FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 4 No. 1, March, 2020, pp 210 – 217

PHOTODEGRADATION OF METHYL RED USING Cd-Al/C LAYERED DOUBLE HYDROXIDE CATALYST

Garzali, F. A. and Muhammad, A. S.

Department of Pure and Industrial Chemistry Bayero University Kano Nigeria

Email: asmuhammed.chm@buk.edu.ng Tel: 08186615765

ABSTRACT

This paper evaluate the degradation of Methyl Red using cadmium aluminum carbon (Cd-Al/C) catalyst under visible light irradiation. The catalyst was successfully prepared from cadmium fluoride (CdF_2), aluminium chloride ($AlCl_3$), and rice husks activated carbon, and then characterized by using X-ray Diffraction (XRD), Scaning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) techniques. The peaks at 23.4 and 35.5 in the XRD result confirmed the presences of LDH. The effect of contact time, catalyst dosage, pH and initial concentration, on the photodegradiation of Methyl Red were investigated. The experimental results showed that after 100 min visible light irradiation, the percentage degradation using 200 mg Cd-Al/C, pH 7 and 3 ppm Methyl Red concentration reached to 83.80%. For kinetics studies the data obtained were analyzed using pseudo first order and pseudo second order kinetic models. From the linear regression coefficient values the data were found to be best fitted to pseudo second order kinetics. The results revealed that the Cd-Al/C show good catalytic activity.

Keywords: Photodegradation, Layered Double Hydroxide (LDH) Cadnium fluoride, Aluminium Chloride and Methyl Red.

INTRODUCTION

Dye pollutants are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem (Martin *et al.,* 2003). Considering their high toxicity, wide prevalence and poor biodegradability, it is necessary to remove them from wastewaters before discharge into water bodies (Majewski, 2007). Unlike conventional biodegradation, adsorption and chemical treatment, advanced oxidation processes (photo catalysis) especially layered double hydroxide technology provided a powerful oxidation technique in the treatment of persistent organic pollutants by mineralizing into CO_2 and water (Parida and Mohapatra, 2012).

A number of researches have been carried out on photocatalytic degradation of dyes using layered double hydroxide catalysts. Shahid *et al.,* (2016) investigated the efficiency of Cd-Al/C and Cd-Sb/C layered double hydroxides in the decoloration and decomposition of organic dyes. Ayawei *et al.,* (2017) reported that the ability of Mg/Fe- CO_3 to degrade Congo red in aqueous solution was investigated under various experimental conditions. In this research, Cd-Al/C LDH was synthesized and explored its efficiency in the degradation of Methyl Red from aqueous solution.

Materials and Methods

All chemicals used in this research work were of analytical grade, and they include; Phosphoric acid (98% Sigma Aldrich), Cadmium Flouride (CdF_2) (Sigma Aldrich), Aluminum chloride ($AlCl_3$) (Sigma Aldrich), Ethanol (99%), Sodium hydroxide (NaOH) (99% Sigma Aldrich) and Hydrochloric Acid (HCl) (97% Sigma Aldrich).

Synthesis of the LDH catalyst

Cd-Al/C LDH catalyst was synthesized by mixing salts of Cadmium fluoride (CdF_2) and Aluminium chloride ($AlCl_3$) in double distilled water and then mixed with activated carbon through co-precipitation method (Khan *et al*., 2016). Briefly salt of $AlCl_3$ and CdF_2 were completely dissolved in double distilled water in 1:3 molar ratio. To this reaction mixture, 1g of activated carbon was added and well dispersed by continuous stirring with the help of magnetic stirrer. To this mixture freshly prepared 0.1 M NaOH solution was added and continuously monitored till pH 9. After this, the reaction mixture was placed on a hot plate for 6 hours at 60 °C with homogenous stirring. After completion of the reaction the surplus solution is removed and the precipitate was washed three times with C_2H_5OH : H_2O mixture (8:2). The resultant product was dried in an oven for overnight at 50 °C and store in clean tube for further characterization.

Characterization of LDH

The Cd-Al/C was characterized by using X-ray Diffaraction (XRD), Scanning electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR).

Photocatalytic experiment

In a typical experiment 100 mg of Cd-Al/C was dispersed in 100 cm^3 of dye solution having a concentration 3 ppm in a beaker. The resulting suspension was magnetically stirred for 25 minutes in the dark to obtained adsorption-desorption equilibrium to eliminate the error due to any initial adsorption effect. This was then irradiated using 500 W high-pressure Hg lamp of intensity 0.0129 w/m^2. A 5 cm^3 aliquot was taking at 25 minutes interval, centrifuged at 2000 rpm prior to absorbance measurement in order to eliminate error due to scattering.

The photocatalytic activity of Cd-Al/C-LDH was examined against the dye under visible light irradiation. The influence of operational parameters such as time, catalyst dosage, pH and concentration were investigated. The percentage removal efficiency R.E. (%) of catalyst was evaluated by using the following equation.

$$R.E.(\%) = \left(\frac{Co-Ct}{Co}\right) \times 100 = \left(\frac{Ao-At}{Ao}\right) \times 100$$

C_0 represents the initial concentration of the dye solution at time = 0, Ct is the concentration of dye solution after some time = t as indicated in equation. Similarly, A_0 represent the absorbance of the original concentration of the dye solution at time = 0 and At is the absorbance of dye solution during reaction progress after passing some time = t (Li *et al.*, 2008).

Results and Discussion

Characterization of the LDH catalyst

Cd-Al/C LDH was characterized using X-ray Diffraction (XRD), Scanning electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR).

X-ray Diffaraction (XRD) of Cd-Al/C LDH

The crystalline phase of the prepared samples was characterized by XRD analysis.

The XRD pattern of Cd-Al/C is as shown in figure (1).

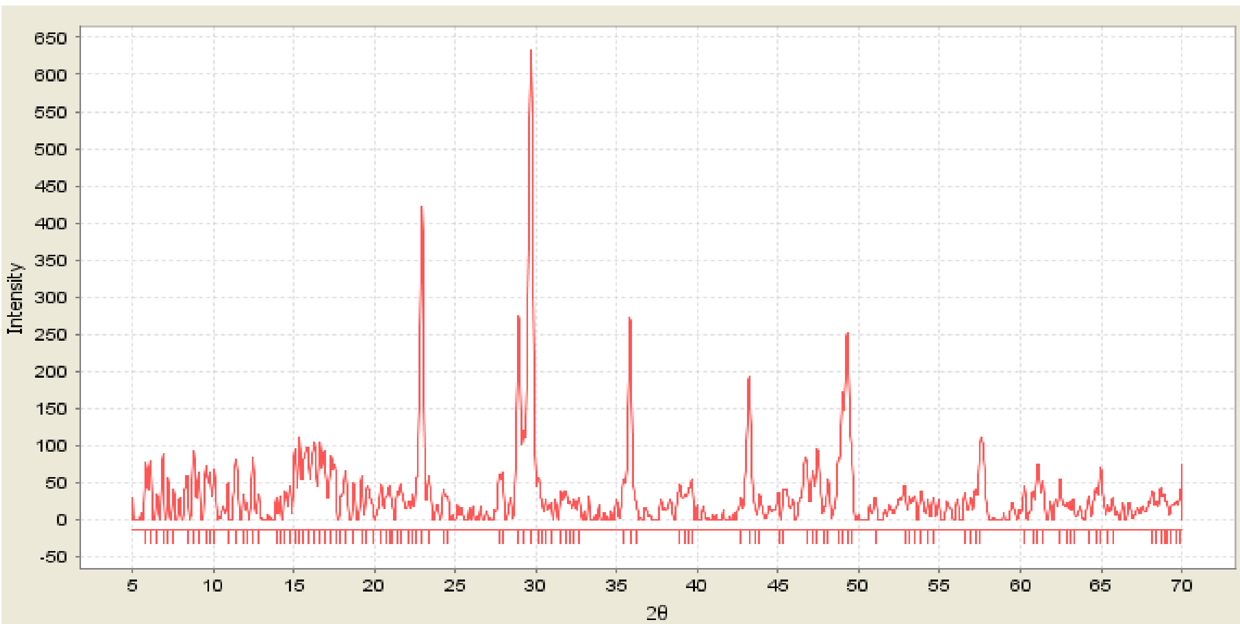

Fig. 1: XRD of Cd-Al/C LDH

The crystalline phases of the Synthesized Cd-Al/C LDH was characterized by XRD analysis. Figure 1 display the XRD patterns of the prepared Cd-Al/C LDH. The characteristic peak for Cd-Al/C appeared at 2θ = 23.4 (006) and 2θ = 35.5 (012) suggesting the formation of Cd-Al/C-LDH. The 006 corresponding to the basal reflection of the successive stacking of brucite like layers (El Gaini *et al.*, 2009). The strong diffraction peaks at low angle due to basal planes (006) were sharp and symmetric compared to the peaks at high angle, which are characteristic of clay minerals having a layered structure (Parida *et al.*, 2006). From figure 1, It can be observed that strong signals in 2θ range 2-30°. These peaks indicate that the prepared LDHs are characterized by high crystalinity and consistent to great extent, with the peaks of hydrotalcite structure (Ren *et al*., 2007).

Powder X-rays diffraction (XRD) patterns were recorded with a Thermo scientific XRD machine of model ARL X" TRA with X-ray diffractometer. The intensities were obtained in the 2θ ranges between 20° and 70°. The FULPROF software was used for data handling. FULPROF software allowed estimating the average size of the crystallites. Refinement was performed on the diffraction patterns to determine the crystallite size and relative abundance of phases.

The average crystallite sizes of particles were estimated by the Scherer's formula as shown

$$D = 0.89\lambda / \beta\cos\theta$$

Where D is the crystallite size, λ is the X-ray wavelength, β is the broadening of the diffraction peak and θ is the diffraction angle for maximum peak. The D value of Cd-Al/C is 101 nm

Scanning Electron Microscopy (SEM) of Cd-Al/C

Scanning Electron Microscopy give further insight into the morphology of the Cd-Al/C LDH. The surfaces morphology of Cd-Al/C LDH is as shown in figure (2).

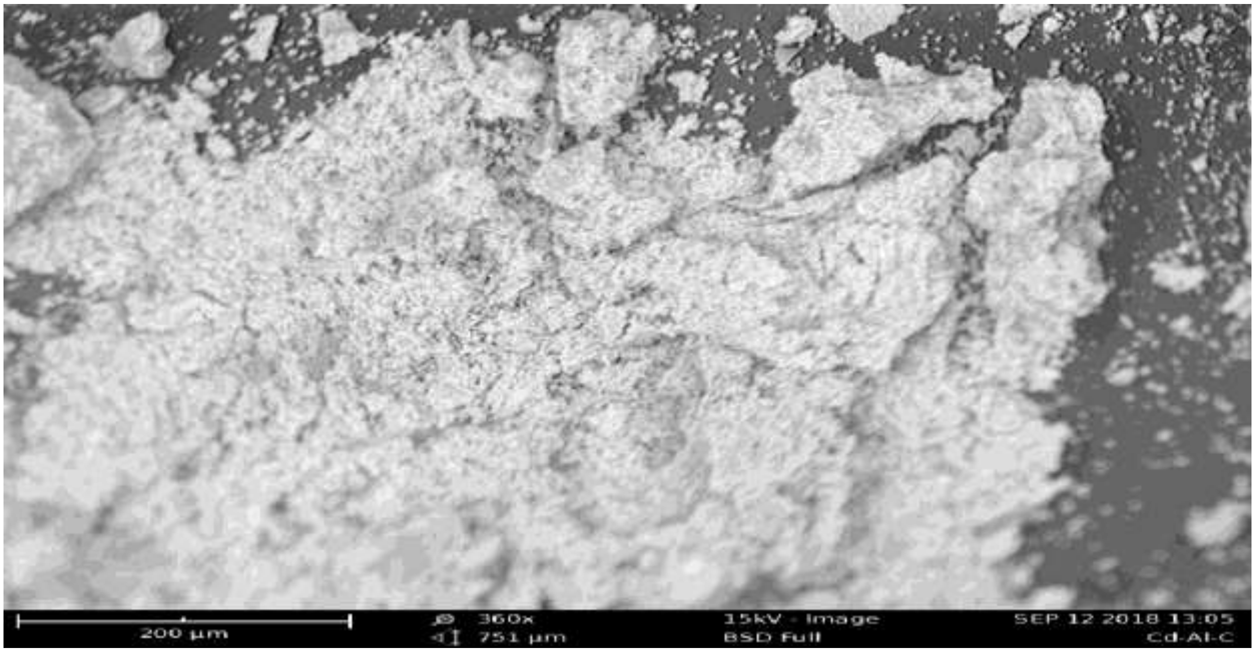

Fig. 2 SEM image of Cd-Al/C LDH.

Figure 2 shows the of SEM image for Cd-Al/C LDH. The SEM image shows the sheet morphology of Cd-Al/C, which indicate the agglomerated grains are not uniform. The agglomerated pattern is evidence in the formation of LDHs and the morphology of the LDHs are in line with report for LDHs (Hibino and Kobayashi, 2005).

Fourier Transform Infrared Spectroscopy (FT-IR) of Cd-Al/C LDH

FT-IR spectroscopy was used to determine the main functional group responsible for the formation of Cd-Al/C LDH and other important available functional groups. The Cd –Al/C LDH FTIR spectra is as shown figure (3).

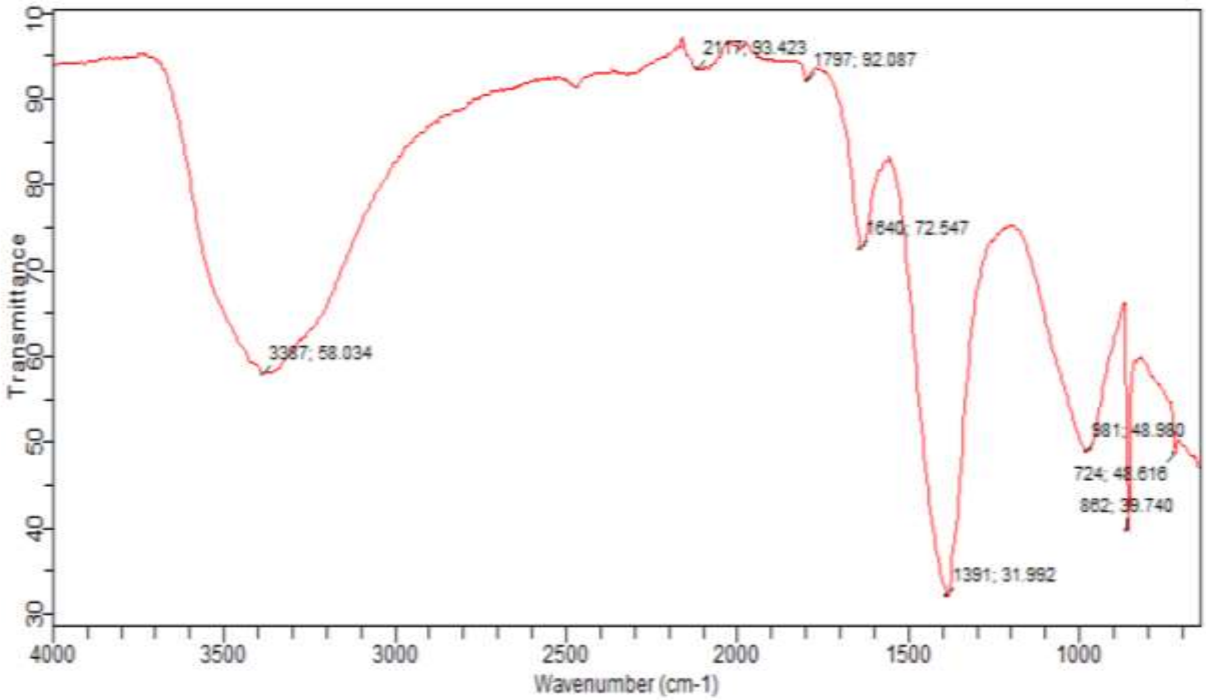

Fig. 3: FT-IR Spectra of Cd-Al/C LDH

The FTIR spectra of the synthesized Cd –Al/C LDH is represented in figure 3. The spectra showed a broad absorption band, which is referred to O-H stretching mode of the hydroxyl group in the layers that is found in the region of 3387.58 cm^{-1}. These bands are commonly observed in the LDHs materials (Cavani *et al*., 1991). At about 1391 cm^{-1} and there is a characteristic signal of CO_3^{2-} stretching vibrations which is present in Cd-Al/C (Zhang *et al.*, 2004). The absorption peaks in the low frequency region, for M-O is below 862 cm^{-1} (Tanaka *et al* ., 2010).

Band Gap Energy of Cd-Al/C

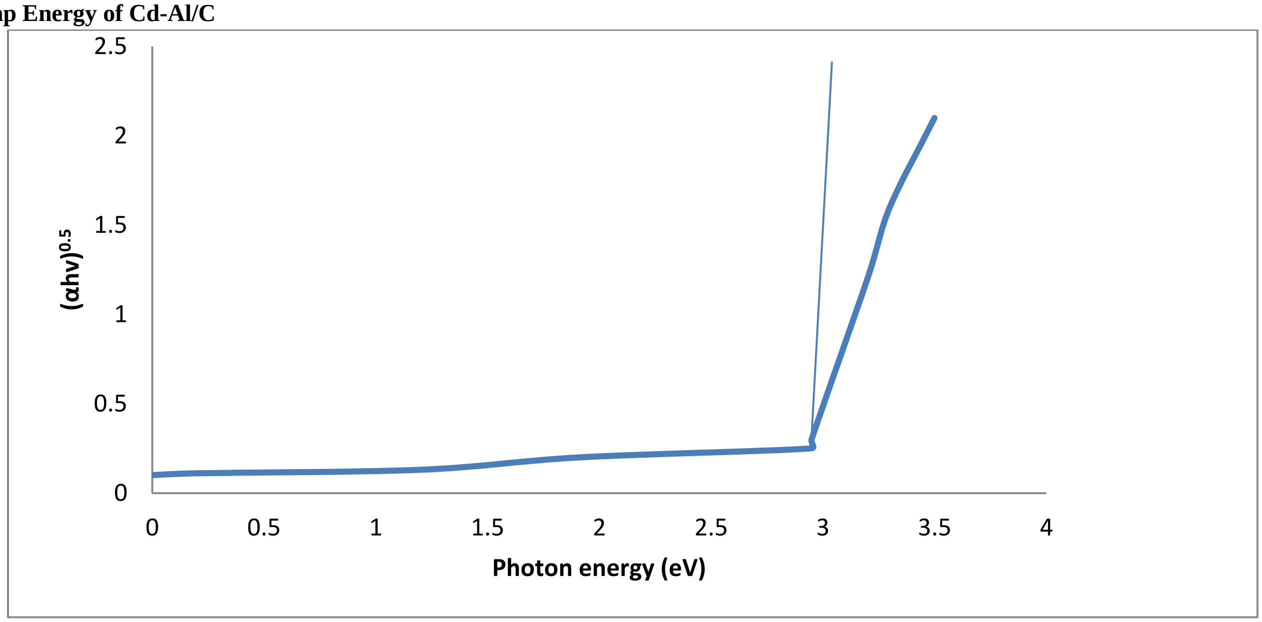

Fig. 4: The Tauc plot showing the energy band gap of Cd-Al/C

The band gap energy of the samples sample was calculated by extrapolating the curve drawn between (h ν) and $(\alpha h\nu)^{1/2}$ as shown in the figure 4. The band gap energy obtained by extrapolating the curves was found to be 2.95 eV for Cd-Al/C.

Effect of Operational Parameters

The influence of operational parameters such as concentration, catalyst dosage, pH and temperature, were tested using Cd-Al/C LDH on degradation Methyl red.

Effect of Catalyst Dosage on Photodegradation of Methyl Red using Cd-Al/C

The effect of catalyst dosage is as shown in figure (5).

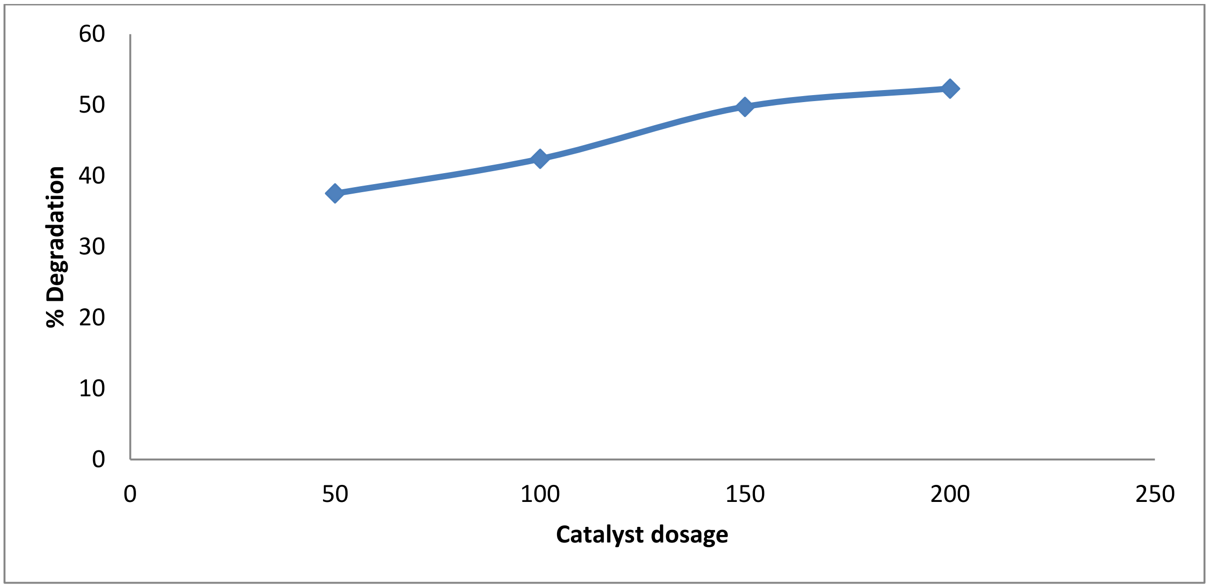

Fig. 5: Effect of catalyst dosage on degradation of MR using Cd-Al/C LDH.

Degradation of dye is also subjective by the amount of the photocatalyst. The dye degradation increases with increasing catalyst concentration, which is characteristic of heterogeneous photocatalysis. The increase in catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the number of •OH radicals which can take part in actual discoloration of dye solution (Shankar *et al*., 2004).

From figure 5 most of the photocatalytic studies, investigation of percentage removal is found to be proportional to the dose of the catalyst and very vital. Influence of photocatalyst dose on the MR dye degradation was investigated for the dye solutions at an initial concentration of 3 ppm. The visible light photodegradation was done for 100 min with Cd-Al/C catalyst doses in the range of 50–200 mg. The total degradation of MR increased with the increase in Cd-Al/C dose, the increase was from 37.52-52.32 %. These results are in line with the results obtained by Singh *et al.,* (2014) in their study of ‘’Methyl red degradation under UV illumination and catalytic action of commercial ZnO in which their results shows same trend’’.

Effect of pH on Degradation of Methyl Red using Cd-Al/C

The effects of pH is as shown in figure (6).

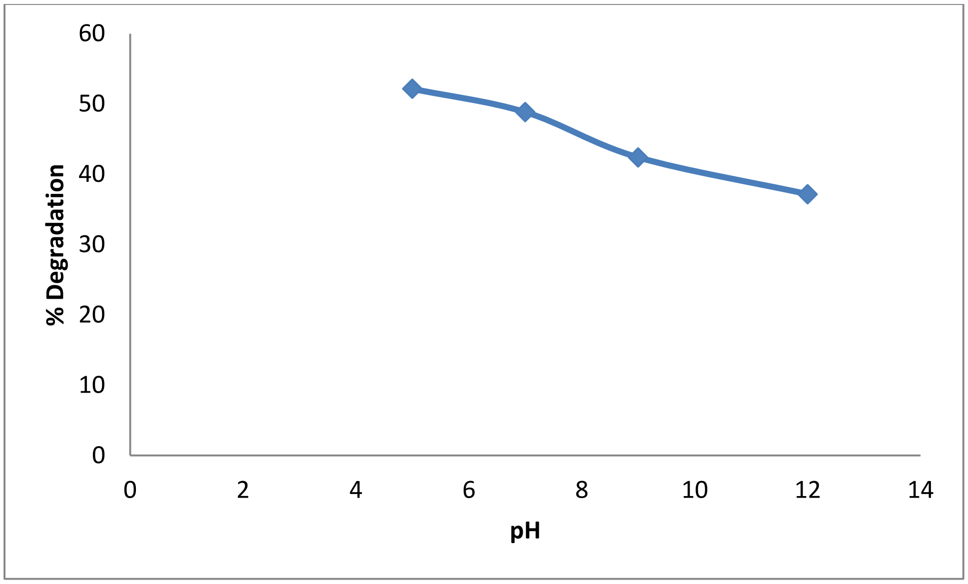

Fig. 6: Effect of pH on degradation of MR using Cd-Al/C LDH.

From figure 6 the pH solution is important factors that hinders or support a certain reaction. Therefore, in order to study the effect of pH in photodegradation of MR using Cd-Al/C pH values of 5-12 were selected. It was found that at lower pH value of 5 the highest percentage photodegradation 52.14 % of the dye was observed. This is due to the electrostatic interactions between a semiconductor surface, substrate, and charge radicals strongly depend on the pH of the solution. This result is in agreement with the results obtained by Thota *et al.,* (2014) in their study of ‘’visible light induced photocatalytic degradation of methyl red with codoped titania.’’

Effect of Concentration on Degradation of Methyl Red using Cd-Al/C

The effects of concentration is as shown in figure (7).

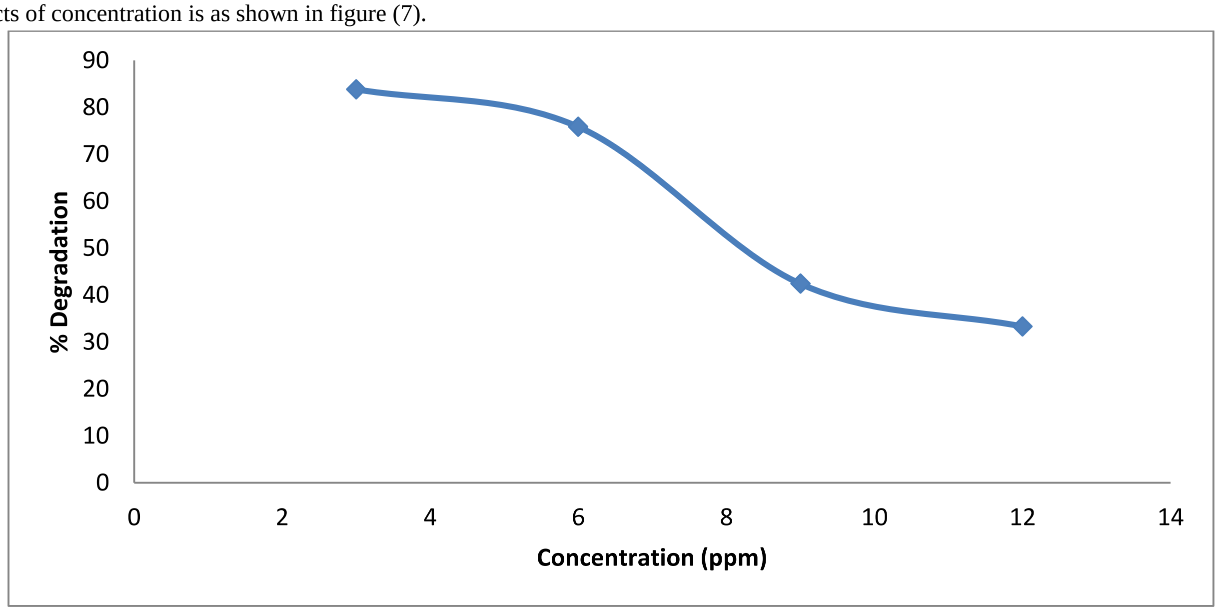

Fig. 7: Effect of concentration on degradation of M.R using Cd-Al/C LDH.

By varying the initial concentration from 3 to 12 ppm at constant catalysts load (200 mg) of Cd-Al/C, its effect on the degradation rate were determined, and the results are shown in Figures 7. As seen in the figures, degradation efficiency of MR increased with decreased in the dyes concentration, the decrease was from 83.80 - 33.3 % after 100 min time of irradiation These results are in line with results reported by Anitha and Auguetine, 2014 in their study of ‘’Photocatalytic Degradation of Alizarin Red S and Bismarck Brown R Using TiO_2 Photocatalyst’’.

Kinetic studies

The degradation of Methyl Red was carried out and tested kinetically by plotting graphs of the corresponding Pseudo order with the slope of the graph is equal to K (rate constant) the result summarized and presented in table (1).

DYE	CATALYST	Pseudo First Order		Pseudo Second Order	
		K	R^2	K	R^2
Methyl Red	1) Cd-Al/C	0.0225	0.9958	0.045	0.9778

The calculated correlation coefficients (R^2) is also close to unity for pseudo-second order kinetic than the other tested kinetic model. Therefore, the adsorption can be approximated more appropriately by pseudo second order kinetic model (Sumanjit *et al.,* 2006).

CONCLUSION

In this research work, the catalyst (Cd-Al/C) was synthesized by co-precipitation method. The efficiency of the catalyst in the degradation of methyl red was explored. The experimental results showed that after 100 min visible light irradiation, the photocatalytic efficiency using 200 mg Cd-Al/C, pH 5 and 3 ppm Methyl Red concentration reached to 83.8 %. The kinetics of the degradation process was studied and the data obtained were modeled using pseudo first order and pseudo second order. From the linear regression coefficient values the data were found to be best fitted to pseudo second order kinetics.

REFERENCES

Anitha P and Auguestine A., (2014). Photocacatalytic degradation of Alizarin Red S and Bismarck Brown R using TiO_2. *Phocatalyst Journal of Chemistry and Applied Biochemistry* (1) 1-7

Ayawei, N, Angaye S. S. and Wankasi, D (2017). Mg/Fe Layered Double Hydroxide as a Novel Adsorbent for the Removal of Congo red, *International Journal of Applied Science and Technology* (7) 2-9.

Cavani, F. Trifiro, A. Vaccari, (1991) Hydrotalcite-type anion clays: preparation, properities and applications, *Catalalysis Today* (11)173-180.

El-Gain L., Lakarami M., Sebbar E., and Maghea A. (2009). Removal of Indigo Carmine dye From Water Mg-Al-CO_3 Calcined Layered Double Hydroxide, *Journal of Hazard Material* (161) 624-632.

Habino T. and Kobayashi M. (2005). Determination of Layered double Hydroxide in water, *Journal of Material Chemistry* (15) 653-656.

Khan, S. B., Khan, S. A. & Asiri, A. M. (2016). A fascinating combination of Co, Ni and Al nanomaterial for oxygen evolution reaction. *Applied surface sciences* (370)445–451.

Li J., S. Liu, and J. Wang (2008). Adsorption and degradation of the cationic dyes over Co doped amorphous mesoporous titania-silica catalyst under UV and visible light irradiation, Microporus Meroporous Material 115(3) 416-425.

Majewski P. J. (2007). Removal of organic matter in water by functionalized self-assembled monolayers on silica, *Separation and Purification Technology* (57) 283–288.

Martin M. J., A. Artola, M.D. Balague and M. Rigola (2003). Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, *Chemical Engineering Journal* (94) 231–239.

Parida K. M. and Mohapatra L. (2012) Carb.onate intercalated Zn/Fe layered double hydroxide: A novel photocatalyst for the enhanced photo degradation of azo dyes, *Chemical Engineering Journal* (179) 131–139.

Parida, K. M., Baliarsingh, N., SairamPatra, B. and Das J. (2006). Copper Phthalocyanine Immobilized Zn/Al LDH as Photocatalyst under Solar Radiation for Decolorization of Methylene Blue, *Journal of MolecularCatalysis A*: Chemical (267) 202-8.

Ren N., Charlton J. and Alder P.N. (2007). The flare gene, which encodes the AIPI protein Dros Phila, function to regulate F-action disassembly in popular epidermis cells Genetics 176 (4) 2223-2234.

Shahid A. K., Sher B. K., and Abdullahi M. A. (2016).Layered double hydroxide of Cd-Al/C for the Mineralization and Decoloration of Dyes in Solar and Visible Light Exposure.*Scientific report*, (10) 1038-1045.

Shankar M.V.; KK Cheralathan; B Arabindoo; M Palanichamy; V Murugesan(2004). Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by TiO_2, *Journal Molecular Catalysis A* Chemical. (223) 195-200.

Singh N.k., Sandip S. and Anjali P. (2014). Methyl Red Degradation under UV illumination and catalytic action of commercial ZnO, *Journal of Desllination and Water Treatment* (56) 1066-1076.

Sumanjit K. Seema R. and Rakesh K.M. (2006). Adsorption Kinetics for Removal of the Hazardous Dye Congo Red by Biowaste material as adsorbents, *Journal of Chemistry* (10) 1155-1160.

Tanaka T., S. Nishimoto, Y. Kameshima, J. Matsukawa, Y. Fujita, Y. Takaguchi, M. Matsuda, M. Miyake, (2010) " A novel nanocomposite material prepared by intercalating photoresponsivedendrimers into a layered double hydroxide, *Journal solid state chemical* (183) 479-485.

Thota S., Siva R. T and Sreedhar B. (2014). Visible light photocatalytic Degradation of Methyl Red with Codoped Titanium, (1155) 9624-9628

Zhang X.H., Axton J.M., Drinjakovic J., Lorenz L White-Cooper H. and Renault A.D. (2004). Spatial and Temporary Control of Mitotic Cyclins by the Gnu regulator by the embryonic mitosis in Drosophila. *Journal of Cell Sciences*. (16) 3571-3578.