

Photocatalytic Degradation of Eosin Blue, Acid Orange and Orange G using H₂O₂ Sensitized Bi₂WO₆ and Visible Light

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Photocatalytic degradations of eosin blue, acid orange and orange G have been studied with Bi₂WO₆ as photocatalyst under visible light irradiation. Addition of H₂O₂ enhanced the rate of degradation in each case. Formation of *OH free radicals during irradiation is established in terms of photoluminescence studies using terephthalic acid. Degradation times of 3, 3 and 1 h are obtained for eosin blue, acid orange and orange G dyes, respectively.

Keywords: Photocatalytic degradation, Eosin blue, Acid orange, Orange G, Synergetic effect.

INTRODUCTION

Remediation of industrial effluents from toxic organic pollutants prior to their discharge into aquatic sources is a prime ecological concern since they pose a severe threat to human health and animal life. Though several methods were proposed in terms of adsorption, biosorption, reverse osmosis, ion exchange, wet chemical oxidation, *etc.*, none of these methods is completely satisfactory to treat large volumes of effluents effectively, efficiently and economically. Over the past few decades attention has been focussed on heterogeneous photocatalysis making use of TiO₂ and UV irradiation for non-selective mineralization of several organic pollutants of which dyes were studied as model pollutants. Despite the advantages of being inexpensive, inert and non-photodegradable, TiO₂ as a photocatalyst suffers from two major disadvantages namely the wide band gap necessitating UV irradiation and the rapid recombination rate of photogenerated charge carriers. In order to overcome these demerits and enhance photocatalytic efficiency in visible region, TiO₂ is modified through (i) doping, codoping, tri-doping and quadra-doping with suitable anions, cations, noble metal atoms, transition and inner transition metal ions, (ii) coupling with more visible light photo absorptive compounds and (iii) converting into nanocomposites with special architecture of higher surface area. Since the success yielded by these approaches is limited due to inherent methodologies involved, research is simultaneously focussed on non-TiO₂ based binary and ternary metal oxide semiconductors with band gaps that are visible light active like α -Fe₂O₃, WO₃, MoO₃, Cu₂O, V₂O₅, ZnWO₄, LaFeO₃, BaBiO₃, BiFeO₃,

Zn₃(VO₄)₂, BiVO₄, Bi₂MoO₆, Bi₂Mo₂O₉, Bi₂MoO₁₂, Bi₂WO₆, NaBiO₃, Fe₂Mo₃O₁₂ *etc.*, a detailed discussion of which can be had from the review article [1]. Of the different Bi-based mixed metal oxides, Bi₂WO₆ is an Aurivillius compound of layered structure with a band gap around 2.8 eV and was reported to be successful in the photocatalytic degradation of rhodamine B [2,3], methylene blue [4,5], crystal violet [6,7], malachite green [8,9] and eosin Y [10]. Present paper describes visible light photocatalytic degradation of eosin blue, acid orange and orange G using H₂O₂ assisted Bi₂WO₆. Molecular structures and molecular formulas of eosin blue, acid orange and orange G are shown in Fig. 1.

EXPERIMENTAL

Bi₂WO₆ is prepared using solid-state metathetic reaction between BiOCl and Na₂WO₄ as precursors. Stoichiometric amounts of BiOCl and Na₂WO₄ are mixed and ground for 1 h. The homogeneous mixture is heated to 600 °C for 4 h. After cooling, the mixture is thoroughly washed with water to remove the by-product NaCl and the sample is subjected to X-ray diffraction studies for phase identification using CuK α and 4 °C/min scan rate.

Photocatalytic studies: Photocatalytic activity of Bi₂WO₆ is evaluated in terms of degradation of eosin blue, acid orange and orange G blue under visible light. 100 mg of the catalyst is dispersed in 100 mL eosin blue (10 ppm)/acid orange (10 ppm)/orange G (10 ppm) aqueous solution and the suspension is magnetically stirred for 0.5 h in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye

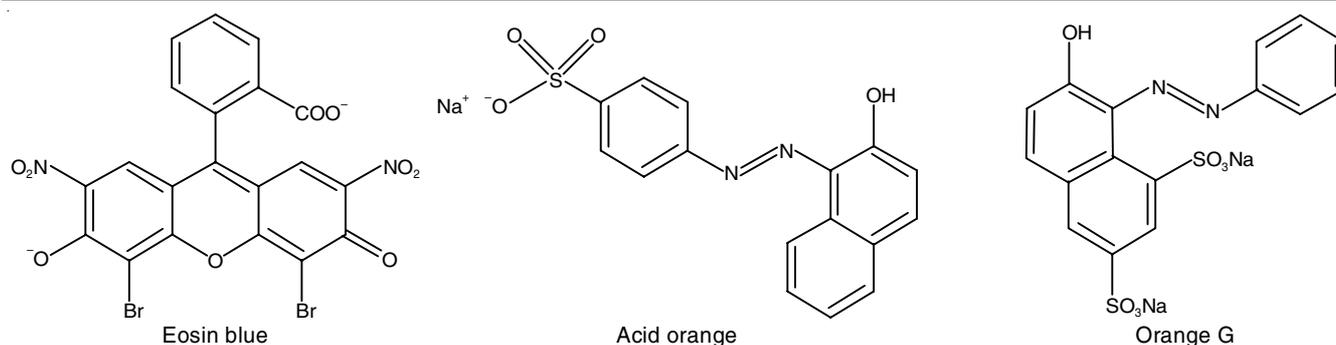


Fig. 1. Molecular structure of dyes

solution. The suspension is then exposed to 400 W metal halide lamp; 5 mL aliquots are pipetted at periodic time intervals and filtered through 0.45 μ Millipore filters to remove any suspended powder. The spectra as a function of irradiation time are recorded using UV-visible spectrophotometer (Shimadzu). The extent of photo degradation is calculated using the following equation:

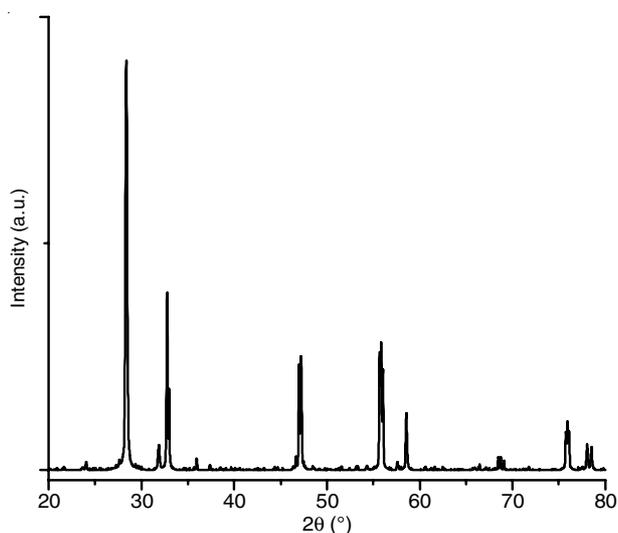
$$\text{Photodegradation (\%)} = [(A_0 - A_t)/A_0] \times 100$$

where A_0 and A_t correspond to initial absorbance and absorbance at time 't', respectively.

Photoluminescence studies: 50 mg Bi_2WO_6 catalyst is added to the beaker containing 100 mL of terephthalic acid (TPA) solution (0.25 mmol L^{-1} in 1 mmol L^{-1} NaOH solution) and 10 $\mu\text{mol H}_2\text{O}_2$. The solution is stirred for 0.5 h in dark followed by irradiation by 400 W metal halide lamp for 1 h. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectrofluorometer (Fluoromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

XRD pattern of ground mixture consisting of BiOCl and Na_2WO_4 heat treated at 600 $^\circ\text{C}$ for 4 h and washed after cooling is shown in Fig. 2. All the diffraction peaks could be indexed to Bi_2WO_6 of JCPDS file No: 39-0256. Since there are no extra peaks that could not be accounted for the sample is ascertained to be mono phasic Bi_2WO_6 .

Fig. 2. XRD pattern of ground mixture of $\text{BiOCl} + \text{Na}_2\text{WO}_4$ heat treated at 600 $^\circ\text{C}$ for 4 h and washed with water

Photocatalytic degradation of eosin blue has been reported using ZnO [11], SnO_2 [12] under UV light and over Nd, N, S-doped TiO_2 [13] and BiVO_4 [14] under visible light. Temporal variations of spectral contours as a function of irradiation time for aqueous solution of eosin blue, eosin blue + H_2O_2 , eosin blue + Bi_2WO_6 and eosin blue + H_2O_2 + Bi_2WO_6 are shown in Fig. 3. It can be seen from Fig. 3a, eosin blue has a characteristic absorption at about 520 nm and undergoes photolysis to an extent of 32 % for irradiation of 2 h. In presence of H_2O_2 , photodegradation of eosin blue to an extent of 55 % is noticeable as observed in Fig. 3b. In presence of Bi_2WO_6 , photodegradation of eosin blue to an extent of 17 % is observed for irradiation of 3 h (Fig. 3c). However, in presence of both Bi_2WO_6 and H_2O_2 , complete photocatalytic degradation of eosin blue is achieved for 3 h (Fig. 3d).

Photocatalytic degradation of acid orange was reported over TiO_2 under UV irradiation by Lucarelli and co-workers [15]. The dye abatement was monitored by diffuse reflectance FTIR. According to these investigators, addition of H_2O_2 accelerated the rate of dye removal from solution using anatase was more effective compared to using rutile as photocatalyst. Fernandez *et al.* [16] studied factorial experimental design of acid orange photocatalytic discoloration in terms of three variables, concentration of acid orange, pH and concentration of TiO_2 under UV irradiation. Feng *et al.* [17] developed a novel laponite clay-based Fe nanocomposite for photoassisted degradation of Orange II under UV light in presence of H_2O_2 . Mu *et al.* [18] reported significant determinately effect of Mn^{2+} on the photocatalytic degradation of acid orange by TiO_2 under UV light. Styliidi and co-workers [19] reported visible light activated photocatalytic degradation of acid orange in aqueous TiO_2 suspension in presence of H_2O_2 for 47 h of irradiation. Bessekhoud *et al.* [20] reported UV-visible *versus* visible degradation of acid orange using a compound CdS/TiO_2 suspension and realized only 40 % degradation under visible light. Bojinova *et al.* [21] studied influence of the mixing ratio of anatase to rutile on the photocatalytic degradation of acid orange in slurry under UV irradiation. Stengl and Bakardjieva [22] reported extraordinary photocatalytic activity for molybdenum-doped anatase for degradation of acid orange in UV and visible regions yielding 80 and 40 % degradations, respectively. Yang *et al.* [23] used BiOCl/ZnO heterojunction photocatalysts for degradation of acid orange under UV light and by Susmita *et al.* [24] using Mn, P-codoped TiO_2 nanocatalyst under visible light.

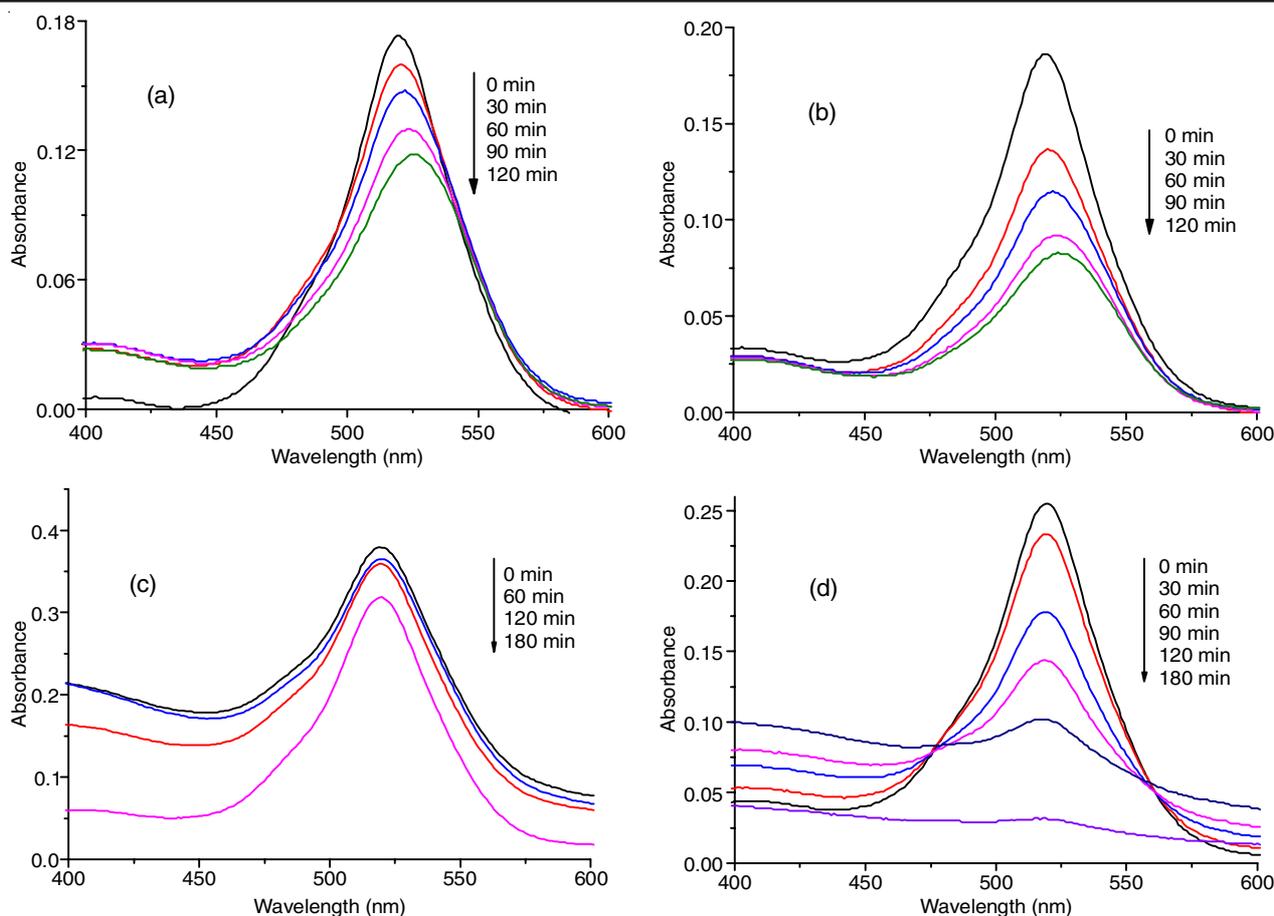


Fig. 3. Variation of spectral intensity as a function of irradiation time for (a) eosin blue, (b) eosin blue + H₂O₂, (c) eosin blue + Bi₂WO₆ and (d) eosin blue + Bi₂WO₆ + H₂O₂

Time dependent spectral intensities as a function of irradiation time for aqueous solution of acid orange, acid orange + H₂O₂, acid orange + Bi₂WO₆ and acid orange + H₂O₂ + Bi₂WO₆ are shown in Fig. 4. From the figure, it can be seen that acid orange exhibits absorption at $\lambda = 485$ and 430 nm attributing to hydrazone form and azo form, respectively (Fig. 4a) and the extent of photolysis undergone by acid orange for 3 h of irradiation is extremely small. In presence of H₂O₂, acid orange undergoes photodegradation to an extent of 8 % for 2 h of irradiation (Fig. 4b). In presence of Bi₂WO₆, photodegradation of acid orange occurred to an extent of 40 % for irradiation of 3 h (Fig. 4c). However, in presence of both H₂O₂ and Bi₂WO₆, photocatalytic degradation to an extent of 80 % acid orange occurred for 3 h of irradiation (Fig. 4d).

Photocatalytic degradations of orange G was reported by Shi-Ying *et al.* [25] using TiO₂ and UV radiation, by Sun *et al.* [26] over nano-sized Sn-TiO₂/Activated Carbon and UV light, by Mahata *et al.* [27] GdCoO₃ as well as TiO₂ under UV radiation by Sun *et al.* [28] using N-doped TiO₂ under visible light and sunlight irradiation, by Madhavan *et al.* [29] using sono-photocatalysis and by Thennarasu co-workers [30] using nanocrystalline ZnO under solar light time dependent spectral variations for aqueous orange G, orange G + H₂O₂, orange G + Bi₂WO₆ and orange G + H₂O₂ + Bi₂WO₆ under visible light irradiation are shown in Fig. 4. From the figure it can be seen that orange G has a characteristic absorption at $\lambda = 480$ nm and does not undergo any photodegradation for irradiation

time of 60 min (Fig. 5a). In presence of H₂O₂, orange G shows an exceedingly small photodegradation for irradiation of 60 min (Fig. 5b). Likewise, there is no photocatalytic degradation due to Bi₂WO₆ as well (Fig. 5c). However, in presence of both Bi₂WO₆ and H₂O₂, orange G shows complete 100 % degradation for 1 h of irradiation indicating a clear synergetic effect between Bi₂WO₆ and H₂O₂ (Fig. 5d).

In view of the enhanced photocatalytic degradations observed for eosin blue, acid orange and orange G dyes in presence of Bi₂WO₆ and H₂O₂, the following mechanism is suggested:



Formation of $\cdot\text{OH}$ free radicals during irradiation is ascertained by photoluminescence studies using terephthalic acid (TPA) as probe molecule. Terephthalic acid reacts with $\cdot\text{OH}$ free radicals to form 2-hydroxy terephthalic acid (HTPA) instantaneously which shows a characteristic photoluminescence peak at 419 nm. Fig. 6 shows photoluminescence spectra of Bi₂WO₆ + terephthalic acid suspensions in water with and without H₂O₂ prior to and after irradiation. The intense photoluminescence peak at 420 nm for sample after irradiation clearly indicates formation of $\cdot\text{OH}$ free radicals during irradiation.

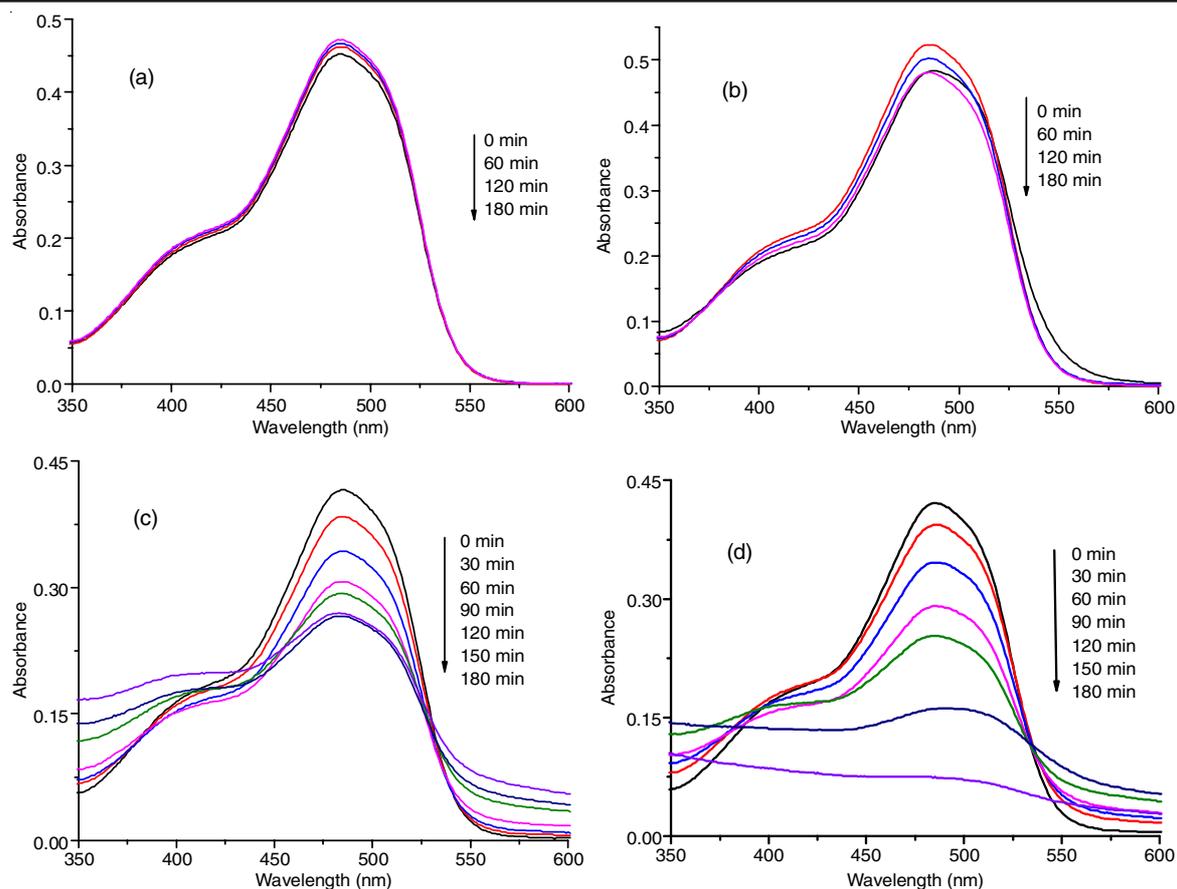


Fig. 4. Variation of spectral intensity as a function of irradiation time for (a) acid orange, (b) acid orange + H₂O₂, (c) acid orange + Bi₂WO₆ and (d) acid orange + Bi₂WO₆ + H₂O₂

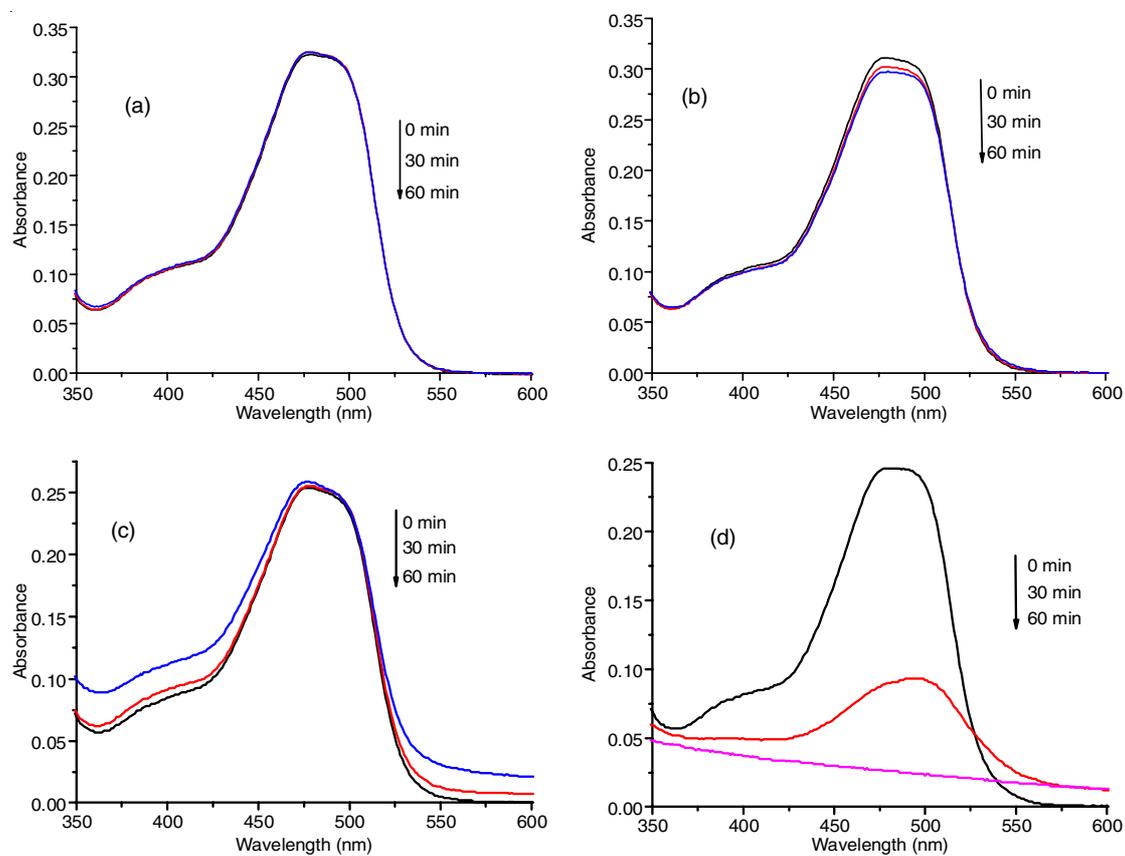


Fig. 5. Variation of spectral intensities as a function of irradiation time for (a) orange G, (b) orange G + H₂O₂, (c) orange G + Bi₂WO₆ and (d) orange G + Bi₂WO₆ + H₂O₂

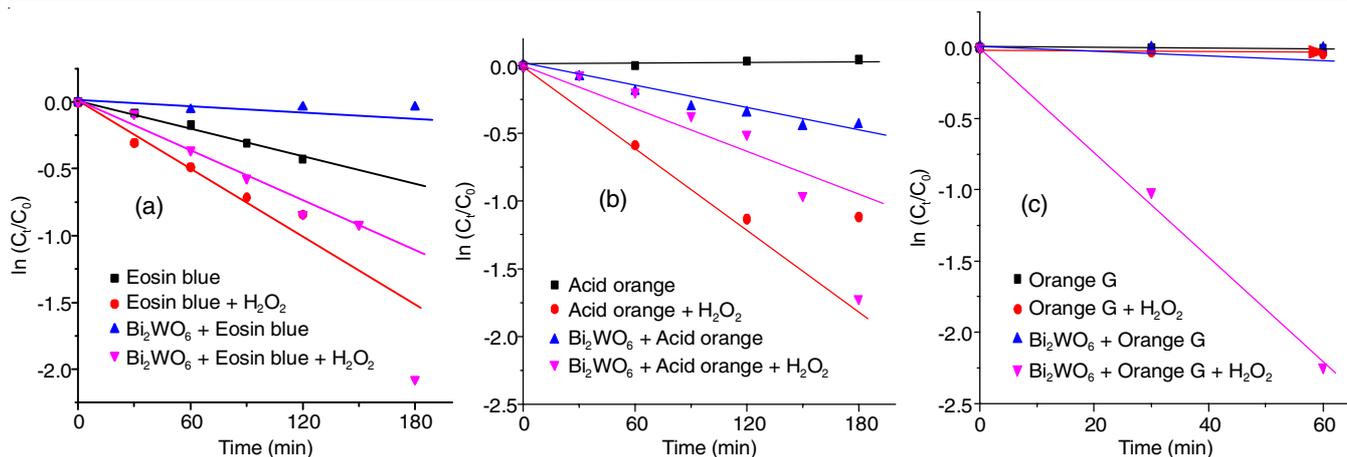


Fig. 7. Plot of $\ln(C_t/C_0)$ vs. irradiation time for dye, dye + H₂O₂, dye + Bi₂WO₆ and dye + Bi₂WO₆ + H₂O₂ (a) eosin blue, (b) acid orange and (c) orange G

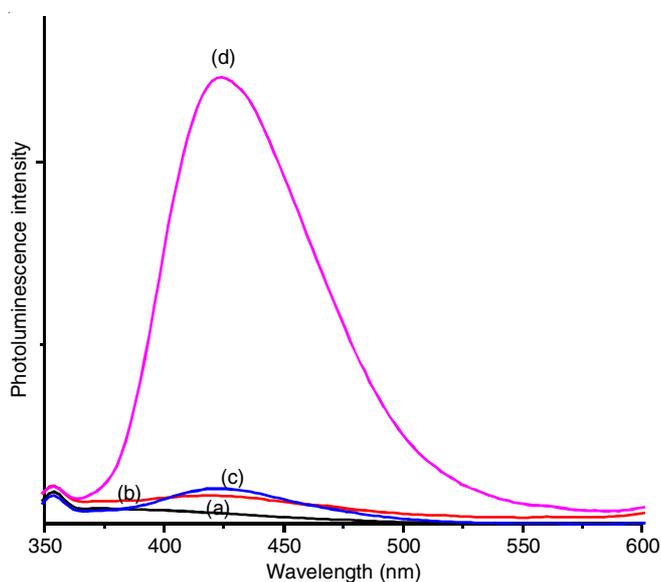


Fig. 6. Photoluminescence spectra of Bi₂WO₆ + terephthalic acid (a) before, (b) after 1 h irradiation and spectra of Bi₂WO₆ + terephthalic acid + H₂O₂ (c) before, (b) after 1 h irradiation

Plots of $\ln(C_t/C_0)$ vs. irradiation time for different photodegradation reactions of eosin blue, acid orange and orange G are shown in Fig. 7. Rate constants computed from the respective slopes for each are presented in Table-1.

TABLE-1
CALCULATED RATE CONSTANTS FOR
PHOTODEGRADATION OF EOSIN-BLUE, ACID ORANGE
AND ORANGE G WITH AND WITHOUT CATALYST AND H₂O₂

Photodegradation	Rate constant, k (min ⁻¹)		
	Eosin blue	Acid orange	Orange G
Dye alone	2.2×10^{-5}	0.0	0.0
Dye + H ₂ O ₂	3.8×10^{-5}	3.0×10^{-5}	0.0
Dye + Bi ₂ WO ₆	0.0	1.1×10^{-5}	0.0
Dye + Bi ₂ WO ₆ + H ₂ O ₂	4.4×10^{-5}	3.8×10^{-5}	6.0×10^{-4}

Conclusion

Photocatalytic degradation of eosin blue, acid orange and orange G have been studied under visible light irradiation using H₂O₂ sensitized Bi₂WO₆. Addition of H₂O₂ enhanced the rate

of degradation in each case. Complete degradation of eosin blue and orange G was achieved for 3 and 1 h, respectively. Degradation to an extent of 80 % acid orange is noticed for irradiation of 3 h. Presence of H₂O₂ enhanced photocatalytic degradation and formation of [•]OH free radicals during irradiation is ascertained by photoluminescence studies using terephthalic acid.

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