



## **VISIBLE LIGHT ACTIVATED PHOTOCATALYTIC DEGRADATION OF EOSIN-Y USING H<sub>2</sub>O<sub>2</sub> SENSITISED Cu<sub>2</sub>O**

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### **ABSTRACT**

Photocatalytic degradation of Eosin-Y is studied using Cu<sub>2</sub>O and visible light. Complete degradation of 20 ppm Eosin-Y occurred in 90 min over 100 mg Cu<sub>2</sub>O assisted by H<sub>2</sub>O<sub>2</sub>. Addition of H<sub>2</sub>O<sub>2</sub> is found to enhance the rate of degradation significantly. Formation of OH free radicals during irradiation is ascertained by means of photoluminescence studies making use of terephthalic acid as probe molecule.

**Key words:** Eosin-Y, Photocatalytic degradation, Synergetic effect, Cu<sub>2</sub>O.

### **INTRODUCTION**

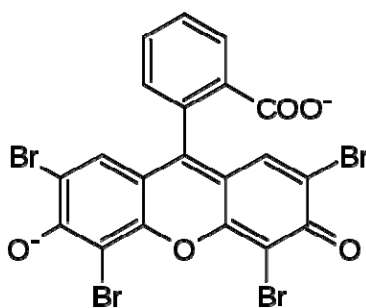
Ever since the discovery of photocatalytic activity of TiO<sub>2</sub> under U.V irradiation, photocatalytic degradation of soluble toxic organic pollutants using semiconductor metal oxides has been the subject of several investigations over the past few decades because of its ability to completely mineralize the contaminants at ambient temperature as a green technology. Though TiO<sub>2</sub> has been widely studied as a photocatalyst, two major drawbacks limit its use, namely its wide band gap and rapid recombination rate of photo generated charge carriers. These factors have been addressed in terms of doping with suitable anions, cations and noble metal atoms, photosensitization, and nano composite formation with materials of suitable band potential. These techniques though yielded better results compared to pure TiO<sub>2</sub>, their success is limited due to their inherent defects. In order to make the process more cost effective, there is a need to exploit the largely available visible light of solar radiation rather than energy constrictive U.V radiation. Scientific research

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around different parts of the globe, led to unravel several binary and ternary metal oxides as potential photocatalysts in place of  $\text{TiO}_2$ . These include  $\text{ZnO}$ <sup>1</sup>,  $\text{Fe}_2\text{O}_3$ <sup>2</sup>,  $\text{Bi}_2\text{O}_3$ <sup>3</sup>,  $\text{WO}_3$ <sup>4</sup>,  $\text{MoO}_3$ <sup>5</sup>,  $\text{V}_2\text{O}_5$ <sup>6</sup>,  $\text{ZnWO}_4$ <sup>7</sup>,  $\text{BiVO}_4$ <sup>8</sup>,  $\text{Bi}_2\text{WO}_6$ <sup>9</sup>,  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ <sup>10</sup>,  $\text{Bi}_2\text{MoO}_6$ <sup>11</sup>,  $\text{BiFeO}_3$ <sup>12</sup>,  $\text{NaBiO}_3$ <sup>13</sup>,  $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ <sup>14</sup> etc. Different structural families of heterogeneous photocatalysts studied thus far, for the degradation of dyes with different chromophores have been discussed in a recent review<sup>15</sup>.

$\text{Cu}_2\text{O}$  is a p-type semiconductor with band gap in the region of 2.0 to 2.2 eV. It is cheap and easily available abundantly.  $\text{Cu}_2\text{O}$  has been reported as an effective photocatalyst for the degradation of rhodamine-B, methylene blue, methyl orange<sup>16</sup>, bromocresol green, rosaniline, eosin blue<sup>17</sup>, mono, di and tri nitrophenols<sup>18</sup> and nitrobenzene<sup>19</sup> from this laboratory. Present paper describes visible light activated photocatalytic degradation of eosin-Y using  $\text{H}_2\text{O}_2$  sensitised  $\text{Cu}_2\text{O}$ . Molecular structure of Eosin-Y is given below.



Structure of Eosin-Y

## EXPERIMENTAL

### Materials and characterization

As purchased A.R grade  $\text{Cu}_2\text{O}$  (99%) obtained from Sigma Aldrich and A.R grade 99%. Aniline and acetophenone were obtained from Merck India Ltd. Phase purity of  $\text{Cu}_2\text{O}$  is ascertained using X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature with Ni filtered  $\text{Cu-K}_\alpha$  radiation and a scan rate of  $2^\circ \text{min}^{-1}$ .

### Photocatalytic studies

100 mg of catalyst powder was added into 100 mL aqueous solution containing 20 ppm Eosin-Y. The suspension was magnetically stirred for 30 mins in dark. The suspension was then exposed to 400 W metal halide lamp; 5 mL aliquots were pipetted at

periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended particles. Extent of degradation was followed by recording the corresponding absorption spectra. All experiments were conducted under ambient conditions. Percent degradation of pollutant is calculated by using the expression.

$$\% \text{ degradation} = (A_0 - A_t) / A_0 \times 100$$

where  $A_0$  and  $A_t$  are respectively initial absorbance and absorbance at time 't'.

### Photoluminescence study

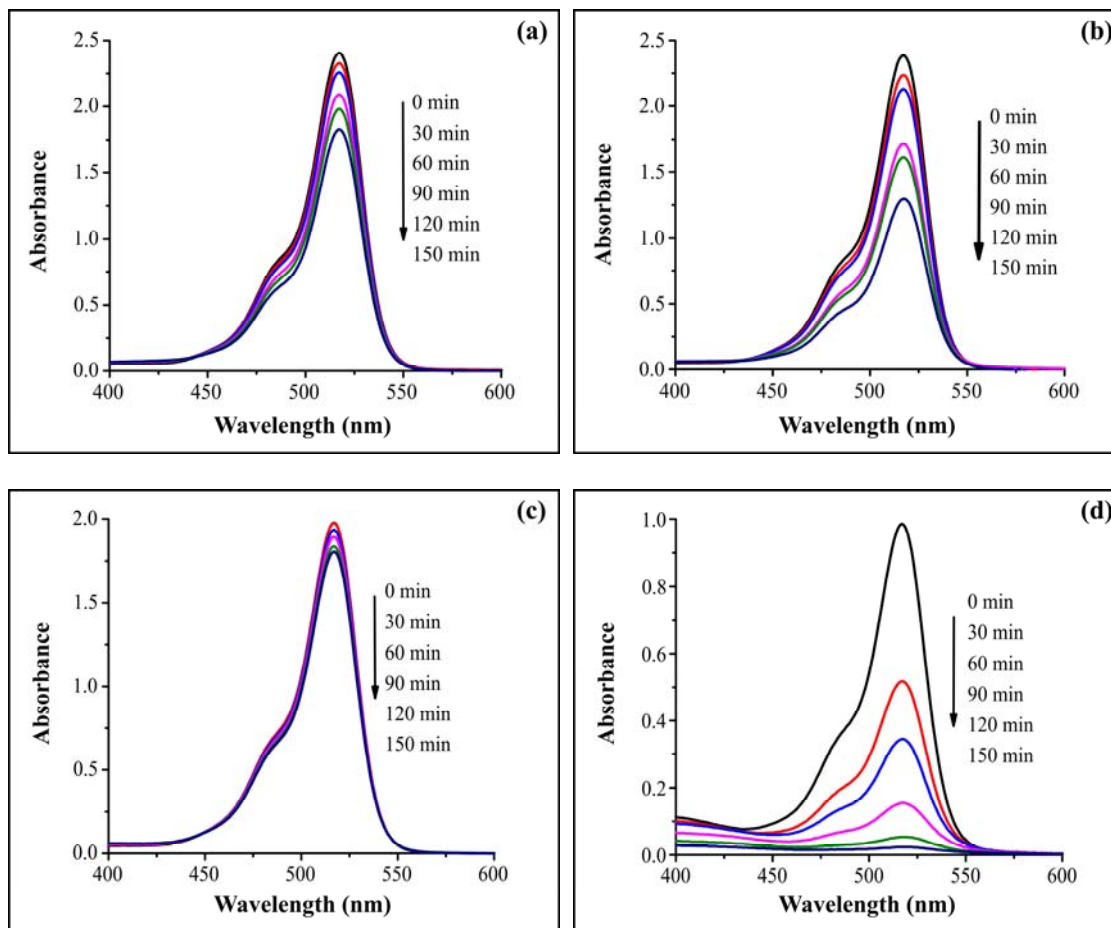
50 mg  $\text{Cu}_2\text{O}$  catalyst is added to the beaker containing 100 ml of terphthalic acid (TPA) solution ( $0.25 \text{ mmol L}^{-1}$  in  $1 \text{ mmol L}^{-1}$  NaOH solution) and  $10 \mu\text{mol H}_2\text{O}_2$ . The solution is stirred for 30 min in dark followed by irradiation by 400 w metal halide lamp for 30 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectro fluorometer (Fluoromax 4) with the excitation wavelength of 315 nm.

## RESULTS AND DISCUSSION

Eosin-Y belongs to xanthine derivative of dyes. Photocatalytic degradation of eosin-Y was reported by Poulis et al.<sup>20</sup> in presence of  $\text{TiO}_2$  and  $\text{ZnO}$ , Chakrabarti and Dutta over  $\text{ZnO}$ <sup>21</sup>, Brahimi et al.<sup>22</sup> using Pts-sensitised  $\text{TiO}_2$  in comparison with  $\text{CdS}/\text{TiO}_2$ ,  $\text{Bi}_2\text{O}_3/\text{TiO}_2$ ,  $\text{Cu}_2\text{O}/\text{TiO}_2$  and  $\text{Bi}_2\text{O}_3/\text{TiO}_2$ , Hu et al.<sup>23</sup> over  $\text{AgI}/\text{Zr}(\text{WO}_4)_2$ , Siva Kumar and coworkers<sup>24</sup> using Ag doped  $\text{TiO}_2$ , Lu et al.<sup>25</sup> over N-doped  $\text{TiO}_2$ , Kuverega and coworkers<sup>26</sup> using N and Os codoped  $\text{TiO}_2$ , Susmita et al.<sup>27</sup> using  $\text{TiO}_2$  and  $\text{ZnO}$ , Suresh et al.<sup>28,29</sup> using  $\text{Fe}_2\text{Mo}_3\text{O}_{12}$   $x\text{MoO}_3$ ,  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$   $x\text{MoO}_3$  and visible light.

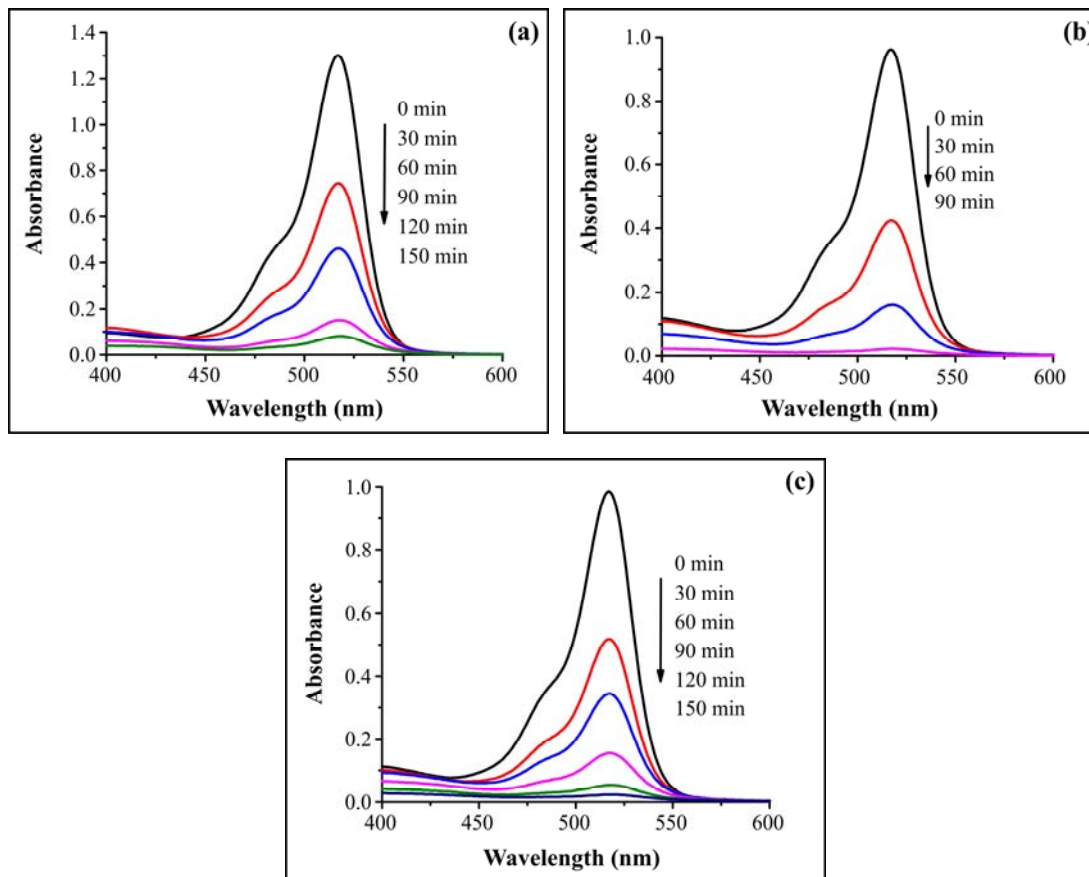
Temporal variation of spectral intensities as a function of irradiation time for aqueous solution of Eosin-Y (EY), EY +  $\text{H}_2\text{O}_2$ , EY +  $\text{Cu}_2\text{O}$  and EY +  $\text{H}_2\text{O}_2$  +  $\text{Cu}_2\text{O}$  are shown in Fig. 1.

From the figure, it can be seen that Eosin-Y shows characteristic absorption at 510 nm and irradiation for 150 min caused nearly 28% of photolysis (Fig. 1a). In presence of  $\text{H}_2\text{O}_2$ , photodegradation to an extent of 50% is noticed for irradiation of 150 min (Fig. 1b). In presence of  $\text{Cu}_2\text{O}$ , EY showed photocatalytic degradation of hardly 10% for 150 min of irradiation (Fig. 1c). However, in presence of both  $\text{Cu}_2\text{O}$  and  $\text{H}_2\text{O}_2$ , complete photocatalytic degradation of EY is achieved for less than 150 min of irradiation (Fig. 1d), suggesting a synergetic effect between  $\text{Cu}_2\text{O}$  and  $\text{H}_2\text{O}_2$ .



**Fig. 1: Temporal variations of spectral intensities as a function of irradiation time for (a) Eosin-Y (b) Eosin-Y+H<sub>2</sub>O<sub>2</sub> (c) Eosin-Y+Cu<sub>2</sub>O and (d) Eosin-Y+Cu<sub>2</sub>O+H<sub>2</sub>O<sub>2</sub>**

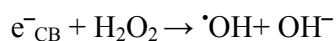
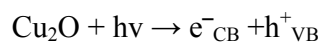
In order to optimize the amount of catalyst and concentration of H<sub>2</sub>O<sub>2</sub>, different photocatalytic degradation studies are performed with varying amounts of catalyst and H<sub>2</sub>O<sub>2</sub>. Fig. 2 shows the variation of spectral intensities for photo degradation of 20 ppm EY in presence of 100 mg Cu<sub>2</sub>O with 8 μmol, 10 μmol and 12 μmol H<sub>2</sub>O<sub>2</sub>. From the variation in spectral intensities, it can be seen that 10 μmol H<sub>2</sub>O<sub>2</sub> is the optimum concentration. Lowering of H<sub>2</sub>O<sub>2</sub> concentration did not yield complete degradation till 150 min of irradiation. Likewise when H<sub>2</sub>O<sub>2</sub> is 10 μmol, complete degradation is noticed only for 150 min of irradiation. Several studies over TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> indicated that excess concentration of H<sub>2</sub>O<sub>2</sub> is detrimental and lowers the photocatalytic efficiency by acting as scavenger for <sup>•</sup>OH free radicals that are formed during irradiation.



**Fig. 2: Effect of concentration of  $\text{H}_2\text{O}_2$  on photocatalytic degradation of Eosin-Y in presence of 100 mg  $\text{Cu}_2\text{O}$  (a)  $8 \mu\text{mol}$  (b)  $10 \mu\text{mol}$  (c)  $12 \mu\text{mol}$**

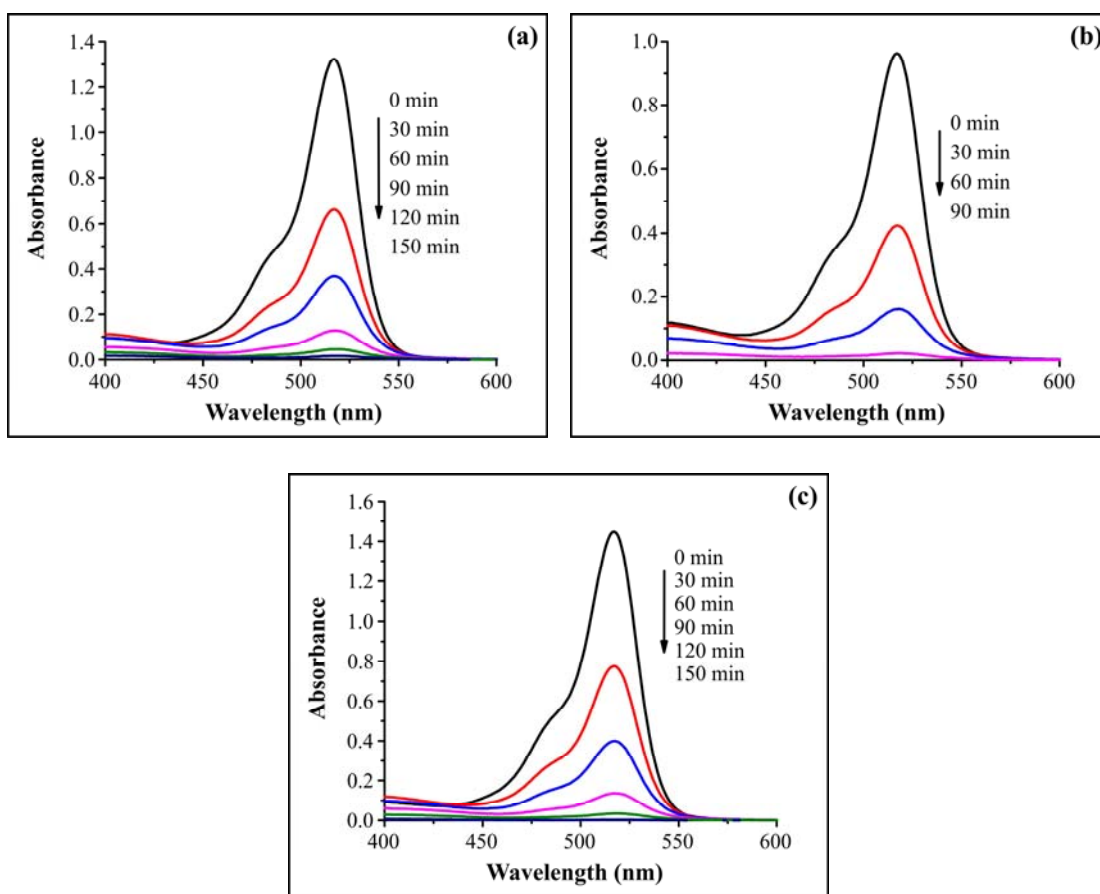
Fig 3 depicts time dependent spectral variations as a function of irradiation time for the photodegradation of Eosin-Y with different amounts of photocatalyst (50, 100 and 150 mg) keeping  $\text{H}_2\text{O}_2$  concentration constant ( $10 \mu\text{mol}$ ). From the figure, it is seen that degradation times of 150, 90 and 150 min have been observed for 50, 100 and 150 mg of  $\text{Cu}_2\text{O}$  respectively. The spectral changes indicate that 100 mg is the optimum amount of  $\text{Cu}_2\text{O}$  for the degradation of 20 ppm Eosin-Y with  $10 \mu\text{mol}$  of 30%  $\text{H}_2\text{O}_2$ .

Synergetic effect between  $\text{Cu}_2\text{O}+\text{H}_2\text{O}_2$  in enhancing the rate of photocatalytic degradation of Eosin-Y can be explained in terms of the following possible mechanism.





Formation of OH free radicals during irradiation is ascertained by means of photoluminescence studies using terephthalic acid (TPA) as a probe molecule. TPA reacts with OH free radicals and forms 2-Hydroxy terephthalic acid (HTPA) which exhibits a characteristic luminescence peak around 420 nm. Fig. 4 shows photoluminescence spectra of aqueous suspensions containing 100 mg Cu<sub>2</sub>O dispersed in 100 ml of water with addition of H<sub>2</sub>O<sub>2</sub> and without H<sub>2</sub>O<sub>2</sub> before irradiation and after irradiation. Intense peak around 419 nm for sample containing Cu<sub>2</sub>O+H<sub>2</sub>O<sub>2</sub> after irradiation clearly indicates that OH free radicals are formed during irradiation.



**Fig. 3: Effect of amount of catalyst on photocatalytic degradation of Eosin-y in presence of 10  $\mu\text{mol}$  H<sub>2</sub>O<sub>2</sub> a) 50 mg b) 100 mg c) 150 mg**

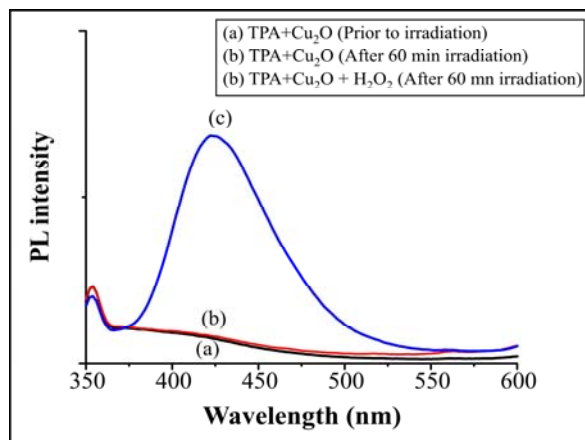


Fig. 4: Photoluminescence spectra of Cu<sub>2</sub>O+TPA with and without H<sub>2</sub>O<sub>2</sub>, Prior to and after irradiation

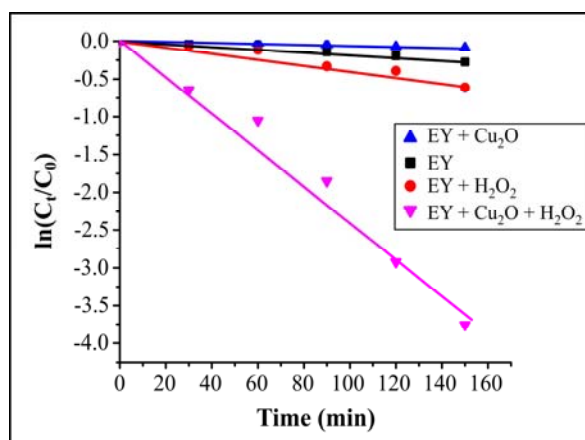


Fig. 5: Plots of  $\ln C_t/C_0$  vs irradiation time for EY, EY+H<sub>2</sub>O<sub>2</sub>, EY+Cu<sub>2</sub>O and EY+Cu<sub>2</sub>O+H<sub>2</sub>O<sub>2</sub>

Table 1: Calculated rate constants for photo degradation of EY, EY+H<sub>2</sub>O<sub>2</sub>, EY+Cu<sub>2</sub>O and EY+H<sub>2</sub>O<sub>2</sub>+Cu<sub>2</sub>O

Photodegradation	Rate constant $k_{EY}$ (min <sup>-1</sup> )
EY only	0.0
EY + H <sub>2</sub> O <sub>2</sub>	$2.0 \times 10^{-5}$
EY + Cu <sub>2</sub> O	0.0
EY + Cu <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	$1.5 \times 10^{-4}$

Plots of  $\ln C_t/C_0$  vs irradiation time for EY, EY + H<sub>2</sub>O<sub>2</sub>, EY + Cu<sub>2</sub>O and EY + Cu<sub>2</sub>O + H<sub>2</sub>O<sub>2</sub> are shown in Fig. 5. Rate constants computed from respective slopes are given in Table 1.

## CONCLUSION

Experimental results indicate that rapid photocatalytic degradation of Eosin-Y can be achieved using Cu<sub>2</sub>O under visible light irradiation. Addition of H<sub>2</sub>O<sub>2</sub> led to synergetic effect between Cu<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, as a consequence the rate of degradation is found to be enhanced. Optimal conditions for the photocatalytic degradation of 20 ppm Eosin-Y are 100 mg of photocatalyst, 10  $\mu$ mol of 30% H<sub>2</sub>O<sub>2</sub> and 90 min of visible light irradiation.

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