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Photocatalytic Degradation of Methylene Blue Dye Using Synthesized CuO:CdO Nanocomposite

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Abstract: **Nanocomposites are comprised of enormous variation of system, such as 1-D, 2-D, 3-D and amorphous material, made up of particularly different components and mixed at nanometre scales. Nanocomposites are high performance material exhibits rare and unique properties, which are due to quantum confinement, surface Plasmon reaction, tunnelling of electrons and density of states. Nanocomposites containing two or more dissimilar band gaps semiconductors provide special properties to photocatalyst. CuO:CdO nanocomposite synthesized by simple, chemical, co-precipitation method. XRD technique used to characterize the prepared nanocomposite. The XRD spectra confirms the characteristics vibration of Cu-O and Cd-O. The crystallite particle size calculated by Debye Scherer formula is confirming the particle is nanoparticle. The photocatalytic efficiency of CuO:CdO nanocomposites was assessed using methylene blue dye in the presence of sun light. Variation in the concentration of Cu with respect to Cd in the nanocomposites affect the photodegradation efficiency in this investigation. Our results here indicate that the ability for dye removal from wastewaters can be change by changing the composition of nanocomposite catalyst.**

Index Terms: **Degradation, Methylene blue, Nanocomposites, Photocatalysis, Wastewater.**

I. Introduction

In recent years, the increasing population with its better needs has stimulated many industrial progresses. This has headed to the escalation in pollution, largely uncleanness of surface and ground water. Investigates nowadays have been targeting on the transition metal oxide nanoparticles in single or composite form owing to their exceptional optical, electrical, magnetic and catalytic properties (Saravanan et. al., 2013, Essam et al., 2013). Photocatalysis is a developing technology that agreement a broad range of uses, including degradation of organic compounds and dyes, antibacterial activity. Photo catalyst also help in fuel generation through water splitting and carbon dioxide reduction (Shen S, et. al., 2017).

Semiconductor photocatalysis is an efficient method of converting toxic and non-biodegradable organic compounds into carbon dioxide, water and inorganic salts, which help in environmental detoxification. (Ying et.al., 2018).

Generally, dying process used in textile, dyestuff, paper and plastic industries to colour their product while consuming substantial volume of water. Large amount of wasted produced from the colour-based industries particularly contained considerable amount of coloured wastewater. Most commonly used dye in industries is methylene blue (Engku et.al., 2019 , Banat, et.al., 1996). This is polluting the local environment and spreading many diseases like cyanosis, vomiting, increase in heartbeat, quadriplegia, shock, jaundice, tissue necrosis in human being and carcinogenic disorders (Kushwaha et al., 2014).

Hence, for the degradation and detoxification of wastewater a persistent and effective treatment technique should employed. Therefore, there is an exigent requirement to develop an environment friendly and cost effective process for the definite degradation and detoxification of methylene blue for environmental welfare (Yi et. al., 2008). Abundant methods reported for effective elimination of methylene blue dye from contaminated water (Karthik et al., 2016). Amongst them, the adsorption and photocatalyst played a very significant role in the water treatment. The key challenges in the adsorption process is restoration of the adsorbents and stowage of toxic sludge. In the recent years, toxic effluents eliminated from wastewater by various types photocatalyst (Fanourakis et al., 2020, Kim and Farnazo et al.,2017)). Water purification via semiconductor photocatalysis is an environment friendly and inexhaustible process which converts dyes into the gaseous products and does not pile-up toxic sludge (Nallendran et al., 2019). A semiconductor photocatalyst absorb photons with energy higher than its bandgap, causing electrons to jump into conduction band and leaving holes in the valence band. These holes and electrons are powerful oxidant and reductant and decontaminates organic and inorganic pollutants present in the water respectively (Maria et. al., 2016). The high band gap, rapid electron-hole recombination and weak semiconductor-pollutants interaction are the important challenges need to overcome for the effective harvesting of solar energy for different applications (Tadjarodi et al., 2013).

CuO is p-type semiconductor with many applications in sensors, catalysis, batteries, high temperature superconductors, solar cells, and field emitters (Y. Li et al., 2008, Ramírez et al., 2001, Cun et al., 2002). While CdO is an n-type semiconductor, exhibits high electrical conductivity and optical transparency. Cadmium oxide applicable in almost all fields such as solar cells, phototransistors, photodiodes, gas sensors, UV absorbers, oxygen storage materials and automobile exhaust catalysts (Gopidas et al., 1990). Due to its high charge carrier mobility and favourable visible light absorption. Cadmium oxide nanoparticles was found to be act as photocatalyst for dye degradation (Long et. al. 2006, Xue et al., 2008).

However, the Combination of two or more semiconductors enhance the waste degradation efficiency due to synergistic effect of each semiconductor (Saravanana et al., 2011, Li et. al., 2008, Y. He et. al., 2008). The two types of energy-level systems in coupled semiconductor materials show significant character in recognizing charge separation. Higher photocatalytic activity achieved by coupling of different semiconductor oxides, causing shrinking of the band gap, which increases the absorbance range to visible region leading to electron–hole pair separation under irradiation (Cun et al., 2002, Gopidas et. al., Bandara et. al., 2006, Marci et. al., 2001, Mclaren et. al., 2009). "The ZnO/CuO (Li et. al., 2008), CuO/TiO_2 (Huang et al., 2006), CuO / Fe_2O_3 (Cheng et. al., 2007), ZnO/TiO_2 (Gaurav et. al., 2019), ZnO/SnO_2 (Dharmadasa et. al., 2010), TiO_2/MgO (Lopez et. al., 1999), and ZnO-CdO (Sahu et. al., 2013) are the types of successfully combined coupled semiconductors. Thus increasing the photocatalytic activity in the visible region (Zhang et. al., 2019).

II. MATERIALS AND METHODS

Materials: Cadmium nitrate hexa hydrate ($Cd(NO_3)_2·6H_2O$, 99%), cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$, 99.5%), sodium hydroxide , ethanol, methyl alcohol , were sourced from S.D. Fine Chem. limited. All chemical reagents were of analytical grade and used without further purification.

A. *Synthesis of CdO-CuO Nanocomposites*

CuO -CdO nanocomposite was synthesized by simple co-precipitation method from ($Cu(NO_3)_2.3H_2O$ and $Cd(NO_3)_2·6H_2O$, dissolved in deionized water with 1:1, 2:1 and 1:2 ratio of CuO-CdO respectively. 4N sodium hydroxide was added to metal ions solution to form precipitate . The precipitates were filtered and washed several times with distilled water. Final washing was given with methanol. Precipitate was dried at 110^0 C for 24 hours in an electrical oven. The dried samples were calcined in tube furnace at 500^0 C for 6 hours (Kim et. al. 2019, Maria et. al. 2016, and Tadjarodi et. al. 2013). The obtained products were labelled cdc, cdc2 , cd2c corresponding to the molar ratio of the CuO-CdO nanocomposites.

B. *Structural Characterization*

UV-Vis spectrophotometer (systronic UV-2203) in the range of 300–800 nm was employed to measures the optical absorption spectrum. Schimadzu xrd-7000 was used to record X-ray diffraction pattern, using CuKα, wavelength of radiation (λ = 0.15406 nm) in the range of 2theta 10nm to 80nm.

C. *Photocatalytic activity studies*

The photocatalytic degradation of methylene blue was performed in a 250 cm^3 conical flask using as synthesized CuO:CdO as photocatalyst under the sunlight for various time intervals. 10mg of synthesized CuO:CdO powder was equilibrated with 50 cm^3 of 10ppm methylene blue dye solution by shaking on shaker for 30min, i.e. CuO:CdO, before exposing to the sunlight. A 5.0 cm^3 sample was taken at regular time intervals and the photocatalytic decomposition of methylene blue was examined using UV–visible spectrophotometer (systronic UV-2203) at 695 nm wavelength.

Activity of the recycled catalysts was evaluated by collecting the catalyst using filter paper after the degradation reaction. The next run was carried out using the fresh methylene blue solution and recovered catalyst. The experiment was replicated five times (Sajid et al., 2021, Shekoohiyan et al., 2020).

III. RESULTS AND DISCUSSION

A. *Binding energy*

Higher molar ratio CuO with respect to CdO in nanocomposites decreases the binding energy (3.543eV) of CuO:CdO nanocomposite by 0.135 eV. Binding energy of nanocomposite CuO:CdO in the ratio 1:1 having 3.678eV ,which is higher than the binding energy of CuO (3.612eV) and CdO (3.56eV). Therefore it is expected that CuO-CdO nanocomposite with 2:1 ratio with respect to CuO:CdO possess comparatively good semiconductor property.(Engku et. al., 2019)

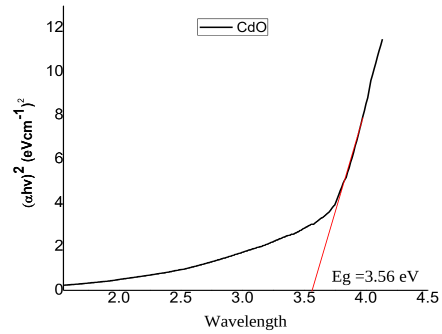
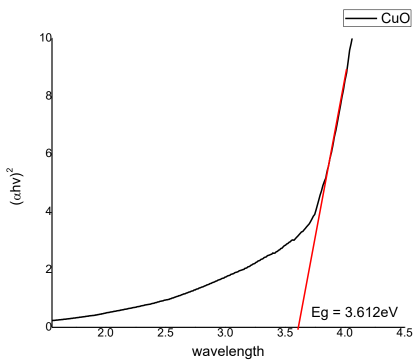
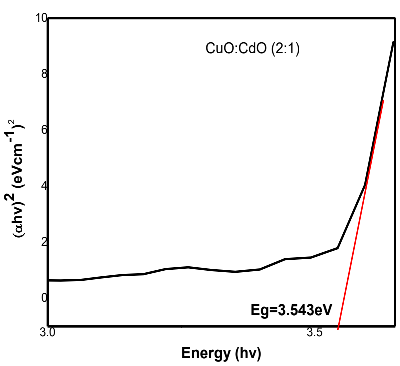


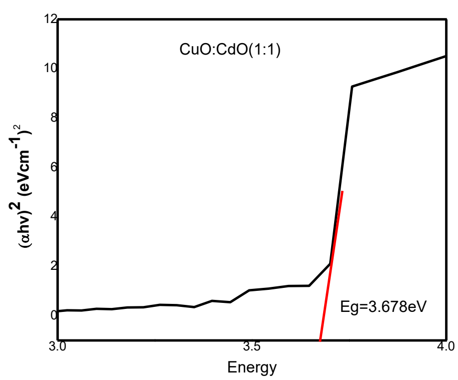
Figure1: a) Binding energy curve of CdO



b) Binding energy curve of CuO



c) Binding energy curve of CuO:CdO nanocomposite(2:1)



d) Binding energy curve of CuO:CdO nanocomposite(1:1)

B. XRD Analysis

The potential peaks intensity with indication for 2θ values were assigned at 2θ values of 33.16°, 38.48°, 55.46°, 66.1° and 69.42° corresponds to (111), (200), (220), (311), (222) crystalline planes of CdO nanoparticles respectively. These peaks are in good agreement with the standard JCPDS data (File no. 05-0640) (Mohammed et. al. 2017). The potential peaks intensity with indication for 2θ values of CuO were assigned in the spectrum at 31.72°(112), 35.6°(111), 38.9°(110), 45.4°(002), 48.9°(202), 56.5°(202), 61.7°(113), 66.2°(311), and 75.2°(222) is according to the JCPDS card No.00-04(Tauseef et. al., 2021). According to the XRD analysis, good number of crystalline CuO-CdO was existing in the prepared nanocomposites. Debye-Scherer's formula was used to calculate crystalline particle size, and found to be between 20-40 nm. (Gopidas et. al., 1990)

Average particle size (D) = $\frac{0.9\lambda}{\beta cos\theta}$

Where, D = crystalline particle size, λ= wavelength of X-ray ,β= diffraction peak broadening ,θ = angle of diffraction

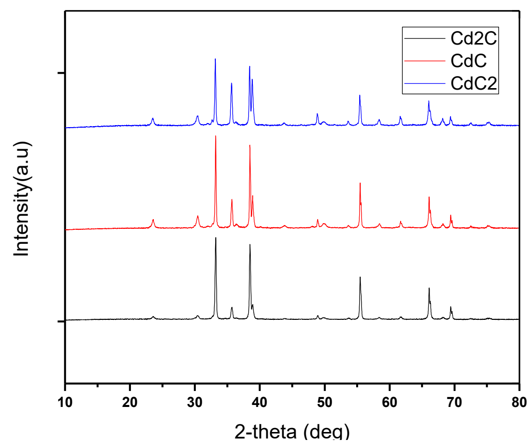


Figure 2: XRD spectra of CuO:CdO nanocomposite

C. Photo catalytic activity

In this study, CuO:CdO nanocomposites with 1:1, 1:2 and 2:1 molar ratios was used for degradation reaction of methylene blue. Maximum Degradation efficiency was 98.78% for 2:1 ratio of CuO:CdO at 180 minutes. While degradation of methylene blue at the same time was 95.99% for 1:1 ratio and 90.22% for 1:2 ratio of CuO:CdO as shown in figure 5a. Thus present study on degradation of methylene blue using CuO:CdO nanocomposites confirms that the increase in ratio of CuO compare to CdO favor the charge separation hence degradation is better than the other ratio where CdO percentage is higher than CuO.

Linearity of the analysis response was inspected through the linearity of calibration line, attained from 18 standard solutions, which exhibited, a linear regression coefficients = 0.99078 and slope = 0.19739± 0.00462 (Figure 3). Blank determination method used to calculate the limit of detection (LOD) and limit of quantitation (LOQ) and found to be 0.182478 mg/L and 0.575594mg/L respectively. The slope of least-squares line is given by b= 0.2000, Intercept of least-squares line= 0.0140 The equation for the regression line, y=0.2000x + 0.0145. Six replicate measurement of 0.1 ppm methylene blue was used to determined repeatability in terms of relative standard deviation (RSD) in percentage and found to be 5.2814% (Dilip et. al. 2016).

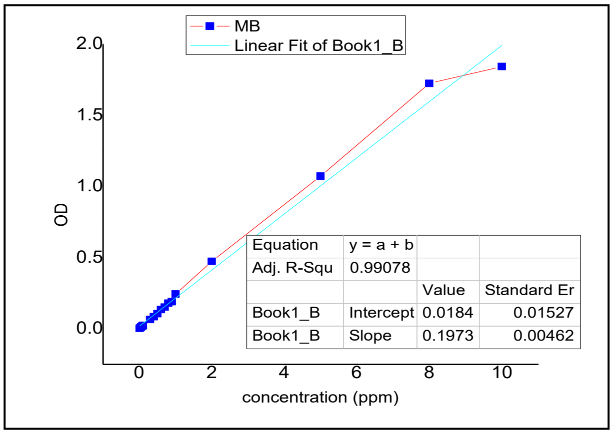


Figure 3: calibration curve of methylene blue

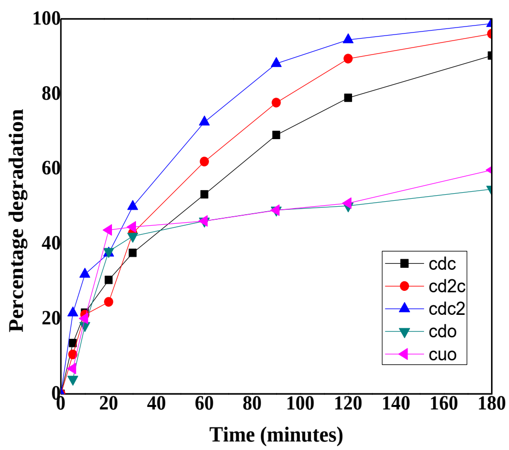


Figure 4: a) Plots of percentage degradation of methylene blue dye as function of time under visible light irradiation.

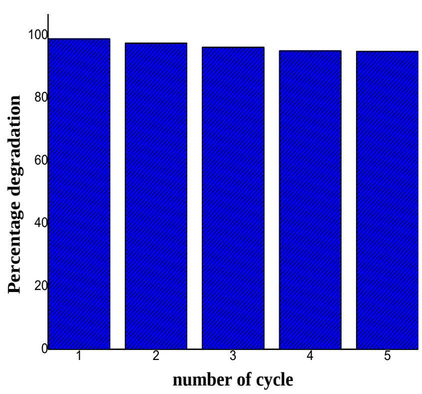


Figure 4(b): Recycling of 2:1 CuO:CdO nanocomposite during the degradation of methylene blue in presence of sun light.

D. *Order of reaction*

The linearity of plot show that the degradation reaction of methylene blue dye using 1:1, 2:1 and 1:2 of nanocomposite CuO:CdO as catalyst show good agreement with first order kinetics with the regression value of 0.9979, 0.9959 and 0.9962 respectively as shown in figure 5I, 5II, and 5III(Sidney et. al. 2019, Raees et. al., 2021).

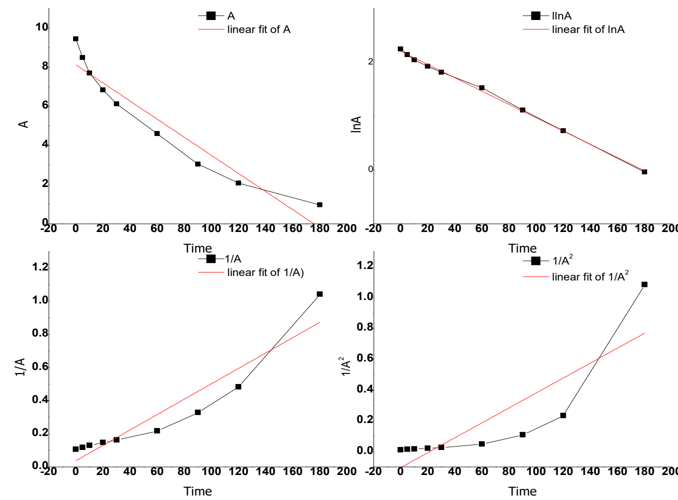


Figure 5I: (a) zero order of reaction (b) first order of reaction (c) second order of reaction (d) third order of reaction plot for degradation of methylene blue using CuO:CdO (1:1) nanocomposite

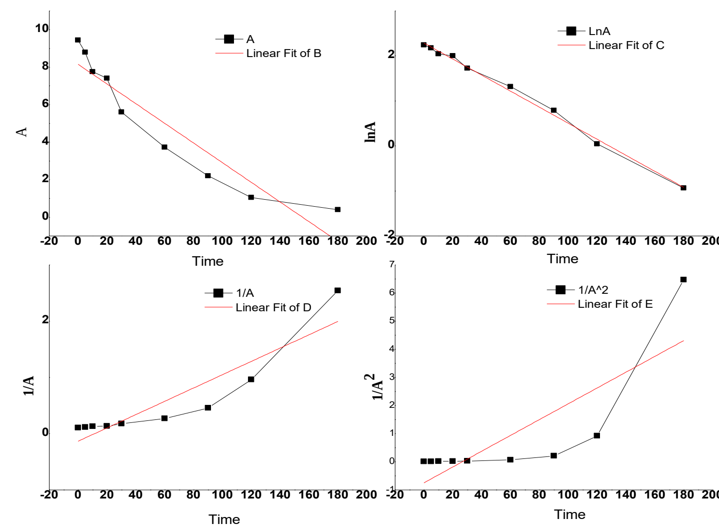


Figure 5II: (a) zero order of reaction (b) first order of reaction (c) second order of reaction (d) third order of reaction plot for degradation of methylene blue using CuO:CdO (1:2) nanocomposite.

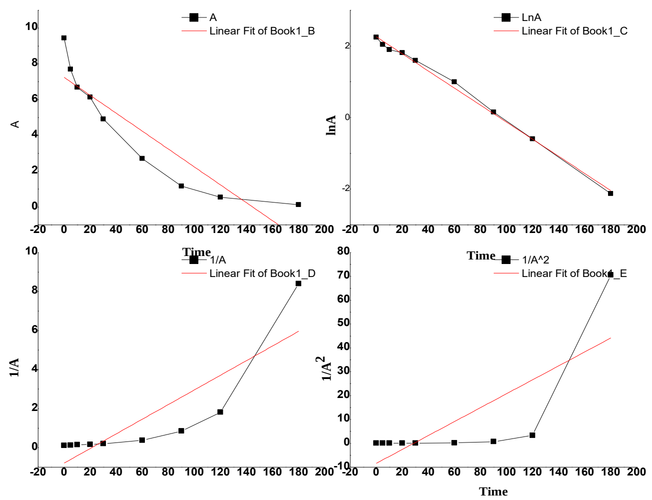


Figure 5III: (a) zero order of reaction (b) first order of reaction (c) second order of reaction (d) third order of reaction plot for degradation of methylene blue using CuO:CdO (2:1) nanocomposite.

The above results concluded that the variation of CuO with CdO in nanocomposite has great impact on photo catalytic activity of methylene blue. Due to the formation of 2:1 of CuO:CdO nanocomposite resulting in controlled recombination of photo created electron and hole and help in better degradation.

CONCLUSIONS

CuO:CdO nanocomposites synthesized by simple, co-precipitation method. The XRD results revealed that prepared sample was nanosized and its strong peaks show the presence of CuO:CdO nanocomposites. The photocatalytic activity of the nanocomposite with molar ratio of 1:1, 1:2 and 2:1 of CuO:CdO possess good photo response under visible light irradiation and follow firs order kinetics with the regression 0f 0.9979, 0.9959 and 0.9962 respectively. The improved photocatalytic activity of prepared nanocomposite might be due to coupling of two semiconductor and the increased percentage of CuO with respect to CdO in the nanocomposites. The degradation efficiency of prepared samples are in the sequence of CuO:CdO(2:1) (98.78%)>CuO:CdO(1:2) (95.99%) > CuO:CdO(1:1)(90.22%) > CuO(59.68%) > CdO (54.63%), respectively Moreover, good recycle property of nanocomposite was observed after decomposition of dye.

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