 65, 51-59.
  7. Mall, I.D., Srivastava, V.C., Agarwal, N.K. and Mishra, I.M., "Adsorptive Removal of Malachite Green Dye from Aqueous Solution by Bagasse Fly Ash and Activated Carbon - Kinetic Study and Equilibrium Isotherm Analyses", *Colloids and Surfaces: A physicochemical. Eng. Aspects*, **2005.**, 264, 17-28.
  8. Amin, S., Jayson, G.G., Humic substance uptake by hydrotalcites and PILCs. *Water Res.* **1996.**, 30, 299 – 977.
  9. Cavani, F., Trifiro, F., Vaccari, A., Hydrotalcite-type anionic clays: preparation, properties and application. *Catal. Today* **1991.**, 11, 173 – 301.
  10. G., Ramos, E., Olguin, M.T., Bosh, P., Lopez, T., Bulbulian, S., Sorption of 131I by hydrotalcites. *J. Radioanal. Nucl. Chem.* **1997.** 222, 63 – 66.
  11. Gutmann, N.H., Spiccia, L., Turney, T.W., Complexation of Cu(II) and Ni(II) by nitriloacetate intercalated in Zn – Cr layered double hydroxides. *J. Mater. Chem.* **2000.**, 10, 1219 – 1224.
  12. Hermosín, M.C., Pavlovic, I., Ulibarri, M.A., Cornejo, J., Trichlorophenol adsorption on layered double hydroxide: a potential sorbent. *J. Environ. Sci. Health, Part A, Environ. Sci. Eng.* **1993.**, 28 (9), 1875 – 1888.
  13. Hermosín, M.C., Pavlovic, I., Ulibarri, M.A., Cornejo, J., Hydrotalcite as sorbent for trinitrophenol: sorption capacity and mechanism. *Water Res.* **1996** 30, 171 – 177.
  14. Hourri, B., Legrouri, A., Barroug, A., Forano, C., Besse, J.P., Use of the ion exchange properties of layered double hydroxides for water purification. **(1998)**.
  15. J.Tronto, K.C. Sanchez, E.L. Crepaldi, Z. Naal, I.K. Stanlei, J.B. Valim Synthesis, characterization and electrochemical study of layered double hydroxide intercalated with 2thiophenecarboxylate anions, *J. Phys. Chem. Solid* **(2004)**, 65 493-498.
  16. M.Z. Hussein, A.H. Yahaya, Z. Zainal, L.H. Kian, Nanocomposite-based controlled release formulation of an herbicide, 2, 4-dichlorophenoxyacetate incapsulated in zinc-aluminiumlayered double hydroxide, *Sci. Technol. Adv. Mat.* **2005.**, 6., 956-962.
  17. Pavlovic, I., Ulibarri, M.C., Hermosín, M.C., Cornejo, J., Sorption of an anionic surfactant from water by a calcined hydrotalcite-like sorbent. *Fresenius Environ. Bull.* **1997.**, 6, 266 – 271.
  18. Pavlovic, I., Barriga, C., Hermosín, M.C., Cornejo, J., Ulibarri, M.C., Adsorption of acidic pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite. *Appl. Clay Sci.* **2005.**, 30, 125 – 133.
  19. Rives, V., Ulibarri, M.A., Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. *Coord. Chem. Rev.* **1999** 181, 61 – 120.
  20. Tarasov, K.A., O'Hare, D., Isupov, V.P., Solid state chelation of metal ions by ethylenediaminetetraacetate intercalated in a layer double hydroxide. *Inorg. Chem.* **2003.** 42 (6), 1919 – 1927.
  22. Tsyganok, A.I., Suzuki, K., Hamakawa, S., Takehira, K., Hayakawa, T., Mg – Al layered double hydroxide intercalated with [Ni (edta)] 2 " chelate as a precursor for an efficient catalyst of methane reforming with carbon dioxide. *Catal. Letters* **2001.** 77 (1–3), 75 – 86.
  23. Ayawei, N., Ekubo, A. T., Wankasi, D., and Dikio, E. D. Mg/Fe Layered Double Hydroxide For Removal Of Lead (II): Thermodynamic, Equilibrium And Kinetic Studies. *European Journal of Science and Engineering.* **2015.** 3, 7; 1-17.
  24. Ayawei, N., Ekubo, A. T., Wankasi, D., and

- Dikio, E. D.. Equilibrium, Thermodynamic and Kinetic Studies of the Adsorption of Lead(II) on Ni/Fe Layered Double Hydroxide. *Asian Journal of Applied Sciences* ., **2015.**, 3 – Issue 2; 2., 7-217.
25. Ayawei, N., Ekubo, A. T., Wankasi, D., and Dikio, E. D. "Synthesis and Application of Layered Double Hydroxide for the removal of Copper in Wastewater". *International Journal of Chemistry*. **2015.**, 7., 1; 122 - 132.
26. a) Arivoli S, Venkatraman B R, Rajachandrasekar T and Hema M, Adsorption of ferrous ion from aqueous solution by low cost activated carbon obtained from natural plant material, *Res J Chem Environ*. **2007.**, 17, 70-78. b)
27. Dawodu F. A., Akpomie G. K., and Ogbu I. C., "Isotherm Modeling on the Equilibrium Sorption of Cadmium (II) from Solution by Agbani Clay", *International Journal of Multidisciplinary Sciences and Engineering*, **2012**. 3, 9.
28. K.K.H. Choy, G.Mckay and J.F. Porter "Sorption of acidic dyes from effluents using activated carbons", *Resource. Conserv. Recycling*, **1999**, 27., 57-71.
29. Chongrak, K., Eric, H., Nouredine A. and Jean P. G., "Application of Methylene Blue Adsorption to Cotton Fiber Specific Surface Area Measurement: Part I. Methodology", *The Journal of Cotton Science* **1998.**, 2: 164 - 173.