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VISIBLE LIGHT ACTIVATED PHOTOCATALYTIC DEGRADATION OF EOSIN-Y USING H_2O_2 SENSITISED Cu_2O

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ABSTRACT

Photocatalytic degradation of Eosin-Y is studied using Cu_2O and visible light. Complete degradation of 20 ppm Eosin-Y occurred in 90 min over 100 mg Cu_2O assisted by H_2O_2. Addition of H_2O_2 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_2O.

INTRODUCTION

Ever since the discovery of photocatalytic activity of TiO_2 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_2 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_2, 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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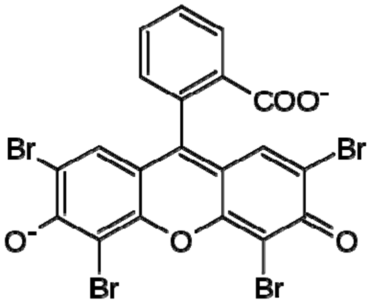
around different parts of the globe, led to unravel several binary and ternary metal oxides as potential photocatalysts in place of TiO_2. These include ZnO[1], Fe_2O_3[2], Bi_2O_3[3], WO_3[4] MoO_3[5], V_2O_5[6], $ZnWO_4$[7], $BiVO_4$[8], Bi_2WO_6[9], $Bi_2Mo_3O_{12}$[10], Bi_2MoO_6[11], $BiFeO_3$[12], $NaBiO_3$[13], $Fe_2Mo_3O_{12}$[14] 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[15].

Cu_2O 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. Cu_2O has been reported as an effective photocatalyst for the degradiation of rhodamine-B, methylene blue, methyl orange[16], bromocresol green, rosaniline, eosin blue[17], mono, di and tri nitrophenols[18] and nitrobenzene[19] from this laboratory. Present paper describes visible light activated photocatalytic degradation of eosin-Y using H_2O_2 sensitised Cu_2O. Molecular structure of Eosin-Y is given below.



Structure of Eosin-Y

EXPERIMENTAL

Materials and characterization

As purchased A.R grade Cu_2O (99%) obtained from Sigma Aldrich and A.R grade 99%. Aniline and acetophenone were obtained from Merck India Ltd. Phase purity of Cu_2O is ascertained using X-ray diffractometer (PANalytical- X’ Pert PRO, Japan) at room temperature with Ni filtered Cu-K_α radiation and a scan rate of 2^0 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 Cu_2O catalyst is added to the beaker containing 100 ml of terpthalic acid (TPA) solution (0.25 mmol L^{-1} in 1mmol L^{-1} NaOH solution) and 10 µmol H_2O_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 flourometer (Flouromax 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.[20] in presence of TiO_2 and ZnO, Chakrabarti and Dutta over ZnO[21], Brahimi et al.[22] using Pts-sensitised TiO_2 in comparsion with CdS/TiO_2, Bi_2O_3/TiO_2, Cu_2O/TiO_2 and Bi_2O_3/TiO_2, Hu et al.[23] over $AgIZr(WO_4)_2$, Siva Kumar and coworkers[24] using Ag doped TiO_2, Lu et al.[25] over N-doped TiO_2, Kuverega and coworkers[26] using N and Os codoped TiO_2, Susmita et al.[27] using TiO_2 and ZnO, Suresh et al.[28,29] using $Fe_2Mo_3O_{12}$ $xMoO_3$, $Bi_2Mo_3O_{12}$ $xMoO_3$ and visible light.

Temporal variation of spectral intensities as a function of irradiation time for aqueous solution of Eosin-Y (EY), EY + H_2O_2, EY + Cu_2O and EY + H_2O_2 + Cu_2O 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 H_2O_2, photodegradation to an extent of 50% is noticed for irradiation of 150 min (Fig. 1b). In presence of Cu_2O, EY showed photocatalytic degradation of hardly 10% for 150 min of irradiation (Fig. 1c). However, in presence of both Cu_2O and H_2O_2, complete photocatalytic degradation of EY is achieved for less than 150 min of irradiation (Fig. 1d), suggesting a synergetic effect between Cu_2O and H_2O_2.

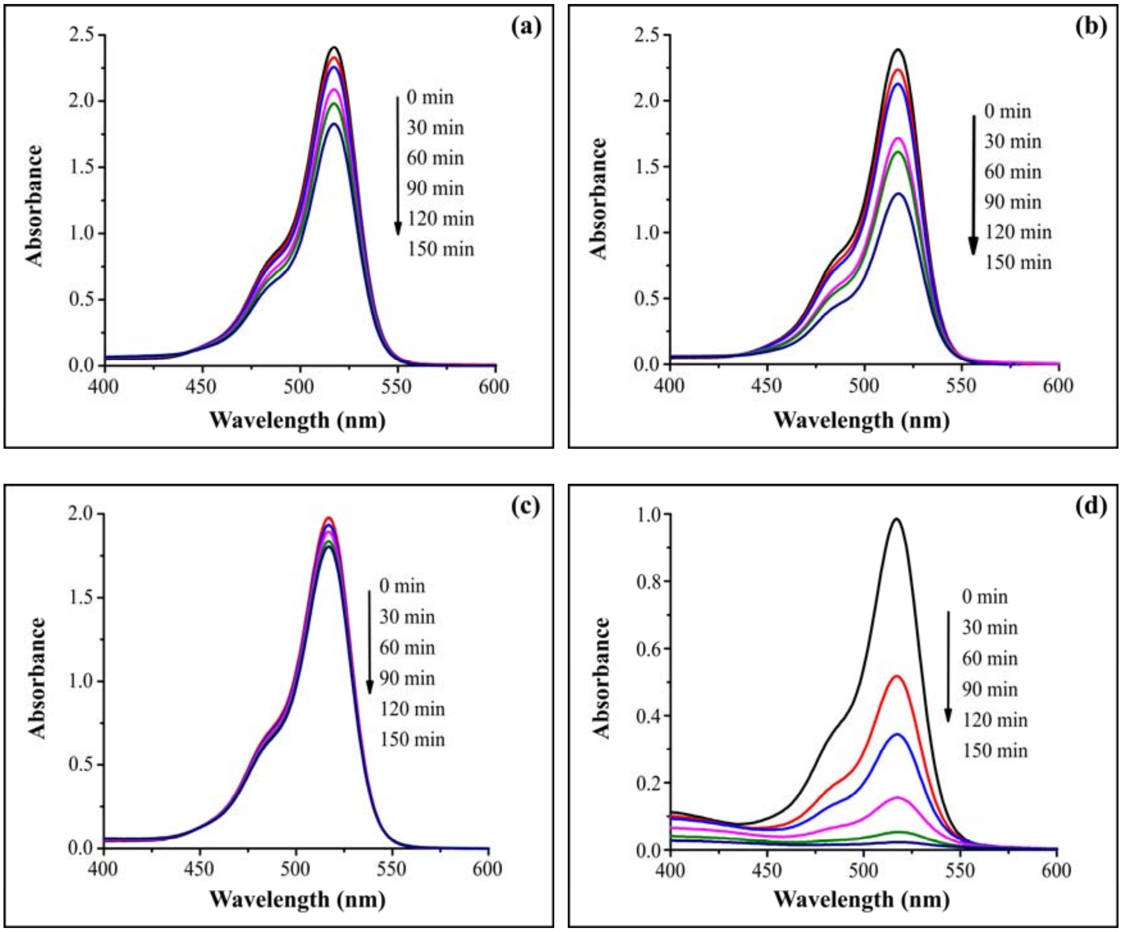


Fig. 1: Temporal variations of spectral intensities as a function of irradiation time for (a) Eosin-Y (b) Eosin-Y+H_2O_2 (c) Eosin-Y+Cu_2O and (d) Eosin-Y+Cu_2O+H_2O_2

In order to optimize the amount of catalyst and concentration of H_2O_2, different photocatalytic degradation studies are performed with varying amounts of catalyst and H_2O_2. Fig. 2 shows the variation of spectral intensities for photo degradation of 20 ppm EY in presence of 100 mg Cu_2O with 8 µmol, 10 µmol and 12 µmol H_2O_2. From the variation in spectral intensities, it can be seen that 10 µmol H_2O_2 is the optimum concentration. Lowering of H_2O_2 concentration did not yield complete degradation till 150 min of irradiation. Likewise when H_2O_2 is 10 µmol, complete degradation is noticed only for 150 min of irradiation. Several studies over TiO_2 and H_2O_2 indicated that excess concentration of H_2O_2 is detrimental and lowers the photocatalytic efficiency by acting as scavenger for $^{\bullet}OH$ free radicals that are formed during irradiation.

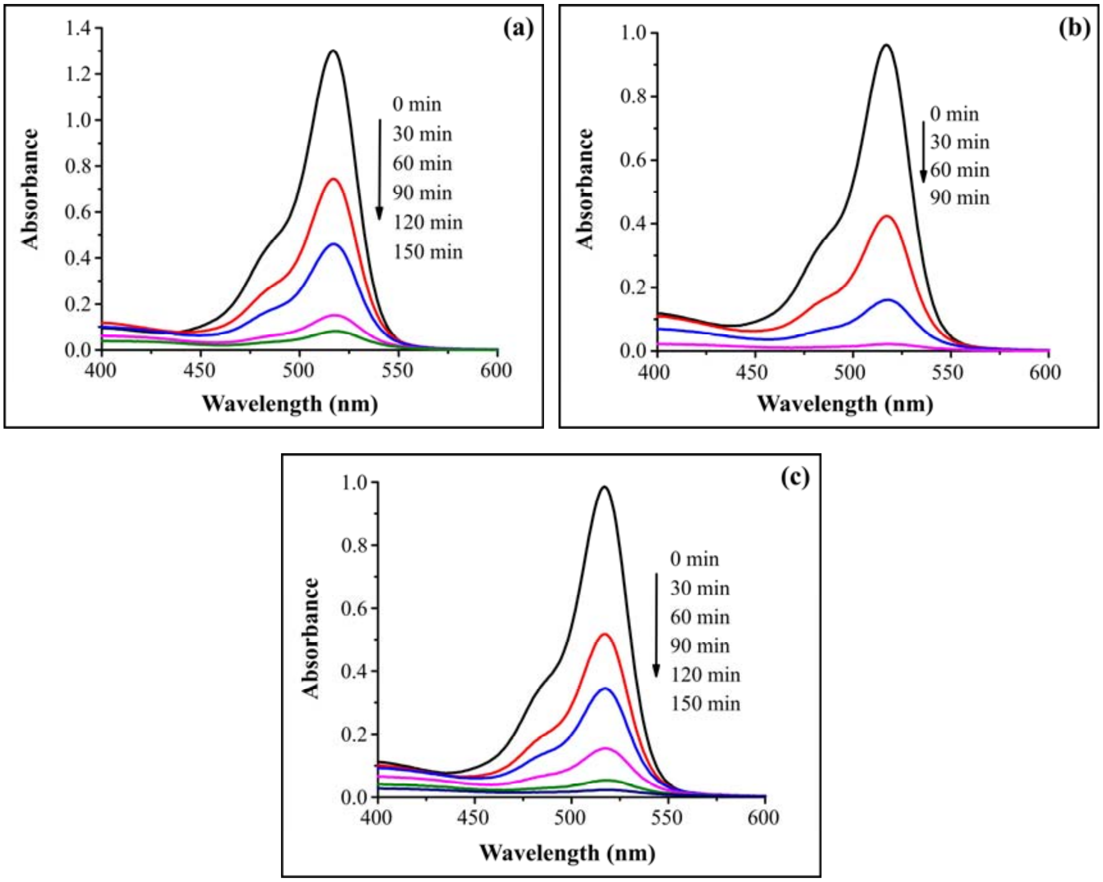


Fig. 2: Effect of concentration of H_2O_2 on photocatalytic degradation of Eosin-Y in presence of 100 mg Cu_2O (a) 8 µ mol (b) 10 µ mol (c) 12 µ mol

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 H_2O_2 concentration constant (10 µmol). 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 Cu_2O respectively. The spectral changes indicate that 100 mg is the optimum amount of Cu_2O for the degradation of 20 ppm Eosin-Y with 10 µmol of 30% H_2O_2.

Synergetic effect between Cu_2O+H_2O_2 in enhancing the rate of photocatalytic degradation of Eosin-Y can be explained in terms of the following possible mechanism.

$$Cu_2O + h\nu \rightarrow e^-_{CB} + h^+_{VB}$$

$$e^-_{CB} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^-$$

$$h^{+}_{VB} + OH^{-} \rightarrow {}^{\bullet}OH$$

$${}^{\bullet}OH + \text{Eosin-Y} \rightarrow \text{Degradation products}$$

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 terepthallic acid (HTPA) which exhibits a characteristic luminescence peak around 420 nm. Fig. 4 shows photoluminescence spectra of aqueous suspensions containing 100 mg Cu_2O dispersed in 100 ml of water with addition of H_2O_2 and without H_2O_2 before irradiation and after irradiation. Intense peak around 419 nm for sample containing Cu_2O+H_2O_2 after irradiation clearly indicates that OH free radicals are formed during irradiation.

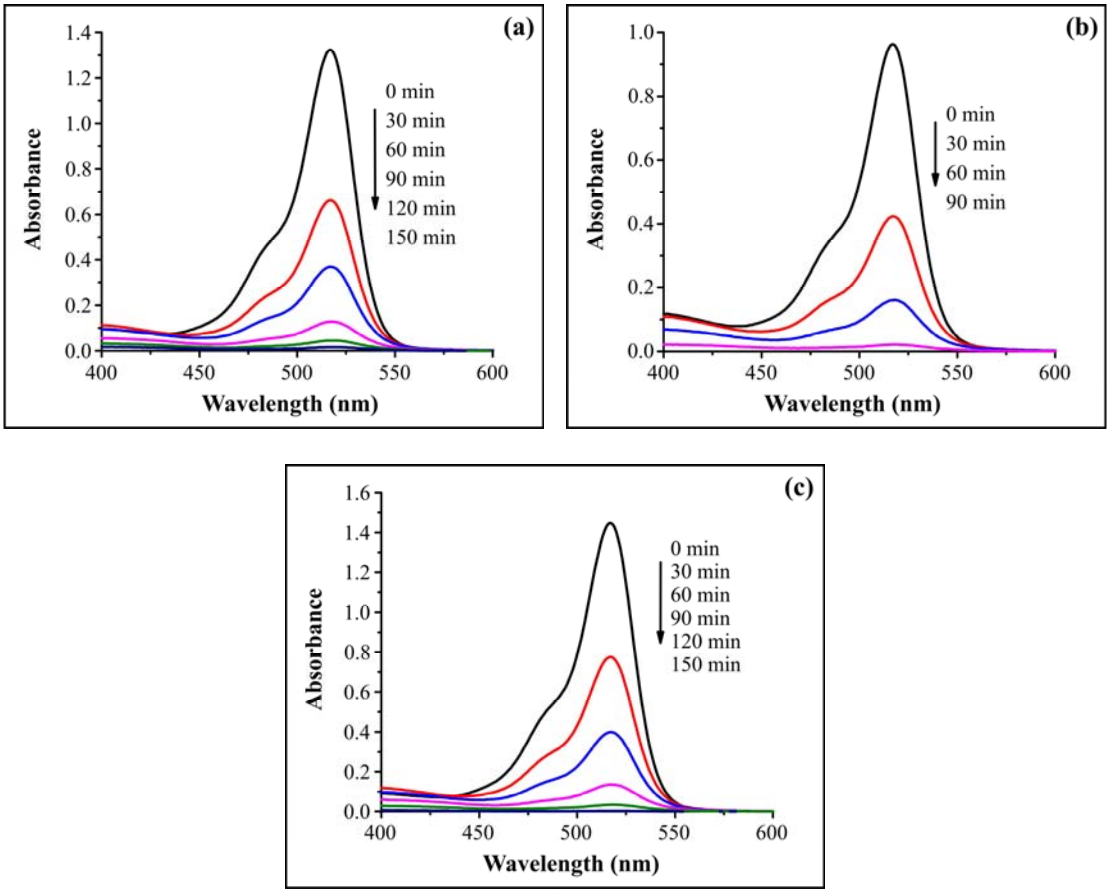


Fig. 3: Effect of amount of catalyst on photocatalytic degradation of Eosin-y in presence of 10 µmol H_2O_2 a) 50 mg b) 100 mg c) 150 mg

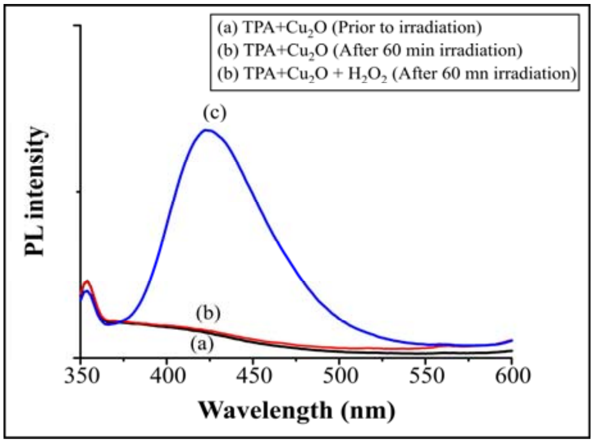


Fig. 4: Photoluminiscence spectra of Cu_2O+TPA with and without H_2O_2, Prior to and after irradiation

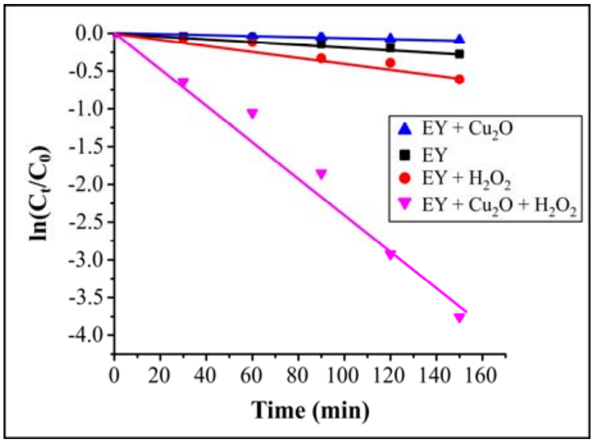


Fig. 5: Plots of ln C_t/C_0 vs irradiation time for EY, EY+H_2O_2, EY+Cu_2O and EY+Cu_2O+H_2O_2

Table 1: Calculated rate constants for photo degradation of EY, EY+H_2O_2, EY+Cu_2O and EY+H_2O_2+Cu_2O

Photodegradation	Rate constant k_{EY} (min^{-1})
EY only	0.0
EY + H_2O_2	2.0×10^{-5}
EY + Cu_2O	0.0
EY + Cu_2O + H_2O_2	1.5×10^{-4}

Plots of ln C_t/C_0 vs irradiation time for EY, EY + H_2O_2, EY + Cu_2O and EY + Cu_2O + H_2O_2 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_2O under visible light irradiation. Addition of H_2O_2 led to synergetic effect between Cu_2O and H_2O_2, 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 µmol of 30% H_2O_2 and 90 min of visible light irradiation.

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