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Photocatalytic degradation of Bromocresol green, Rosaniline and Eosin blue using H₂O₂ sensitized Cu₂O and visible light

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ABSTRACT

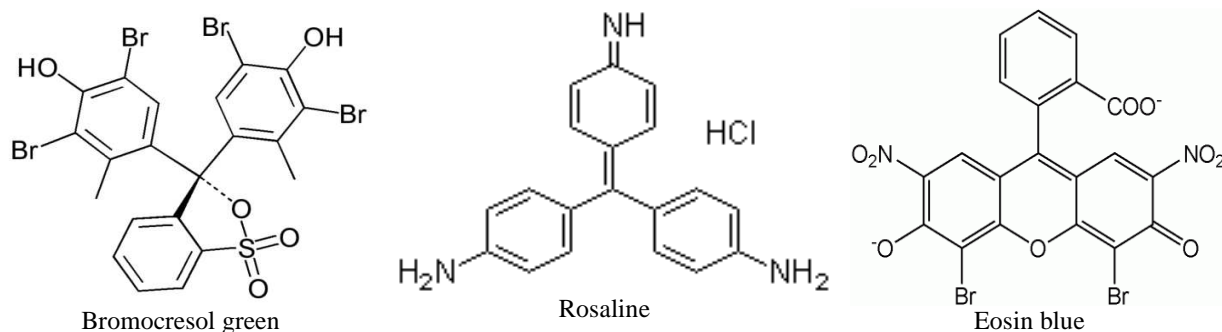
Visible light irradiated photocatalytic degradation of Bromocresol green, Rosaniline and Eosin blue has been studied using Cu₂O as photocatalyst. Addition of H₂O₂ led to synergetic effect between Cu₂O and H₂O₂ and enhanced the rate of degradation. Complete degradation of Bromocresol green, Rosaniline and Eosin blue occurred for 180, 180 and 120 min of irradiation respectively. Formation of ·OH free radicals during irradiation is ascertained by photoluminescence studies using terphthalic acid as probe molecule.

Key words: Cu₂O, Bromocresol green, Rosaniline, Eosin blue, Photocatalysis, Synergetic effect.

INTRODUCTION

Majority of synthetic organic dyes used in textile, dyeing, tannery and printing industries are less biodegradable as well as mutagenic or carcinogenic. Treatment of exhausts from such industries to get rid of unused or remnant toxic organic pollutants is an ecological necessity in order to protect aquatic sources from contamination. Different methods based on adsorption, ion exchange, reverse osmosis, biosorption have been proposed from time to time for remediation of pollutants, but these methods are not completely satisfactory since they generate secondary pollutants. Likewise chemical oxidation, ozonation, Fenton and photo Fenton processes are also not cost effective. However, during the past few decades, semiconductor mediated heterogeneous photocatalysis has been reported to be highly successful for mineralization of several organic pollutants of very low concentration (in ppm range) at ambient temperature without generation of any hazardous intermediates. TiO₂ is claimed as an excellent photocatalyst, because it is chemically inert and easy to synthesize, but it has its own demerits. The photo absorption is restricted to U.V region and the photo generated electrons and holes undergo rapid recombination, both of which lower the photocatalytic efficiency. Several investigators tried to improve the photocatalytic performance of TiO₂ in terms of (i) doping with noble metal atoms, transition metal ions, lanthanide ions and anions, (ii) enhancing photo absorptivity in the visible region through surface sensitization with dyes, pthalocyanins, porphyrins, and (iii) formation of nano/meso structures of special architectures with high surface to volume ratio. Though each approach has its own merit, the proposed methods do have some inherent defects as well. For instance in doping, optimum dopant concentration is extremely crucial since the excess dopants turn into traps and lower photocatalytic efficiency of TiO₂. In surface sensitization, photocatalytic oxidation involves both the pollutant and the sensitizer. Fabrication of nano composites involves energy constrictive technologies like microwave, hydrothermal etc. which are not cost effective on an industrial scale. To overcome these disadvantages, use of non-TiO₂ binary metal oxides such as ZnO [1], SnO₂ [2], α-Fe₂O₃ [3], WO₃ [4], Bi₂O₃ [5], MoO₃ [6] and ternary metal oxides like ZnWO₄ [7], Bi₂WO₆ [8], Bi₂MoO₆ [9], α-Bi₂Mo₃O₁₂ [10], Fe₂Mo₃O₁₂ [11], NaBiO₃ [12], BaBiO₃ [13] and BiVO₄ [14] have been extensively

investigated to exploit their photo absorptivities in the visible region of solar radiation that renders the process both economical and environmental friendly [15]. Cu_2O is an n-type semiconductor with a band gap in the region of 2.0 to 2.2 eV. It is easily available in abundance. Recently photocatalytic degradation of mono, di and tri nitrophenols and nitrobenzene using Cu_2O has been reported from this laboratory [16, 17]. Present paper describes visible light assisted photocatalytic degradation of Bromocresol green, Rosaniline and Eosin blue over Cu_2O . Molecular structures of Bromocresol green, Rosaniline and Eosin blue are given below:



MATERIALS AND METHODS

Materials and Characterization:

As purchased A.R grade Cu_2O (Sigma Aldrich) and A.R grade Bromocresol green, Rosaniline hydrochloride and Eosin blue and 30% H_2O_2 are used in the photocatalytic studies. Phase purity of Cu_2O was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} .

Photocatalytic Studies:

100 mg of catalyst powder was added into 100 ml aqueous solution containing 10 ppm Dye. The suspension was magnetically stirred for 30 minutes in dark. The suspension was then exposed to 400 watts metal halide lamp; 5ml 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 terphthalic acid (TPA) solution (0.25 mmol L^{-1} in 1 mmol L^{-1} NaOH solution) and $10 \mu\text{M}$ H_2O_2 . The solution is stirred for 15 min in dark followed by irradiation by 400 w metal halide lamp for 60 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

X-ray diffraction pattern of Cu_2O is shown in Fig 1. All the diffraction peaks could be indexed to cubic Cu_2O of JCPDS File No 78-2076. As there are no extra peaks, the sample is considered as phase pure Cu_2O .

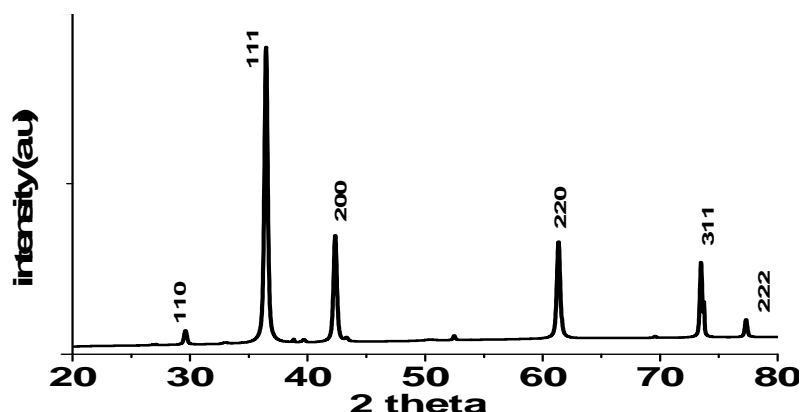


Fig. 1. X-ray diffraction pattern of Cu₂O sample used in this study

Bromocresol green belongs to triphenyl methane family of dyes. It is used as a pH indicator as well as a tracking dye for DNA agarose gel electrophoresis. Photocatalytic oxidation of Bromocresol green has been reported by Ghorai *et al* [18] using Fe (III) doped TiO₂ under U.V.irradiation. Ghorai *et al* [19] also reported the use of Mn₂O₃/TiO₂ for the photocatalytic degradation of Bromocresol green under visible light. Fassi *et al* [20] made a comparative study of degradation of Bromocresol green by direct UV photolysis, acetone/UV with H₂O₂/UV, S₂O₈²⁻/UV. Farbod and coworkers [21] reported fabrication of Cu/Cu₂O/CuO nanowires and their photocatalytic properties towards degradation of Bromocresol green. Kalpagam and Kannadasan [22] investigated degradation of Bromocresol green using Ag and Ni doped TiO₂ under U.V. light. Nezamzadeh-Ejhi *et al* [23] reported sunlight photodecomposition of a mixture of methyl orange and Bromocresol green by CuS incorporated in a Zeolite. Temporal variation of spectral contours for Bromocresol green (BCG), BCG+H₂O₂, BCG+Cu₂O and BCG+Cu₂O+H₂O₂ as a function of irradiation time are shown in Fig 2. From the figure, it can be seen that BCG has characteristic absorption at $\lambda=614$ nm along with two smaller intense peaks, one at $\lambda=400$ and the other at 300 nm respectively. BCG shows no photolysis when irradiated for 180 min (Fig 2a). In presence of H₂O₂, BCG showed 45% photodegradation with progressive irradiation for 180 min (Fig 2b). BCG with Cu₂O did not show any significant photo degradation for 180 min of irradiation (Fig 2c). But, in presence of Cu₂O+H₂O₂, BCG exhibited 100% photocatalytic degradation for irradiation of 150 min (Fig 2d). These results indicate that Cu₂O and H₂O₂ exert a synergetic effect in the photocatalytic degradation of Bromocresol green.

Rosaniline is a derivative of triphenyl methane structure. Photocatalytic degradation of Rosaniline was reported by Kosanic and Trickovic using Degusa P-25 and H₂O₂ under visible light [24]. Fig.3 depicts variation of spectral intensities as a function of irradiation time for Rosaniline, Rosaniline+H₂O₂, Rosaniline+Cu₂O and Rosaniline+Cu₂O+H₂O₂. From the figure, it can be seen that Rosaniline has a characteristic absorption at $\lambda_{max}=530$ nm. When irradiated, Rosaniline shows photolysis to an extent of 13% for 150 min of irradiation (Fig 3a). In presence of H₂O₂, Rosaniline exhibits photodegradation with progressive irradiation. Nearly 58% photodegradation of Rosaniline is evident from Fig 3b for irradiation of 150 min. In presence of Cu₂O, Rosaniline showed photodegradation to an extent of 18% for 180 min of irradiation (Fig 3c). However, in presence of both Cu₂O and H₂O₂, complete photocatalytic degradation of Rosaniline is achieved for 120 min of irradiation, indicating a synergetic effect between Cu₂O and H₂O₂.

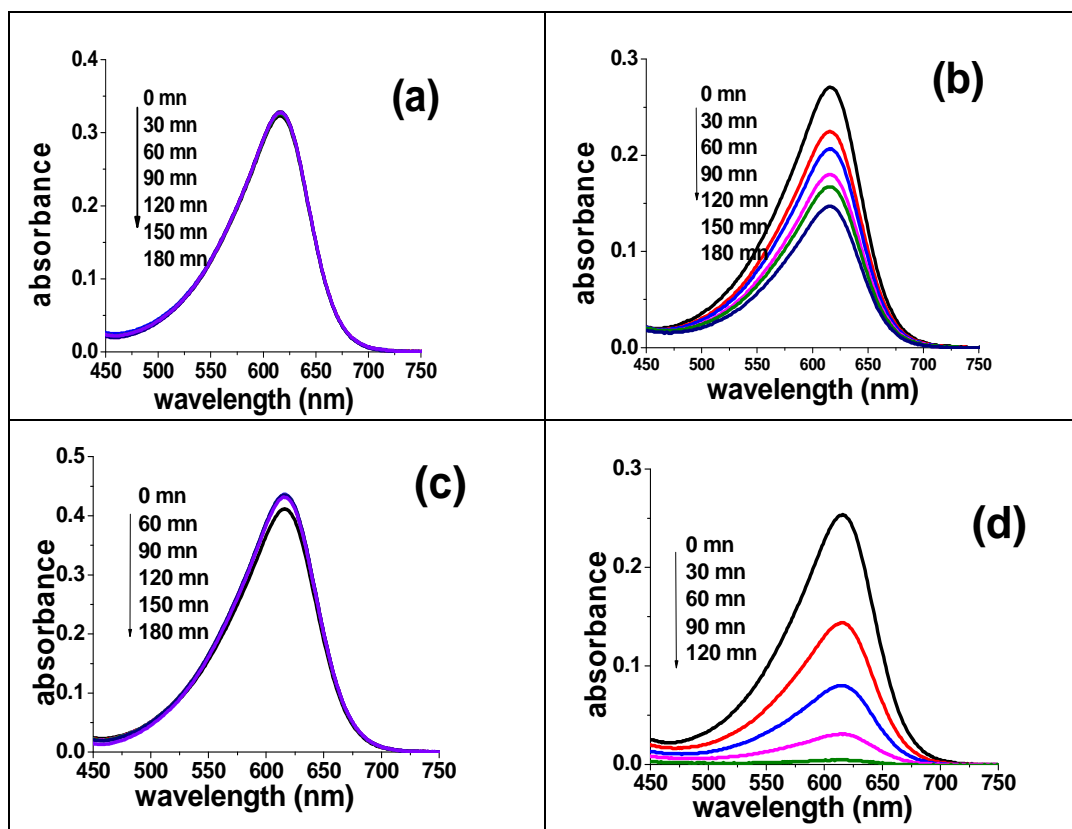


Fig. 2. Variation of spectral intensity as a function of irradiation time for (a) BCG, (b) BCG+H₂O₂, (c) BCG+Cu₂O and (d) BCG +Cu₂O+H₂O₂

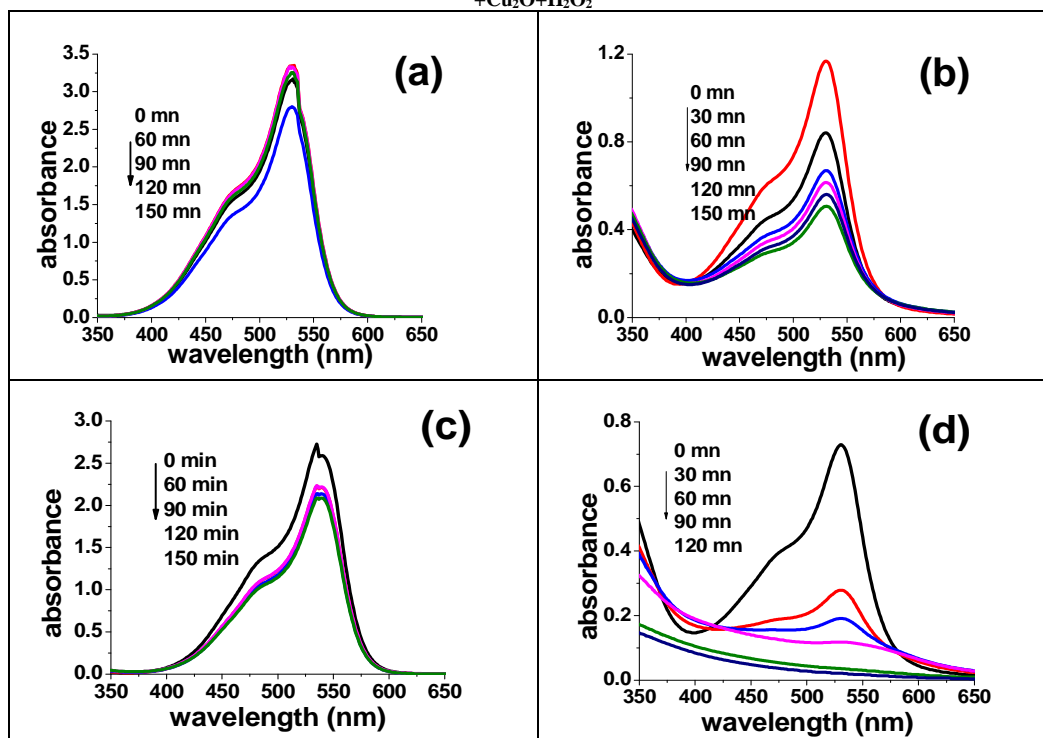


Fig. 3. Time dependent variation of spectral intensities with irradiation time for (a) Rosaniline, (b) Rosaniline + H₂O₂, (c) Rosaniline + Cu₂O and (d) Rosaniline + Cu₂O + H₂O₂

Photocatalytic degradation of Eosin blue (EB) was reported by Ye et al [25] using ZnO and U.V. light, Chen et al [26] using SnO₂ and U.V light, and by Mamha et al [27] using Nd, N,S tridoped TiO₂ decorated onto single walled carbon nano tubes, Umabala et al [28] over BiVO₄ under visible light. Temporal variation of spectral intensities for EB, EB+H₂O₂, EB+Cu₂O and EB+Cu₂O+H₂O₂ as a function of irradiation time are shown in Fig.4. From the figure it can be seen that EB exhibits a characteristic absorption at $\lambda=519$ nm and undergoes photolysis to an extent of 32% for irradiation of 120 min (Fig 4a). In presence of H₂O₂, photo degradation of EB occurred to an extent of 56% for irradiation 180 min (Fig 4b). In presence of Cu₂O, EB showed hardly 6% photodegradation for irradiation of 180 min (Fig 4c). However, in presence of both Cu₂O and H₂O₂, complete degradation is achieved for 120 min of irradiation as seen from Fig 4d. These results suggest a synergetic effect between Cu₂O and H₂O₂.

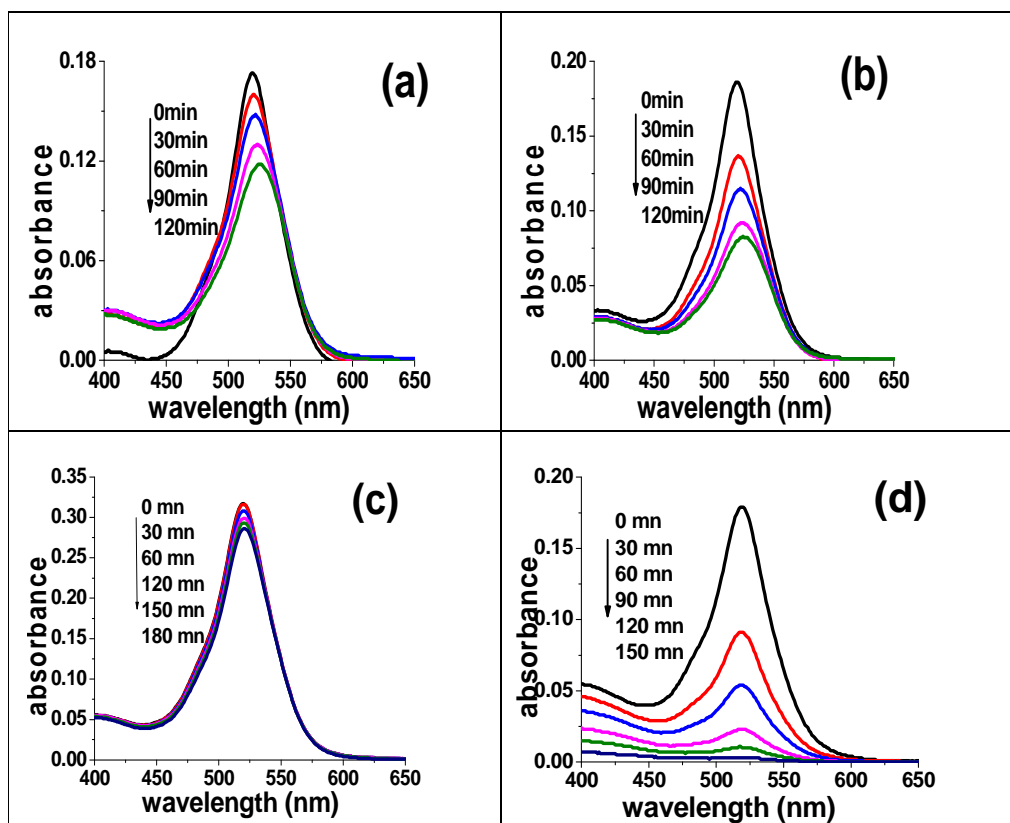
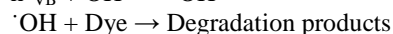
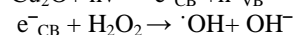
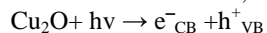


Fig. 4. Temporal variation of spectral contours as a function of irradiation time for (a) EB, (b) EB+H₂O₂, (c) EB+Cu₂O and (d) EB+Cu₂O+H₂O₂

Based on these results, the following photocatalytic mechanism is proposed for the degradation of these dyes.



Formation of $\cdot\text{OH}$ free radicals is ascertained by means of photoluminescence studies using Terphthalic acid (TPA) as a probe molecule. TPA is known to react with $\cdot\text{OH}$ free radicals to yield 2-Hydroxy terphthalic acid (HTPA) which exhibits a characteristic luminescence peak at 420 nm. Fig 5 shows photoluminescence spectra for Cu₂O+TPA with and without H₂O₂ prior to and after irradiation. The intense luminescence peak at 420 nm for sample containing Cu₂O+TPA and H₂O₂ after irradiation for 60 min clearly establishes the presence of $\cdot\text{OH}$ free radicals during irradiation.

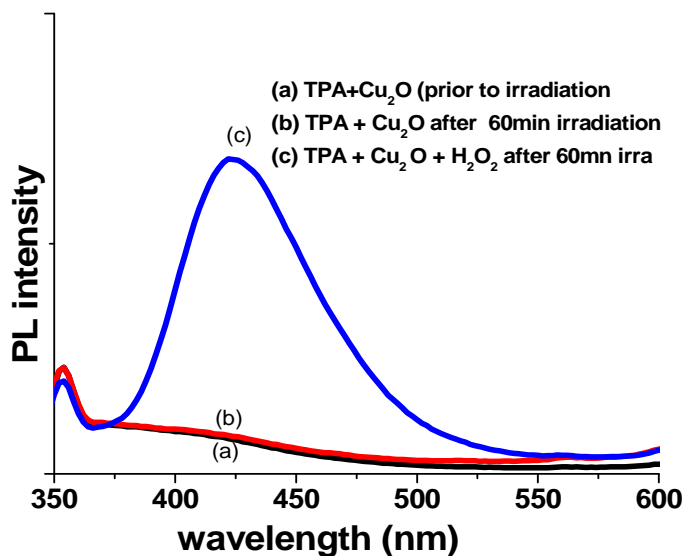


Fig. 5. Photoluminescence spectra of $\text{Cu}_2\text{O}+\text{TPA}$ with and without H_2O_2 , Prior to and after irradiation

From the data presented above for Bromocresol green, Rosaniline and Eosin blue, it is apparent that external oxidant H_2O_2 is playing a significant role in enhancing the rate of degradation. The rate constants computed from the respective graphs of $\ln C_t/C_0$ vs time shown in Fig. 6 are given in Table 1.

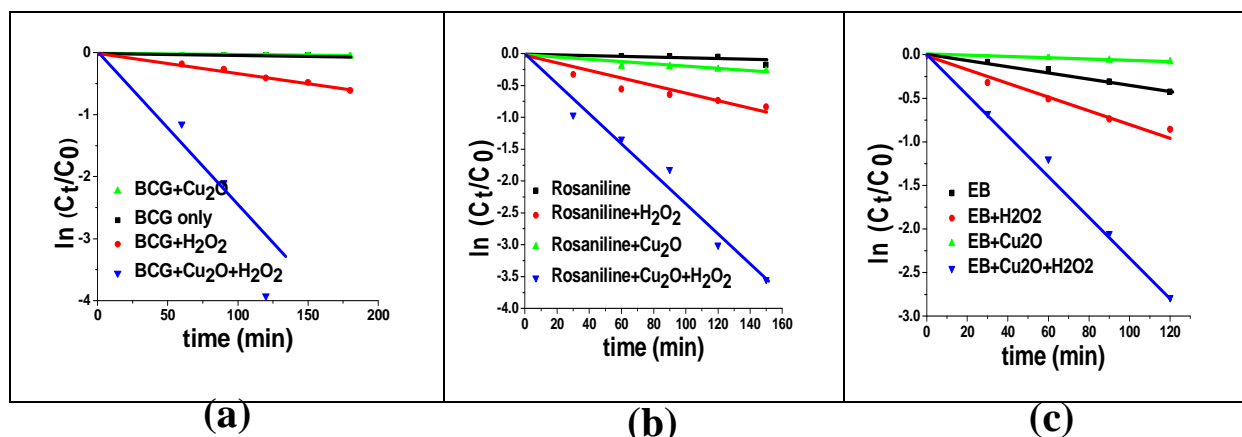


Fig. 6. Plot of $\ln C_t/C_0$ vs irradiation time for dye, dye+ H_2O_2 , dye+ Cu_2O and dye+ $\text{Cu}_2\text{O}+\text{H}_2\text{O}_2$ (a) Bromocresol green, (b) Rosaniline and (c) Eosin blue

Table. 1. Calculated rate constants for photodegradation of BCG, Rosaniline and EB with and without catalyst and H_2O_2

photodegradation	Rate constant k (min^{-1})		
	BCG	Rosaniline	EB
Dye alone	0.0	0.0	3.0×10^{-5}
Dye+ H_2O_2	2.0×10^{-5}	1.0×10^{-5}	6.0×10^{-5}
Dye+ Cu_2O	0.0	4.0×10^{-3}	0.0
Dye+ $\text{Cu}_2\text{O}+\text{H}_2\text{O}_2$	2.3×10^{-4}	1.5×10^{-4}	1.8×10^{-4}

CONCLUSION

Photocatalytic degradation of Bromocresol green, Rosaniline and Eosin blue has been studied under visible light using Cu_2O as photocatalyst. Complete degradation of Bromocresol green, Rosaniline and Eosin blue occurred for 180, 180 and 120 min of irradiation respectively. Synergetic effect is observed between Cu_2O and H_2O_2 which

generated more ·OH free radicals which enhance the rate of degradation. ·OH free radical formation is ascertained by means of photoluminescence studies using terphthalic acid as probe molecule.

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