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Research Paper

Adsorption of Congo Red a Basic Dye by Zn/Fe-CO₃

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Abstract: Adsorption of Congo Red dye from aqueous solution by Zn/Fe-CO₃ layered double hydroxide was accomplished under the optimized conditions of variable temperature, initial concentration and contact time. 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) to give it a signature print before and after adsorption studies. The kinetics of interactions were tested with Zero-order kinetic model, first-order kinetic model, second-order kinetic model and pseudo-second-order kinetic model respectively with the best fits been first-order kinetic model ($R^2 = 0.9999$) and pseudo-second-order kinetic model ($R^2 = 0.9993$). The applicability of Langmuir, Freundlich and Temkin adsorption isotherm equations for the present system was also tested. The experimental data are fitted Langmuir, Freundlich and Temkin isotherm equations with correlation coefficient values of 0.9925, 0.9936 and 1 respectively. The kinetics of interactions were tested with Zero-order kinetic model, first-order kinetic model, second-order kinetic model and pseudo-second-order kinetic model respectively with the best fits been first-order kinetic model ($R^2 = 0.9999$) and pseudo-second-order kinetic model ($R^2 = 0.9993$). Thermodynamic parameters like ΔG° , ΔH° , ΔS° and ΔH_x were calculated. The results shows an endothermic, favourable and feasible adsorption system.

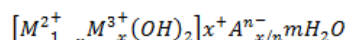
Keywords: Layered double hydroxides, Kinetic, Dye, Adsorption, isotherms, Congo Red, thermodynamics.

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Introduction

The layered double hydroxide (LDH) is also known as hydrotalcite-like material or anionic clay, are the large group of natural or synthetic materials that are layered, containing the hydroxide of two or more different kinds of metal cations and possessing an overall positive charge, which neutralized by the incorporation of exchangeable anion¹. In addition, the spent adsorbent can be easily regenerated and its adsorption capacities are comparable with the fresh LDH adsorbents^{2,3}.

Layered double hydroxides have the general formula given below⁴⁻⁶:



where M^{2+} represents divalent cations (Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+}), M^{3+} represents trivalent cations (Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Mn^{3+}) represents

inorganic or organic anions (Cl^{3+} , NO_3^- , $ClO_{1/1}^-$, CO_3^{2-} , SO_4^{2-}), m is the number of interlayer water and X ($=M^{2+}/(M^{2+}+M^{3+})$) is the layer charge density of LDH.

LDHs have anionic exchange capacity and the ability to capture organic and inorganic anions make them almost unique in multiple applications⁷⁻¹¹.

It is estimated that approximately 40,000 tones of dyes out of roughly 450,000 tones in total production are not used but discharged into wastewaters. A large variety of dyestuffs is available under the categories of acid, basic, reactive, direct, disperse, sulphur and metallic dyes¹². Dyes are synthetic aromatic compounds, which have various functional groups¹³. Some dyes and their degradation products may be carcinogens and toxic, and consequently their treatment cannot depend on biodegradation alone¹⁴⁻¹⁷. Therefore, extensive research has been conducted to find an effective and efficient alternative for the removal of dyes.

Adsorption is an efficient and economical method for removing dyes from industrial effluents. In this process, a substance (soluble dye) from liquid phase (wastewater) is transferred to the surface of a solid, highly porous material (adsorbent), to which it binds physically or chemically¹⁸. Most wastewater effluents usually contain pollutants with either positive or negative charge. The LDH anion exchange ability, large surface area and regeneration ability ensure that this adsorbent can be excellently utilized in wastewater purification¹⁹. Therefore, layered double hydroxide was selected in our work to optimize the removal of congo red from aqueous solution. This work aims to replicate clay like materials in a laboratory condition, optimize process conditions for the removal of dyes in aqueous solutions.

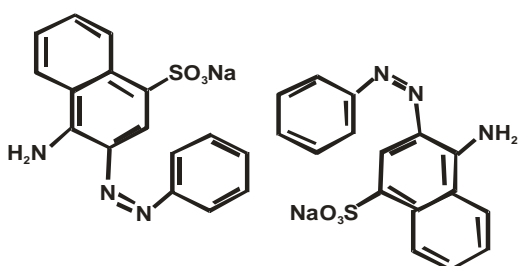


Figure 1: Molecular Formula of Congo Red

Material and Methods

Synthesis of Zn/Fe-CO₃

Carbonate form of Zn-Al LDH was synthesized by co-precipitation method. A 50 ml aqueous solution containing 0.3 M Zn (NO₃)₂·6H₂O and 0.1 Fe (NO₃)₃·9H₂O with Zn/Al ratios 2:1, was added drop wise into a 50 ml mixed solution of (NaOH (2M) + Na₂CO₃ (1M) with vigorous stirring and maintaining a pH of greater than 10 at room temperature. After complete addition which last between 2 hours 30 minutes to 3 hours, the slurry formed was aged at 60°C for 18 hours. The products were centrifuged at 5000 rpm for 5 minutes, with distilled water 3-4 times and dried by freeze drying.

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 by measuring the absorbance of different known concentrations of CR solutions at λ_{max} =497 nm using a UV-vis spectrophotometer (Shimadzu, Kyoto, Japan).

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 α radiation (λ = 1.54 Å) 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 θ / 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⁻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.

Experimental Procedure

The batch adsorption experiments were performed with 0.2g of adsorbent and carefully done to acquire good results.

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° C.

The results of Congo Red adsorbed on layered double hydroxide were quantified by mass balance. To test the system at equilibrium, the following parameters were used: adsorption capacity of the layered double hydroxide (q_{eq}) expressed in terms of dye amount adsorbed on the unitary sorbent mass (mmol/g), i.e. ([Congo Red]_{uptake}); and sorption efficiency of the system (R%) indicated from the percentage of removed dye relative to the initial amount, i.e. [Congo Red]%. These parameters have been calculated as indicated in the equations 1 and 2 below:

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

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

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).

Adsorption Isotherms analysis

The uptake of congo red by the LDH at different concentrations was analyzed by the linearized forms of the Langmuir and Freundlich and Temkin isotherms equations.

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

$$\frac{1}{q_{\text{eq}}} = \frac{1}{K_1 q_{\text{max}} C_{\text{eq}}} + \frac{1}{q_{\text{eq}}} \quad (3)$$

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

$$S_f = \frac{1}{1 + a C_0} \quad (4)$$

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).

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

$$\ln q_{\text{eq}} = \ln K_f + \frac{1}{n} \ln C_{\text{eq}} \quad (5)$$

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. The linear form of the Temkins isotherm model equation is given in (6).

$$q_e = B \ln A + B \ln C_e \quad (6)$$

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.

Kinetic Parameters

The experimental data were further subjected to certain kinetic parameters.

Zero-order kinetic model,

$$q_t = q_0 + K_0 t \quad (7)$$

First-Order Kinetic model,

$$\ln q_t = \ln q_0 + K_1 t \quad (8)$$

Second-Order Kinetic model,

$$\frac{t}{q_t} = \frac{t}{q_0} + K_2 t \quad (9)$$

Third-order kinetic model

$$\frac{1}{q_t^2} = \frac{1}{q_0^2} + K_3 t \quad (10)$$

Pseudo-second order model

$$\frac{t}{q_t} = \frac{1}{h_0} + \frac{1}{q_e t} \quad (11)$$

Thermodynamic parameters

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

$$\Delta G^\circ = -RT \ln K_d \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (13)$$

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 ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows:

$$\theta = \left[1 - \frac{C_e}{C_i} \right] \text{ or } \frac{C_e}{C_i} = 1 - \theta \quad (14)$$

$$S^* = (1 - \theta) e^{-\frac{E_a}{RT}} \quad (15)$$

$$\ln S^* = \ln(1 - \theta) - \frac{E_a}{RT} \quad (16)$$

$$\ln(1 - \theta) = \ln S^* + \frac{E_a}{RT} \quad (17)$$

The differential isosteric heat of adsorption (ΔH_x) at constant surface coverage was calculated using the Clausius-Clapeyron equation¹⁸:

$$\frac{d \ln(C_{\text{eq}})}{dT} = -\frac{\Delta H_x}{RT^2} \quad (18)$$

Integration gives the following equation¹⁷:

$$\ln(C_{\text{eq}}) = \frac{\Delta H_x}{R} \frac{1}{T} + k \quad (19)$$

where K is a constant. The differential isosteric heat of adsorption was calculated from the slope of the plot of $\ln(C_{\text{eq}})$ 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 temperatures⁸.

Results and Discussion
Characterization of LDH

SEM

Figures 2 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.

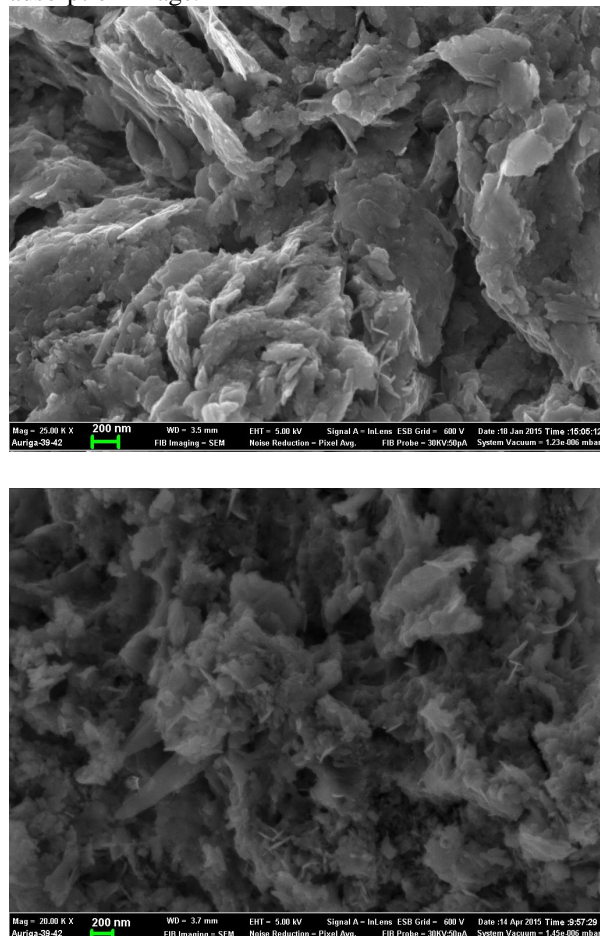


Figure 2: Scanning Electron Microscope (SEM) micrograph of Zn/Fe-CO₃ before (a) and after (b) adsorption studies

FT-IR

Figure 3 shows the pre and post FT-IR spectra of Zn/Fe-LHD. The strong bond around 3400 cm⁻¹ as shown in 3(a) is 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 cm⁻¹ was assigned to the bending vibration of the interlayer water molecules. The carbonate ion peak is around 1400cm⁻¹ which is consistent with layered double hydroxides. The low wave number region of <1000cm⁻¹, the lattice vibration

modes of the layered double hydroxides sheets such as M-O is assigned between 840 - 550 cm⁻¹. New peaks around 1100cm⁻¹ - 1200 cm⁻¹, 650 cm⁻¹ - 900 cm⁻¹ are consistent with symmetric stretching and asymmetric stretching of phosphate and wagging bending vibration of primary amines which are the precursor functional groups present in congo red^{20,21}.

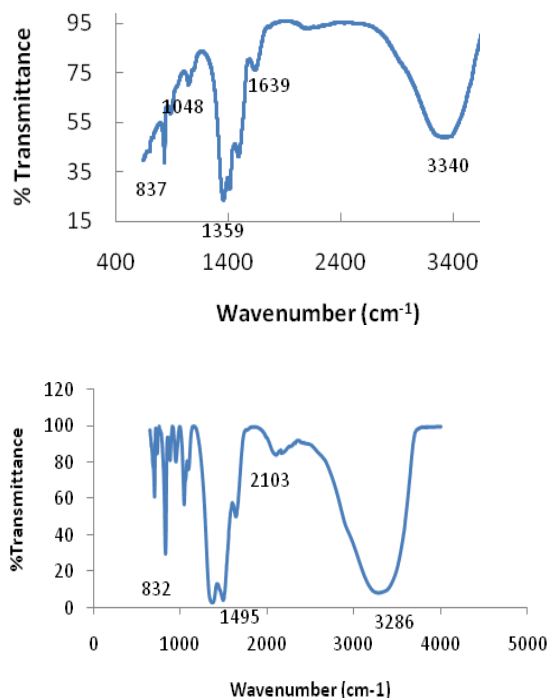


Figure 3: Zn/Fe-CO₃ Fourier transform infrared spectroscopy, before (a) and after (b) adsorption studies

XRD

Figure 4 shows the XRD patterns of the Zn/Fe. XRD patterns of Zn-Fe-CO₃-LDH prepared at different Zn²⁺/Fe³⁺ molar ratios.

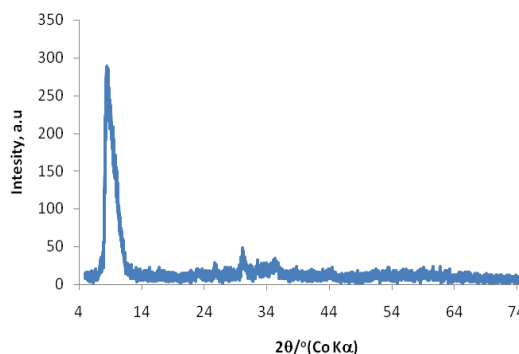


Figure 4: Zn/Fe-CO₃ X-ray powder diffraction

XRD patterns exhibit two characteristic intense peaks of basal reflection of Zn-Fe-CO₃-LDH which were located near 2θ of 8.46° and 30.14° 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.

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 (47.5%, 46.7% and 43%) respectively, this is probably due to rapid adsorption at all available sites and relatively small amount of adsorbent that was used.

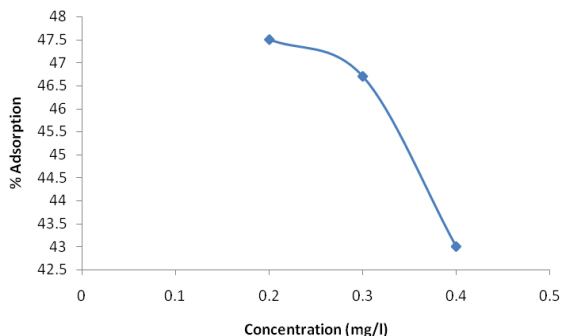


Figure 5: Effect of Concentration on adsorption of Congo Red onto layered double hydroxide

Isotherm Analysis

The Langmuir plot in figure 6 fitted the experimental data with $R^2 = 0.9925$ and therefore, confirm monolayer coverage.

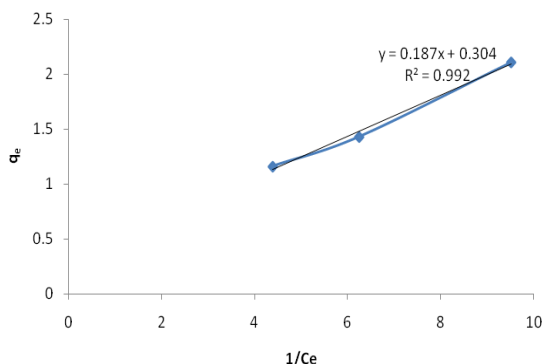


Figure 6: Langmuir Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide

For a Langmuir type adsorption process, the isotherm shape can be classified by a dimensionless constant separation factor (R_L), given by Eq. (4). The calculated value of R_L from figure 5 is 0.8022, which is within the range of 0–1, thus confirms the favourable uptake of the layered double hydroxide adsorption process.

The adsorption capacity of the layered double hydroxide was extrapolated from the slope of the plot of Freundlich to be 0.92 in figure 7.

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.

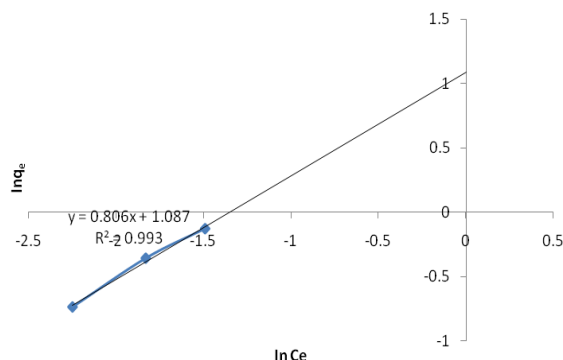


Figure 7: Freundlich Isotherm plot for adsorption of Congo Red onto Layered Double Hydroxide

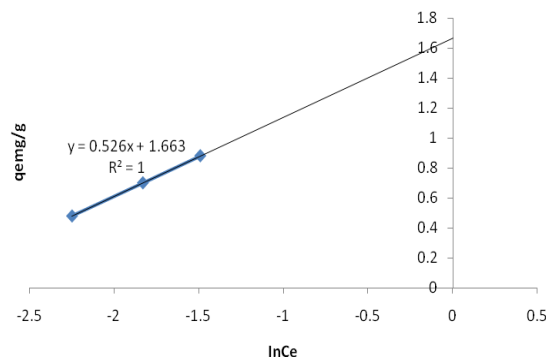


Figure 8: Temkin Isotherm Model plot for adsorption of Congo Red onto Layered Double Hydroxide

The Temkin isotherm derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. From the plot in figure 8, the following values were estimated: $A = 1.372 \text{ L/g}$, $B = 1.6637 \text{ J/mol}$ which is an indication of the heat of sorption, indicating a physical adsorption predominated process and the $R^2 = 1$.

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	1.0875
	R^2	0.9936
Langmuir	K_L , mg/l	0.8022
	R^2	0.9925
Temkin	A	1.6637
	b	1.36×10^3
	B	1.6637
	R^2	1

Effect of Temperature

As shown in figure 9 adsorption was lowest at 313K (53%), and increased slightly to 333K (55.5%) and 353K (57%). This means that adsorption capacity increase with higher temperature.

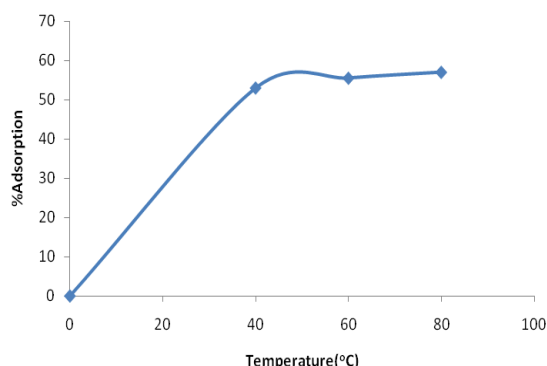


Figure 9: Effect of Temperature on adsorption of Congo Red onto layered double hydroxide

The values of the enthalpy change (ΔH°) and entropy change ΔS° were calculated from equation 15 to be 3.665KJ/mol and 12.8J/molK respectively, as shown in figure 10. A positive ΔH° suggests that sorption proceeded favourably at a higher temperature and the sorption mechanism was endothermic. A positive value of ΔS° (12.8J/molK) reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value of ΔS° 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^{5,8}, thus allowing for the prevalence of randomness in the system. The positive ΔS° value also corresponds to an increase in the degree of freedom of the adsorbed species.

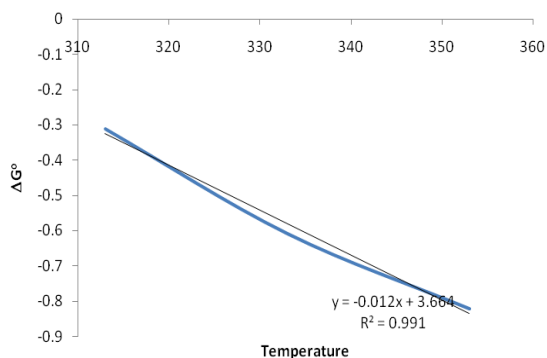


Figure 10: Plot of ΔG° vs. Temperature for the adsorption of Congo Red onto layered double hydroxide

Isosteric heat of adsorption ΔH_x , an essential characteristic for design purposes is calculated from the slope of the plots of $\ln C_e$ against $1/T$ as shown in

figure 11. The value of ΔH_x derived from equation 21 was 40.285KJ/mol which indicates that adsorption mechanism was physical adsorption and in a heterogeneous surface^{8,11}.

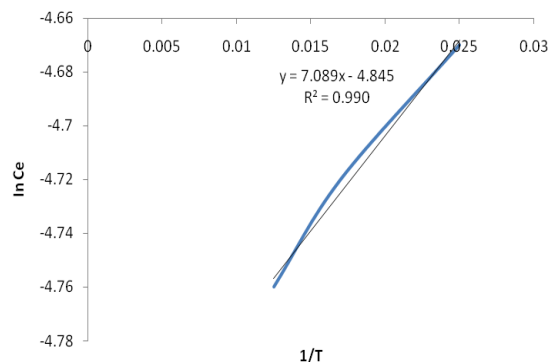


Figure 11: Plot of $\ln C_e$ vs. $1/T$ for the adsorption of Congo Red onto layered double hydroxide

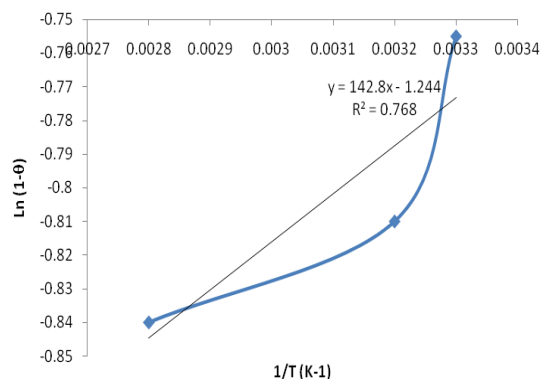


Figure 12: Plot of $\ln(1-\theta)$ vs. $1/T(K^{-1})$ for the adsorption of Congo Red onto layered double hydroxide

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

T, K	ΔG° , KJ/mol	ΔH° , KJ/mol	ΔS° , J/mol K	E_a KJ/mol	ΔH_x J/mol K
313	-0.312	3.665	12.8	-10.3	40.285
333	-0.609				
353	-0.822				

From the plot of $\ln(1-\theta)$ vs $1/T$, the values of activation energy and the sticking probability were calculated as shown in figure 12. The value of activation energy shows that the sorption process was predominantly physical (< 4.2 KJ/mol) [7]. The sticking probability S^* also indicates favourable sticking – physic-sorption.

Kinetic Study

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 64mg CR/L at three different times (10, 20 and 30 minutes) is presented in Figure 13.

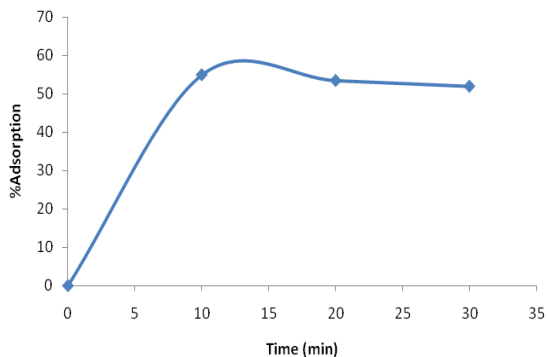


Figure 13: Effect of Contact Time on adsorption of Congo Red onto layered double hydroxide

The result shows that adsorption was highest at 10 minutes, thereafter, a gradual decrease occurred (10=55%, 20=53.5% and 30=52%).

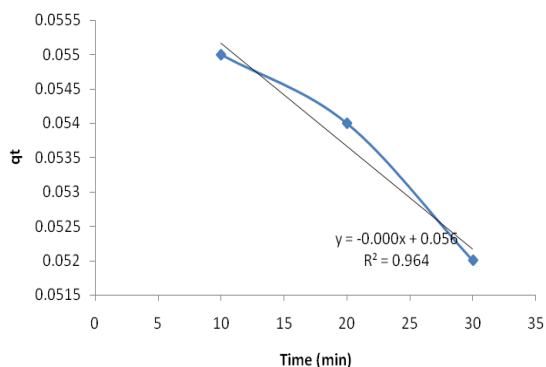


Figure 14: Plot of qt vs. t for the adsorption of Congo Red onto layered double hydroxide

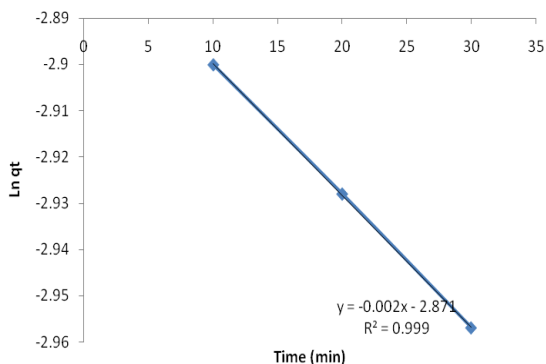


Figure 15: Plot of 1/qt vs. t for the adsorption of Congo Red onto layered double hydroxide

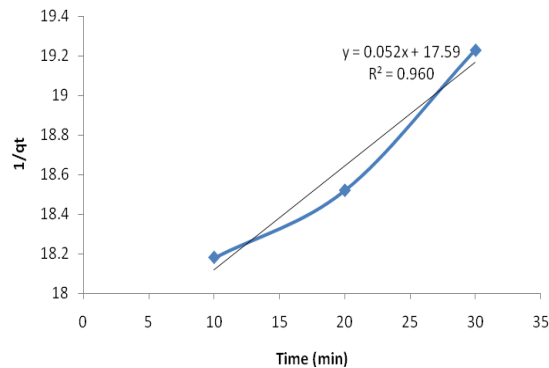


Figure 16: Plot of 1/qt vs. t for the adsorption of Congo Red onto layered double hydroxide

The experimental data were fitted into different kinetic models including (figures 14 - 18) 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^{5,11}. The correlation coefficient values of 0.9643, 0.9999, 0.9603, 0.9993 and 0.9564 respectively confirm the applicability of the above models.

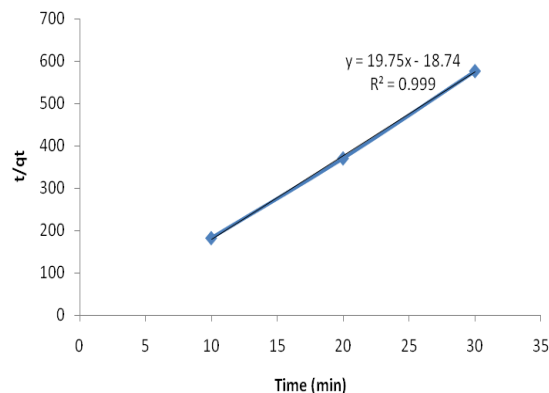


Figure 17: Plot of t/qt vs. t for the adsorption of Congo Red onto layered double hydroxide

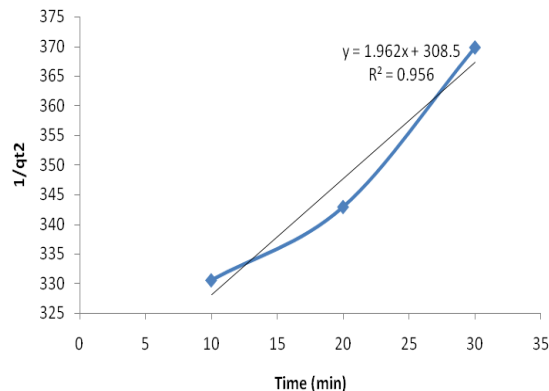


Figure 18: Plot of 1/qt^2 vs. t for the adsorption of Congo Red onto layered double hydroxide

Conclusion

The degradation of Congo Red dye from aqueous solution was possible using Zn/Fe-CO₃ layered double hydroxide. It was seen that the overall adsorption process was dependent on temperature. The Langmuir, Freundlich and Temkin isotherms models provided the best fits to predict the adsorption for the removal of Congo Red dye onto the layered double hydroxide while first-order kinetic and pseudo-second-order kinetic models provided the best fit to determine the adsorption kinetics of the reaction systems. Thermodynamic study showed that the adsorption process was spontaneous and endothermic because ΔG° values were negative and ΔH° value positive. To maximize the degradation of the Congo Red dye, varying system conditions like temperature and amount of adsorbent could further enhance the adsorption process.

References

- Oh J.M., Biswick T.T. and Choy J.H., Layered material for green materials, *J. Mater. Chem.*, **19**: 2553-2563 (2009)
- Marangoni R., Bouhent M., Gueho C.T., Wypych F. and Leroux F., Zn₂Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: A physico-chemical characterization, *Journal of Colloid and Interface Science*, **333**: 120–127 (2009)
- Zhang P., Qian G., Shi H., Ruan X., Yang J. and Frost R.L., Mechanism of interaction of hydrocalumites (Ca/Al-LDH) with methyl orange and acidic scarlet GR, *Journal of Colloid and Interface Science*, **365**: 110–116 (2012)
- Hamzah Z., Rahman M. N. Ab, Yasin Y., Sumari S.M. and Ahmad S., Removal Of Copper From Aqueous Solution By Adsorption Using Magnesium Aluminium Hydrogenphosphate Layered Double Hydroxides, *Journal of Nuclear and Related Technologies*, **8(2)**: 60-67 (2011)
- Ayawei N., Ekubo A.T., Wankasi D., and Dikio E.D., Adsorption Dynamics of Copper Adsorption by Zn/Al-CO₃, *IJACSA*, **3(1)**: 57-64 (2015)
- Xuefeng L., Wanguo H., Yingming X., Guohong S., Lin W., Yang S. and Xu Q., Sorption of lead ion by layered double hydroxide intercalated with diethylenetriaminepentaacetic acid, *Colloids and surface a: physicochemical and engineering aspects*, **366**: 50-57 (2010)
- 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*, **3(1)**: 1-17 (2015)
- 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*, **7(1)**: 122 – 132 (2015)
- Hu Q., Xu Z., Qiao S., Haghseresht F., Wilson M. and Lu G.Q., A novel color removal adsorbent from heterocoagulation of cationic and anionic clays, *Journal of Colloid Interface Science*, **308**: 191–199 (2007)
- Mehdi R. and Mehdi V. , Langmuir, Freundlich and Temkin Adsorption Isotherms of Propranolol on Multi-Wall Carbon Nanotube, *Journal of Modern drug discovery and drug delivery research*, 1-3 (2014)
- 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*, **3(2)**: 207-217 (2015)
- Marangoni R., Bouhent M., Gueho C.T., Wypych F. and Leroux F., Zn₂Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: A physico-chemical characterization, *Journal of Colloid and Interface Science*, **333**, 120–127 (2009)
- Borisover M., Graber E., Bercovich F. and Gerstl Z., Suitability of dye–clay complexes for removal of non-ionic organic compounds from aqueous solutions, *Chemosphere*, **44**, 1033–1040 (2001)
- Marsh H. and Rodríguez-Reinoso F., *Activated carbon*, 1st edition, Amsterdam: Elsevier. (2006)
- Noroozi B., Sorial G. A., Bahrami H. and Arami M., Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent- Silkworm pupa, *J. Haz. Mater.*, **B139**, 167–174 (2007)
- Reife A., Dyes, environmental chemistry. In Kirk-Othmer (Ed.). *Encyclopedia of chemical technology*. Washington: John Wiley & Sons, 753 (1993)
- Pagga U. and Braun D., The degradation of dye stuffs: part II. Behaviour of dyestuffs in aerobic biodegradation tests, *Chemosphere*, **154**: 79–489 (1986)

18. Zaharia C., and Suteu D., Coal fly ash as adsorptive material for treatment of a real textile effluent: operating parameters and treatment efficiency, *Environ. Sci. Pollut. Res. Int.* **20(4)**: 2226-2235 (2013)
19. Yasin Y., Abdul Malek A.H. and Sumari S.M., Adsorption of eriochrome black dye from aqueous solution onto anionic layered double hydroxides, *Oriental Journal of Chemistry*, **26(4)**: 1293-1298 (2010)
20. Ahmet G., Synthesis and characterization of hybrid congo red from chloro-functionalized silsesquioxanes, *Turk. J.Chem.*, **34**: 437-445 (2009)
21. Flavio A.P., Silvio L.P.D., Ede C.L., Edilson V.B., Removal of Congo red from aqueous solution by anilinepropylsilica xerogel", *Dyes and Pigments*, **76**: 64 – 69 (2008).