ChemSearch Journal 10(2): 123 – 129, December, 2019
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 06/11/2019 Accepted: 04/12/2019
http://www.ajol.info/index.php/csj

Degradation of Methyl Red Using Cd-Sb/C Layered Double Hydroxide Catalyst under Visible Light

Garzali, F. A. and *Muhammad, A. S.
Department of Pure and Industrial Chemistry Bayero University, P. M. B. 3011, BUK, Kano, Nigeria
***Correspondence Email:** asmuhammed.chm@buk.edu.ng

ABSTRACT

This research work presents the degradation of Methyl red using cadmium-antimony-carbon (Cd-Sb/C) catalyst under visible light. The double layered hydroxide was successfully prepared from cadmium fluoride (CdF_2), antimony chloride ($SbCl_3$), and rice husks activated carbon, and then characterized by X-ray Diffaractometry (XRD) Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) methods. The peaks at 2ϴ 10.0, 23.4 and 35.5 in the XRD result confirmed the presence of double layered hydroxide. The effect of catalyst dosage, pH and initial concentration, on the photo degradation of Methyl red was investigated. The experimental results showed that after 100 min visible light irradiation, the percentage degradation using 200 mg Cd-Sb/C, pH 5 and 3ppm Methyl red concentration reached to 50.36%. For kinetics studies the data obtained were analysed 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-Sb/C show good catalytic activity.

Keywords:

INTRODUCTION

Organic dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem (Martin *et al.*, 2003). Various methods have been suggested to handle the removal of dyes from water; these include precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration. Most of these methods suffer from various drawbacks (Jeanette *et al*., 2005). These methods are fairly effective in removing pollutants. However the main drawback of these techniques is formation of secondary waste product which cannot be treated again and dumped (Ferreira *et al*., 2001). Advanced oxidation processes (Perez *et al.*, 2006) appear to be a promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants fromwaters and soils, because they can provide an almost total degradation (Petala *et al*., 2006).

A number of researches have been carried out on photocatalytic degradation of dyes using double layered hydroxide catalysts. Shahid *et al.*, (2016) investigated Cd-Al/C and Cd-Sb/C double layered hydroxides nanocatalyst for the decoloration and mineralization 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, the adsorption was endothermic and the computation of the parameters ΔG^o, ΔH^o and ΔS^o indicated that the ineractions were thermodynamically favorable. In this research work, we used synthesized Cd-Sb/C LDH to degraded Methyl Red.

MATERIALS AND METHODS

Chemicals and Reagents

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), Antimony chloride ($SbCl_3$) (Sigma Aldrich), Ethanol (99%), Sodium hydroxide (NaOH) (99% Sigma Aldrich) and Hydrochloric acid (HCl) (97% Sigma Aldrich).

Synthesis of Cd-Sb/C Catalyst

Salts of Cadmium fluoride (CdF_2) and Antimony chloride ($SbCl_3$) were well mixed in double distilled water and further mixed with activated carbon through co-precipitation method (Khan *et al*., 2016). Briefly salts of $SbCl_3$ and CdF_2 were dissolved thoroughly 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 solutions was added and continuously monitored till pH 9. After this, the reaction mixture was placed on a hot plate for 6 h at 60 °C with homogenous stirring. On completion of the reaction the surplus solution was 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 overnight at 50 °C and stored in clean tube for further characterization.

Characterization of Catalyst

X-ray Diffaractometry (XRD), Scanning electron Microscopy (SEM) and Fourier Transform Infrared (FT-IR) Spectroscopy were employed in the characterization of the Cd-Sb/C double layered hydroxide.

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 (equation 1).

$$D = 0.89\lambda / \beta\cos\theta \qquad (1)$$

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 is 128nm for Cd-Sb/C.

Photocatalytic Experiment

In a typical experiment 100 mg of Cd-Sb/C was dispersed in 200 cm^3 of 3ppm dye solution in a beaker. The above suspension was magnetically stirred for 25 minutes in the dark to in order to obtained an adsorption-desorption equilibrium and to eliminate the error due to any initial adsorption effect. The suspension was then irradiated with 500W high-pressure Hg lamp of intensity 0.0129w/m^2. A 10 cm^3 aliquot was taken at 25 minutes interval, centrifuged at 2000rpm prior to absorbance measurement in order to eliminate error due to scattering.

The catalytic activity of Cd-Sb/C-LDH was evaluated against the dye under visible light. The effect of operational parameters such as catalyst dosage, pH and concentration were investigated, the percentage removal efficiency R.E. (%) of catalyst was evaluated by using the equation (2).

$$R.E.(\%) = \left(\frac{Co - Ct}{Co}\right) \times 100 = \left(\frac{Ao - At}{Ao}\right) \times 100 \; \ldots.(2)$$

C_0 represents the original concentration of each dye solution at time = 0, C_t is the concentration of dye solution after adding the catalyst at time, t as indicated in equation (2). Similarly, A_0 designated the absorbance of the original concentration of the dye solution at time = 0 and A_t is the absorbance of dye solution during reaction progress after passing at time, t (Li *et al.*, 2008).

RESULTS AND DISCUSSION

Characterization of Cd-Sb/C

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

X-ray Diffaractometry (XRD) of Cd-Sb/C

The crystalline phase of the prepared samples was characterized by XRD analysis.
The XRD pattern of Cd-Sb/C is as shown in Figure (1).

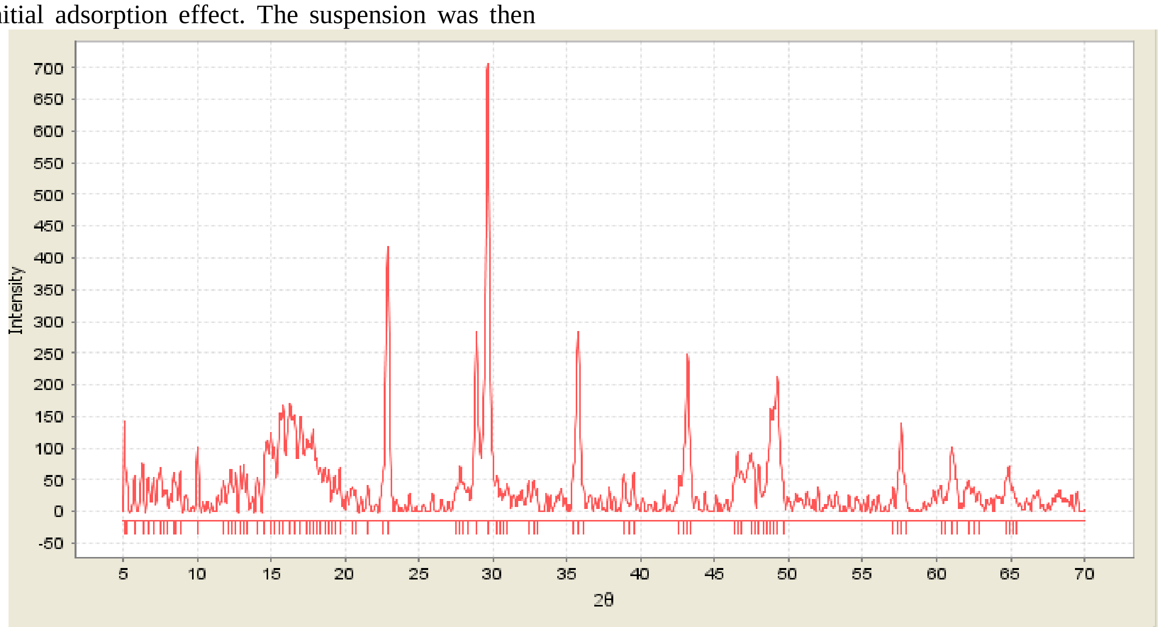

Figure 1: XRD of Cd-Sb/C

The crystalline phases of the Synthesized Cd-Sb/C LDH was characterized by XRD analysis. From Figure 1 the characteristic peak for Cd-Sb/C appeared at 2θ = 10 (003) 23.4 (006) and 35.5 (012) suggesting the formation of Cd-Sb/C-LDH. The 006 corresponds 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^{o} which 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).

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

Scanning Electron Microscopy gave further insight into the morphology of the Cd-Sb/C LDH. The surface morphology of Cd-Sb/C LDH is as shown in Figure (2).

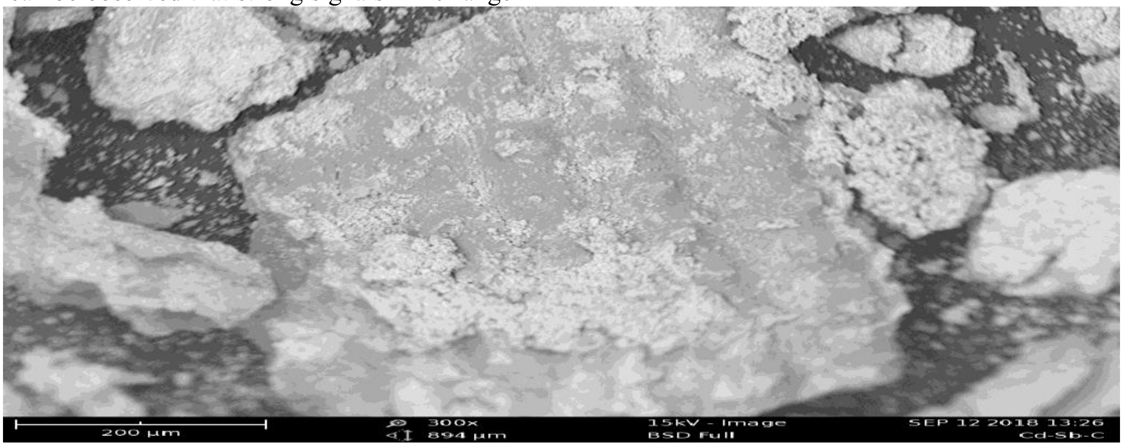

Figure 2 SEM image of Cd-Sb/C

Figure 2 shows the of SEM image for Cd-Sb/C LDH. The SEM image shows the sheet morphology of Cd-Sb/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-Sb/C LDH

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

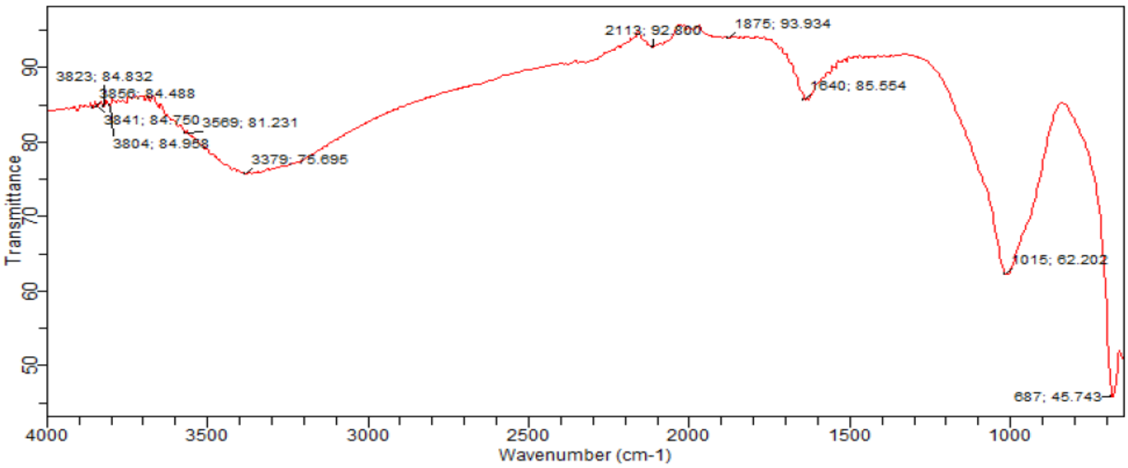

Figure 3: FT-IR Spectrum of Cd-Sb/C LDH

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 3379.75 cm^{-1}.These bands are commonly observed in the LDHs materials (Cavani *et al*., 1991). The absorption peaks in the low frequency region, for M-O is below 687.45cm^{-1} (Tanaka *et al*., 2010).

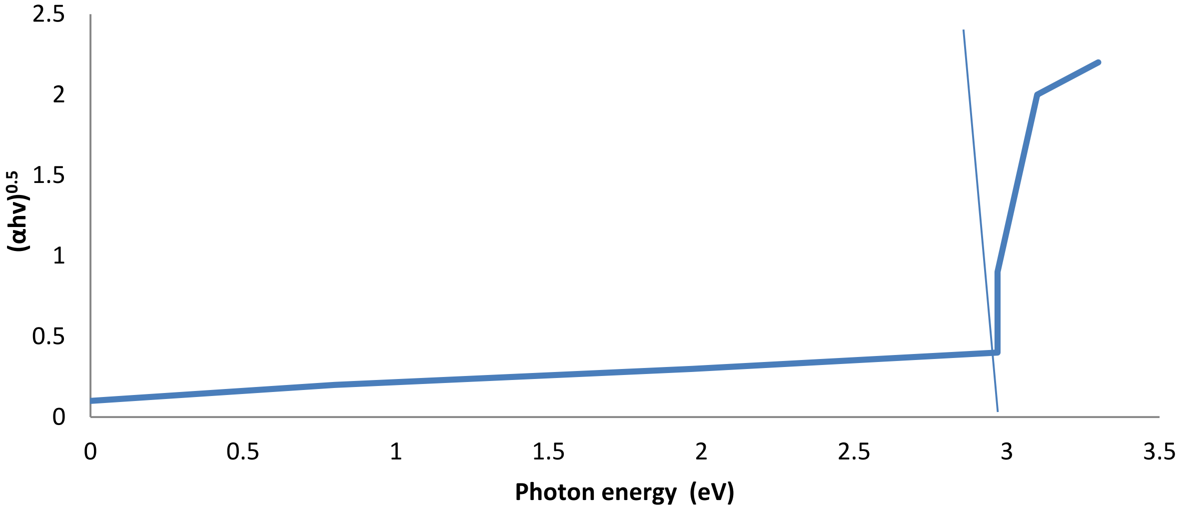

Figure 4: The Tauc plot showing the band gap energy of Cd-Sb/C

The band gap energy of the 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 2.97eV for Cd-Sb/C. The band gap suggested that catalyst work well in visible range.

Effect of Operational Parameters

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

Effect of Catalyst Dosage on Degradation of Methyl Red using Cd-Sb/C

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

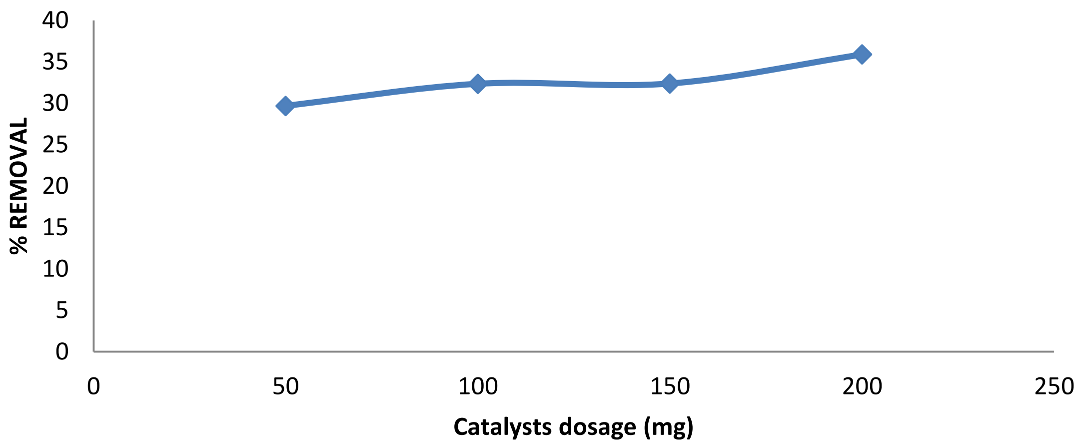

Figure: 5 Effect of catalyst dosage on degradation of MR using Cd-Sb/C LDH.

Dye degradation is also subjective to the amount of the photocatalyst. The dye degradation increases with increasing catalyst concentration, which is characteristic of heterogeneous photocatalysis (Shankar *et al.*, 2004). The increase in amount of catalyst 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 degradation of photodegradation was found to be proportional to the dose of the catalyst and very vital. The influence of photocatalyst dose on the MR dye degradation was investigated for the dye solutions at an initial concentration of 3ppm. The visible light photodegradation was done for 100min with Cd-Sb/C catalyst at varying doses in the range of 50–200 mg. The total degradation of MR increased with the increase in Cd-Sb/C dose, the increase was from 29.67-35.87%. These results are in agreement 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''

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

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

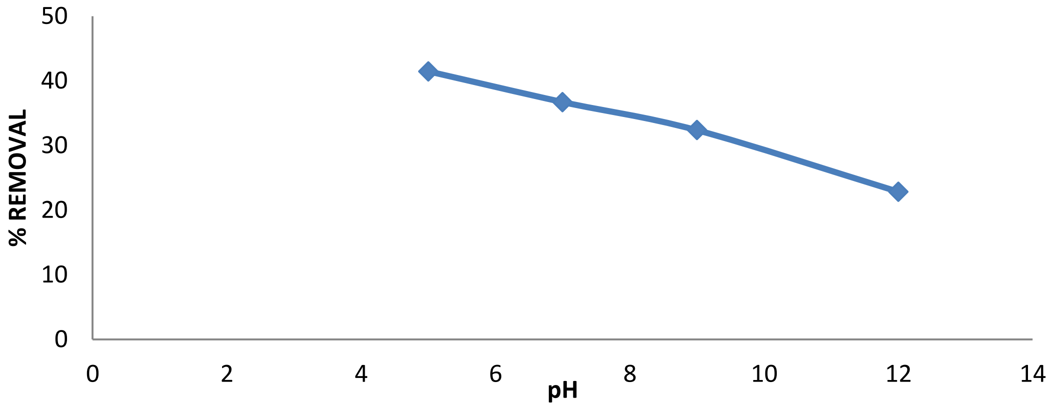

Figure: 6 Effect of pH on degradation of MR using Cd-Sb/C LDH.

From Figure 6 the pH of solution is an important factor that hinders or support a certain reaction. Therefore, in order to study the effect of pH in photodegradation of MR using Cd-Sb/C pH values of 5-12 were selected. It was found that at lower pH value of 5 the highest percentage photodegradation 41.46% 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-Sb/C

The effects of concentration is as shown in Figure (7). By varying the initial concentration from 3 to 12ppm at constant catalysts load (200 mg) of Cd-Sb/C, its effect on the degradation rate were determined, and the results as shown in Figures 7. As seen in the figures, degradation efficiency of MR increased with decreased in the dyes concentration, the decrease was from 50.36-24.24% after 100min time of irradiation These results are in line results with reported by Anitha and Auguestine (2014) in their study of ''Photocatalytic Degradation of Alizarin Red S and Bismarck Brown R Using TiO_2Photocatalyst''.

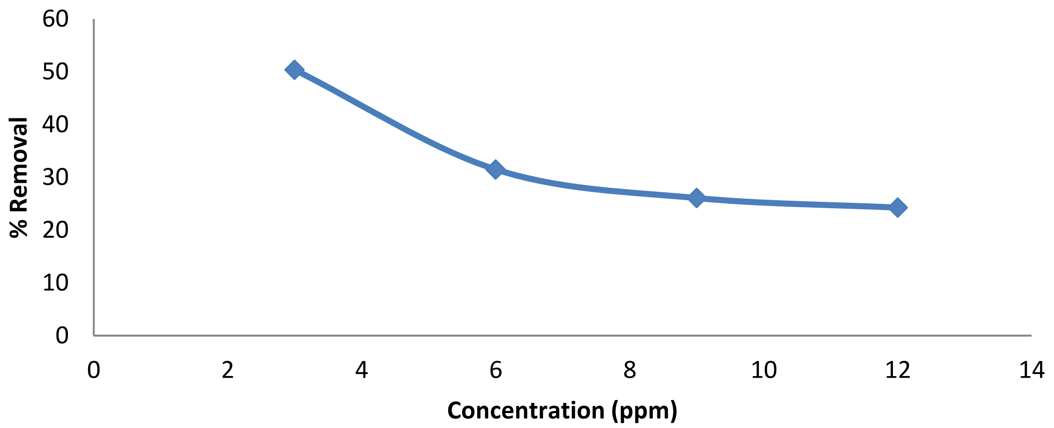

Figure 7: Effect of concentration on degradation of M.R using Cd-Sb/C LDH.

KINETIC STUDIES

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

Table 1: Kinetic Models and Calculated Parameters on Photodegradation of Methyl red using Cd-Sb/C.

model	Kinetic parameter	
Pseudo First Order	K	0.0070
	R^2	0.8530
Pseudo First Order	K	0.0089
	R^2	0.9702

CONCLUSION

In this research work, the catalyst (Cd-Sb/C) was synthesized by co-precipitation method. The catalyst was characterized via X-ray Diffractometry (XRD), Fourier Transform infrared spectrophotometer (FT-IR) and scanning electron microscope (SEM). Effects of operational parameters such as contact time, catalyst dosage, initial dye concentration, and effect of pH were all studied. The experimental results showed that after 100min visible light irradiation, the photocatalytic efficiency using 200mg Cd-Sb/C, pH 5 and 3ppm Methyl Red concentration reached to 50.36%. The data obtained were studied 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.

REFERENCES

Anitha P and Augustine A., (2014). Photocacatalytic degradation of Alizarin Red S and Bismarck Brown R using TiO_2 phocatalyst *Journal of Chemistry and Applied Biochemistry* 1(1):105 – 111.

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): 83-92.

Cavani, F. Trifiro, F. and Vaccari, A. (1991) "Hydrotalcite-type anion clays: preparation, properities and applications", *Catalysis Tod*ay 11(2):173 - 301.

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 *J Hazard Mater* (161) 624-632.

Ferreira C, Domenech S, Lacaze P (2001). Synthesis and characterization of polypyrrole/TiO_2 composites on mild steel, *J of Applied Electrochemistry* 31(1): 49-56.

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

Jeanette M.C. Robertson, Peter K. J. Robertson, and Linda A. Lawton (2005). A comparison of the effectiveness of TiO_2 photocatalysis and UV photolysis for the destruction of the the destruction of three pathogenic micro-organism. *J. Photochem. Photobio. A: Chemistry.*175 (1): 51-56.

Khan, S. B., Khan, S. A. and Asiri, A. M. (2016).A fascinating combination of Co, Ni and Al nanomaterial for oxygen evolution reaction''*Appl. Surf. Sci.* (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.

Martin M. J., Artola A., Balague M. D. and Rigola M. (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., 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 Molecular Catalysis A: Chemical*, 267(1):202 - 208.

Perez M. H, G. Penuela, M.I. Maldonado, O. Malato, P.F. Iba˜nez, I. Oller, W. Gernjak and S. Malato, (2006). Degradation of pesticides in water using solar advanced oxidation processes, *Applied Catalysis B: Environmental* (64) 272–281.

Petala M., V. Tsiridis, P. Samaras, A. Zouboulis and G.P. Sakellaropoulos (2006) Wastewater reclamation by advanced treatment of secondary effluents, *Desalination* (195) 109–118.

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 De-coloration of Dyes in Solar and Visible Light Exposure. *Scientific report*, 6, 35107(2016) http://doi.org/10.1038/srep35107.

Shankar M.V., Cheralathan K.K., Arabindoo B., Palanichamy M. and Murugesan V. (2004). Enhanced photocatalytic activity for the destruction of monocrotophos pesticide by TiO_2, *Journal of Molecular Catalyst A Chemistry.* (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 Desallination and Water Treatment* (56) 1066-1076.

Tanaka T., S. Nishimoto, Y. Kameshima, J. Matsukawa, Y. Fujita, Y. Takaguchi, M. Matsuda and M. Miyake, (2010) " A novel nanocomposite material prepared by intercalating photoresponsive dendrimers into a layered double hydroxide**",** *J. Solid State Chem***.** 183(2):479-484.

Thota S., Siva R. T and Sreedhar B. (2014). Visible light photocatalytic Degradation of Methyl Red with Codoped Titanium, *Journal of Catalysts, Hindawi Publishing Corporation*, http://dx.doi.org/10.1155/2014/962419.