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Synthesis, Characterization and Isothermal Studies of Mg-Fe Layered Hydroxide with Bentonite Clay for the Removal of Alizarin Blue Dye from Aqueous Solution

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This research aimed to prepare and characterize Mg-Fe layered Hydroxide clay for removal of alizarin blue dye from aqueous media using batch adsorption technique. The Mg-Fe layered Hydroxide prepared was characterized by SEM, FT-IR and XRD before and after adsorption. The result obtained from SEM shows a large surface area before and a rough and filled surface after adsorption. The presence of OH, C=O and N-CH stretching at 3644 cm⁻¹, 1771 cm⁻¹ and 2884 cm⁻¹ respectively was analyzed by FT-IR. It was verified that the crystalline structure was not altered during the pillaring process as evidenced by XRD. Various parameters such as initial dye concentration (10 – 50 mg/l), contact time (10 – 50 mins), adsorbent dose (0.1 – 0.5 g) and Temperature (30 – 70 °C) were investigated. The experiments showed the following results; dye concentration decreased from 95.70% - 72.6%, contact time increased from 87.70% - 98.0% and adsorbent dose showed 87.7% - 92.3% removal respectively. The Adsorption isotherms of Freundlich, Langmuir, Temkin and Harkin's-Jura Isotherms were used to observe the adsorption condition. Freundlich adsorption Isotherm fitted best with maximum removal of 6.97 mg/g and R² value of 0.999. In this work, Mg-Fe layered hydroxide with bentonite clay which is low cost became effective adsorbent for the removal of Alizarin blue dye.

Keywords: Mg-Fe layered Hydroxide, Synthesis, Characterization, Adsorption, Alizarin blue.

1. Introduction

Several conventional treatment methods such as chemical precipitation, ultra-filtration, electrolysis etc have been developed for the removal of heavy metals, dyes and other organic pollutants (Abdullahi and Audu, 2017). Dyes are widely used by several industries like plastics, textile and paper, to color their final products. The use and discharge of synthetic dyes from these industries is an environmental health concern specially to developing countries (Ying *et al.*, 2014). The presence of dyes in industrial influent possess a great threat to the environment. It interferes with the normal photo synthetic activities of aquatic life by decreasing light penetration for photosynthesis and gas dissolution in lakes, rivers and other water bodies. Most of these dyes have been shown to cause allergy dermatitis, skin irritation and intestinal cancer to humans. Without adequate treatment these dyes are persistent in the environment and henceforth serious threat to

survival of both terrestrial and aquatic eco system (Ahmad and Kumar, 2010). Therefore, the elimination of dyes from waste water is one of the most important environmental problems for research (Fu *et al.*, 2011). Various techniques have been developed for removal of dyes from waste water, among which adsorption is the most efficient. Different adsorbents were tested for removal of dyes, such as agricultural waste, activated carbon among others. In recent studies, there is growing interest in the removal of heavy metals and dyes by adsorption method using locally sourced natural materials prepared as adsorbents. Some of the materials include chitosan-clay composite, walnut shell. Kaolinite and montmorillonite and palm kernel shell charcoal (Oyedoh and Ekwonu, 2016). The method of adsorption for dyes removal is very useful due to the cost effectiveness, availability of naturally sourced materials and efficiency in the treatment of high strength industrial waste

water with quality effluent. Recently, bentonite clay is being considered to be a novel low-cost adsorbent and has proven its efficiency in removing heavy metals and dyes (Gueye *et al.*, 2014). The important modifications recorded are the exchange of interlayer cations by organic or inorganic moiety, acid treatment, supporting active species on clay surface for catalysis, pillaring by inorganic poly-cations, and preparation of clay-polymer nano composite materials (Mishra and Mahato, 2016).

In this work, Mg-Fe layered hydroxide with bentonite clay was synthesized for the removal of alizarin blue dye. This adsorbent is easily available and economically favorable.

2. Materials and Methods

2.1 Preparation of Adsorbent

The Mg-pillared clay was prepared by dissolving 5% of the clay suspension in water, the solution was then mixed with the pillaring solution to provide 20meq of Mg³⁺/g of the clay. The beaker containing the solutions mixture was placed in an ultrasonic bath at ambient temperature (300 K/27 °C) for 20 min. The product was centrifuged at 4500 rpm for 5 minutes and was washed with distilled water 5 times until the filtrate was free of chloride ions. This was tested using silver nitrate (AgNO₃ test). The resulting residue was dried in an oven at 60 °C for 4hours. The dried pillared bentonite clay was grounded in to fine powder using mortar and pestle to about more than 40 mesh size. The intercalated sample was calcined in a furnace at 500 °C for 6 hours (Palinko *et al.*, 1997).

2.2 Fe Doping

The Mg-pillared clay was doped with Fe (III) according to a method adopted from Palinko *et al.* 1997) by dissolving 4 g of the calcined layered clay in 20 cm³ of 20% FeCl₃ solution. It was ultrasonicated at 30 °C for 5 min, and then dried in an oven at 60 °C for 24 hours, after which it was grounded and calcined again in a furnace at 500 °C for 6 hours.

2.3 Preparation of Adsorbate

Alizarin blue dye (1.0 g) was taken in 1000 ml measuring flask and dissolved in distilled water, making volume up to the mark. This was 1000 ppm stock solution of dye. Standard solution of the dye was prepared by successive dilution of stock solution. 1000 ppm stock solution was prepared by dissolving 1.0 g of alizarin dye in 1000 ppm volumetric flask and serial dilution was conducted using the relation;

$$C_1V_1 = C_2V_2$$

Where

C₁ = Initial dye concentration

C₂ = Final dye concentration

V₁ = Initial volume of dye

V₂ = Final volume of dye

2.4 Batch Adsorption

Experiment on adsorption of alizarin blue on Mg-Fe layered hydroxide bentonite clay was carried out by batch adsorption on accordance to the procedure reported by Ibrahim and Ahmad (2017). The influence of various parameters such as initial dye concentration (10 - 50 mg/l), Contact time (10 – 50 mins), temperature (30 – 70°C), adsorbent dose (0.1 – 0.5 g) were studied at constant agitation speed of 100rpm in triplicate.

2.5 Fourier Transform Infrared Spectroscopy (FT-IR)

The spectra of Mg-Fe layered hydroxide were recorded on a carry 630 FT- IR Agilent spectrometer. All spectra (32 scans at 8.0 cm⁻¹ resolution) were recorded at a range 4000 – 650 cm⁻¹.

2.6 Scanning Electron Microscopy (SEM)

SEM was conducted in order to investigate the surface morphology of Mg-Fe layered hydroxide before and after adsorption. The samples were analyzed using the microscopic operated at an accelerated voltage of 15kv and 500 magnifications.

2.7 X- Ray Diffraction (XRD)

The crystallinity of the Mg-Fe layered hydroxide bentonite clay was analyzed on a Bruncker X-ray diffractometer and the intensity at 2θ angle, XRD analyses were conducted using powdered samples. The diffraction patterns were recorded on a Thermo scientific Switzerland with model number 197492086 ARL X'TRA X- ray diffractometer, using Ni-filtered Cu Ka radiation (k =1.5405 Å⁰) and scintillation counter at 40 V and Ma at ambient temperature. All the samples were scanned for 2hours at a diffraction angle ranging from 0 to 120. The powdered sample with uniform surfaces were exposed to X- rays and the scattering angles of the diffracted X- rays with respect to the angle of the incident beam were measured.

3. Results and Discussion

3.1 Fourier Transform infrared (FT-IR)

The FT-IR Spectra of Mg-Fe layered Hydroxide in Figure 1 showed Hydroxyl absorption band at

3644 cm^{-1} . Another absorption band with an unsaturated function at 1771 cm^{-1} correspond to C=O, while N-CH peaks was shown at 2884 cm^{-1} .

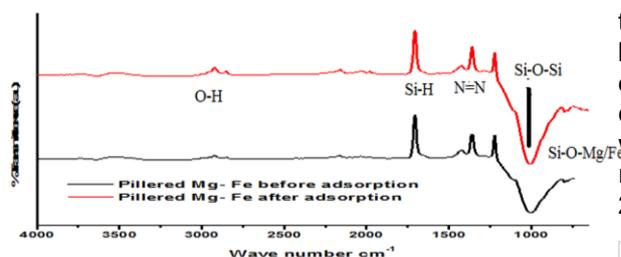


Figure 1. FT-IR Spectra of Mg-Fe layered Hydroxide

3.2 Effect of initial Dye Concentration

Figure 2 show that adsorption capacity decreases from 95.7%-72.6% as dye concentration increases from 10 to 50 mg/l. the trend is that of the result of the progressive decreases in the electrostatic interaction between the alizarin blue dye and the adsorbent active sites. Moreover, this can be explained by the fact that less adsorption site was being covered as the dye concentration decreases. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively large number of adsorbing species at lower concentration. The experimental results of adsorption of alizarin blue dye on Mg-Fe layered hydroxide at various initial concentrations was shown in figure 2. Its reveals that, the actual amount of dye absorbed per unit mass of Mg-Fe layered hydroxide decreases with increase in dye concentration. Adsorption is maximum when the initial concentration of Alizarin blue dye was 10 mg/l. as the concentration increases, all the adsorption sites are being filled up and there remains unadsorbed dye, hence the decrease in percentage adsorption. This result is in favour of only monolayer coverage and suggests the application of the Langmuir isotherm model. Since 95.7% adsorption occurs when the initial concentration was 10 mg/l, Mg-Fe layered hydroxide appears to be very effective adsorbent in removing dye (Lakshmi *et al.*, 2015).

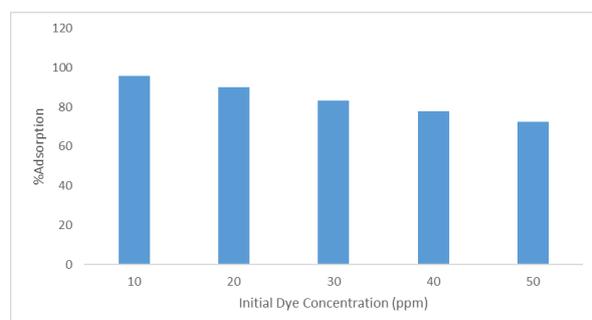


Figure 2: Effect of initial dye concentration

3.3 Effect of Contact time

The contact time has a vital role in adsorption studies, it helps in determining the maximum time required for the removal of alizarin blue dye by Mg-Fe layered hydroxide. It has been observed that, the adsorption increases as the contact time increases, the maximum adsorption was 98% at 50 min and 87.7% at 10 min. this result was in line with the work of (Rabia *et al.*, 2015).

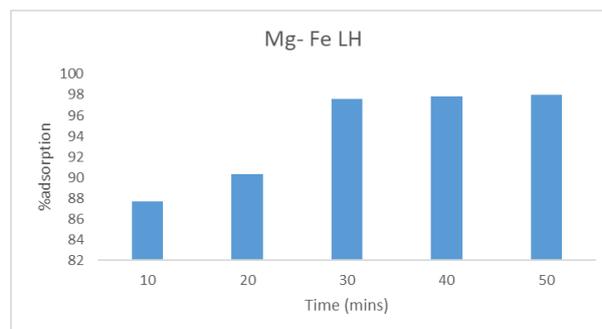


Figure 3: Effect of contact time

3.4 Effect of adsorbent dose

Adsorbent dose is an important factor in the determination of Dye uptake by adsorbent. It shows that, the percentage removal of alizarin yellow dye increases with increased in adsorbent dose. It has been observed that, amount of dye uptake increased from 87.7%-92.3% with 0.1g-0.5g dose of Mg-Fe layered Hydroxide adsorbent. This because of the availability of more space site for the adsorption to take place which is in line with the work of (Lakshmi *et al.*, 2015 and Rabia *et al.*, 2015).

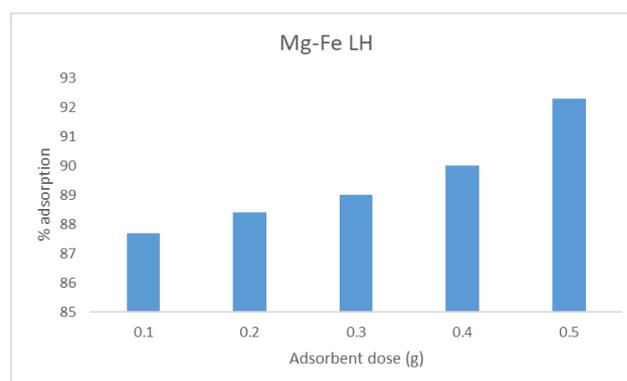


Figure 4: Effect of adsorbent Dose

3.5 Scanning Electron Microscopy (SEM)

Figure 5a and 5b show the SEM Micrograph of Mg-Fe layered Hydroxide before and after adsorption. It showed more tightly packed pattern pores before adsorption and a rough surface after adsorption.

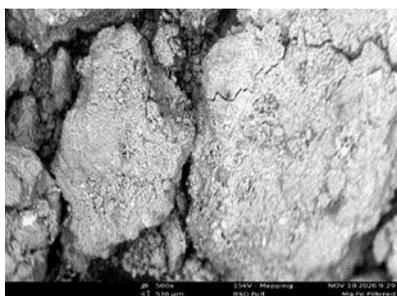


Figure 5a: SEM before adsorption

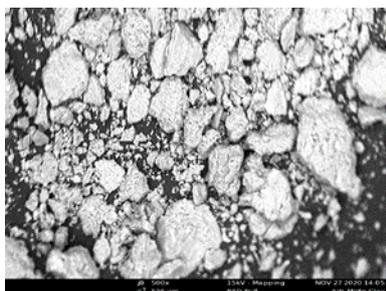


Figure 5b: SEM after adsorption

3.6 X-ray Diffraction Spectroscopy (XRD)

Figure 6a and 6b Showed XRD Studies of the adsorbent Mg-Fe layered hydroxide before and after adsorption of the dye which were carried out using Bruncker X- ray diffractometer 40 V/ 30 mA. The XRD result confirmed the pillaring was done successively by Mg-Fe layered hydroxide. Therefore, the diffraction reflection corresponding to Mg-Fe layered hydroxide, verifying that the crystalline structure was not altered after pillaring process. This observation was also in line with the work of Baloyi *et al.*, (2018).

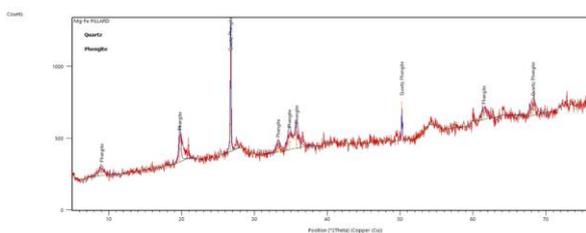


Figure 6a: Mg-Fe layered hydroxide before adsorption

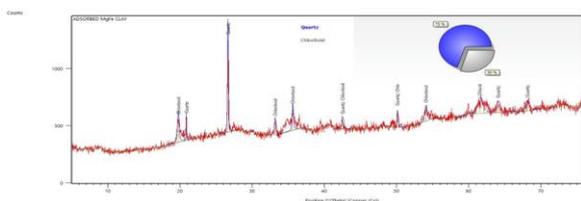


Figure 6b: Mg-Fe layered hydroxide after adsorption

3.7 Adsorption Isotherms

The Freundlich Isotherm assumes heterogeneous surface with a non-uniform distribution of adsorption and describes the

adsorption process as the ratio of the amount of solute adsorbed onto adsorbent to residual concentration is not the same at different concentration. It's in liner form is expressed by the following equation.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots 1.0$$

Where K_f and n are the Freundlich constant which predict the amount of dye adsorbed per gram of adsorbent at equilibrium concentration and strength of the adsorption process, respectively. It was well known that values between 0.1 and 1.0 indicate beneficitation of adsorption and also, high K_f values shows the excellent adsorption (Mahida and Patel, 2016).

The Langmuir model assumes that all the sites are identical, containing one molecule and are all energetic and sterical. The linear form of the Langmuir isotherm described by equation;

$$\frac{C_e}{q_e} = \frac{1}{K_I Q_m} + \frac{C_e}{q_e} \dots \dots \dots 1.1$$

Where q_e is the amount of the dye adsorbed(mg/g) toward hydrogels, q_m is the maximum adsorption capacity relating for Langmuir adsorption(mg/g), and C_e is the residual concentration of dyes at equilibrium (mg/L) and K_I is Langmuir adsorption constant (Abdel-Halim and Al- Hoqbani, 2015).

Temkin Isotherms and Harkin's-Jura Isotherm

The derivation of the Temkin isotherms assumes that the fall in the heat of sorption is linear than logarithmics, as implied in the Freundlich equation (Aharoni and Sparks, 1991). This isotherm contains a factor that explicitly takes into account of the adsorbent-adsorbate interactions. It based on the assumption that due to the adsorbate-adsorbate repulsion, the heat of the adsorption of all molecules in the layer decreases linearly with the coverage of molecules and the adsorption of adsorbate is uniformly distributed. (Temkin and Pyzhev, 1940). The model is given by the following equation (Temkin and Pyzhev, 1940):

$$Q_e = B \tau \ln (A \tau C_e) \dots \dots \dots 1.2$$

The linearized form of the equation is given as:

$$Q_e = B \ln A \tau + B \ln C_e \dots \dots \dots 1.3$$

B is further determined from expression as:

$$B = \frac{RT}{bT} \dots \dots \dots 1.4$$

Where $A \tau$ is the Temkin isotherm equilibrium binding constant (L/g), bT is the Tamkin isotherm constant, R is the universal gas constant (8.314j/mol/K), T is the temperature at 298K and B is the constant related to heat of adsorption (j/mol).

3.8 Harkin's-Jura Isotherm

The Harkin's-Jura adsorption isotherm account for multilayer adsorption and explains the existence of heterogenous pore distribution. The Harkin's-Jura adsorption isotherms is expressed in equation 1.10 (Samarghandiet al., 2009)

$$Q_e = \left(\frac{AHJ}{BHJ} + \log C_e \right)^{1/2} \dots \dots \dots 1.5$$

This equation can be linearized as follows:

$$\frac{1}{q_e^2} = \frac{BHJ}{AHJ} - \frac{1}{AHJ \log C_e} \dots \dots \dots 1.6$$

Where AHJ is the Harkin's-Jura isotherm parameter, BHJ is the isotherm constant. If the value of $1/q_e^2$ is plotted against $\log C_e$, a straight-line graph should be obtained (Suyamboo and Perumal, 2012).

Table 1: Adsorption Isotherms

Isotherm model	Parameters	RBC	Mg-FeHBC
Langmiur	qm (mg/g)	2500	0.002176
	K _L (l/mg)	104.846	0.0586
	R ²	0.9696	0.0586
Freundlich	K _f (mg/g)	13633269	679360
	n (g/l)	6.345178	1.021138
	R ²	0.2894	0.999
Temkin	B _T	6777.12	6460.17
	B (J/mol)	2.5	0.252
	A _T (L/g)	1.454	8.137
	R ²	1	0.981
Harkins-Jura	B _{HJ}	0.616	-0.099
	A _{HJ}	0.022	0.029
	R ²	0.0116	0.3941

4. Conclusion

Preparation of Mg-Fe layered hydroxide clay was successful. Adsorption of alizarin dye under the variation of initial dye concentration, contact time, adsorbent dose and temperature show interesting results. FT-IT result validate the preparation of the adsorbent and also, SEM and XRD analysis show clearly the difference in the surface morphology of the adsorbent before and after adsorption.

Conflict of interest

The authors declare no conflict of interest.

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