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RESEARCH ARTICLE

VISIBLE LIGHT ACTIVATED PHOTOCATALYTIC DEGRADATION OF BRILLIANT GREEN, ORANGE G AND CRYSTAL VIOLET USING H_2O_2 SENSITIZED BI_2MOO_6.

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Abstract

Photocatalytic degradation of Brilliant green, Orange G and Crystal violet dyes is investigated under visible light irradiation using Bi_2MoO_6 synthesised by coprecipitation and calcined at 450^0 C for 20 h. Addition of H_2O_2 is found to enhance the rate of degradation. The above dyes are degraded for 210, 180 and 60 min of irradiation, respectively. Formation of $^{\cdot}OH$ free radicals during irradiation is ascertained by means of photoluminescence studies using Terephthalic acid as probe molecule. A possible mechanism for photocatalytic degradation is suggested.

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Introduction:-

Remanent organic pollutants in waste water discharges from industries relating to dyes, painting, leather, paper, ink, pesticides, petrochemicals and pharmaceuticals pose a severe threat to aquatic sources of being continuously polluted with mutagenic/carcinogenic and less biodegradable toxic contaminants. During past few decades, heterogeneous photocatalysis making use of semiconductor metal oxides has been proven to be a useful technique for remediation of many soluble organic pollutants, because the method renders complete mineralisation of several organic pollutants non-selectively at ambient temperature. Many investigations projected TiO_2 as a potential photocatalyst since TiO_2 is chemically inert, photostable, easy to synthesise and abundantly available. However, the wide band gap associated with anatase/rutile restricts its absorptivity to UV region which is hardly 4% of solar radiation. In order to exploit the largely available visible region of solar radiation, a good number of binary and ternary metal oxides have been explored (1). These studies led to the observation that Bi-based composite oxides such as $BiVO_4$ (2), Bi_2WO_6 (3), Bi_2MoO_6 (4), $Bi_2Mo_2O_9$ (5), $Bi_2Mo_3O_{12}$ (6), $NaBiO_3$ (7), $BaBiO_3$ (8), $BiFeO_3$ (9) are extremely useful because of the upshifted valance band and smaller band gaps resulting from the hybridisation of Bi 6s and O 2p orbitals. Among the various Bi-composite metal oxides, Bi-Mo and Bi-W oxides exist as layered compounds that provide more transition for charge carriers. $[Bi_2O_2]^{2+}$ layers sandwiched between MO_6 octahedral layers with corner sharing structural arrangement allows easy migration of photogenerated charge carriers to the surface and contributes to the photocatalytic efficiency under visible light. Bi_2MO_6 (M=Mo, W) samples have been reported to photocatalytically degrade Rhodamine-B, Methylene blue, Methyl orange, Caramine indigo, Congo red and Malachite green under visible light irradiation(10-16).Recently, photocatalytic degradation of Brilliant green, Caramine Indigo and Toluidine blue using H_2O_2 sensitized Bi_2WO_6 synthesized by solid-state metathetic reaction has been reported from this laboratory (17). Present paper describes visible light activated photocatalytic degradation of Brilliant green, Orange G and Crystal violet using H_2O_2 sensitized Bi_2MoO_6. Molecular structures of these dyes are given below.

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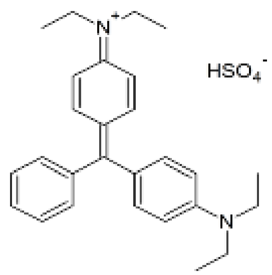
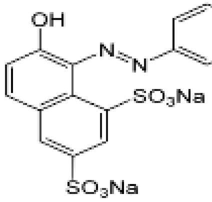
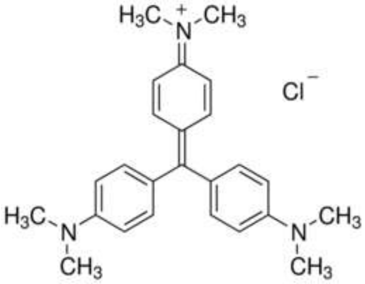


Brilliant green



Orange G



Crystal violet

Experimental:-

Materials and Methods:-

γ-Bi_2MoO_6 is synthesized by co-precipitation method reported by Matrinez and Obregon (18).

9.5439g of $Bi(NO_3)_3.5H_2O$ is dissolved in 100 m L of HNO_3(10% v/v) and 1.7369g of $(NH_4)_6Mo_7O_{24}.4H_2O$ is dissolved in 100m L distilled water separately. Bismuth nitrate solution is added dropwise(~5m L min^{-1}) to molybdate solution under vigorous stirring. pH of the solution is adjusted to 3 by using NH_4OH. Resulting yellow suspension is maintained at 70^0 C and the yellow powder obtained is used as the precursor for γ-Bi_2MoO_6 which is calcined using a thermal treatment of 5^0 C min^{-1} in air at 450^0 C for 20 h.

Photocatalytic studies:-

Photocatalytic activity of Bi_2MoO_6 is evaluated in terms of degradation of Brilliant Green, Orange G and Crystal violet under visible light. 100 mg of the photocatalyst is dispersed in 100 ml Brilliant Green (10 ppm)/ Orange G (10 ppm)/ Crystal violet (10 ppm) aqueous solution and the suspension is magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye solution. The suspension is then exposed to 400 W metal halide lamp; 5ml aliquots are pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove any suspended particles. UV-Visible spectra as a function of irradiation time are recorded using UV-Visible spectrophotometer (Schimadzu). Extent of photo degradation is calculated using the following equation

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

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

Photoluminescence studies:-

50 mg Bi_2MoO_6 catalyst is added to the beaker containing 100 ml of terepthalic 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 60 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectroflourometer (Flouromax 4) with the excitation wavelength of 315 nm.

Results and Discussions:-

X-ray diffraction pattern of precipitate calcined at 450^{0}C for 20 h is shown in Figure 1. All the observed diffraction peaks can be assigned to Bi_2MoO_6 of JCPDS file No.76-2388. Absence of any extra peaks due to any contamination indicates the sample to be phase pure Bi_2MoO_6. The sample is further characterised by FT-IR and UV- Visible diffuse reflectance spectroscopy. In the FT-IR spectrum shown in figure 2, three sharp bands at 739, 797 and 842 are present which are assigned to Mo-O stretching bands. The observed spectrum is in good agreement with literature reports. FT-IR data further corroborates that the sample obtained is phase pure Bi_2MoO_6. UV-Visible diffuse reflectance spectrum is shown in figure 3 from which the band gap is computed as 2.6 eV. Reported band gaps for Bi_2MoO_6 samples prepared by different methods range from 2.56 e V to 2.79 eV. Band gap obtained in present study lies within the range of literature reports(19).

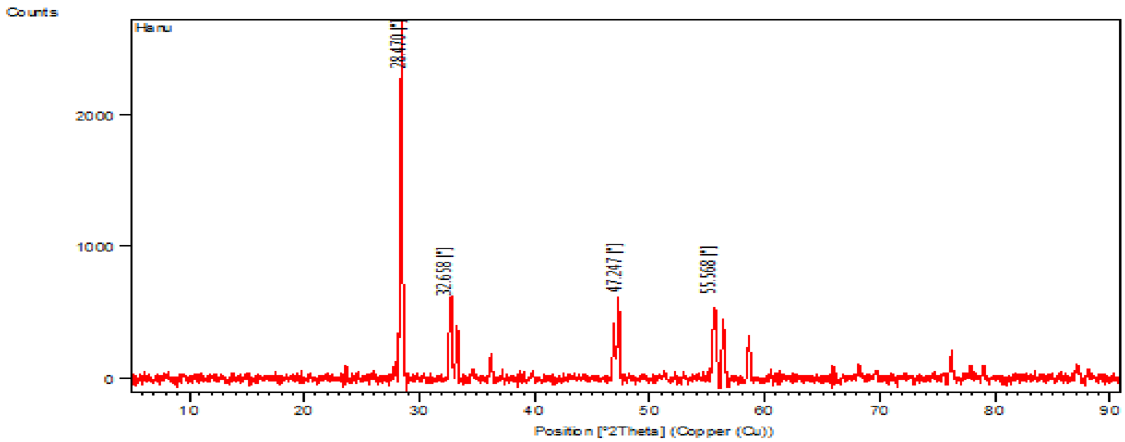


Fig. 1:- XRD pattern of Bi_2MoO_6 precursor powder heat treated at 450^0C for 20 h.

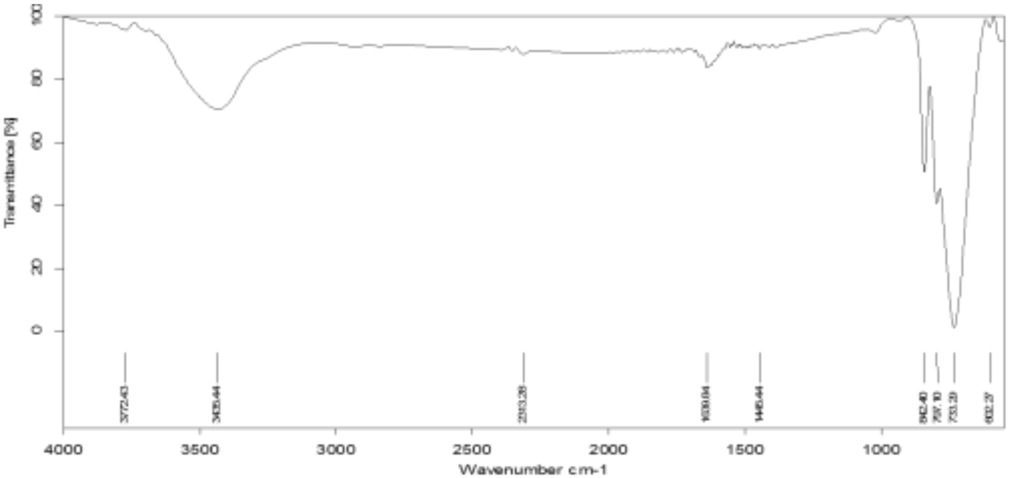


Fig. 2:- FT-IR spectrum of Bi_2MoO_6 precursor precipitate heat treated at 450^0C for 20 h

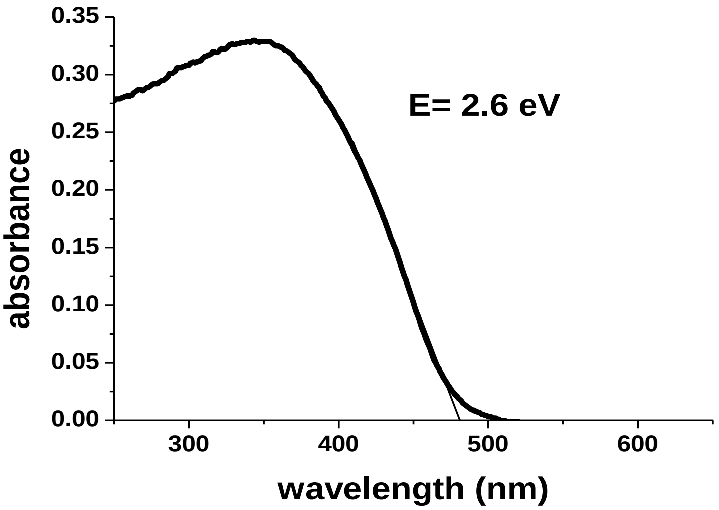


Fig. 3:- UV-Visible Diffuse reflectance spectrum of Bi_2MoO_6

Brilliant green (BG), a triphenyl methane dye is highly toxic and it is banned in many countries because of its carcinogenic nature. Photocatalytic degradation of BG was reported using N, S- codoped TiO_2 by Ankit Kumar Jain and co-workers (20), over Nb_2O_5-graphene by Hae Soo Park and Weon Bee Ko (21), over CeO_2-(NaX) Zeolite by SudhaSubrahmaniyan (22), over TiO_2 by Chon et al (23), over Sr-doped TiO_2 by Swati Sood et al (24), over TiO_2-SiO_2 mesoporous nanocomposites by Dong et al (25), over SnO_2 by Shanmugam et al (26), over nanoTiO_2 on activated carbon by Ragupathy and co-workers (27) and over $BiVO_4$ by Umabala et al (28). Temporal variations of spectral intensities as a function of irradiation time for BG, BG+H_2O_2, BG+Bi_2MoO_6 and BG+H_2O_2+Bi_2MoO_6 are shown in figure 4. From the figure it can be seen that BG has a characteristic absorption at λ=625 nm and BG shows very little photolysis for irradiation of 240 min (Fig. 4a). In presence of H_2O_2, BG undergoes extensive photodegradation to an extent of 85% for irradiation for 240 min (Fig. 4b). In presence of Bi_2MoO_6, photocatalytic degradation of BG occurred only to an extent of 27% for 240 min (Fig. 4c). However, in presence of H_2O_2+Bi_2MoO_6, complete decolouration of BG is achieved for 210 min. of irradiation (Fig. 4d).

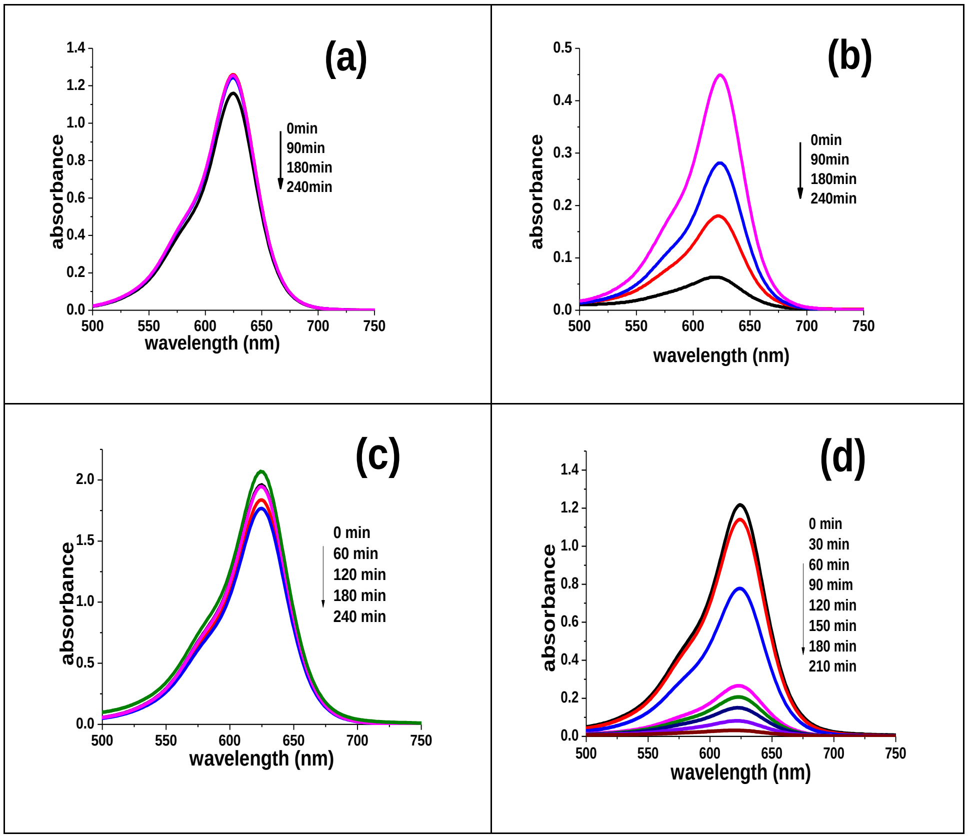


Fig. 4:- Time dependent variations of spectral intensities as a function of irradiation time for (a) BG, (b) BG+ H_2O_2, (c) BG + Bi_2MoO_6 and (d) BG + Bi_2MoO_6 + H_2O_2

Photocatalytic degradation of azo dye Orange G was reported over TiO_2 by Shi-Ying et al (29), over nano SnO_2-TiO_2/activated carbon by Sun et al (30), over $GdCoO_3$ by Mehata et al (31), over N-doped TiO_2 by Sun et al (32) and over nanocrystalline ZnO by Thennerasu and co-workers (33). Temporal variations of spectral intensities as a function of irradiation time for OG, OG+H_2O_2, OG+Bi_2MoO_6 and OG+H_2O_2+Bi_2MoO_6 are shown in figure 4. From the figure it can be seen that OG has a characteristic absorption at λ=480 nm and does not undergo any photolysis under irradiation for 180 min (Fig. 5a). In presence of H_2O_2, OG shows negligible photodegradation as shown in Figure 5b. In presence of Bi_2MoO_6, OG shows photocatalytic degradation to an extent of (Fig. 5c). However, in presence of H_2O_2+Bi_2MoO_6, complete photocatalytic degradation of OG is achieved for 180 min. (Fig. 5d).

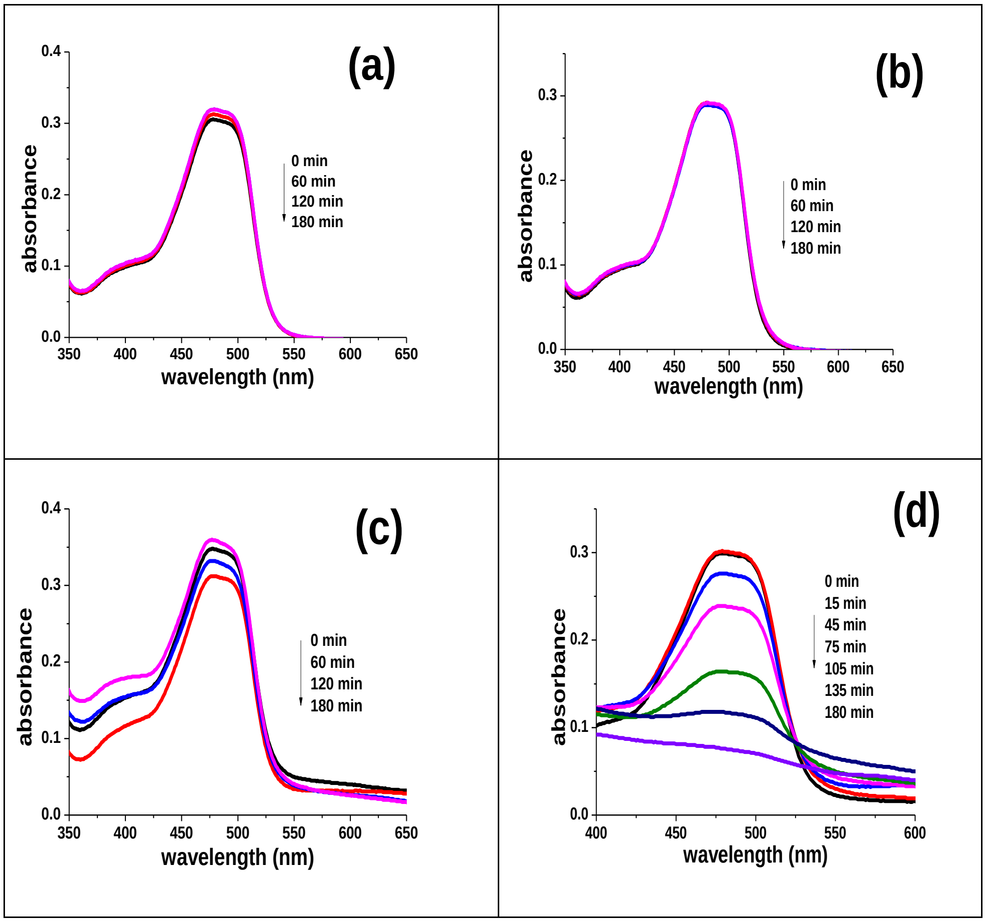
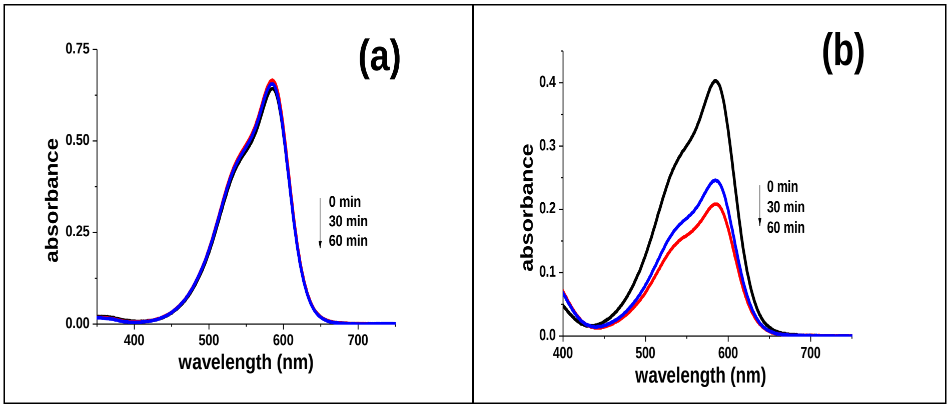


Fig. 5:- Time dependent variation of spectral intensities as a function of irradiation time for (a) OG, (b) OG+ H_2O_2, (c) OG + Bi_2MoO_6 and (d) OG + Bi_2MoO_6 + H_2O_2

Crystal Violet (CV), a triaryl-methane dye used in paper, textile, and leather industries is considered to be carcinogenic. Photocatalytic degradation of CV has been reported with ZnO (34-37), iron oxide (38), Ba-$SrTiO_3$ (39), nano TiO_2 (40-42), V-doped TiO_2 (43), Ni-containing polytungastometallate (44), Sm_2InTaO_7 (45), TiO_2 doped Bi_2O_3 (46), Bi_2WO_6 (47), ZnS (48), Fenton like systems (49) and $Bi_2Mo_3O_{12}$ (50). Time dependent variations of spectral intensities with progressive irradiation for CV, CV+H_2O_2, CV+Bi_2MoO_6 and CV+H_2O_2+Bi_2MoO_6 are shown in figure 6. From the figure it can be seen that CV has a characteristic absorption at λ= 585 nm and undergoes no photolysis for 60 min of irradiation (Fig. 6a). In presence of H_2O_2, photodegradation of CV occurred to an extent of 50% for 60 min of irradiation (Fig. 6b). In presence of Bi_2MoO_6, photocatalytic degradation of CV to an extent of 23% has occurred for 60 min of irradiation (Fig. 6c). However, in presence of both H_2O_2+Bi_2MoO_6, near complete degradation of CV is achieved for 60 min. of irradiation (Fig. 6d).



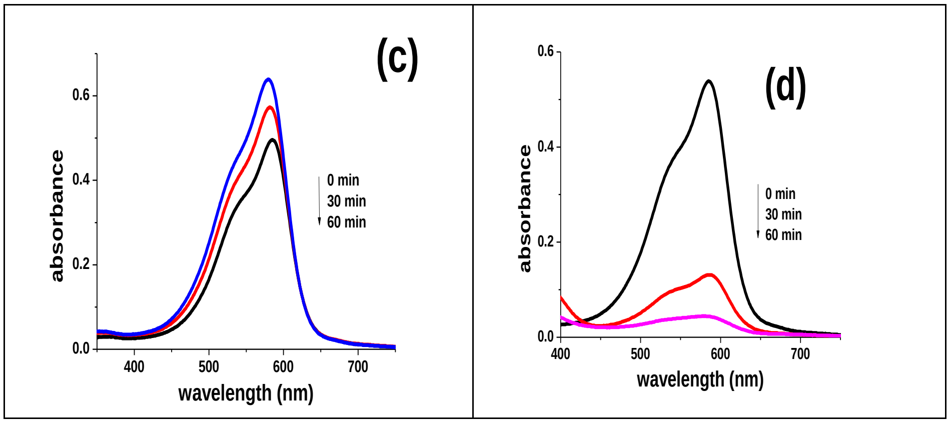


Fig. 6:- Time dependent variation of spectral intensities as a function of irradiation time for (a) CV, (b) CV+ H_2O_2, (c) CV + Bi_2MoO_6 and (d) CV + Bi_2MoO_6 + H_2O_2

The above results suggest that the role of H_2O_2 is critical in enhancing the rate of degradation of BG, OG and CV dyes. Since BG and OG did not show any significant photolysis, the photocatalytic degradation mechanism may be suggested as follows:

$$Bi_2MoO_6 + h\nu \longrightarrow e^-_{CB} + h^+_{VB}$$
$$e^-_{CB} + H_2O_2 \longrightarrow {}^{\cdot}OH + OH^-$$
$$h^+_{VB} + OH^- \longrightarrow {}^{\cdot}OH$$
$${}^{\cdot}OH + \text{Dye} \longrightarrow \text{Degradation products}$$

Presence of $^{\cdot}OH$ during irradiation is ascertained by Photoluminescence studies using Terephthalic acid (TPA) as probe molecule. TPA reacts with $^{\cdot}OH$ to form 2-hydroxy Terephthalic acid (HTPA) which exhibits photoluminescence around 420 nm. Figure 7 shows photoluminescence spectra of aqueous suspension containing Bi_2MoO_6+TPA with and without H_2O_2 subjected to irradiation and no irradiation. Intense peak at 419 nm observed for Bi_2MoO_6+TPA+H_2O_2 after irradiation indicates formation of $^{\cdot}OH$ free radicals during irradiation.

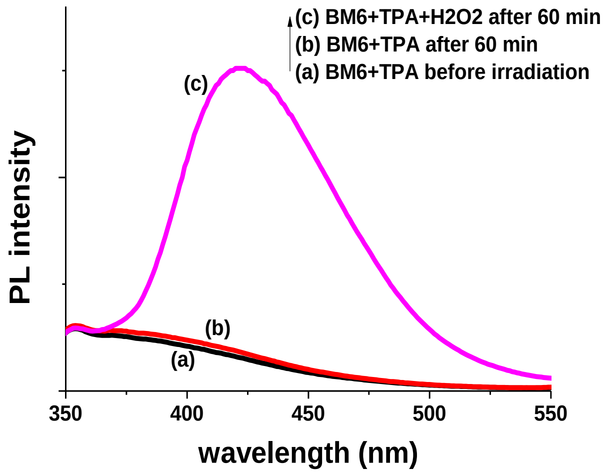


Fig. 7:- Photoluminescence spectra of Bi_2MoO_6+TPA with and without H_2O_2, prior to and after irradiation

Plots of ln C_t/C_0 vs time for different degradation reactions relating to BG, OG and CV are shown in Figure 7. Rate constants calculated from their respective slopes are given in Table 1.

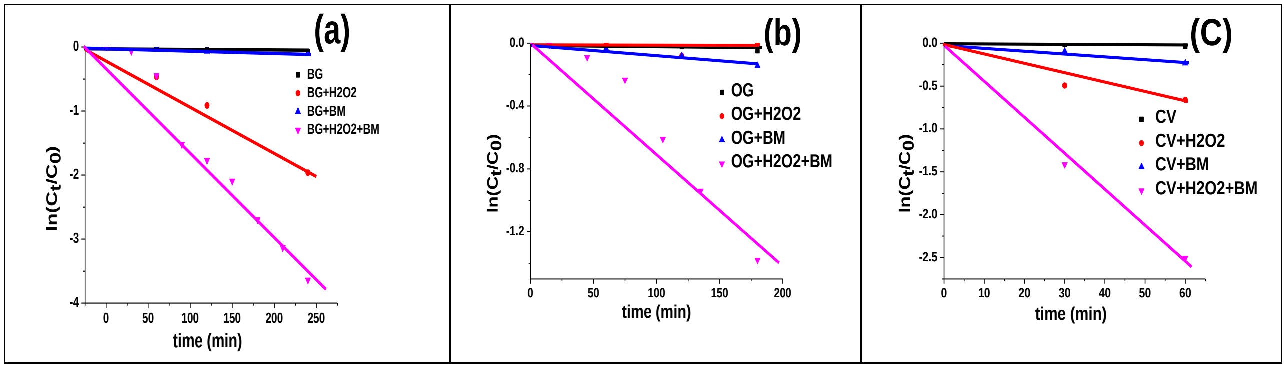


Fig. 8:- Plots of ln C_t/C_0 vs irradiation time for dye, dye+H_2O_2, dye+Bi_2MoO_6 and dye+ Bi_2MoO_6+H_2O_2 (a) BG, (b) OG and (c) CV

Table. 1:- Calculated rate constants for photodegradation of BG, OG and CV with and without catalyst and H_2O_2

photodegradation	**Rate constant k (min^{-1})**		
	BG	**OG**	**CV**
Dye alone	0	0	0
Dye+H_2O_2	$3.3X10^{-5}$	0	$2x10^{-4}$
Dye+Bi_2MoO_6	0	0	$5x10^{-5}$
Dye+ Bi_2MoO_6+ H_2O_2	$5.8x10^{-5}$	$3.3x10^{-5}$	$7x10^{-4}$

Conclusions:-

Based on the experimental results, it is concluded that Brilliant green, Orange G and Crystal Violet dyes can be photocatalytically degraded under visible light irradiation using Bi_2MoO_6 in presence of external oxidant H_2O_2. Combination of H_2O_2+Bi_2MoO_6 showed synergetic effect in enhancing rate of degradation. Complete degradation of Brilliant green, Orange G and Crystal violet occurred for 210, 180 and 60 min of irradiation respectively.

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