Mg/Fe Layered Double Hydroxide as a Novel Adsorbent for the Removal of Congo red

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Abstract

The ability of Mg/Fe- CO_3 to degrade Congo Red in aqueous solution was investigated under various experimental conditions. The layered double hydroxide was synthesized by co-precipitation method and characterized by X-ray diffraction (XRD), Fourier Transform Infrared spectroscopic (FTIR) and Energy-Dispersive X-ray Spectroscopic (EDX). Batch mode experiments were conducted to assess the potential of the layered double hydroxide for the removal of Congo Red from aqueous solution. Laboratory experimental investigation was carried out to identify the effect of agitation time (10 - 30min), varying temperature (40-80˚C) and varying concentration (20 - 40m/L). The adsorption was endothermic and the computation of the parameters $\Delta G˚$, $\Delta H˚$, $\Delta S˚$ and ΔH_x indicated that the interactions were thermodynamically favorable. Langmuir, Freundlich, Temkin and the Dubinin–Kaganer–Radushkevich (DKR) adsorption isotherm models were used to qualify the experimental data with the best fits been Langmuir and Freundlich isotherms with regression coefficient values of 0.9995 and 0.9998 respectively.

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

Introduction

Approximately 10% of total dye production per year is not used but discharged into water bodies. This has placed premium on scientists and governments all over the world to look at the impacts of such discharges. A large variety of dyestuffs is available under the categories of acid, basic, reactive, direct, disperse, sulphur and metallic dyes [1]. Dyes are synthetic aromatic compounds, which have various functional groups [2]. Some dyes and their degradation products may be carcinogens and toxic, and consequently their treatment cannot depend on biodegradation alone [3,4]. Several methods such as phytoremediation, flocculation, membrane separation, adsorption etc are usually employed for the removal of dye in aqueous media. Adsorption process in recent times is the most effective method for removal dyes from waste sewage [5,6]. The process of adsorption has an advantage over other methods due to its sludge free clean operation and complete removal of dyes even from diluted solutions. Layered double hydroxides (LDHs) are a class of anionic clays with high anion exchange capacities which can be used as an effective adsorbent for the removal of variety of anionic pollutants. The empirical formula of LDH can be described by $[M^{2+}1-x\ M^{3+}x(OH)2]^{x+}\ (A^{n-})x/n.mH_2O$ where M^{2+} and M^{3+} are metal cations, for example Mg^{2+} and Al^{3+} respectively, that occupy octahedral sites in the hydroxide layers, A^{n-} is an exchangeable anion and x is the ratio $M^{3+}/(M^{2+} + M^{3+})$. Carbonates are the interlayer anions in the naturally occurring mineral hydroxides, which is a member of this class of materials [7,8]. It is known that many substances in waste water, such as humic acid substances, dye in the effluents carry negative charges [9]. Species that carry negative charges account for a large part of water in contaminated water bodies [10].

Because of the large surface area, anion exchange ability, and regeneration ability, LDHs are been used as adsorbents for purification of wastewater [11, 12]. This work aims to replicate clay like materials in a laboratory condition, optimize process conditions for the removal of Congo Red in aqueous solutions.

Figure 1: Molecular Formula of Congo Red
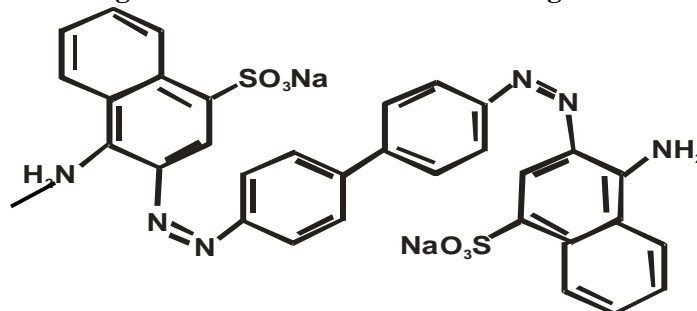
Materials and Methods

Synthesis of Mg/Fe-CO₃ Carbonate form of Mg-Fe LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3M Mg $(NO_3)_2.6H_2O$ and 0.1M Fe $(NO_3)_3.9H_2O$ with Mg/Fe ratios 2:1, was added drop wise into a 50 ml mixed solution of (NaOH (2M) + Na_2CO_3 (1M) with vigorous stirring and maintaining a pH of greater than 10 at room temperature. After complete addition which last between 2 hours 30 minutes to 3 hours, the slurry formed was aged at 60°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 diffract meter, 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 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 4000cm^{-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.

Preparation of Congo Red Solution

The analytical grade Congo red dye supplied by Labchem Laboratory was used as received. Stock solution of the dye was prepared by dissolving 1g solute in 1000ml volumetric flasks to make 1000 mg/L of the dye solution. Model and working calibration standards were prepared by serial dilution of the stock solution to concentrations of 20, 30 and 40mgl^{-1}. The supernatant from each experiment were determined using UV-vis spectrophotometer (Shimadzu, Kyoto, Japan) at a wavelength of 497nm.

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. The adsorption experiments were performed at three different temperatures viz., 40, 60 and 80°C in a thermostat attached with a shaker (Remi make). The constancy of the temperature was maintained with an accuracy of ± 0.5° C. 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. 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 substrate equilibrium adsorption capacity (q_{eql}) and percentage adsorption (R) were evaluated using equations 1 and 2 respectively.

$$q_{eql} = \frac{C_{init} - C_{eql}}{m} \qquad 1$$

$$R\% = \frac{C_{init} - C_{eql}}{C_{eql}} \ x \ 100 \qquad 2$$

Where C_{init} and C_{eql} 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

Four adsorption isotherms were used to characterize the equilibrium between the amount of adsorbate that accumulated on the adsorbent and the concentration of the dissolved adsorbate namely, Freundlich, Langmuir, Temkin and Dubinin–Kaganer–Radushkevich (DKR).

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

$$\frac{1}{q_{eql}} = \frac{1}{K_l q_{mas} C_{eql}} + \frac{1}{q_{eql}} \qquad\qquad 3$$

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

$$S_f = \frac{1}{1 + a C_o} \qquad\qquad 4$$

With C_o 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).

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

$$In q_{eql} = In K_f + \frac{1}{n} In C_{eql} \qquad\qquad 5$$

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 [13].

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

$$In q_e = In X_m - \beta \varepsilon^2 \qquad\qquad 6$$

where X_m is the maximum sorption capacity, β is the activity coefficient related to mean sorption energy, and ε is the Polanyi potential, which is equal to

$$\varepsilon = RT In \left(1 + \frac{1}{C_e}\right) \qquad\qquad 7$$

Where R is the gas constant (kJ/kmol) . The slope of the plot of ln e q versus ε^2 gives β (mol^2/J^2) and the intercept yields the sorption capacity, Xm (mg/g) as shown in Fig. 6. The values of β and Xm, 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 β increase as temperature increases while the values of Xm decrease with increasing temperature.

The values of the adsorption energy, E, was obtained from the relationship [14]

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

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 [15]. The linear form of the Temkins isotherm model equation is given in (9).

$$qe = BlnA + BlnCe \qquad\qquad 9$$

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.

Thermodynamic studies

The thermodynamic parameters such as change in free energy ΔG^o, enthalpy change ΔH^o and entropy change ΔS^o were determined by using the following equations:

$$\Delta G^o = -RT In K_d \qquad\qquad 10$$
$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad\qquad 11$$

where K_d equals the ratio of C_{solid} and C_{liquid}. C_{solid} is the equilibrium concentration of adsorbate on the adsorbent (mg/L), C_{liquid} is the equilibrium concentration of adsorbate in solution (mg/L), T is temperature (K) and R is the ideal gas constant ($8.314 \, J.mol^{-1}K^{-1}$)

The differential isosteric heat of adsorption (ΔH_x) at constant surface coverage was calculated using the Clausius-Clapeyron equation:

$$\frac{dIn(C_{eql})}{dT} = -\frac{\Delta H_x}{RT^2} \qquad\qquad 12$$

Integration gives the following equation [13]:

$$In(C_{eql}) = \frac{\Delta H_x}{R}\frac{1}{T} + k \qquad\qquad 13$$

where K is a constant. The differential isosteric heat of adsorption was calculated from the slope of the plot of $\ln(C_{eql})$ vs $1/T$ and was used for an indication of the adsorbent surface heterogeneity.

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 19.

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

where θ is the degree of surface coverage, T is absolute solution temperature and R is gas constant ($8.314\,J/mol^{-1}K^{-1}$).

Results and Discussion

Characterization of LDH
FT-IR

The pre and post adsorption FT-IR spectra of the layered double hydroxide is shown in Figure 2. The band at $3400\,cm^{-1}$ which could be attributed to the stretching vibration of hydroxyl group 4(a). The low intensity band at $1738\,cm^{-1}$ is assigned to bending vibration of strongly adsorbed water (solvation water for compensating anion vibration). The band at $1355\,cm^{-1}$ is assigned to carbonate vibration (CO_3^{2-}). Figure 4(b) shows additional vibration peaks in the range of $1100\,cm^{-1}$ - $1200\,cm^{-1}$, and $650\,cm^{-1}$ - $900\,cm^{-1}$ corresponding to phosphate stressing, aromatic ring presence and characteristic primary amine bending vibration respectively , this implies the adsorption process involves the formation of complex between the adsorbent and the congo red [16].

Figure 2: Mg/Fe-C03 Fourier transform infrared spectroscopy, before (a) and after (b) adsorption studies
**XRD**
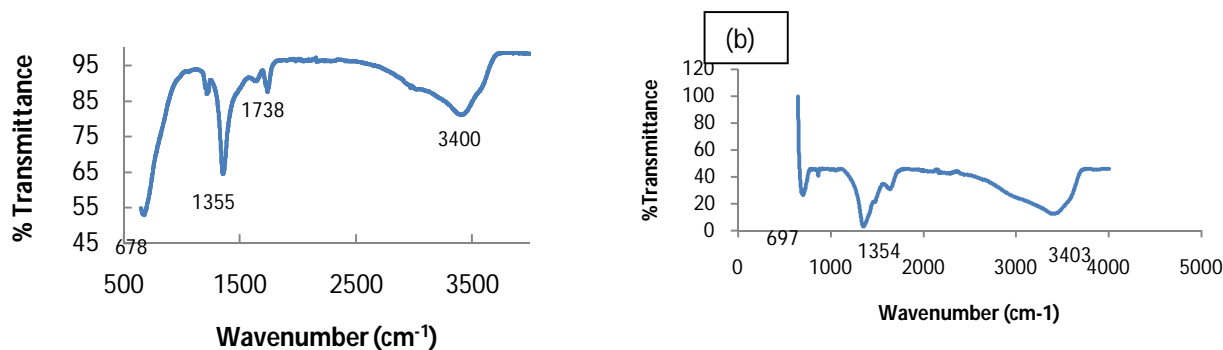
The typical XRD pattern (Figure 3) shows a lar CO_3-
LDH prepared at different Zn^{2+}/Fe^{3+} molar ratios. XRD patterns exhibit two characteristic intense peaks of basal reflection of Zn-Fe-CO_3-LDH which were located near 2θ of 8.46^o and 30.14^o corresponding to diffraction by (003) and (006) planes and d-spacing of 1.04 and 0.2911 respectively. These two peaks show the presence of an ordered layered structure.

Figure 3: Mg/Fe-C03 X-ray powder diffraction
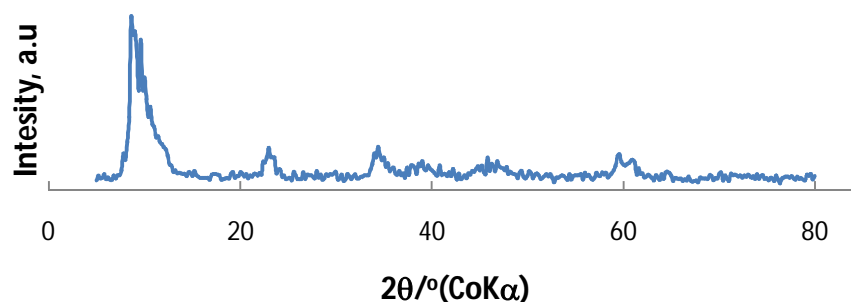
SEM

Figures 4 clearly show the pre & post adsorption SEM images. The SEM image of post adsorption shows coverage of available pores in relation to pre-adsorption image.

Figure 4: Scanning Electron Microscope (SEM) micrograph of Mg/Fe-CO3 before (a) and after (b) adsorption studies.
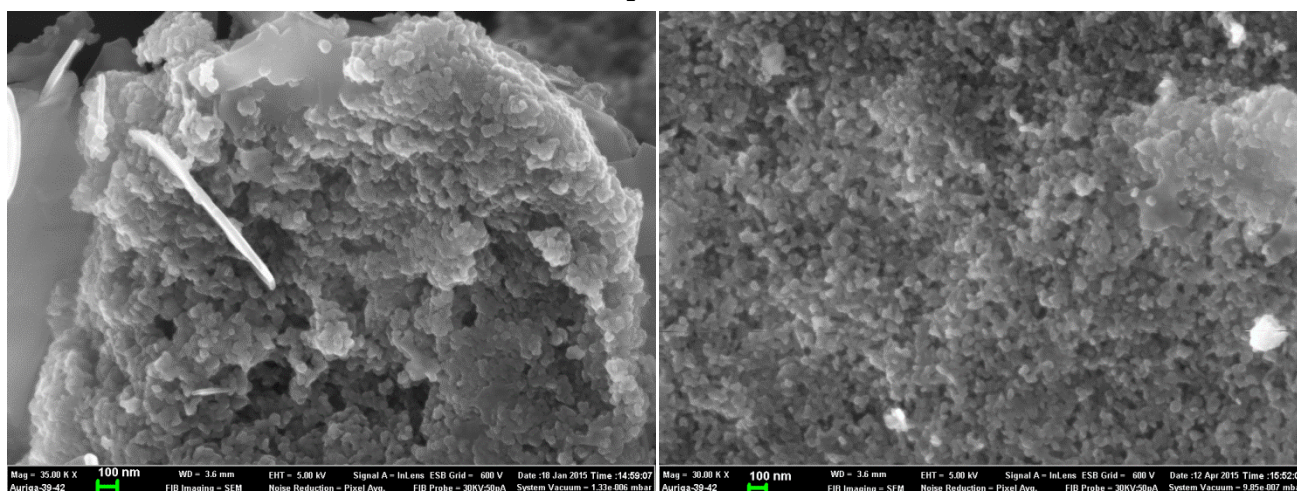

Effect of Concentration

Removal efficiency of Congo Red by adsorbents is illustrated in figure 5. It shows that removal efficiency decreased with increasing of initial concentration (54%, 51% and 48.8%) respectively, this is probably due to rapid adsorption at all available sites and the relatively small amount of adsorbent that was used, thus an increase in the amount of adsorbent may therefore further increase the uptake of the Congo Red dye.

Figure 5: Effect of Concentration on adsorption of Congo Red onto layered double hydroxide
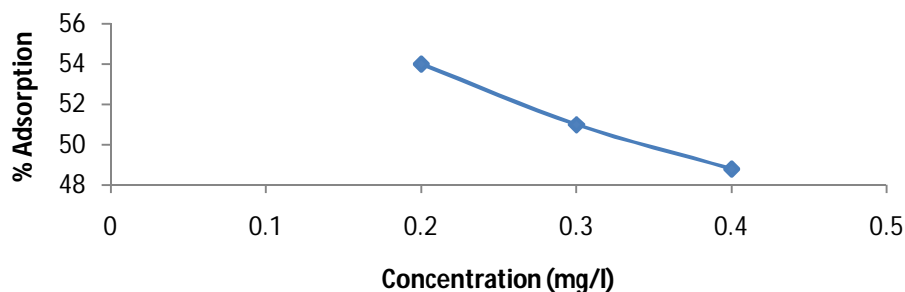
Isotherm Analysis

To investigate an interaction of adsorbate molecules and adsorbent surface, four well-known models, the Langmuir, Freundlich, Dubinin-kaganer-radushkevic and Temkin isotherms, were selected to explicate LDH interaction in this study. The influence of isotherm shape on whether adsorption is favorable or unfavorable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant separation factor (R_L), given by Eq. (4). The calculated value of R_L from figure 6 is 0.872, which is within the range of 0–1, thus confirms the favorable uptake of the layered double hydroxide adsorption process. The degree of favorability is generally related to the irreversibility of the system, giving a qualitative assessment of the layered double hydroxide interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

Figure 6: Langmuir Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide
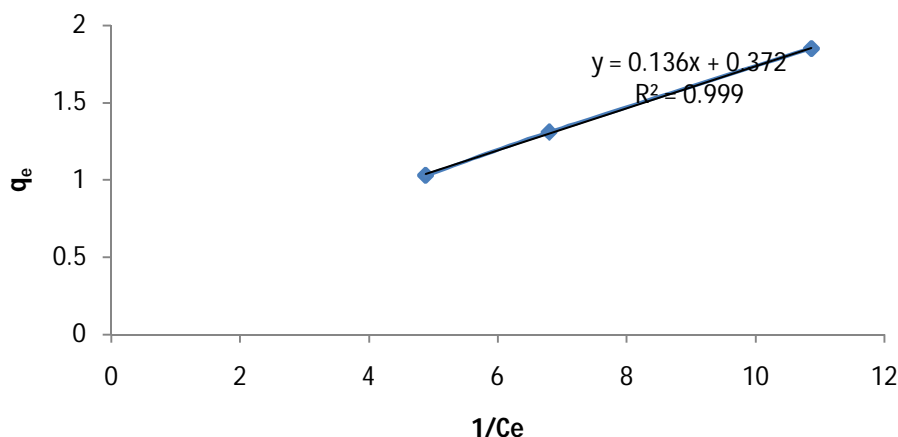

From the slope and intercept values of K_f and $1/n$ were determined. The constants K_f and $1/n$ are empirical parameters, K_f is the adsorption constant related to the bonding energy and $1/n$ is associated to the surface heterogeneity. The Freundlich constant n is the measure of the deviation from linearity of the adsorption. If a value for n is blew to unity, this implies that adsorption process is govern by a chemical mechanism, but a value for n is above to unity, adsorption is favorable a physical process. The values of K_f and n are 2.0664 and 0.893 respectively. The fraction of the layered double hydroxide surface covered by the Congo Red is given as 0.54 (table 1). This value indicates that 54% of the pore spaces of the Layered double hydroxide surface were covered by the Congo Red which means high degree of adsorption.

Figure 7: Freundlich Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide
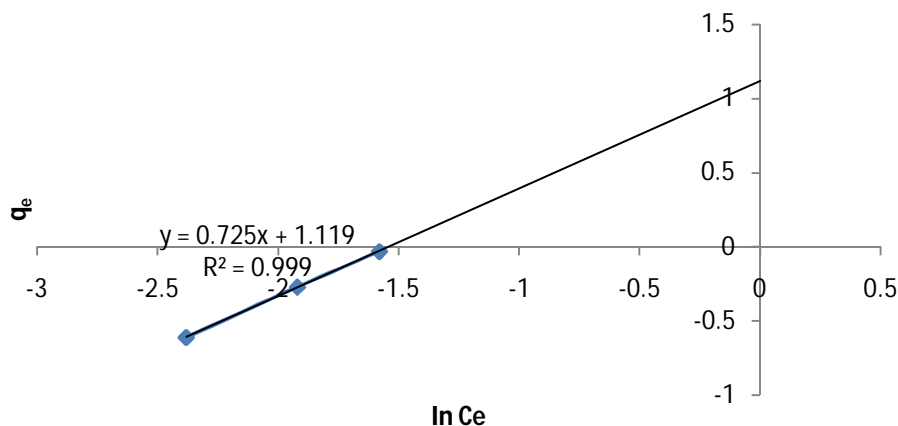
The plot of Inq$_e$ against ε^2 as shown in figure 8 gives a straight line which confirms the applicability of Dubinin-kaganer-radushkevic. From the slope and the intercept of the graph the DKR constants were calculated and the apparent energy determined from the equation 8. The values of the constants q$_D$(mol/g) is the D-R constant representing the theoretical saturation capacity and B$_D$(mol^2/J^2) is a constant related to the mean free energy of adsorption per mol of the adsorbate are 0.961 and 1.0375 while the apparent energy was 0.694KJ/mol.

Figure 8: Dubinin-kaganer-radushkevic (DKR) Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide
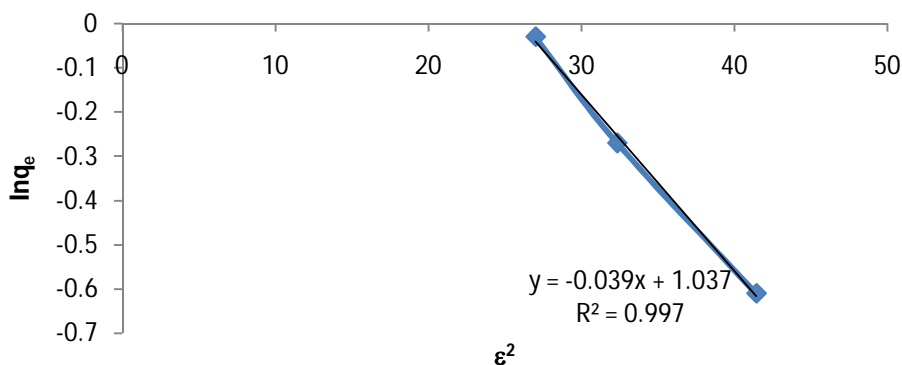
Temkin adsorption isotherm model is usually chosen to evaluate the adsorption potentials of an adsorbent for the adsorbate from an experimental data. This model gives the mechanism and adsorption capacity of an adsorbate in a sorption process. From the slope and intercept of the Temkin plot as shown in figure 8, the Temkin constants B= [RT/b$_T$] (J/mol) corresponding to the heat of adsorption, A (mg/L) is the equilibrium binding constant corresponding to the maximum binding energy. The values of the constants B = 1.8357 and A = 1.347 while the correlation coefficient R^2 = 0.9964.

Figure 9: Temkin Isotherm Model plot for adsorption of Congo Red onto Layered Double Hydroxide
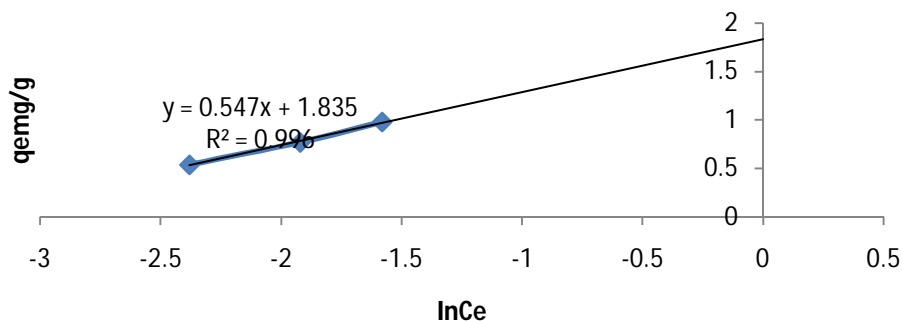

Table 1: Characteristic Parameters of the Adsorption Isotherm Models for Congo Red adsorption by Layered Double Hydroxide

| Isotherm Model	Isotherm Parameter	Results
Freundlich	1/n	1.1192
	K$_f$	2.0664
	R^2	0.9998
Langmuir	R$_L$, mg/l	0.872
	R^2	0.9995
Dubinin- kaganer-Radushkevich	E, KJ/mol	0.694
	β_D, mol^2/KJ^2	1.0375
	q$_D$, mg/g	0.961
	R^2	0.9973
Temkin	A	1.347
	b	1.24x10^3
	B	1.8357
	R^2	0.9964

Effect of Temperature

As shown in figure 10 adsorption was lowest at 313K (51.5%), and increased slightly to 333K (52%) and 353K (53.5%). This means that adsorption capacity increase with higher temperature.

Figure 10: Effect of Temperature on adsorption of Congo Red onto layered double hydroxide
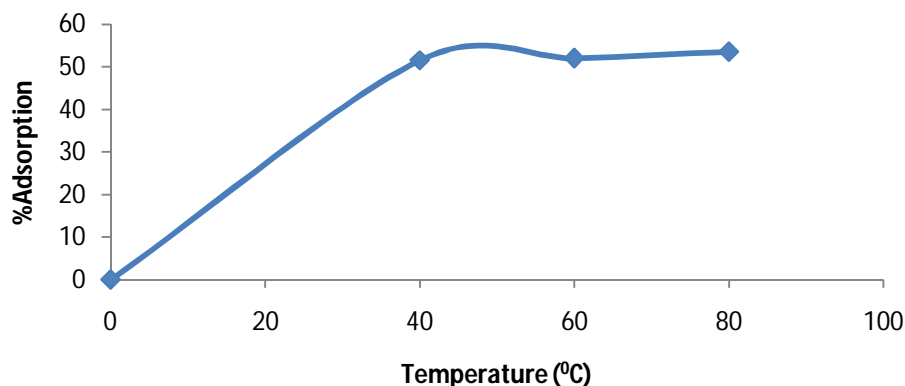

The values of the enthalpy change (ΔH^o) and entropy change ΔS^o were calculated from equation 10 to be 2.3107KJ/mol and 7.7J/molK respectively, as shown in figure 10. A positive ΔH^o suggests that sorption proceeded favorably at higher temperature and the sorption mechanism was endothermic. A positive value of ΔS^0 (7.7J/molK) reflects the affinity of the adsorbent towards the adsorb ate species. In addition, positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorb ate and the adsorbent [11]. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorb ate ions/molecules, thus allowing for the prevalence of randomness in the system. The positive ΔS^0 value also corresponds to an increase in the degree of freedom of the adsorbed species.

Figure 11: Plot of ΔG^o vs. Temperature for the adsorption of Congo Red onto layered double hydroxide
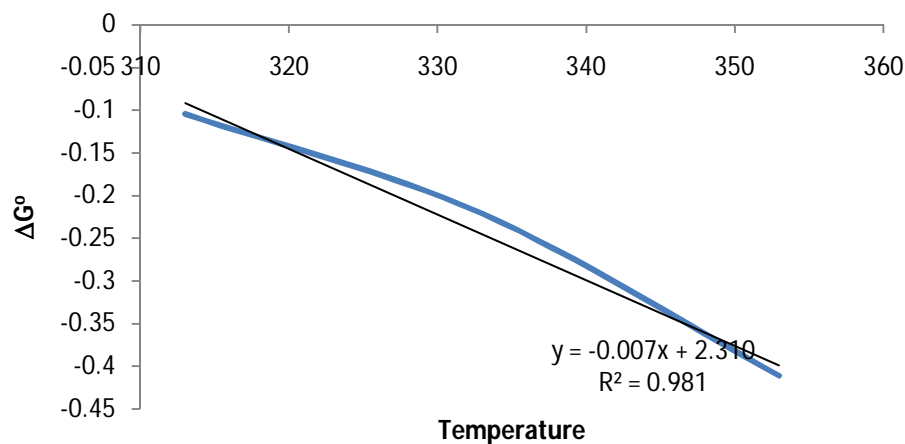
A plot of InCe against 1/T in figure 12 gives a slope equal to ΔHx. The value of ΔHx derived from equation 11 was 39.165KJ/mol which indicates that adsorption mechanism was physical adsorption and in an heterogeneous surface [12].

Figure 12: Plot of In Ce vs. 1/T for the adsorption of Congo Red onto layered double hydroxide
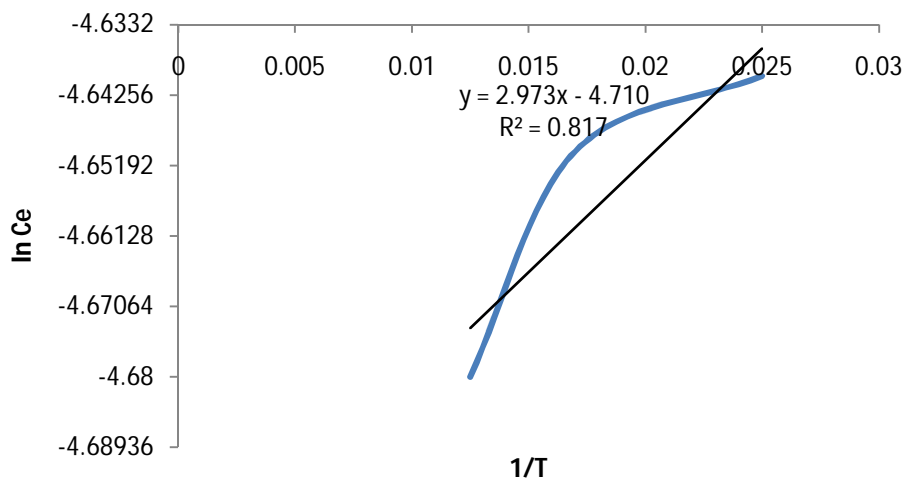
The activation energy Ea and the sticking probability S* were calculated from equation 12, the value shown in table 2 for Ea and S* are -8.673KJ/mol and 0.49 respectively, as shown in the plot in figure 13. The value of activation energy shows that the sorption process was a physical one less than 4.2KJ/mol. The sticking probability S* indicates the measure of the potential of an adsorb ate to remain on the adsorbent [11, 12]. It is often interpreted as S*>1 (no sorption), S*=1 (mixture of physic-sorption and chemisorption), S* = 0 (indefinite sticking – chemisorption), 0<S*<1 (favourable sticking – physic- sorption).

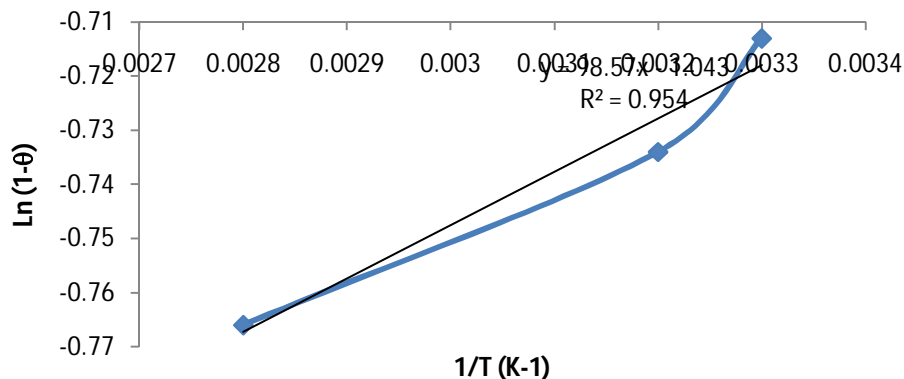**Figure 13: Plot of Ln(1-☐) vs. 1/T(K-1) for the adsorption of Congo Red onto layered double hydroxide**

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

T, K	ΔG^o, KJ/mol	ΔH^o, KJ/mol	ΔS^o, J/molK	E_a KJ/mol	ΔH_x J/molK
313	-0.104				
333	-0.221	2.310	7.7	-8.673	39.165
353	-0.411				

Conclusion

In this study, Congo Red uptake by $Mg/Fe-CO_3$ was investigated. The performance of the layered double hydroxide was examined as a function of the operating conditions such as contact time, initial dye concentration and variable temperature. The experimental evidence shows that the overall adsorption process is dependent on temperature. The experimental data were best defined by Langmuir, Freundlich, Dubinin-kaganer-Radushkevich and Temkin isotherms. The determination of thermodynamic parameters shows an endothermic reaction, feasible and favorable adsorption process. The variables showed that $Mg/Fe-CO_3$ is indeed a novel adsorbent.

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