



## Sunlight assisted photocatalytic degradation of Indigo Carmine using eco-friendly synthesized CdSnO<sub>3</sub>

Ashok V. Borhade

Research Centre, Department of Chemistry, HPT Arts and RYK Science College, Nashik, 422005 MS, India.

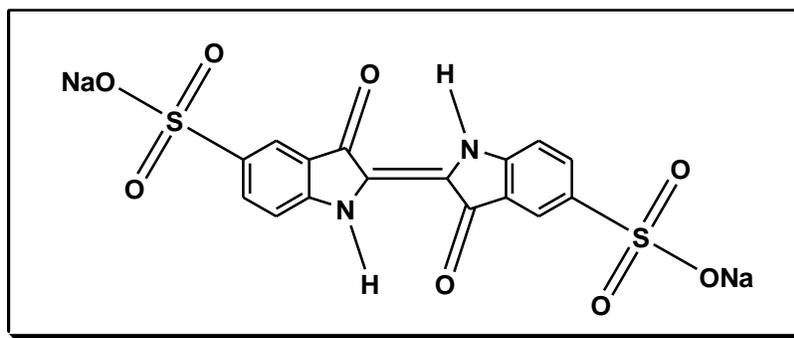
**Abstract:** In the present study I have developed an eco-friendly mechanochemical solid state method with green chemistry approach for the synthesis of CdSnO<sub>3</sub>. The photocatalyst was characterized to carry out physicochemical characterization by various analytical techniques like, Fourier Transform Infrared (FT-IR), Ultraviolet diffused reflectance Spectroscopy (UV-DRS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Tunnelling Electron Microscopy (TEM) and Brunauer–Emmett–Teller (BET) surface area. The synthesized CdSnO<sub>3</sub> particles had an average size of 105 nm with band gap 3.17 eV. The surface area by BET isotherm method highlight for the synthesized photocatalyst (S<sub>BET</sub>) is 54.45 m<sup>2</sup>/g, with pore volume (V<sub>p</sub>) is 0.021 cc/g, and pore diameter (D<sub>p</sub>) is 24.85 Å. Photocatalytic activity of CdSnO<sub>3</sub> was demonstrated by degradation of Indigo carmine dye under influence of sunlight in aqueous solution

**1. Introduction:** Water is one of the fundamental requirements of life and any undesired addition of chemical substances lead to its contamination and become unfit for human use. Speedy industrialization has provided much comfort to human beings; however, its adverse effects have emerged in the shape of environmental deterioration. Industries discharging pollutants into the environment include oil refineries, tanneries, textile plants, and the food, pharmaceutical, paint and coal processing industries. Various dyes found in industrial effluents, at the end go into the aquatic ecosystem generating various environmental hazards. These may have adverse, sometimes irreversible effects on animals and plants. Therefore, it becomes essential to completely degrade these organic compounds before their discharge.

Synthetic dyes are toxic refractory chemicals, which generates murky color to the water and are hazardous to the environment. The dyes were detected in dissolved state in wastewater [1]. Most of these dyes are toxic and carcinogenic in nature [2]. One must note down that, a wide spectrum of compound can transform themselves into potentially dangerous substances during the water treatment process. A non-biodegradable pollutant present in wastewater is a point of major serious pain to the researchers in the world.

Various methods have been suggested for purification of polluted water, these includes; surface adsorption [3, 4] bio-degradation [5-7] and use of membrane [8]. The light induced photocatalytic process has received considerable attention in the last few decades. The photocatalytic reactions on semiconductors have been utilized for many applications, such as air cleaners [9], self-cleaning materials [10] and antibacterial materials [11]. Literature survey shows that, very little attention is given to the mixed oxide photocatalyst. TiO<sub>2</sub> is widely studied catalyst and demonstrated its photocatalytic activity [12-15]. The ZnO is another broadly studied photocatalyst for the dye degradation [16, 17]. Few

reports are available on the studies related to the photocatalytic activity of coupled semiconductor photocatalyst, such as  $\text{TiO}_2\text{-CeO}_2$  [18],  $\text{TiO}_2\text{-SnO}_2$  [19] and  $\text{ZnO-SnO}_2$  [20, 21].



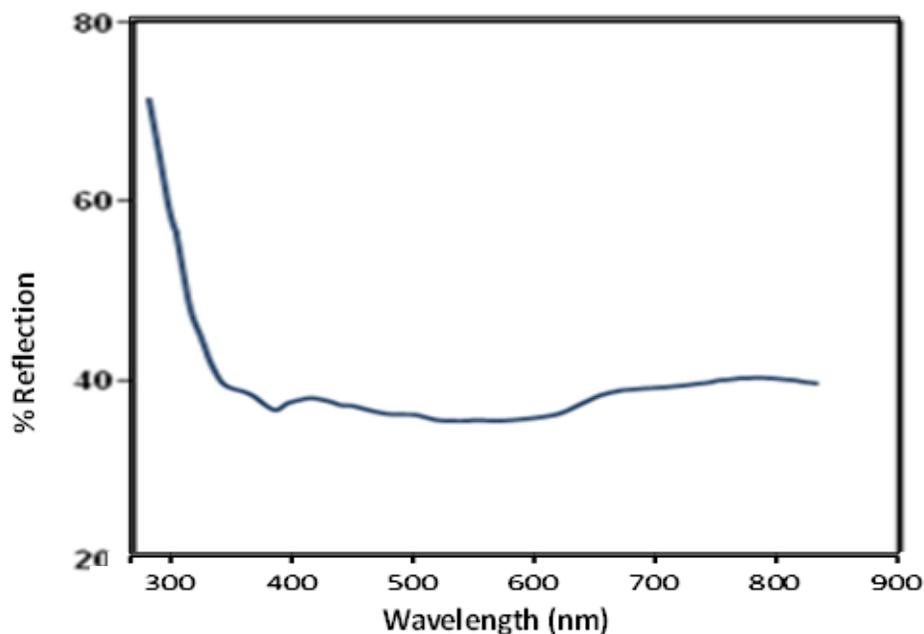
**Figure (1):** Structure of Indigo carmine dye.

Indigo carmine is an anionic dye usually used in the textile, food and cosmetics industries. The indigo carmine is considered as highly toxic indigoid class of dye. Contact with it can cause skin and eye irritations. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye can also prove fatal, as it is carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity. It may also cause gastrointestinal irritations with nausea, vomiting and diarrhea.

**2. Experimental:** I report herein the synthesis of  $\text{CdSnO}_3$  photocatalyst by simple one-pot mechanochemical method using a green chemistry approach. Various routine methods are available for the synthesis of mixed metal oxide such as; sol-gel [22, 23], hydrothermal [18]. These methods are complicated, cost effective and cause environmental pollution, whereas the solid-state mechanochemical synthesis method is an eco-friendly method, easy, also gives less energy to the environment. The aim of this work is to optimize the synthesis of  $\text{CdSnO}_3$  catalyst. For this purpose, a solid state-mechanochemical synthesis method, with a green chemistry approach was employed. High energy mechanical milling is a very effective way of mixing of metal oxides. For the synthesis of  $\text{CdSnO}_3$ , starting reagents were,  $\text{CdO}$  (Sr. no.-361 Batch No 600220109, 99.9 % pure) and  $\text{SnO}_2$  used in the synthesis is of high purity, (Loba Chem. Batch No 27685, CAS No 18282-10-5, 99.9 % pure). For the synthesis of  $\text{CdSnO}_3$ , equimolar mixture of  $\text{CdO}$  and  $\text{SnO}_2$  was grinded with mortar and pestle to acquire fine powder for 25 min. and calcinated at  $500\text{ }^\circ\text{C}$  for 3 h. Again, the obtained powder was further calcinated at  $800\text{ }^\circ\text{C}$  following milling after each interval of three-hour of time. The calcination was continued for next twenty hours with milling. Afterwards, the mixture was heated up to the terminal temperature. The furnace was programmed as  $10\text{ }^\circ\text{C}$  per min from one temperature to subsequent higher temperature. The dark brown colored product  $\text{CdSnO}_3$  obtained, was characterized and utilized to evaluate catalytic activity.

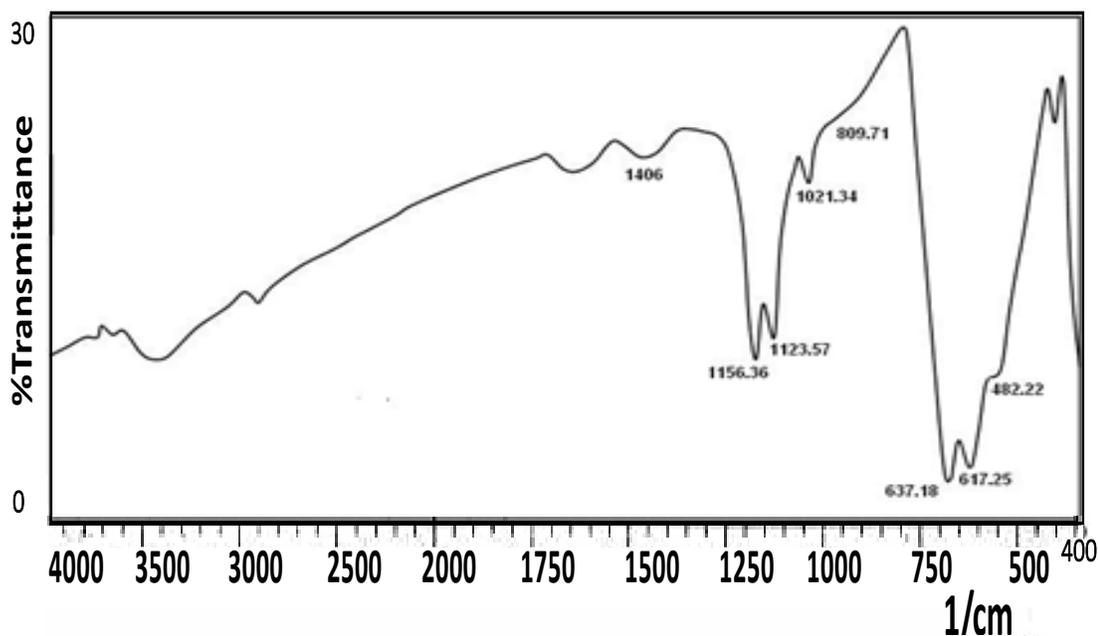
### 3. Characterization of $\text{CdSnO}_3$ :

**3.1 UV diffused reflectance spectroscopy (UV DRS):** The optical property of the synthesized product was studied by using Perkin Elmer- $\lambda$ -950, UV spectrophotometer. The catalysts were scanned over the wavelength range of 250-850 nm. Figure (2) depicts the UV diffused reflectance spectrum of synthesized  $\text{CdSnO}_3$ , catalyst. The spectrum has absorption edge cut-off at 390 nm with corresponding band in the ultraviolet region. The band gap energy for the synthesized compound was found to be 3.17 eV by using formula,  $E=h\nu$ .



**Figure (2):** UV diffused reflectance spectrum of synthesized CdSnO<sub>3</sub>.

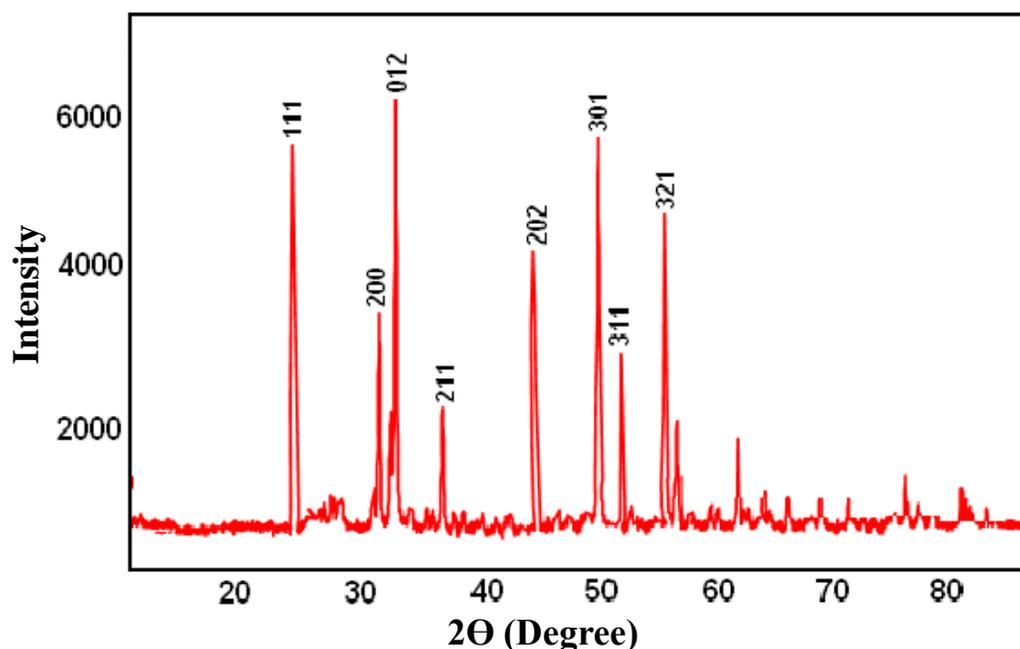
**3.2. Fourier Transform Infrared (FTIR) Spectroscopy of CdSnO<sub>3</sub>:** The vibrational frequency of the synthesized catalyst was studied by FTIR, 8400S-Shimadzu, in the range of 400-4000 cm<sup>-1</sup>. The infrared absorption spectrum of the synthesized ZnSnO<sub>3</sub> catalyst is shown in Figure (3). The vibrational frequency band at 450 cm<sup>-1</sup>, 482.22 and 545 cm<sup>-1</sup> indicate vibration due to Cd-O and vibrations at 617 cm<sup>-1</sup>, 637 cm<sup>-1</sup> and 809 cm<sup>-1</sup> indicates vibrations occurred by Sn-O.



**Figure (3):** FTIR spectra of synthesized CdSnO<sub>3</sub>.

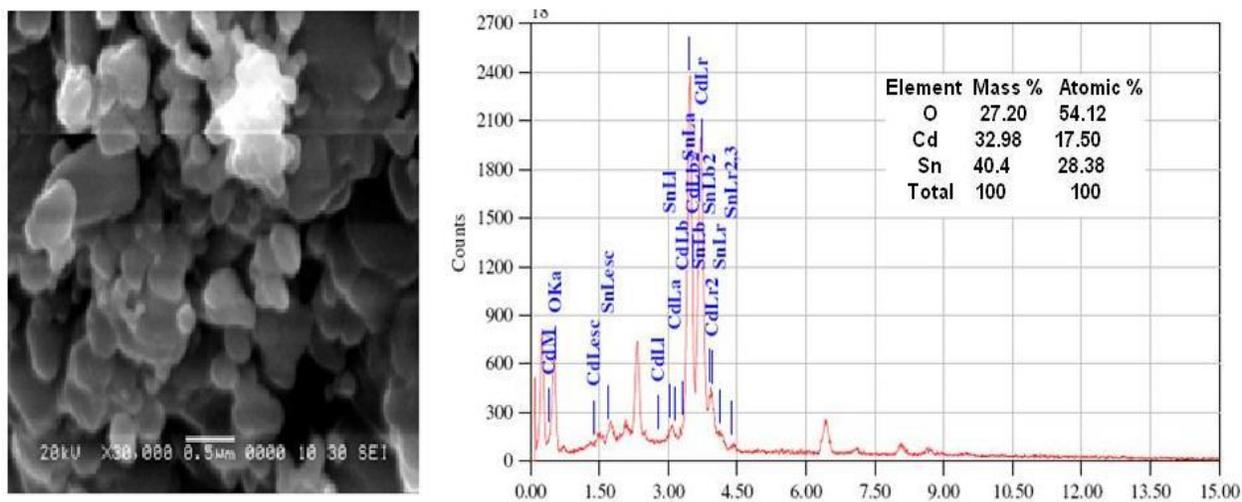
**3.3. X-Ray Diffractogram (XRD) of CdSnO<sub>3</sub>:** The structural properties of the material was studied by using X-ray diffractometer, Rigaku-D/MAX-2500 with Cu-K $\alpha$  radiation, having  $\lambda = 1.5406 \text{ \AA}$ . Figure (4) shows XRD pattern of CdSnO<sub>3</sub> powder formed after heating. The d-line patterns of the X-ray

diffraction pattern matches with the standard JCPDS data card No-13.0360. The peaks at scattering angles ( $2\theta$ ) of 25.35, 32.29, 38.06, 46.25, 53.43 and 58.47 corresponds to the reflection from 111, 200, 012, 211, 202, 311 and 321 crystal planes (hkl) respectively confirming the orthorhombic structure of the  $\text{CdSnO}_3$ .



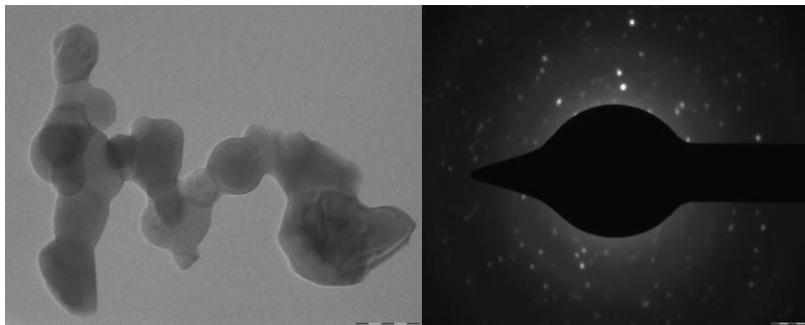
**Figure (4):** XRD spectrum of synthesized  $\text{CdSnO}_3$ .

**3.4. Scanning Electron Microscopy (SEM) and EDAX of  $\text{CdSnO}_3$ :** The surface morphology and associated chemical composition of synthesized photocatalyst was analyzed by using a scanning electron microscope (SEM) coupled with EDAX. Figure 5 indicate the SEM picture with EDAX of synthesized  $\text{CdSnO}_3$ . SEM image shows that particles are polycrystalline and well agglomerated with each other. The EDAX data confirms elemental composition in conformity with the respective molar proportions taken. The observed mass percentage of Cd in the  $\text{CdSnO}_3$  is 32.98%, Sn in the  $\text{CdSnO}_3$  is 40.4 % and that of oxygen is 27.20 %, which confirm the  $\text{CdSnO}_3$ .



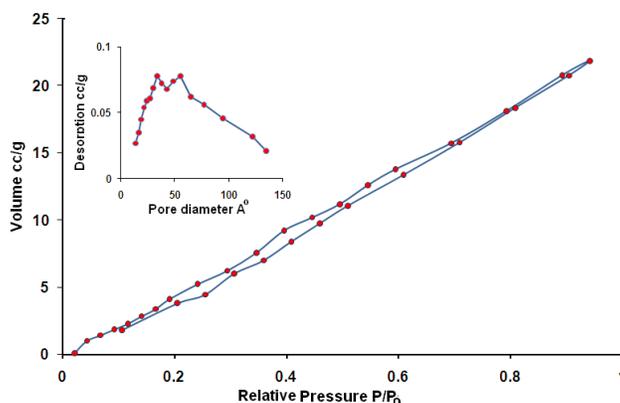
**Figure (5):** SEM and EDAX of synthesized  $\text{CdSnO}_3$

**3.5. Transmission Electron Microscopy (TEM) with SAED of CdSnO<sub>3</sub>:** The TEM image along with the selected area of the diffraction pattern (SAED) recorded for the sample corresponding to the CdSnO<sub>3</sub> is shown in Figure (6). TEM image along with SAED pattern of synthesized CdSnO<sub>3</sub> catalyst. It is clear from SAED pattern, Crystal structure of the material found to be orthorhombic. The dark spot in the SAED pattern reveals orthorhombic perovskite phase of CdSnO<sub>3</sub> which is in good agreement with XRD pattern.



**Figure (6):** Transmission Electron Microscopy (TEM) with SAED of CdSnO<sub>3</sub>.

**3.6. BET (Brunauer, Emmett and Teller) Surface area of CdSnO<sub>3</sub>:** The Surface area ( $S_{BET}$ ), Pore volume ( $V_p$ ) and Pore diameter ( $D_p$ ) was evaluated on Quntachrome autosorb automated gas sorption system, Autosorb-1 NOVA-1200 and Mercury porositymeter autosorb-IC. The typical N<sub>2</sub> adsorption-desorption isotherm and BJH pore size distribution of synthesized CdSnO<sub>3</sub>, catalyst are nearly similar in shape and are depicted in Figure (7). To obtain detailed information about the pore size, the specific surface area, the mesopore volume and the pore size distribution, N<sub>2</sub> adsorption and desorption isotherms were performed. The total surface area and pore volume were determined using BET and the three point method respectively. N<sub>2</sub> adsorption-desorption isotherm leads to the identification of the isotherm profile, as type IV in the BDDT (Brunauer, Deming, Deming and Teller) system which is typical for mesoporous material with pore diameter between 2 to 50 nm. The BJH pore size distribution demonstrates that, all the samples have narrow pore diameter range, the surface area ( $S_{BET}$ ) is 54.45 m<sup>2</sup>/g, pore volume ( $V_p$ ) is 0.021 cc/g, and pore diameter ( $D_p$ ) is 24.85 Å,



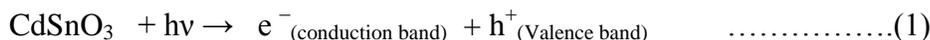
**Figure (7):** BET surface area along with pore volume of synthesized CdSnO<sub>3</sub>.

#### 4. Photocatalytic Degradation of Indigo carmine dye Using Synthesized CdSnO<sub>3</sub> :

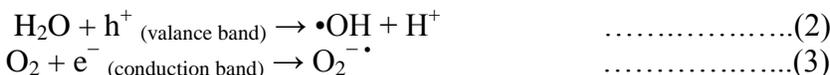
The photocatalytic activity of the synthesized CdSnO<sub>3</sub>, photocatalyst was carried out by studying photodegradation of Indigo carmine dye in an aqueous solution. Experiment was conducted with 20 ppm dye solution with 6 and 10 g/L CdSnO<sub>3</sub> photocatalyst. During the experiment, three types of observations were recorded. In one set of the experiment, the effect of photocatalyst in presence of

sunlight was evaluated by irradiating 50 ml dye solution with 0.3 g of photocatalyst to the sunlight. To study effect of photocatalyst in absence of sunlight, in a second set of experiment, dye solution containing photocatalyst was kept in dark. In the third set of experiment, to evaluate effect of sunlight in absence of photocatalyst on dye solution only dye solution was exposed to the sunlight. The decreases in the absorbance due to the photocatalytic degradation of the dyes were measured on systronics double beam spectrophotometer after every 30 minutes. The change in absorbance was measured at 610 nm. The change in sunlight intensity during time to time was monitored by using Lux meter Kusam-meko, KMLUX.

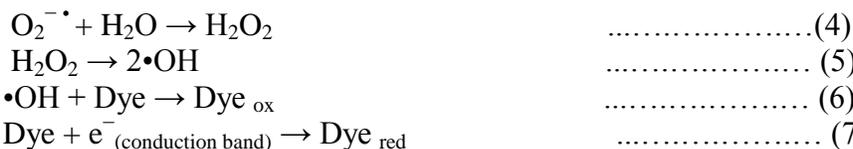
The effect of catalyst for degradation of Indigo carmine (20 ppm) was studied by taking the amount 10 g/L of CdSnO<sub>3</sub>. In the Figure (8) curve-a indicate degradation of Indigo carmine dye solution in presence of 6 g/L, curve-b indicate degradation of Indigo carmine containing 10 g/L photocatalyst when exposed to the sunlight and curve-c indicate when dye solution containing 10 g/L photocatalyst was kept in dark. From Fig. curve-a and curve-d depicts degradation of indigo carmine increases rapidly in presence of photocatalyst when exposed to the sunlight. Further, curve-c depict that there is no effect of photocatalyst on degradation of indigo carmine when dye solution containing photocatalyst was kept in the dark. The photodegradation of indigo carmine takes place very slowly in absence of the photocatalyst when only dye solution was exposed to the sunlight. Figure (9a and b) illustrates the UV-visible spectrum of indigo carmine dye before and after exposed to the sunlight in presence of the photocatalyst. It also depicts that, before degradation λ<sub>max</sub> value observed at 610 nm vanishes and new peak generates at 215 nm indicating degradation of indigo carmine dye. The result further shows that, on increase in the photocatalyst amount resulting faster degradation. This may be due to fact that, the increase in the photocatalyst amount actually increases the active sites on the photocatalyst surface causing increase in number of electrons and holes resulting faster degradation. The photocatalytic degradation of the dye is believed to take place according to the following mechanism (Figure 10). When a CdSnO<sub>3</sub> photocatalyst was exposed to UV-visible radiation, electrons are promoted from the valence band to the conduction band, as a result of this, an electron–hole pairs are produced.



Where, e<sup>-</sup><sub>(conduction band)</sub> and h<sup>+</sup><sub>(valence band)</sub> are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both of these entities migrate to the catalyst surface, where they can enter in a redox reaction. In most of the cases h<sup>+</sup><sub>(valence band)</sub> react easily with surface bound H<sub>2</sub>O to produce •OH radicals, whereas e<sup>-</sup><sub>(conduction band)</sub> react with O<sub>2</sub> to produce superoxide, O<sub>2</sub><sup>-•</sup> radical anion of the oxygen

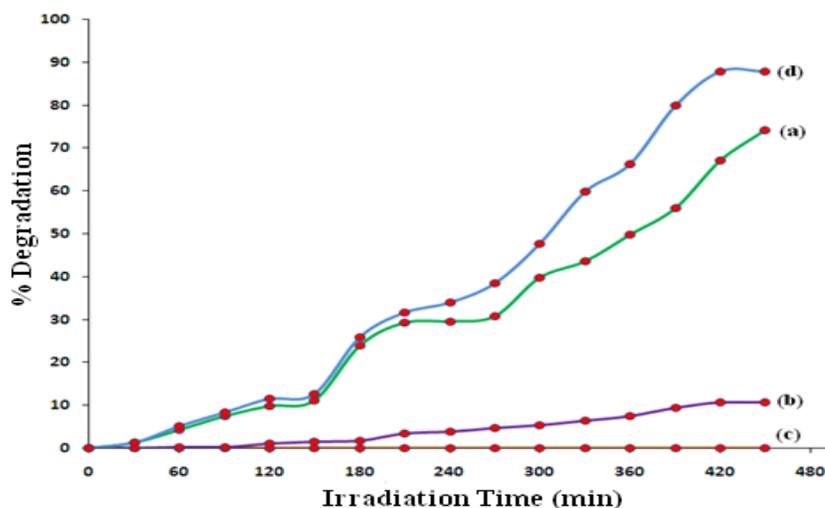


This reaction prevents the combination of the electron and the hole, which are produced in the first step. The •OH and O<sub>2</sub><sup>-•</sup> produced in the above manner can then react with the dye to form other species and is thus responsible for the degradation.

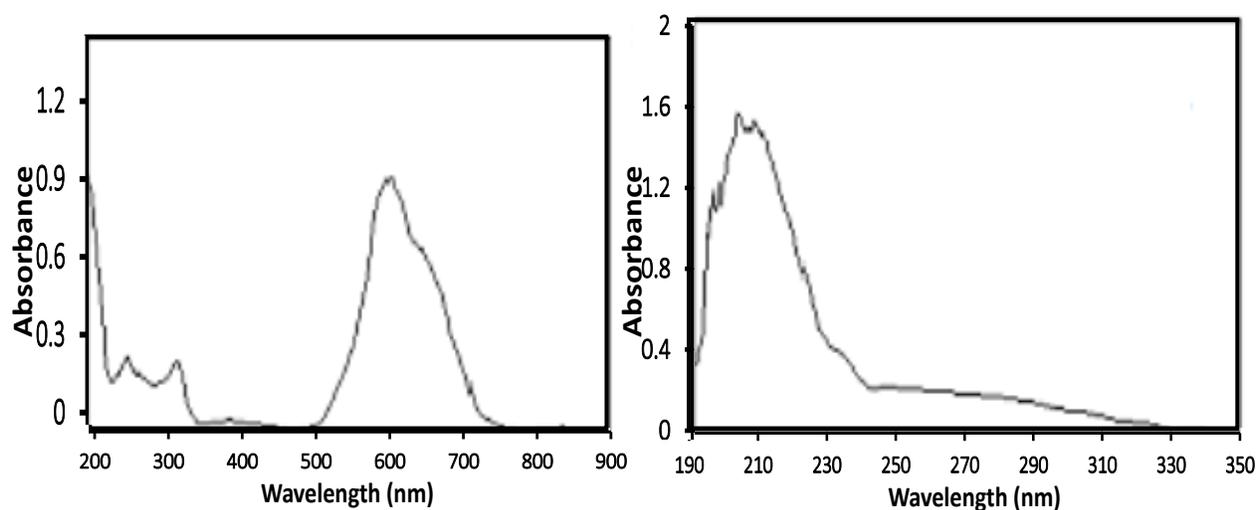


It may be noted that, all these reaction in the photocatalysis are possible due to the presence of both dissolved oxygen and water molecules. The change in sunlight intensity during progress of time was

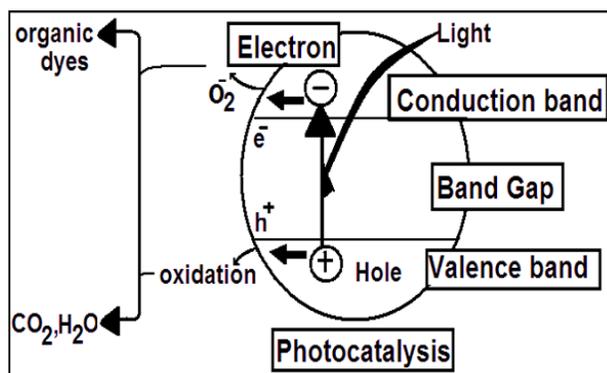
monitored by lux meter. The variation in light intensity was found to be  $940 \times 50000$  to  $650 \times 50000$  Lux during experiment time. Overall degradation of indigo carmine in presence of  $\text{CdSnO}_3$  photocatalyst obeys first order kinetics with rate constant  $0.0023 \text{ min}^{-1}$  (Figure 11).



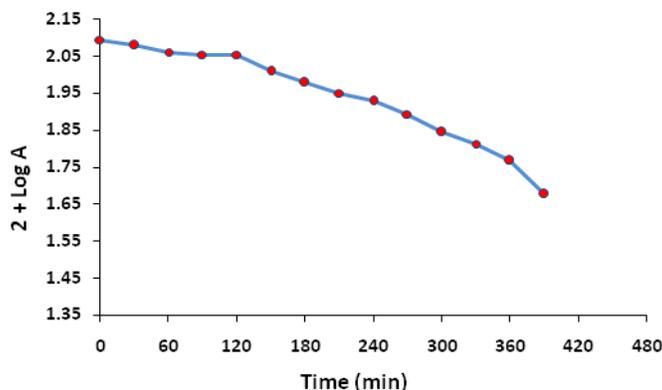
**Figure (8):** Photodegradation of indigo carmine by using  $\text{CdSnO}_3$  photocatalyst.



**Figure (9):** UV-visible spectra of indigo carmine dye a) before, and b) after degradation by using  $\text{CdSnO}_3$  photocatalyst.



**Figure (10):** Pathway of Indigo carmine degradation by using  $\text{CdSnO}_3$  photocatalyst.



**Figure (11):** Kinetic study of Indigo carmine degradation by using CdSnO<sub>3</sub> photocatalyst

**Conclusions:** The photocatalyst, CdSnO<sub>3</sub> was synthesized by green chemistry using solid state mechanochemical method followed by calcination. Its mean size, band gap energies as well as its photocatalytic activity was studied in detail by photodegradation of Indigo carmine dye. The decay follows pseudo first order kinetic to the visible absorption of the test dyes. The effective photodegradation of dyes by CdSnO<sub>3</sub> photocatalyst under stimulated sunlight is a very exciting respect in the photocatalytic area, and this work may provide new insight into the development of novel sunlight photocatalyst.

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#### References:

- [1] F. Esther, C. Tibor, O. Gyula, *Environ. Inter.* 30 (2004) 953.
- [2] D. Blake, P. Maness, *Sap. Puri. Methods* 28 (1999) 1.
- [3] V. Meshko, L. Markovska, *Water Resource* 35 (2001) 3357.
- [4] J. Iqbal, H. Watto, *Arab. J. Chem.* 4 (2011) 389.
- [5] Elias, C. Silgia, *App. Environ. Micro*(2000) 3357.
- [6] R. G. Saratale, G. D. Saratale, *J. Hazard. Mater* 166 (2009) 1421.
- [7] P. D. Shah, S.R. Dave, M.S. Rao, *Int. Biodeter. Biodegrad.* 69 (2012) 41.
- [8] H. Joong, H. Yong, *Dyes Pigm.* 76 (2008) 429.
- [9] M. R. Hoffmann, S. T. Martin, *Chem. Reviews* 95 (1995) 69.
- [10] W. F. Libby, *Science* 171 (1971) 499
- [11] H. Wang, H. Yang, *Chin. J. Pro. Eng.* 10 (2010) 1025
- [12] F. Chen, Z. Weiwei, (2009). *Catal. Comm.*, (2009) 10,1510
- [13] L. Konstantinou, T. Albanis. *App. Catal. B Chem. Env.* 49 (2004) 1.
- [14] V.K. Gupta, R. Jain, *Mat. Sci. Eng.* 31 (2011) 1062.
- [15] A. V. Borhade, Y. R. Baste, D.R. Tope, *Carb. Sci. Technol.*, 5(1) (2013) 192.
- [16] S. Chakrabarti, B. K. Dutta, *J. Hazard. Mater.* 112 (2004) 269.
- [17] N. Daneshvar, D. Salari, *J. Hazard. Mater.* 156 (2008) 194.
- [18] X. Bao, S. Yan, *Mater. Lett.* 59 (2005) 412.
- [19] H. Tada, A. Hattori, *J. Phy. Chem. B* 104 (2000) 4585.
- [20] F. Azam, R. M. Ali, *World Academy of Science, Eng. Tech.* 76 (2011) 138.
- [21] Wang, X. Wang, *J. Photochem. Photobio. A: Chemistry* 168 (2004) 47.
- [22] Y. Gao, W. Yu, *Chin. Chem. Let.* 13 (2002) 1115.
- [23] P. Wongkalasin, S. Chavadej, T. Sreethawong, *Col. Surf. A: Physico. Eng. Asp.* 384 (2011) 519.