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PHOTODEGRADATION OF RHODAMINE B IN AQUEOUS BY VISIBLE LIGHT IRRADIATED Cd-Sb/C LAYERED DOUBLE HYDROXIDE

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ABSTRACT

The degradation of Rhodamine B (RB) by cadmium antimony carbon (Cd-Sb/C) catalyst under visible light was examined. The layered double hydroxide was successfully prepared from cadmium fluoride (CdF_2), antimony chloride ($SbCl_3$), and rice husks activated carbon, and then characterized by X-ray Diffraction (XRD) Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) methods. The peaks at 2Ɵ 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 photo degradation of Rhodamine B were investigated. The experimental results showed that after 100min visible light irradiation, the percentage degradation using 200mg Cd-Sb/C, pH 7 and 3ppm Rhodamine B concentration reached to 76.22%. 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: Layered Double Hydroxide (LDH) Cadmium fluoride, Antimony Chloride, Rhodamine B and Activated carbon.

INTRODUCTION

Dyes came up as one of the new chemicals which could be used in many industrial productions. Due to the extensive use of these dyes in industries, they have become part of industrial effluent. In fact, of the 450,000 ton of organic dyes annually produced worldwide, more than 11% is lost in effluents during manufacture and application processes (Forgacs *et al*., 2004). Majority of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem (Persons, 2004). Various methods have been suggested to handle the dye removal from water; these include the ultra-filtration, reverse osmosis, biodecomposition, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process (Derudi *et al*., 2007). Generally these processes have some advantages or disadvantages over the other method. A balanced approach is therefore needed to look into the worthiness on choosing an appropriate method which can be used to degrade the dye in question. Among these techniques, the advanced oxidation processes appear to be a promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants from water, because they can provide an almost total degradation (Rauf and Asharaf, 2009).

Researches have been carried out on photocatalytic degradation of dyes using layered double hydroxide catalysts. Shahid *et al.*, (2016) investigated Cadmium aluminum carbon and Cadmium antimony carbon layered double hydroxides nanocatalyst for the decoloration and mineralization of organic dyes. Ayawei *et al.*, (2017) reported the capability of Mg/Fe- CO_3 to degrade Congo red in aqueous solution under various experimental conditions. Zhe-Ming *et al*., (2017) investigated Zn/M–NO_3-LDHs (M = Al, Fe, Ti, and Fe/Ti) which was synthesized through two different methods and their activities for visible-light photocatalytic degradation on Rhodamine B (RB) were tested. In this research work we used Cd-Sb/C to degraded Rhodamine B

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 the catalyst

The LDH catalyst was synthesis by dissolving salt of Cadmium fluoride (CdF_2) and Antimony chloride ($SbCl_3$) in distilled water and then mixed with activated carbon through co-precipitation method (Khan *et al*., 2016). Briefly salt of $SbCl_3$and CdF_2 were dissolved thoroughly in 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 and then 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 h 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

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

PHOTOCATALYTIC EXPERIMENT

In a typical experiment 100 mg of Cd-Sb/C was dispersed in a beaker containing 200 cm^3 RB (3 ppm) solution. The catlyst 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 10 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-Sb/C-LDH was evaluated against RB under visible light. The effect of operational parameters such as catalyst dosage, pH and concentration were investigated, the percentage removal efficiency R.E. was determined by using the following equation.

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

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

RESULTS AND DISCUSSION

Catalyst Characterization

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

X-ray Diffraction (XRD) of Cd-Sb/C LDH

The XRD analysis presents the crystalline phase of the prepared sample.

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

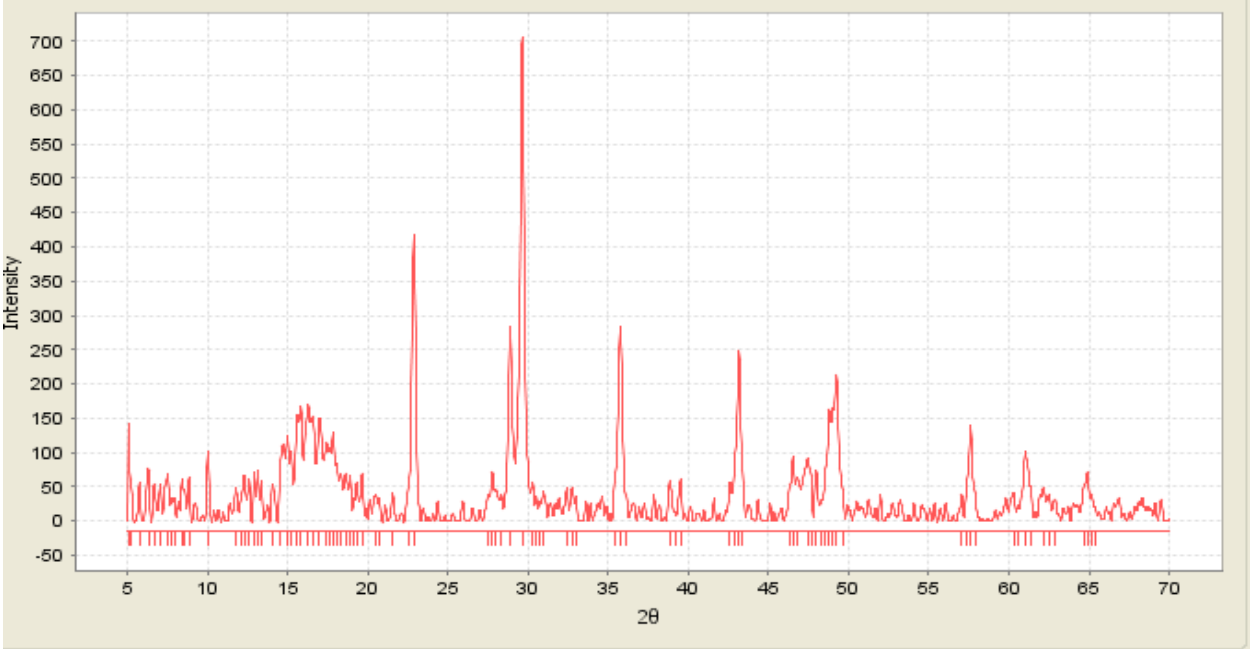

Fig. 1: XRD of Cd-Sb/C LDH

The crystalline phases of the Synthesized Cd-Sb/C LDH was characterized by XRD analysis. Figure 1 display the XRD patterns of the prepared LDH catalyst. 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 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 sharp signals in 2θ range 2-30º. These peaks indicate that the prepared LDHs are characterized by high crystallinity 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 is 128 nm for Cd-Sb/C.

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

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

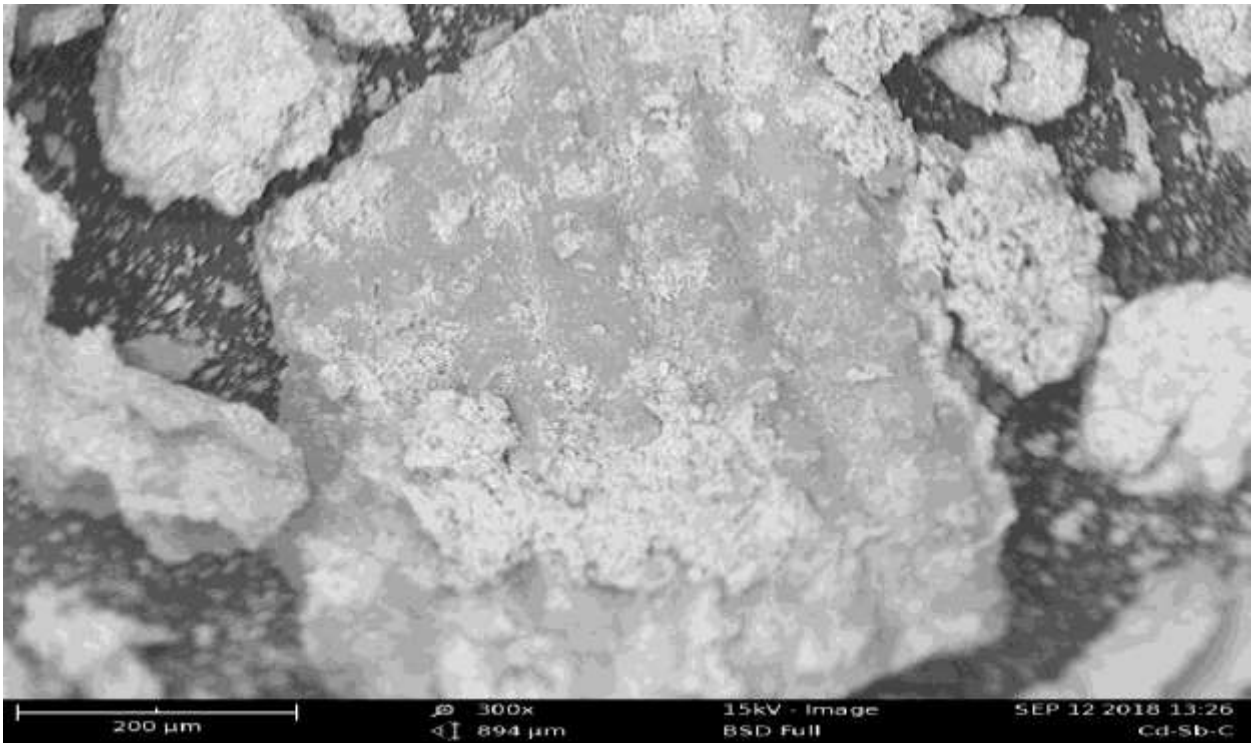

Fig. 2 SEM image of Cd-Sb/C LDH.

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-Al/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).

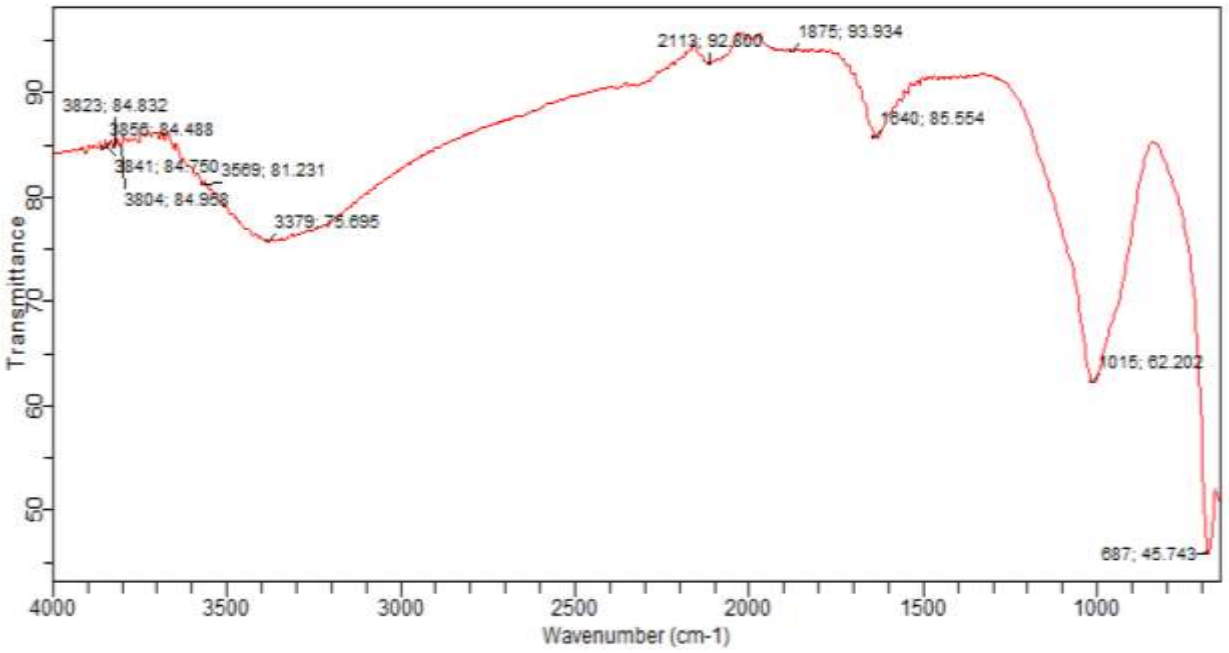

Figure 3: FT-IR Spectrum of Cd-Sb/C LDH

The spectra showed a broad absorption band, which is attributed to O-H stretching mode of the hydroxyl group in the layers that is found in the region of 3379.75 cm^{-1}. The 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 687.45 cm^{-1}(Tanaka *et al*., 2010).

Band Gap Energy of Cd-Sb/C

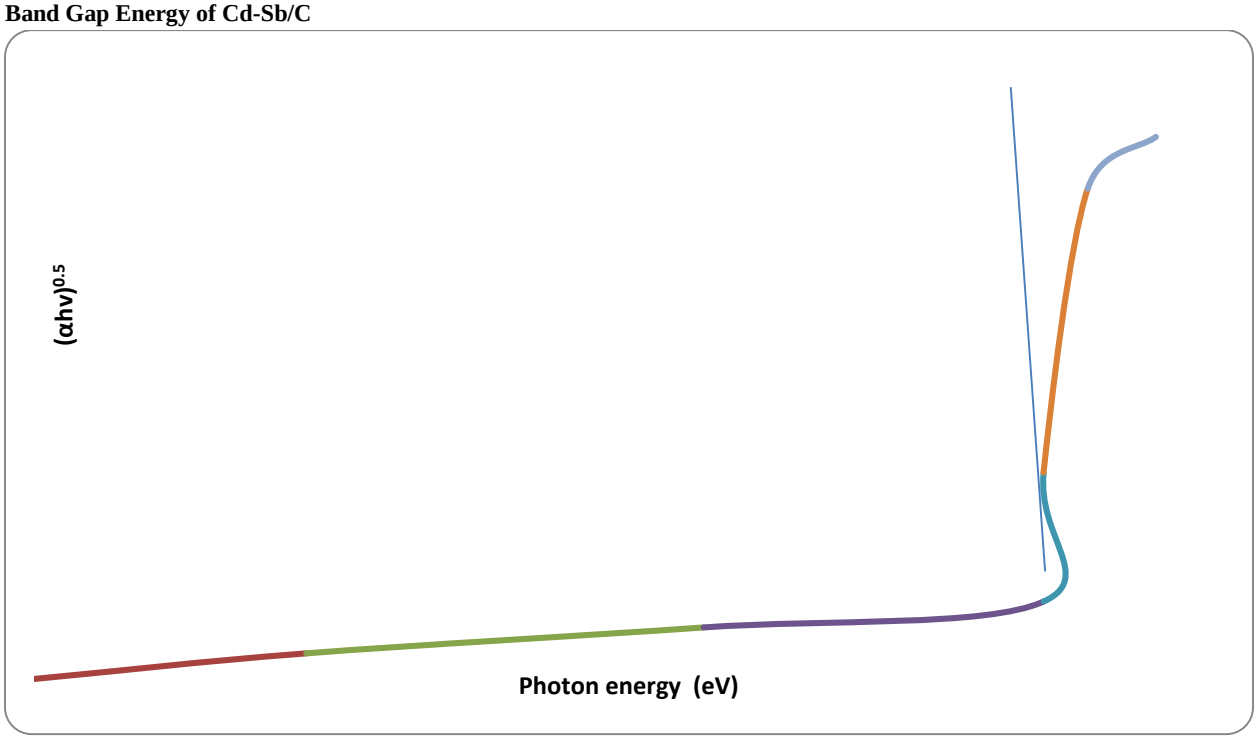

Fig. 4: The Tauc plot showing the energy band gap of Cd-Sb/C

The band gap of the sample was calculated by extrapolating the curve drawn between (h ν) and $(\alpha h\nu)^{1/2}$ (figure 4). The band gap energy was found to be 2.97 eV.

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 RB.

Effect of Catalyst Dosage

Fig. 5 show effect of catalyst dosage.

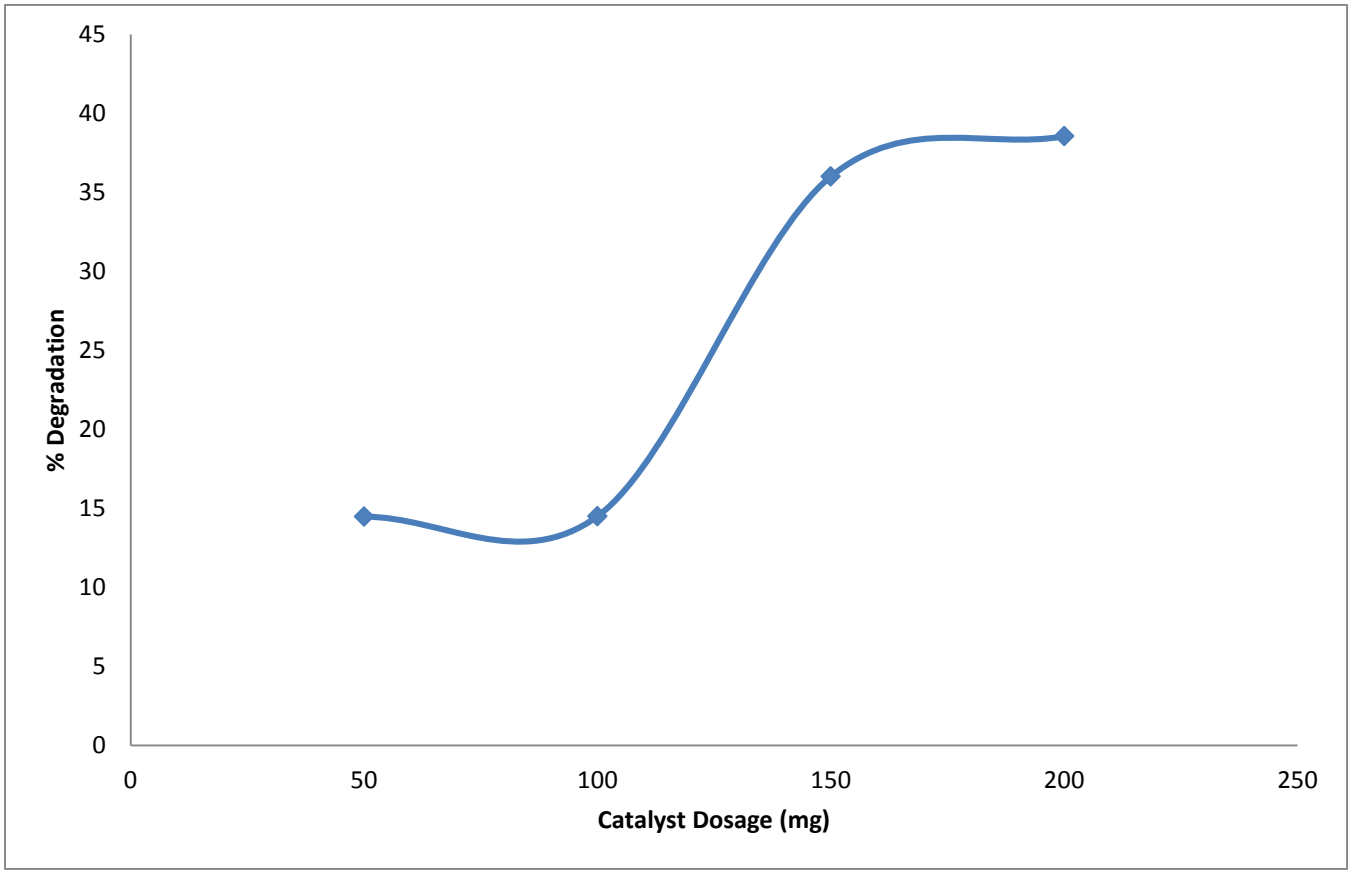

Fig. 5: Effect of catalyst dosage on degradation of RB using Cd-Sb/C LDH.

Figure 5 shows the degradation efficiency of RB using Cd-Sb/C LDH, with different catalyst dosage after 100 min irradiation at neutral pH condition. The photocatalytic decomposition of Rhodamine B increases with increase in the catalyst dosage, the increase was from 14.49-38.56 %. This is due to sufficient number of active site on the catalyst surfaces which result in better penetration of visible light. Similar result was obtained by Jahagir *et al*., (2014) in their study of ‘’Photocatalytic degradation of rhodamine B using nanocrystalline α-Fe_2O_3.’’

Effect of pH

Figure (6) presents the effects of pH on photodegradation of RB.

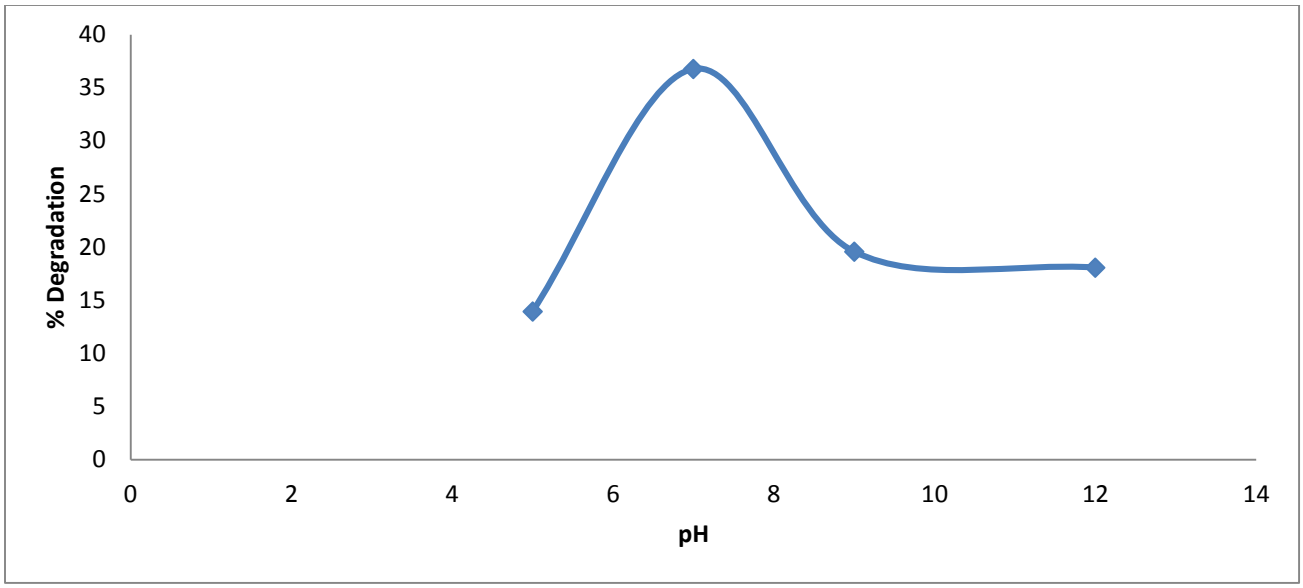

Fig. 6: Effect of pH on degradation of RB using Cd-Sb/C LDH.

Influence of pH on photocatalytic degradation of RB by Cd-Sb/C is shown in figure 6. It was observed that the effect of photodegradation increase with increase in pH, the increase was from 13.94-36.77 % after 100 min time of irradiation. This can be due to the increased of hydroxyl ions which induce more hydroxyl radical formation. This result is in agreement with the results obtained by Rakhi and Kishore (2015) in their study of ''Investigation of Photocatalytic Degradation of Rhodamine B by Using Nano-Sized TiO_2.''

Effect of Concentration

The effects of concentration is presented in figure (7).

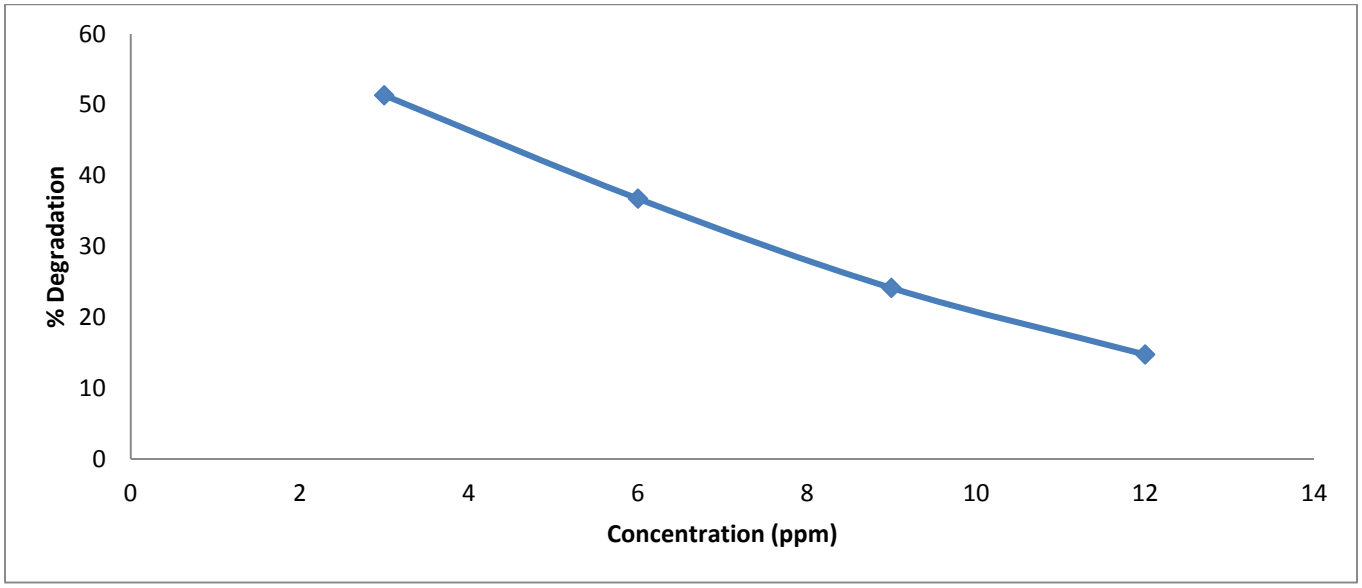

Fig. 7: Effect of concentration on Photodegradation of RB

Figure 7 shows the effect of concentration on photodegradation of RB, in the presences of Cd-Sb/C LDH. It has been observed that the efficiency of photodegradation of RB tend to decrease with increasing the concentration, the decrease was from 51.36-14.76 % after 100 min time of irradiation, which result in reducing the number of active sites and hence decreasing the production of ·OH

on the surfaces. This result is in agreement with the results obtained by Rakhi and Kishore (2015) in their study Investigation of ''Photocatalytic Degradation of RB by Using Nano-Sized TiO_2''

KINETIC STUDIES

The degradation of RB 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).

Table1: Kinetic models and calculated parameters on Photodegradation of RB using Cd-Sb/C

DYES	CATALYST	Pseudo First Order		Pseudo Second Order	
		K	R^2	K	R^2
Rhodamine B	1) Cd-Sb/C	0.026	0.9556	0.02850	0.9863

From table above the value of the correlation coefficients (R^2) calculated is close to unity for pseudo-second order kinetic model. Therefore, the photodegradation can be approximated more appropriately by pseudo second order kinetic model (Sumanjit *et al.* (2006). Zhang *et al*., (2017) reported the correlation coefficients R^2 for the pseudo-second-order model was much larger than that of the pseudo-first-order model.

CONCLUSION

In this research work, the catalyst (Cd-Sb/C) was synthesized by copericipitation method. It was characterized using X-ray Diffraction (XRD), Fourier Infrared Spectrophotometer (FT-IR) and Scanning Electron Microscope (SEM), followed by photo degradation of RB using visible light. The highest degradation efficiencies was achieved at 100 min, using 200 mg of catalyst dosage and at 3 ppm concentration of the dye (RB), with percentage removal of 51.36 %. The data obtained from kinetics studies were modeled using pseudo first order and pseudo second order approaches. From the linear regression coefficient values, the data were found to be best fitted to pseudo second order kinetic model. The LDH catalyst showed good catalytic activity under all conditions and this is probably due to its low band gap energy.

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