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## Synthesis, Characterization and Application of Cu doped ZnO nanopowder for the Solar Photocatalytic Degradation of Textile Dyeing Effluent.

P Logamani<sup>1</sup>, R Rajeswari<sup>2\*</sup>, and G Poongodi<sup>3</sup>.

<sup>1</sup>Research and Development Centre, Bharathiar University, Coimbatore - 641 046.

<sup>2</sup>Department of Chemistry, Quaid-E-Millath Govt. College for Women, Chennai - 600 002

<sup>3</sup>Department of Physics, Quaid-E-Millath Govt. College for Women, Chennai - 600 002

### ABSTRACT

Copper doped ZnO nanocatalyst was synthesized by wet chemical method. X-ray diffraction (XRD), and Field Emission Scanning Electron Microscopy (FESEM) with Energy dispersive X-ray spectroscopy (EDAX) were used to assess the structure and morphological properties of the catalyst prepared. UV-visible transmission spectroscopy assessed optical properties of the samples and the band gap was calculated using Tauc's plot. The XRD diffraction peak confirms that the synthesized Cu doped ZnO has highly crystalline hexagonal wurtzite structure. In addition, the presence of Cu in the ZnO was further evidenced from EDS analysis. FE-SEM images established the morphology of the Cu doped ZnO. The photocatalytic activity of pure and doped ZnO nano powders were tested with Amaranth dye using visible light (365nm) in an annular photo reactor and also in Solar light. The reaction parameters such as pH, catalyst dosage and dye concentration were optimized. The results revealed that maximum degradation was achieved with solar light mediated doped ZnO. Degradation study revealed that doping has distinct influence on the photocatalytic behaviour of ZnO. With the optimized conditions, Decolourisation was 97% and the Degradation was 72% at the end of 180 min. The present research study shows that Cu doped ZnO could be used as an effective photocatalyst for the removal of dyes in textile effluents in a suitably designed solar photocatalytic reactor.

**Keywords:** Solar photocatalysis, Cu doped ZnO, Textile effluent

*\*Corresponding author*

Email: rajikanna99@yahoo.co.in

## INTRODUCTION

Many urban areas and villages all over the country are facing a serious environmental threat due to improper disposal of untreated wastewater from industries which lead to serious health risks in humans. New treatment technologies have been attempted in recent years for the treatment of these wastewaters. In developing country like the India, there is a need to implement these treatment methods which are technically feasible and economically viable to make development sustainable. One such economically viable technology is Advanced Oxidation Processes (AOPs) which uses hydroxyl radical as an oxidant for the degradation of wastewater.

Among different AOPs, heterogeneous semiconductor photocatalyst such as  $\text{TiO}_2$  has been widely used for waste water treatment since Fujishima and Honda reported the photocatalytic splitting of water using  $\text{TiO}_2$  electrode in 1972 [1]. Using semiconductors as photocatalysts has opened a new door to the eradication of harmful pollutants in waste water since it leads to high mineralisation of organic pollutants. Zinc oxide (ZnO) is one of the wide band gap (3.27eV) semiconductor photocatalyst and having similar photocatalytic characteristics that of  $\text{TiO}_2$  have been studied extensively because of their novel properties, such as high chemical stability, excellent optical and electrical response and nontoxic nature. However, the faster recombination of photo-generated charge carriers of ZnO decreases its photocatalytic efficiency. Many techniques have been adopted to overcome this drawback. One of the well-known methods to enhance the photocatalytic efficiency of ZnO is doping metal ions in its lattice which generates defects and vacancies [2–5]. These vacancies act as a trap for photo generated charge carriers and reduces recombination rate.

By doping Cu in ZnO, the physical and chemical characteristics are modified because of different structure of electronic shell and similar size. By neighbouring oxygen vacancy, Cu could enter the ZnO lattice as deep acceptors [6]. Solar light could be harvested efficiently by causing defects in the ZnO structure by narrowing down the band gap.

Environmental contaminants generally vary with nature of source, and the most serious amongst them is the textile dyes which pollute the river, ground water and as well as land. Many researchers have reported the degradation of textile dyes and the removal of colour is comparatively easier than reducing the organic contamination in dyeing wastewater. Kothari *et al* [7] degraded Evans blue and Amaranth by ZnO. Benjamin *et al*. [8] reported increase in photocatalytic activity of ZnO using natural pigments as a coating material. Egzar *et al*. [9] investigated the use of different semiconductors such as ZnO, ZnS and  $\text{SnO}_2$  for the degradation of aniline blue dye. Ahmad *et al*. [10] synthesized Al-doped ZnO which resulted five times enhancement in photocatalytic behavior compared to pure ZnO.

In the present study, photocatalytic degradation of textile dye Amaranth was investigated with Cu doped ZnO nanopowders in the presence of solar light. India being a tropical country has abundant solar energy which could be harnessed for enhancing the photocatalytic activity at the reduced cost. Cu doped ZnO nano powder has been prepared, characterized and the used for the degradation of the Amaranth dye present in the wastewater.

## MATERIALS AND METHOD

### Materials

The commercial azo dye Amaranth was purchased from Shrinathajee Enterprises, (Ahmedabad, India). Zinc acetate dihydrate, Copper(II)acetate monohydrate, sulphuric acid, and sodium hydroxide were purchased from Merck and were used without further purification.

### Preparation of Cu doped ZnO nanopowder

Cu doped ZnO nano powder was prepared using wet chemical precipitation method. Initially, 0.25M of zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) and 5mol% of copper(II) acetate monohydrate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ) were dissolved in distilled water which was then added in drops to 50ml of 0.1M NaOH solution under magnetic stirring. Unwanted ions and impurities were washed and removed

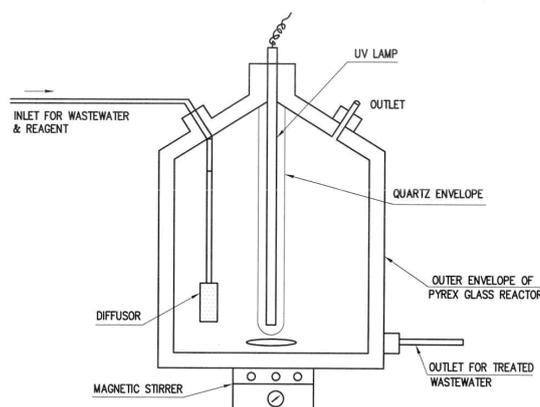
following which the precipitate was collected. The precipitate was dried at 80°C for 24h and calcined at 400°C for 2h.

**Characterization of Cu doped ZnO nanopowder**

Crystalline structure of Cu doped ZnO samples were characterised by XRD. The surface morphology was studied using field emission scanning electron microscopy (FE-SEM) **equipped** with energy dispersive X-ray (EDS) which also confirmed the presence of elements. Optical transmission spectra were taken using LABINDIA T90+ UV-Vis spectrophotometer in the wavelength range of 300-800 nm.

**Photocatalytic degradation of Textile dye Amaranth**

The photocatalytic behaviour of the prepared Cu-doped ZnO nanopowders were assessed by studying the degradation of Amaranth in aqueous solution. Experiments were conducted in an annular reactor with 365 nm UV lamp (Figure 1) and also in plexi glass trays exposed to solar light in the open terrace. 0.2 g/L Cu doped ZnO photocatalyst was added to 500 mL of the prepared dye solution (20 mg/L). These suspensions were stirred thoroughly in the dark for the establishing absorption equilibrium and then exposed to visible light in the annular photoreactor. At regular intervals of time, samples were withdrawn and analysed for the percentage of decolourisation and degradation. Absorbance at 522nm in the UV-visible spectrophotometer depicted decrease in decolourisation and Chemical Oxygen Demand measured by open reflux potassium dichromate titrimetric method showed the decrease in degradation.



**Figure 1: Schematic diagram of annular photoreactor**

**RESULTS AND DISCUSSION**

**Characterization of Photocatalyst**

*Structural studies*

X-ray diffraction analysis confirmed the crystal structure of synthesized Cu doped ZnO. Powder XRD patterns of Cu doped ZnO shown in figure 2 where all the diffraction peaks were indexed and found in wurtzite hexagonal structure (JCPDS No.36-1451). The diffraction peak appeared at 31.47°, 34.09°, 36.02°, 47.28°, 56.35° and 62.6° is corresponding to the diffraction peak (100), (002), (101), (102), (110) and (103), for the Cu doped ZnO sample. No diffraction peaks from copper and any other impurities could be detected in the sample which confirms the incorporation of Cu ions into the crystal lattice of ZnO. Absence of extra peaks in XRD data proves that the sample is in a single phase.

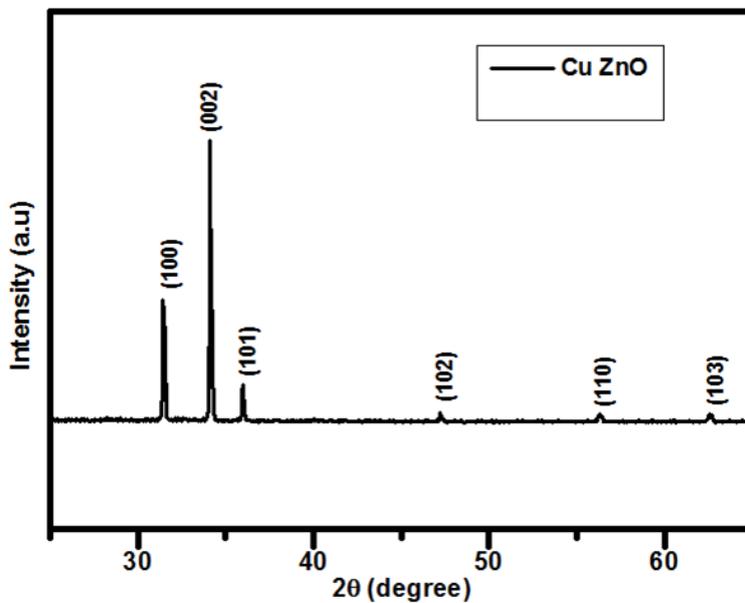


Figure 2: XRD pattern for Cu doped ZnO nanopowders

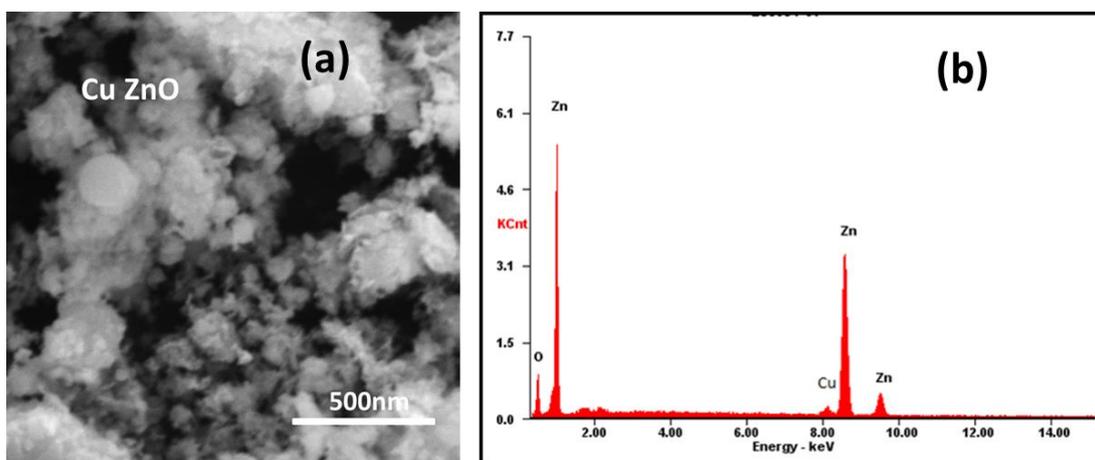


Figure 3: (a) FESEM image of Cu doped ZnO and (b) EDAX spectrum of Cu doped ZnO

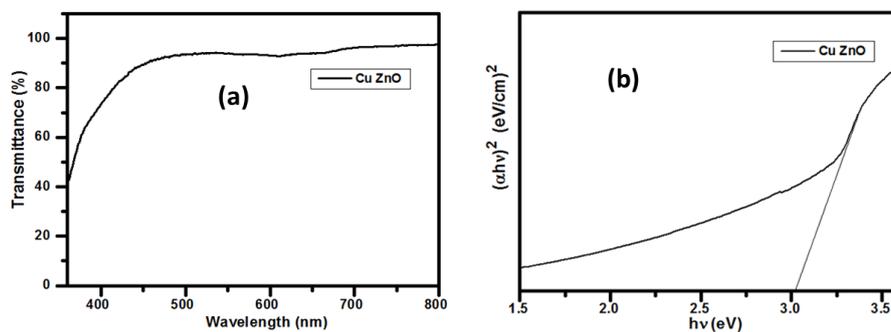
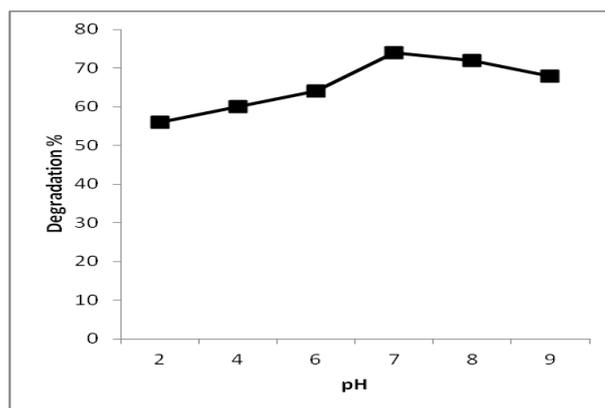


Figure 4: Optical transmission spectra of Cu doped ZnO



**Figure 5: Effect of pH on photocatalytic degradation of Amaranth**

#### *Morphology and compositional analysis*

FESEM studies show the morphology of Cu doped ZnO nanoparticles synthesized. The size and shape of Cu doped ZnO seem to be agglomerated spherical-shaped and of the order of 50 nm as shown in Figure 3(a). Presence of Cu in ZnO is confirmed by the EDAX analysis as indicated in figure 3(b). The results prove that the sample powder consists of Zn, Cu and O and confirms the substitution of Cu in ZnO.

#### *Optical Studies*

The optical transmission spectra of Cu doped ZnO sample shown in figure 4(a) is used to study the optical properties. The optical band gap ( $E_g$ ) was estimated from the Tauc's relation,

$$(\alpha h\nu)^2 = A (h\nu - E_g)^m \quad (1)$$

Where A is an energy dependent constant,  $E_g$  is the optical band gap of the material, m is a constant and is equal to 1 for a direct transition. The optical band gap energy was measured by extrapolation of the linear part of plot between  $(\alpha h\nu)^2$  and  $h\nu$  as shown in Fig.4(b). The observed band gap value of Cu doped ZnO sample is 3.02eV and 3.37eV for pure ZnO. Earlier works by Paneerselvam et al [11] confirmed the decrease in band gap by Cu doping.

#### **Photocatalytic Degradation**

##### *Effect of pH*

Studies showed that pH played a major role in the degradation of any wastewater and hence the samples were analysed at different pH ranging from 2 to 9. The studies were carried out with samples at different pH and with 20 mg/L of dye and 0.2g/L of the catalyst. The degradation of Amaranth was found to be 56, 60, 64, 74, 72 and 68% at pH 2, 4, 6, 7, 8 and 9 respectively. Figure 5 showed that the degradation of Amaranth was greatly influenced by pH of the dye solution and maximum degradation was observed at pH 7.

##### *Effect of catalyst dosage*

Influence of catalyst on the reaction was determined by conducting experiments with different amount of catalyst ranging from 0 to 1.0 g/L (at optimum conditions of pH= 7 and dye concentration=20 mg/L). The degradation rate was found to increase with an increase in the catalyst dosage up to 0.2 g/L as shown in Fig.6 and then decreased. In general, with increase in amount of catalyst, more active sites would be available which in turn increase the reaction rate. However, more photocatalyst would also lead to greater aggregation, which would result in the decrease in the surface area of the photocatalyst and hence the adsorption of dye. Further, as the opacity of the dye solution increase penetration of light becomes difficult and fewer nanoparticles are activated and hence the degradation decreases.

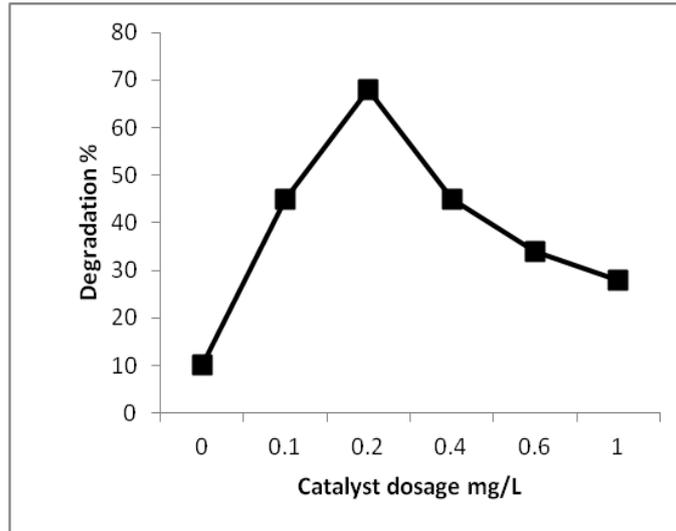


Figure 6: Effect of Catalyst dosage on photocatalytic degradation of Amaranth

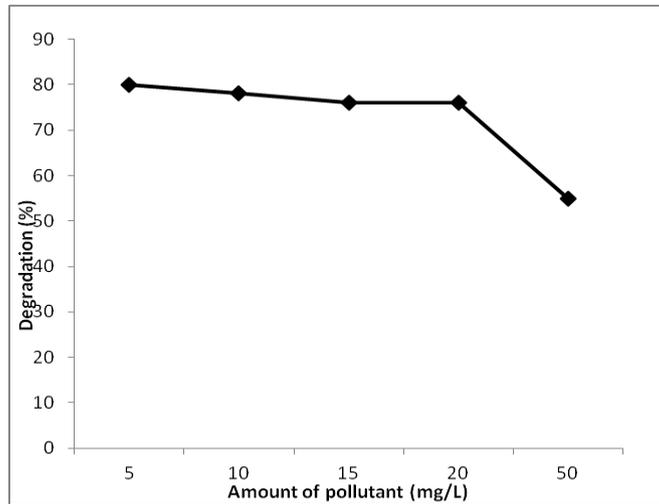


Figure 7: Effect of pollutant concentration on photocatalytic degradation of Amaranth

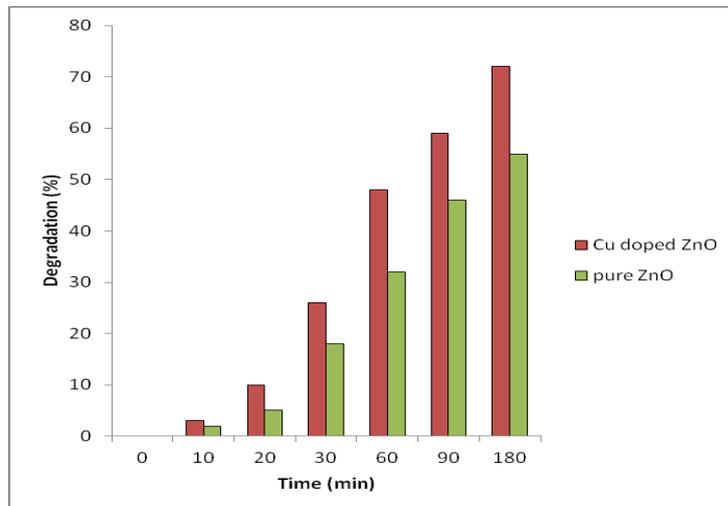


Figure 8: Degradation of Amaranth with Cu doped ZnO and pure ZnO

### *Effect of pollutant Concentration*

The degradation of Amaranth at different concentrations (5,10,15,20 and 50 mg/L) for a catalyst dosage of 0.2g and at pH7 was investigated and shown in Fig.7. The degradation was found to be inversely proportional to the concentration. Further, the figure 7 shows that even at 50 mg/L the degradation efficiency was 55% which means that Cu doped ZnO worked well at high concentration. At lower concentration of the dye, the catalyst surface area available was sufficient for the degradation, but further increase in dye concentration (at 50 mg/L) decreases in OH• radicals generation was observed as active sites of the catalyst were fully occupied by dye molecules which resulted in reduced degradation at higher concentration.

### *Degradation studies*

Solar photocatalytic degradation of Amaranth dye was studied with optimized parameters. With the optimized conditions (i.e. at pH 7, dye concentration 20mg/L and catalyst concentration 0.2g/L), Decolourisation was 97% and the Degradation was 72% at the end of 180 min. Degradation study revealed that doping has distinct influence on the photocatalytic behaviour of ZnO. With pure ZnO, only 55% degradation was achieved in the same optimized conditions as shown in figure 8.

### **CONCLUSION**

Cu doped ZnO nanopowders have been prepared and characterized. Structure and morphology studies revealed the Cu doping in the ZnO photocatalyst. Compared to undoped ZnO, the doped ZnO has reduced band gap and its photocatalytic activity is enhanced. The present preliminary research study shows that with suitably designed solar photocatalytic reactor, Cu doped ZnO could be used as a photocatalyst for the removal of dyes in textile dyeing effluents.

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