# Photodegradation of Methylene Blue Dye Using Nanocomposites of Copper Sulfide Doped with Fe/ Cd/Zr as Nanophotocatalyst

J. William Brown<sup>1</sup>, P.S. Ramesh<sup>2,\*</sup> and D. Geetha<sup>1</sup>

<sup>1</sup>Department of Physics, Annamalai University, Tamil Nadu, India; nirmalamatcdm@gmail.com, geeramphyau@gmail.com <sup>2</sup>Physics Wing DDE, Annamalai University, Tamil Nadu, India; psrddephyau@gmail.com

# Abstract

**Objectives:** To characterize and to know the nature of the synthesized products and identify the photocatalytic response of the hybrid nanocomposites was investigated by the decolourization of (MB) dye under natural Sunlight radiation. Methods/statistical analysis: We report fabrication of mesoporous nanocomposites (Fe-CuS, Cd-CuS, Zr-CuS) with uniform nanostructures via a hydrothermal method employing copper nitrate trihydrate (Cu (NO<sub>3</sub>).3H<sub>2</sub>O), Thiourea (Tu,Sc(NH<sub>2</sub>)<sub>2</sub>, Iron trinitrate (Fe(No<sub>3</sub>)<sub>3</sub>), (Cd(No<sub>3</sub>)<sub>3</sub>) and (Zr(No<sub>3</sub>)<sub>3</sub>) as starting materials with cationic surfactant cetyltrimethylammonium bromide (CTAB) as stabilizer/size controller and ethylene glycol as solvent at 130°C temperature. The products were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy TEM, and UV-Vis spectrum (UV) analysis. Findings: X-ray diffraction (XRD) spectra confirmed the Fe doped copper sulfide nanocomposites are crystalline in nature with the hexagonal CuS phase. XRD pattern showed Fe doped spherical structure of CuS with a grain size of 21 nm. An intense surface Plasmon resonance between 250-300 nm in the UV-Vis spectrum clearly reveals the formation of Fe doped copper sulfide nanocomposites. The XRD pattern of Cd incorporated CuS shows crystallite nature and crystallinity increases with the addition of cadmium on CuS. The observed results show that Zr is homogeneously dispersed on CuS and well separated from one another. The XRD results confirm the presence of well-dispersed cubic ZrS<sub>2</sub> on the covellite CuS surface. Photo reactivity of copper sulfide nanoparticles as undoped and doped with ferrous, cadmium and Zirconium were studied in the decolorization of methylene blue under natural sunlight. The concentration of dopants and concentration of dye are variables that influence the photoreactivity of nanocatalysts. Application/improvements: The prepared nanoparticles CuS, Fe-CuS, Cd-CuS and Zr-CuS show the most degradation efficiency. The optimum dosage of the photocatalyst was 120 mg/L. In the optimized conditions, the degradation efficiency was 86–95% for methylene blue in irradiation time of 150 min.

Keywords: Nanophotocatalyst, Copper Sulfide, Methylene Blue, Photodegradation

# 1. Introduction

To facilitate the recycling and reuse of wastewater by chemical treatment is a sustainable approach. Well-advanced treatment technologies are available to destroy the organic pollutants.<sup>1,2</sup> Semiconducting metal oxides/sulfides have been repeatedly examined in the recent days.<sup>3,4</sup>

The catalytic efficiency depends on some factors viz., material design (morphology, size and surface area) and creating junctions. To achieve all these, preparation methodologies (Co-precipitation, hydrothermal and solvothermal) may vary and play a vital role. If the particle size is very less, the bandgap energy is more; hence it leads to higher redox potentials within it.

\*Author for correspondence

Therefore, nano semiconductors expected to have a very high photocatalytic response.

To eradicate the colored dye effluents which are toxic and non-biodegradable, using heterogeneous photocatalysis is a cost-effective alternative for water remediation and the basic mechanism behind the photodegradation was clearly explained.<sup>5</sup> Covellite CuS is an interesting material, because of its ability to absorb solar energy in the visible region. So, it was used in solar cells, photoelectronic devices and photo degradation.<sup>6</sup> Earlier reports are elaborated  $TiO_2$  is frequently used for the treatment of wastes containing dyes. Whereas, the copper sulfide doped with other transition metals for photodegradation has been not reported much. However, comparative morphology and dopant influenced the photocatalytic study of CuS with different (Fe/Cd/Zr) has not been reported. Considering frequently used dyes, methylene blue is toxic and relevant to environmental pollution. The material morphology onto photodegradation has not been reported before. The present investigation mainly towards the design of different CuS nanocomposites as photocatalysts by a simple hydrothermal via in the presence of CTAB as stabilizing and capping agent and with three dopant ions to evaluate the catalytic activity on MB dye (This dye is stable, incompatible with bases, reducing agents and strong oxidizing agents. It is harmful if swallowed or inhaled or in contact with skin and causes eye irritation) under natural Sun Light.

CuS with different (Fe/Cd/Zr) sulphide is an excellent semiconductor with a direct bandgap of 2.42 ev at room temperature with many outstanding Physio-chemical properties,<sup>7.8</sup> which has promising applications in multiple technical fields viz., solar cells,<sup>9</sup> photo catalysis.<sup>10</sup> Lightemitting diodes for flat-panel display.<sup>11</sup> Different metal sulfide nanostructures with divergent morphologies, such as and nanorods,<sup>12</sup> dendrites,<sup>13</sup> spheres,<sup>14</sup> sea-urchin<sup>15</sup> are reported by many researchers.

Characteristics such as soft-template effect, the capability to modify the chemical kinetics and easy manoeuvrability of the surfactants help to control the nanostructure or the morphology. A few frequently used surfactants in the preparation of Cd–CuS nanostructures are PVP,<sup>16</sup> Tween-80<sup>17</sup> and ethylene diamine SDC<sup>18</sup> as soft templates to synthesize. Ostwald ripening and oriented attachments (OA) are two kinds of mechanism in the growth of nanostructure. The oriented attachment mechanism is the formation of a single crystal from two particles by sharing common crystallographic

orientation.<sup>19</sup> This process is dominant at the nanometer level as they directly modify the nanoparticle surface.<sup>20</sup>

Zirconium Sulfide (ZrS) is an attractive material in various applications due to its excellent textural properties as resistance, low cost, high density, mechanical, thermal, optical and electrical characteristics.<sup>21,22</sup> Nanocomposite containing inorganic metals exhibits different properties compared to individual components, interns of chemical and physical properties which are much better too.

Many researchers have synthesized CuS and FeS, CdS and ZrS separately in the form of powder. But the problem of capping also should be solved, which may change the photocatalysis yet to be studied experimentally in a wide range. Compared to individual components mixed metal sulfides provide better textural, chemical and physical properties than each individual component.

In this report, CTAB molecules are utilized to change the specific surface area and pore-size of CuS. The hydrothermal synthesis method was adopted by thiourea as a sulfur source, enabling the formation of CuS nanostructure. To the best of our insight, Fe/Cd/Zr doped CuS with various morphologies as a photocatalytic material in aqueous catalysts has not been reported.

# 2. Experimental

## 2.1. Material

The Dye methylene blue ( $C_{16}H_{18}N_3ClS_3H_2O$ ) is purchased from Fluka Company. The nitride salts of copper, ferrous, cadmium, zirconium and Thiourea (Na<sub>2</sub>S9 H<sub>2</sub> O) from Sd. fine chemicals were used as such. Cycle tri ammonium Bromide (Tab and ethylene glycol were procured from Merck company and used as suck. The PH of the solution has been modified using HCL and NaOH.

## 2.2. Catalyst Preparation

The precipitated M–CuS nanoparticles were centrifuged at 4000 rpm, washed four times with water to eliminate unreacted ions, and washed with ethanol and dried for about 12 h at 60 °C In the same way, the nanoparticles of CuS, Fe–CuS, Cd–CuS and Zr–CuS were prepared.

## 2.3. Catalyst Characterization

The sample solutions of nanoparticles were prepared with disperses in isopropyl alcohol. The UV-Vis absorption spectra of 10 mm transparent solution were taken for recording by UV-Vis spectra at room temperature.

#### 2.4 Photodegradation Experiment

The beaker was filled with 0.5 mg/L of dye as a pollutant and 50 mg/L of nanoparticles as a nano photocatalyst. All the reactions were done under natural sunlight and stirred by a magnetic stirrer to make the uniform solution. Every 30 minutes the samples were collected for calculating the degradation efficiency.

The degradation efficiency of the synthesized samples before and after irradiation of sunlight can be measured using the relation

% D = 
$$100 \times \frac{n(Ao-A)}{Ao} = 100 \frac{(Co-C)}{Co}$$

Where Ao, A Co and C are initial absorbance and after irradiation time, initial concentration of dye solution and concentration of dye after irradiation time. C is calculated using the Beer-Lambert equation and absorption measurement at  $\lambda_{max}$  of dye solution. The wavelength of absorbance maximum ( $\lambda_{max}$  of methylene blue is 661 nm. The decrease in the absorbance value of samples at  $\lambda_{max after}$  irradiation with time interval will be the rate of degradation.

MB molecule has a major absorption band at  $\lambda_{max} = 660$  nm. From the earlier reports, and from our observation, the colour was found to have disappeared considerably (after 120 min irradiation) indicating that at least the chromophoric structure of dye was destroyed. The molecular structures of Methylene Blue are shown in Figure 1.

The enhanced photocatalytic activity of metals (Fe/Cd/Zr) doped CuS catalysts could be due to reduced hydrogen-related defects. It is worth to mention that the photocatalytic activity of metals (Fe/Cd/Zr) doped CuS nanostructures towards MB are higher than the earlier report. Therefore, the MB from diluted industrial effluents may be easily removed by using these samples.

# 3. Results and Discussion

#### 3.1. Structural Analysis (XRD)

Figures 2.(a)–(d) show crystallographic structures of the CuS and different concentrations of dopant material of Fe–CuS, Cd–CuS, Zr–CuS nanocomposites stabilized by a cationic surfactant (CTAB).

All the diffraction peaks with  $2\theta$  values are positioned at 27.59°, 29.74°, 31.95°, 48.10°, 52.24° and 59.45° corresponding to the (hkl) planes of (101), (102), (103), (110), (108) and (116) of covellite CuS and



Figure 1. Molecular structure of methylene blue.

Fe–CuS nanostructures in good crystalline quality, which is reliable with the hexagonal CuS (JCPDS No.06-0464).<sup>23</sup> No observable other phases are found in the XRD spectra. It reveals the hexagonal phase of CuS only. The material additionally contains a peak which is because of a secondary phase from hematite.<sup>24</sup> The intensity of the peak for the secondary phase becomes stronger. The result is in conformity with similar types of observations made by<sup>25</sup> and<sup>26</sup>. Also, the porous structure is more visible and uniform at 0.30mMconcentration of Fe on CuS.

Figure 2 (c) shows XRD patterns of the CuS and different concentrations of Cd–CuS nanostructures. Good crystalline quality is seen in diffraction patterns with 2θ values at 27.53°, 29.72°, 31.97°, 48.13°, 52.27° and 59.41° corresponding to the planes of (101), (102), (103), (110), (108) and (116) of covellite CuS and Cd–CuS nanostructures.<sup>27</sup> Also, the diffraction peaks of CdS originated from a different set of planes i.e, (100), (200), (101), (102), (110), (103) and (112). These diffraction peaks matched well with the standard JCPDS Code 01-073, corresponding to the cubic phase of CdS. The JCPDS (05-0640) confirms the Cd phase with face-centered crystal structure the Bragg position for reflections like (111) for Cd–CuS nanostructures.

CdS changed its cubic structure into a hexagonal structure of CuS when Cd ions were added to the solution mixture. Structural alteration within the crystal lattice is due to the replacement of bigger size  $Cd^{2+}$  ions (1.71 A°) by the smaller Cu<sup>2+</sup> ions (1.28 A°). These results are in concurrence with the earlier literature reported by.<sup>28</sup> The diffraction peaks are more intense in 0.05 mM of Cd doped CuS as compared to the other two concentrations.

Powder XRD measurements for Zr–CuS are presented in Figure 2 (d). The XRD pattern matched well with standard JCPDS Card no 27-0997. A peak at 30°, which resulted in Zr and CuS precursors, it indicates the presence of the tetragonal ZrS structure<sup>29</sup> and intense sharp peaks at (100), (101), (102), (103) and (006) for hexagonal covellite peaks, (JCPDS Card No 24-0060).<sup>30</sup>



**Figure 2.** (a)–(d) XRD spectrum of (0.1 mM) CTAB stabilized Fe (0.30 mM) doped CuS, (b) Cd (0.05 mM) doped CuS and (c) Zr (0.05 mM) doped CuS nanostructures with SAED pattern.

The diffraction peaks are more intense in 0.05 mM of Cd doped CuS as compared to the other two concentrations

It points out that the structure of Fe–CuS, Cd–CuS, Zr–CuS is strongly controlled by the concentration of the nanoparticles. The average particle size has been calculated using Scherrer's formula.<sup>31</sup>

The average sizes of Fe–CuS, Cd–CuS, Zr–CuS particles are found to be 8, 9, 15 nm for the concentration of Fe–CuS, Cd–CuS, Zr–CuS respectively, which is confirmed by TEM micrographs.

#### 3.2. Morphological Analysis (TEM/SAED)

Interestingly, the particles of the Fe–CuS are porous and loosely assembled (SEM), which allows the electron to still penetrate through the samples while TEM measurements are taken. At higher magnification of the TEM images, all the Fe–CuS samples are composed of a number of interconnected nanoparticles. Figures 3(a) shows the TEM microstructural details of porous Fe doped CTAB templated CuS nanostructures. The morphology of Fe doped CTAB capped CuS consists of thin flake-like shapes with well-defined structures at the edges and an average diameter of around 30 nm. The corresponding selected area electron diffraction (SAED) pattern exposed to the crystalline structure can be indexed to the (101), (102), (103), (110), (108) and (116) planes of the hexagonal Fe doped CuS nanostructures. The SAED pattern reveals well-defined diffraction rings indicating the polycrystalline nature of the sample,

Figure 3(b) illustrates distinctive TEM images of the (0.05 mM) Cd–CuS nanosheets. It is obvious from figures that the length of Cd–CuS nanosheets was 90–110 nm, which explains the capability for high performance. The SAED pattern was obtained from the TEM image of the Cd–CuS samples is shown in the figure. The conclusion has arrived from SEM figures that CTAB plays a vital role in the morphological transformation of the CuS and Cd–CuS nanostructures. The head group of CTAB combines with Cd–CuS nanosheets and detaches outwards. The tail groups of the CTAB project from the neighbouring Cd–CuS nanosheets.<sup>32</sup>



**Figure 3.** (a)–(c) TEM images of (0.1 mM) CTAB stabilized Fe (0.30 mM) doped CuS, (b) Cd (0.05 mM) doped CuS and (c) Zr (0.05mM) doped CuS nanostructures with SAED pattern.

Figure 3(c) shows the typical TEM images of Zr-doped CuS nanocomposite. It is noticed that NPs are quite monodisperse and uniform in size. Induced a slight variation in the reaction condition by dopant (Zirconium) rendered smaller sized Zr–CuS NCs. On the surface of the CuS, the hydroxyl groups of ethylene glycol act as anchors and provide an excellent microenvironment for the nucleation and growth of smaller sized Zr doped CuS nanocomposites.

It is observed that the nanoparticles are relatively uniformly distributed. The diameter of the particles is about only 5–20 nm, and has a mean value at 15 nm. There is a significant morphological difference between CuS and Zr–CuS. There is a significant morphological difference between CuS and Zr–CuS. The hexagon Zr– CuS sheets may be held by weak Vander Waals forces. The precursors' concentration, reaction condition and sulfur source are some other structure promoting factors. Figure 4(c) shows the SAED pattern of (0.05 mM) Zr–CuS with ordered array of hexagonal spot, which confirms the formation of hexagon Zr–CuS and indication of the crystallinity.



**Figure 4.** (a-f) Photocatalytic degradation of methylene blue by Cd–CuS under natural sun light at different time intervals.

# 4. Photo Catalytic Activity of CTAB Templated CuS

The concentration of MB dye removal was estimated using a UV-Vis spectrophotometer. The decreases in MB dye concentration due to reaction between CuS nanoparticles are shown in Figure 5(a–f). Decolourization of MB dye was noted after exposure to the sunlight at periodic time intervals. There was about 25% degradation in the first 60 minutes and later increase up to 75% in 150 minutes was observed. Initially, the degradation is more in the first half an hour after that slow degradation can be observed. Moreover, approximately 80% of MB degradation was observed at the end of 150 minutes.<sup>33</sup>

The absorption peaks decrease with the increase of radiation time in presence of CuS NPs due to their better catalytic property. Moreover, the catalytic response of the nanophotocatalyts is achieved maximum degradation at 150 minutes.

## 4.1. Efficiency of CuS Under Sunlight Irradiation

When CuS nanoparticles are photoexcited under sunlight, the charge transfer from the bonding orbital of Cu3+ to the 2p nonbonding orbital of oxygen. A photon from Sunlight strikes the surface of CuS, an electron from its VB jumps to the CB leaving a positively charged hole. The negative charge production increases in the conduction band and photocatalytic active centers are formed on the surface of CuS.

$$CuS + h\gamma \longrightarrow e_{cb}^{-} + h_{vb}^{+} \qquad (1)$$

The holes in the VB react with the chemisorbed water molecules to form reactive species Viz., OH. Radicals react with dye molecules to achieve their complete degradation. The major role of the catalyst is the consumption of electrons and passes those electrons to H+ or to  $O_2$  ions.

#### 4.2. Photo Catalytic Activity of Fe Doped CuS

The presence of catalysts on MB is insignificant without sunlight due to the fact is that the electron-hole pair generation is not possible without light. The enhancement of oxidation and reduction of any reactions are happening when the electron-hole pair formation exists. Hence the degradation efficiency of MB dye was found to be much larger when the sunlight is incident on the solution<sup>34</sup> when compared to blank solution. The reaction mechanism behind could be explained in two ways.

The catalyst has a very high specific surface area, hence it provides a more active surface site to absorb water molecules and to form active ° oH and Hoo° radicals by trapping the photogenerated holes.

These free radicals influence the reaction (photodegradation) and lead to the decomposition of



**Figure 5.** (a–f) Photocatalytic degradation of methylene blue when 0.5 g of CTAB stabilized CuS under natural sun light at different time intervals.2

organic pollutants. Not only that the higher surface area may facilities the absorption of dye molecules on the surface of the photocatalyst.

When the sunlight is irradiated on the MB molecules are absorbed by the Ncs and liberates electrons. These electrons are absorbed oxygen molecules to yield  $O_2$ and  $Ho_2$  radical the dye, which creates the chance to reach the molecules and speed up the reaction, and then the dye molecules could be mineralized in time by superoxide radical ions. So the size of the NC is favorable for the reduction of  $O_2$  and oxidation of  $H_2o$  molecules by trapping electrons and holes which enriches the catalytic behavior of nanophotocatalyst under sunlight.<sup>35,36</sup>

The pre-adsorption of the dye on the catalytic surface is the main phenomenon for efficient charge transfer, which not only affects the degradation rate, also changes the mechanism of the catalysis. In this process, the decolourisation of the dye solution depends upon the photonanocatalyst concentration. The phase structure, specific surface area and crystalline size are the main parameters that decide the activity of the photocatalyst.

The dopant ions (Fe/Cd/Zr) on CuS may not indicate any crystal structure change, but it changes the crystalline

size which may increase their photocatalytic performance. The reaction processes by the catalyst on the dye are given in Figure 6 (a-f).

 $FeS + h\gamma (UV) \longrightarrow FeS (e_{CB}^{-} + h_{VB}^{+})$ (2)

$$FeS (h_{VB}^{+}) + H_2O \longrightarrow FeS + H^+ + OH^- (3)$$

$$FeS (h^+_{CB}) + OH^- \longrightarrow FeS + OH^-$$
(4)

$$\operatorname{FeS} \left( e^{-}_{\operatorname{CB}} \right) + \operatorname{O}_{2} \longrightarrow \operatorname{FeS} + \operatorname{O}_{2} \cdot \tag{5}$$

$$O_2^{\cdot} + H^+ \longrightarrow HO_2^{\cdot}$$
 (6)

Before examining the catalytic performance of the nanocomposite for the degradation of MB, the pre-absorption of the samples without sun light was measured.

After 90 minutes of sunlight irradiation, the degradation efficiency was 50%. Hence, the catalyst quantity is increased to 30 mg, the irradiation time reaches 180 minutes, and the colour becomes white. The decolourication rate is mainly due to (i) the optimum amount of nanophotocatalyst may increase the adsorption of the dye molecule and (ii) the



Figure 6. (a-f) Photocatalytic degradation of methylene blue by CuS/Fe under natural sun light at different time intervals.



Figure 7. (a-f) Photocatalytic degradation of methylene blue by Zr-CuS under sun light at different time intervals.

nanophotocatalysis density in the area decides the maximum degradation.

### 4.3. Photo Catalytic Activity of Cadmium Doped CuS

The degradation efficiency of Cd–CuS on MB is shown in Figure 7 (a–e). The degradation in the absence of Cd–CuS under Sunlight is not Appreciable.

Results show a higher degradation rate of Cd–CuS when compared to CuS. Spherical structure of Cd–CuS with highly dispersed cadmium metal ions on the copper framework. Interestingly the incorporation of Cd into the CuS matrix gave maximum degradation of MB. From the observed data, the incorporation of Cd onto CuS significantly affects the photocatalytic activity.

The expected reactions at the observed results are expressed as follows

 $CdS + h\gamma (Sunlight) \longrightarrow CdS (e_{CB}^{-} + h_{VB}^{+}) (7)$ 

$$CdS (h^+_{VB}) + H2O \longrightarrow CdS + H^+ + OH^- (8)$$

$$CdS (h^+_{CB}) + OH^- \longrightarrow CdS + OH^-$$
(9)

$$CdS (e_{CB}) + O_2 \longrightarrow CdS + O_2.$$
(10)

$$O_2 \cdot + H^+ \longrightarrow HO_2 \cdot$$
 (11)

 $Dye + OH \rightarrow Degradation products$  (12)

$$Dye + h^+_{VB} \longrightarrow Oxidation products$$
 (13)

 $Dye + e_{CB} \longrightarrow Reduction$  (14)

Photocatalytic reaction on preparation nanocomposite surface can be expressed by the Langmuir-Hinshelwood model. The reaction rate after the adsorption equilibrium can be expressed as

$$-Ln (C/C_0) = Kt$$

Where C and  $C_0$  are the reactant concentration at time t = t and t = 0, respectively, K and t are the apparent reaction rate constant and time.

## 4.4. Mechanism of Cd–CuS Photocatalytic Activity

Incorporation of a small amount of Cd on copper results in increased efficiency in photocatalysis under visible light irradiation. Copper has a Fermi level or electronaccepting region at an energy just below the conduction band. Therefore, after light absorption and charge separation, the electron in the conduction band can be effectively trapped by the silver, while the hole oxidizes water and forms hydroxyl radicals, without the threat of recombination. There is an optimum amount of Copper to rapidly trap electrons, but too much Copper r may cover the titanium dioxide and prevent light absorption. In addition, too much silver may mean that the silver acts as a recombination site itself and as a result a decrease in photocatalytic efficiency.

## 4.5. Photo Catalytic Activity of Zirconium Doped CuS

The benefit of transition metals doping is improved trapping of electrons to inhabit  $e^- - h^+$  recombination during irradiation. Decrease of charge carriers recombination results in enhanced photoactivity. Metal ion implantation with ions such as Zr was found to cause a large shift in the absorption band of CuS towards the visible region.

The relevant reactions at the CuO surface causing the degradation of dyes can be expressed as follows:

 $ZrS + h\gamma$  (Sunlight)  $\longrightarrow$   $ZrS (e_{CB}^{-} + h_{VB}^{+})$  (15)

$$\operatorname{ZrS}(h_{VB}^{+}) + H_2O \longrightarrow \operatorname{ZrS} + H^+ + OH^-$$
 (16)

- $\operatorname{ZrS}(h_{CB}^{+}) + OH^{-} \longrightarrow \operatorname{ZrS} + OH^{-}$  (17)
- $\operatorname{ZrS}(e_{CB}^{-}) + O_2 \longrightarrow \operatorname{ZrS} + O_2^{-}$  (18)

 $O_2 + H^+ \longrightarrow HO_2$  (19)

Dye + OH  $\longrightarrow$  Degradation products (20)

Dye +  $h^+_{VB}$   $\longrightarrow$  Oxidation products (21)

Dye + 
$$e_{CB}^{-}$$
 Reduction products (22)

Initially dye is not discolored. As time increased to half an hour, the degradation started. Moreover, the maximum decolourization was observed at 150 minutes. Temporal variation of spectral changes as a function irradiation of time is shown in Figure 7 for  $MB^+ Zr - CuS$  nanocomposites. From the change in intensity as observed, it can be seen that the nano composites could reach maximum degradation for 150 minutes of sun light irradiation. The reaction takes places during the degradation of MB.

It has been reported that CuS served as photocatalyst did not show the high efficiency of photocatalytic activity because the carriers excitation by light not only being transferred inefficiently but also easily being recombined. But CuS/semiconductors or CuO/Conductive materials composites could solve this problem and improve the photocatalytic activity. Here in this work, the significantly higher photocatalytic activities of nanocomposites M– CuS may due to Ag on the surface of the nanocomposites, which enhance the separation of the photoinduced electron-hole pairs and interfacial charge transfer. Among various compositions, 0.05 mM CuS based nanocomposites show the highest photodegradation efficiency.

The time profiles show enhancement in photocatalytic degradation of dye MB. This is in good agreement with the enhanced photocatalytic activity of Zr doped CuS, reported by many authors. The increased surface area due to the small crystallite size may also contribute to the enhanced photocatalytic activity. A possible explanation for the observed enhancement of photocatalytic activities at different extent is that the photocatalysis is also substrate-specific.

# 5. Conclusions

Under natural sunlight, the synthesized CuS and metal ions doped CuS nanocomposites are used as nanophotocatalyst for degrading Methylene blue. This study reveals that the photocatalytic activity depends on the metal ions doping (Fe/Cd/Zr) on CuS, the best dopant concentrations and used quantity as a catalyst. The highest degradation efficiency was observed CuS in the order of Cd–CuS>Fe–CuS.Zr–CuS.

The photocatalytic activity of these metal ions doped CuS nanocomposites for the elimination of methylene blue was tested at its low concentration. The photodegradation of MB took place within 150 minutes; this suggests that metal ions doped CuS nanocomposites are effective. The enhanced catalytic response of these samples may be due to reduced hydrogen-related defects. It was found that the metal ions doped CuS nanocomposites played a key role in photocatalytic performance through studying the degradation efficiency. The photocatalytic degradation of methylene blue is most efficient at pH 10.

It is observed that suitable doping can accelerate the formation of oxygen anion radicals. The major role of dopants is attributed to the enhancement of photocatalytic activity. In fact, introducing nanoparticles to CuS matrix facilitates longer charge separation by trapping dopant on photogenerated electrons and photoactivity under visible light irradiation.

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