



Rapid Photo Catalytic Degradation Of Crystal Violet And Carmine Indigo Under Sun Light By $\text{Fe}_2\text{Mo}_3\text{O}_{12}$

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ABSTRACT

$\text{Fe}_2(\text{MoO}_4)_3$ with excess MoO_3 has been prepared by combustion method using Ferric nitrate, MoO_3 and glycine. SEM studies revealed particle size in the μm region. The sample as prepared showed excellent photo catalytic activity for the degradation of crystal violet and carmine indigo in presence of H_2O_2 either under visible light irradiation using 400 w metal halide lamp or under sun light. Photo catalytic studies on 100 ml aqueous dye solutions with 100 mg of dispersed catalyst under visible light irradiation indicated degradation of 93% of 5ppm crystal violet and 100% of 20ppm carmine indigo in 70 min and 10 min respectively, whereas, under sun light 100% of 5ppm crystal violet and 100% of 20ppm carmine indigo were degraded in 30 min and 5 min respectively.

Keywords: $\text{Fe}_2(\text{MoO}_4)_3$, Crystal Violet, Carmine Indigo, photo catalytic degradation, Combustion synthesis.

INTRODUCTION

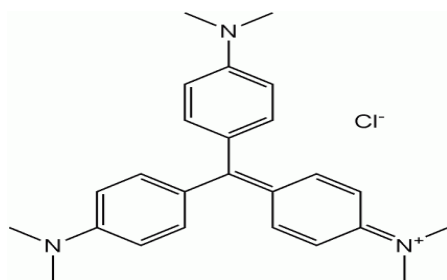
Remediation of organic pollutants from industrial waste water effluents including those of textile, dyeing, printing etc. has been the subject of considerable importance since the chemicals discharged into water are hazardous and have significant impact on the aquatic environment and human health. Various methods like adsorption, osmosis, flocculation have been used traditionally for the removal of dyes, but these methods are not completely satisfactory. During the past two decades, several investigations relating to visible light induced photocatalytic oxidation of dyes have been shown to be exceedingly useful in mitigating this problem since the main advantage of this method is that a lot of organic effluents can be mineralized completely into CO_2 , H_2O and mineral salts. These methods make use of inexpensive metals/metal oxides/mixed metal binary and ternary oxides as photo catalysts.

Crystal violet (CV) is a triaryl methane dye which is widely used in textile dyeing, printing, paper and leather industries. The dye is known to be carcinogenic and therefore its removal is of great importance. Photo catalytic degradation of CV has been reported using TiO_2 [1-5], ZnO [6], Fe_2O_3 [7], (Ba, Sr) TiO_3 [8], aqueous nano- ZnO suspension [9], Ni containing poly tungstate matelate $\text{Na}_2[\text{Cu Ni W}_{18}\text{O}_{62}] 23 \text{H}_2\text{O}$

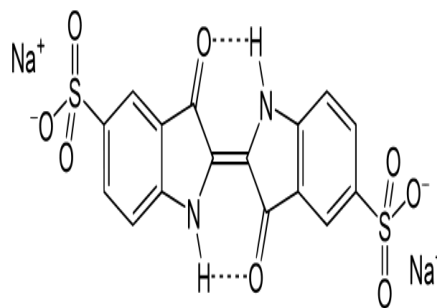
[10], MnO₂ [11], Ag-modified Ti doped- Bi₂O₃ [12]. Irradiation source and time needed for complete degradation in the above cases are listed in table 1.

Carminic acid (CA) is an anionic dye used in textile, food and cosmetic industries. This indigoid class of dye is regarded as highly toxic leading to tumours, eye and skin irritation at the site of contact and is also carcinogenic affecting reproductive, developmental neuron causing acute toxicity. When administered intravenously it may cause gastro intestinal irritations with nausea, vomiting and diarrhea [13-19]. In view of this, its removal from aquatic wastes is highly essential. Photocatalytic degradation of carminic acid has been reported using TiO₂ [20], TiO₂ coated non-woven fibers [21], rubber sheet impregnated with TiO₂ particles [22], TiO₂: AlPO₄-5 zeolites [23], Bi₂Mo₃O₁₂ [24], Bi₂MoO₆ [25], nano TiO₂ particles [26], commercial TiO₂ and natural rutile [27], and Sm₂FeTaO₇ pyrochlore [28]. Irradiation source and time taken for complete degradation in above processes as are given in table 1.

In our previous work we reported rapid degradation of Rhodamine-B, Methylene Blue and Malachite green using Fe₂Mo₃O₁₂ and MoO₃ [29]. The present paper describes the use of Fe₂Mo₃O₁₂ as photocatalyst for rapid degradation of CV and CI under irradiation in the visible region or under direct exposure to sun light without any stirring. Molecular structures of CV and CI are shown below.



Molecular Structure of Crystal violet.



Molecular Structure of Carminic Indigo.

Table 1. Irradiation sources and exposure times reported in literature for CV and CI degradation.

Dye	Photocatalyst	Irradiation source	Time for degradation in minutes	Ref No
1. Crystal violet	Zno	W-lamp	240	6
	Fe ₂ O ₃	W-lamp	360	7
	(Ba,Sr)TiO ₃	W-lamp	45(80% degradation)	8
	Nano TiO ₂	U.V lamp	30	5
	Nano ZnO	Solar radiation	330	9
	Na ₂ [CuNiW ₁₈ O ₆₂] 23 H ₂ O	W-lamp	180	10
	MnO ₂	W-lamp	Not specified	11
	Ag-modified Ti-doped Bi ₂ O ₃	U.V light	90	12

2. Carmine indigo	TiO ₂ impregnated activated carbon	U.V light	240	21
	TiO ₂ impregnated on rubber sheet	U.V light	300	22
	TiO ₂ :AlPO ₄ -5 Zeolites)	U.V light	300	22
	α- Bi ₂ Mo ₃ O ₁₂	U.V light and sun light	210	23
	γ- Bi ₂ Mo ₃ O ₆	Xenon lamp	360	24
	nano TiO ₂	Xenon lamp	360	24
	commercial TiO ₂	U.V light	150	25
	Sm ₂ FeTaO ₇	U.V light	20	26
	Solar radiation	210	27	
		600	28	

MATERIALS AND METHODS

Synthesis of Catalyst: Fe(NO₃)₃·9 H₂O and MoO₃ of AR Quality were starting materials; 6.83g Fe(NO₃)₃ and 7.3004g MoO₃ (Fe: Mo=1:3) were added to 50 ml of water under constant stirring followed by the addition of 0.76149g of glycine. The precursor solution containing dispersed MoO₃ was then heated on a hot plate at 110°C until it became viscous with liberation of large amounts of brown fumes. The dried mass was then calcined at 400°C for 4 h. The resultant powder was ground for homogeneity and used for phase identification.

Characterization Techniques: Phase purity of the calcined powder was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan), using Nickel filtered Cu-K_α radiation (λ= 1.54059 Å), with a scan rate of 2° min⁻¹. UV-visible diffuse reflectance spectrum (UVDRS) of the sample was obtained with the dry pressed disk samples using Shimadzu UV-visible spectrophotometer (UV-3600) between 200 to 800 nm range. Spectral grade BaSO₄ was taken as reference for the reflectance spectra. Microstructural investigation of the sample was performed on the powdered sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

Photocatalytic activity: Photo catalytic activity of Fe₂(MoO₄)₃ + MoO₃ was evaluated in terms of degradation of crystal violet and carmine indigo under visible light irradiation from 400 W metal halide lamp and also in solar radiation as a light source for irradiation. UV radiation below 350nm is eliminated by surrounding the sample with a water jacket, when sample solution irradiated in metal halide lamp. 100 mg of the catalyst powder was added into 100ml CV solution (5 mg/L) and the suspension was magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photo catalyst powder and dye. The suspension was then exposed to lamp/ sun light emanating from the source; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. Progress of decolorization was followed by recording the corresponding absorption spectrum. The same procedure was adopted for CI (20mg L⁻¹) indicator. All the experiments were conducted under ambient conditions.

RESULTS AND DISCUSSION

XRD pattern of resultant powder obtained from the mixture of Ferric nitrate, Molybdenum oxide (Fe: Mo=1:3) and glycine mixed in water and calcined at 400°C is shown in Fig. 1. The observed peaks could be indexed to Fe₂(MoO₄)₃ of JCPDS File no 83-1701 and MoO₃ JCPDS File no 76-1003. Absence of peaks due to Fe₂O₃ indicates that the sample obtained is a mixture of Fe₂(MoO₄)₃ + MoO₃. Scanning electron microscopic study of the calcined powder is depicted in Fig. 2 from which it can be seen that the particle size is in μm region.

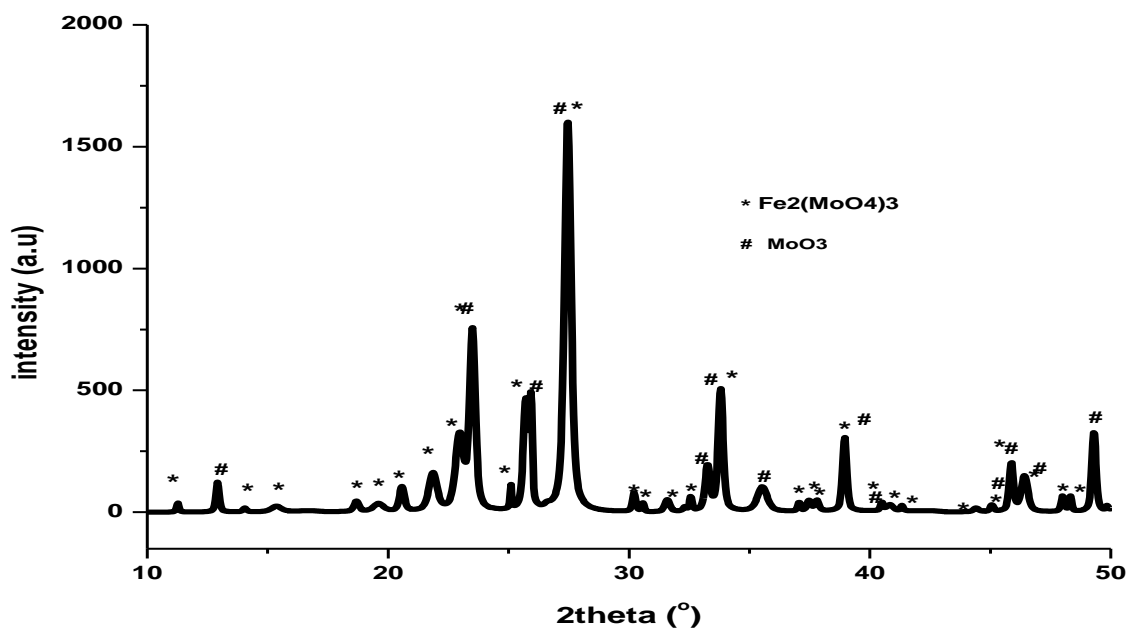


Fig 1. XRD pattern of powder obtained from mixture of Ferric nitrate, Molybdenum oxide and Glycine in water dried at 100°C and calcinated at 400°C for 4 h.

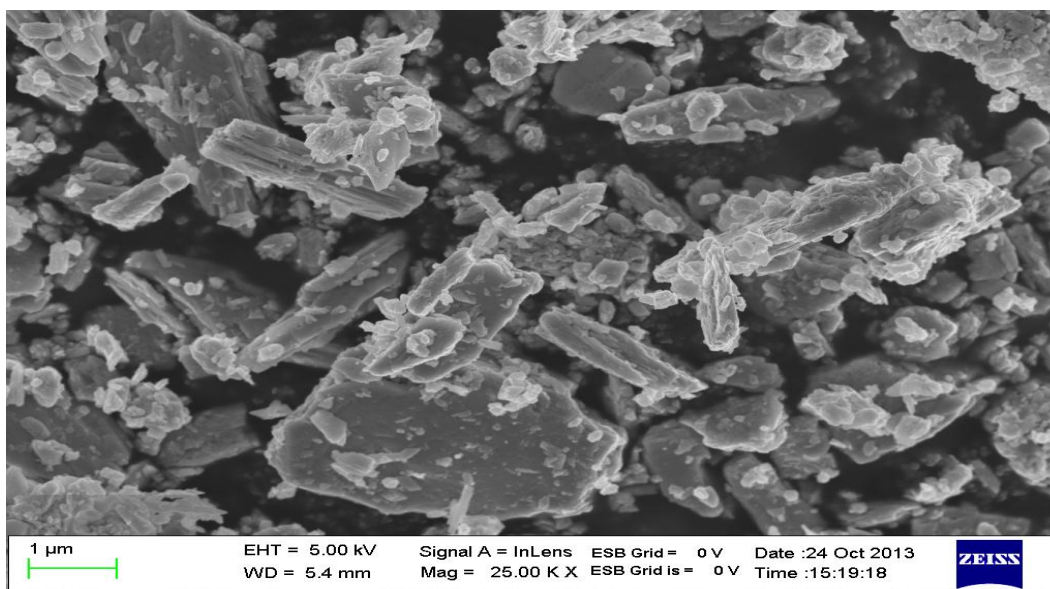


Fig 2. SEM image of $\text{Fe}_2(\text{MoO}_4)_3 + \text{MoO}_3$ calcined powder.

Fig 3 Depicts temporal evolution of spectral changes of aqueous solution of CV as a function of exposure time under different conditions- only dye aqueous solution, dye aqueous solution + H_2O_2 , dye aqueous solution+ catalyst and dye aqueous solution+ H_2O_2 + catalyst and corresponding spectral changes for sun light exposure. Resulting spectra shown in Figs 3A and 3B are obtained with the metal halide source and sun light source respectively.

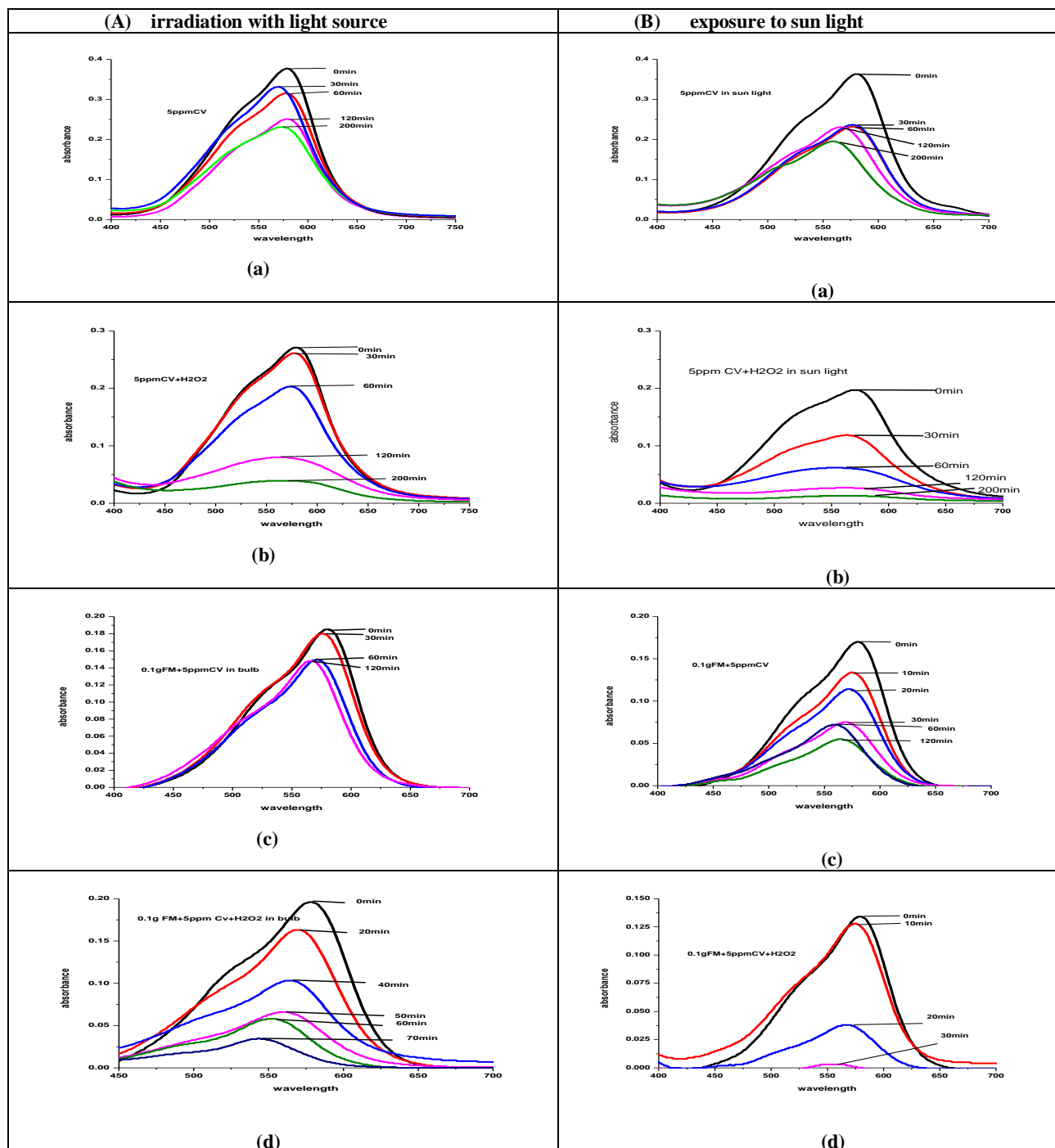
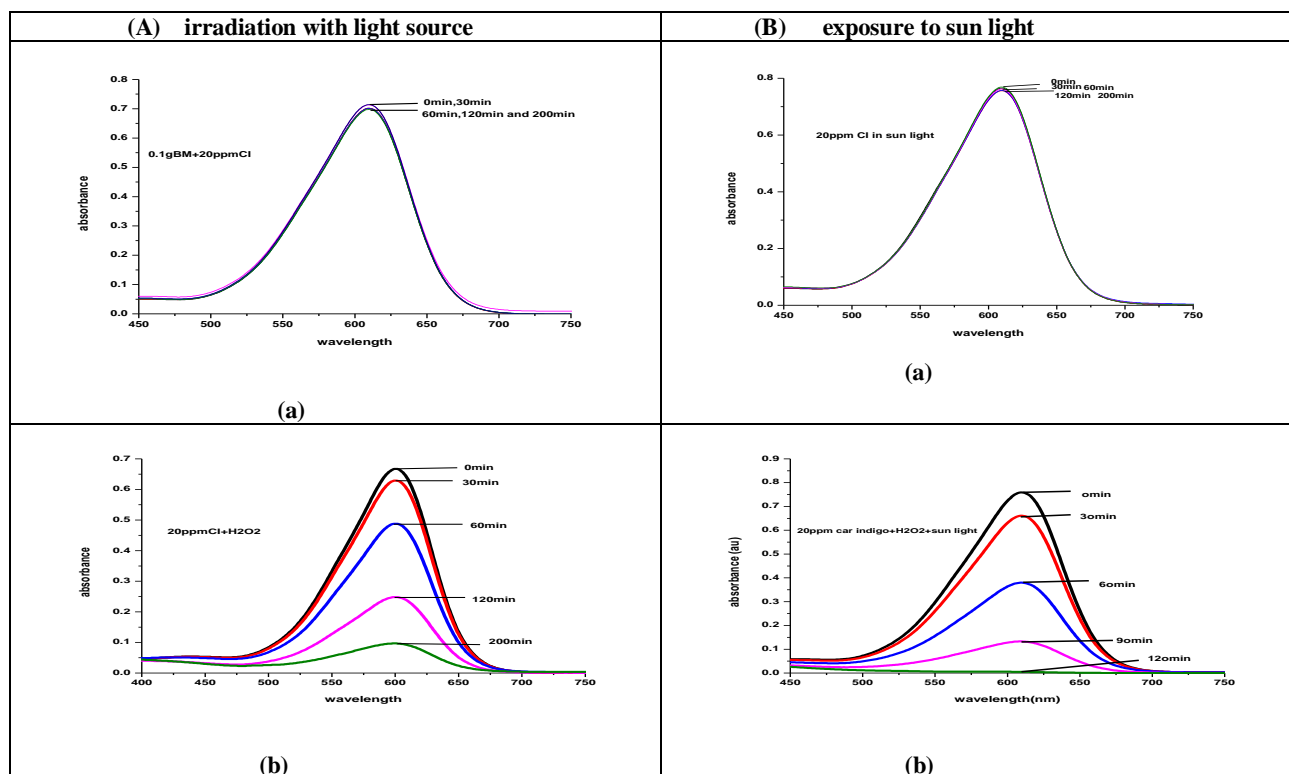


Fig 3. Temporal evolution of spectral changes in CV dye aqueous solution as a function of exposure time under different conditions (a) only dye solution (b) dye solution+H₂O₂ (c) dye solution+ Catalyst (d) dye solution + H₂O₂+ Catalyst with (A) illumination under a bulb and (B) under sunlight.

From Fig 3A (a) and 3B (a), it can be seen that aqueous dye solution showed a small decrease in absorption for an exposure time up to 200 min under light from the bulb or under direct exposure to sun light. From Fig 3A (b) and 3B (b), it can be seen that the dye solution in presence of H₂O₂ showed gradual lowering in absorption as a function of exposure time. Though Fig 3A (c) and 3B (c), do not show that dye

+ catalyst is effective in bringing much decolorization under exposure to sun light, complete bleaching of dye solution occurred in 40 min under direct exposure to sun light (Fig 3d), as compared to the corresponding change under visible light irradiation. From the changes in spectral intensities shown in Fig 3, it is clear that complete bleaching of dye solution could be effected with $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ in presence of H_2O_2 . Fig 4 depicts temporal evolution of spectral changes of aqueous solution of CI as a function of exposure time under different conditions namely - only dye solution, dye solution + H_2O_2 , dye solution + catalyst and dye solution + catalyst + H_2O_2 . Results depicted in Figs 4A and 4B are obtained with the metal halide source and sun light source respectively. Fig 4A (a) and 4B (a), show that there is no change in absorption due to CI aqueous dye solution even after an exposure of 120 min. However, the same dye solution in presence of H_2O_2 showed gradual decrease in absorption with exposure up to 200 min, and no decolorization was observed even at 200 min of exposure. But the dye solution was found to be bleached completely under sun light for an exposure of 120 min (Fig 4A (b) and 4B (b)) even without a catalyst. The dye solution containing only dispersed catalyst showed less bleaching under metal halide lamp compared to exposure to sun light (Fig 4A (c) and 4B (c)). However, in presence of H_2O_2 and catalyst a synergistic effect of bleaching the dye occurred within 5-10 minutes (Fig 4A (d) and 4B (d)).

From the literature reports as shown in table 1, it is clear that degradation of both CV and CI are fast within 20-30 min under U.V irradiation and considerably slow under visible light irradiation i.e from 90-360 min for CV and 150- 600 min for CI. However, the present work, reports that under visible light irradiation 93% decolorization of CV could be obtained in 70 min while 100% bleaching could be obtained in 30 min under sun light. Similarly, for CI, 100% bleaching was observed for an exposure of 10 min under bulb and 5 min under sun light.



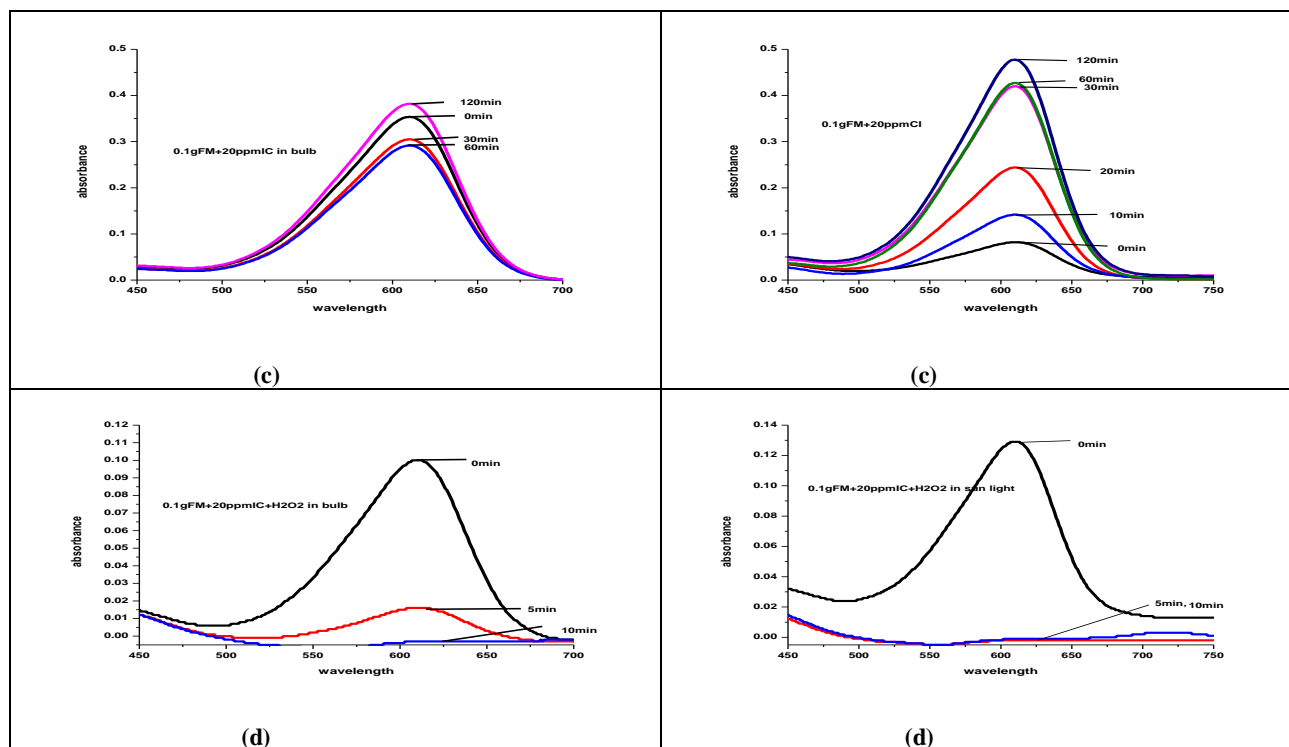
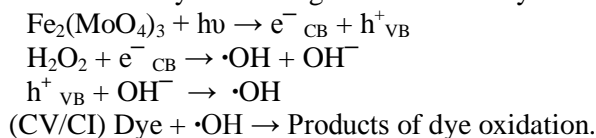
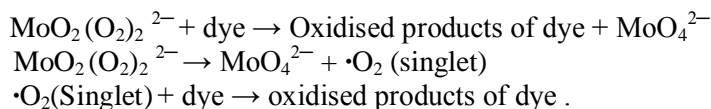


Fig 4. Temporal evolution of spectral changes in CI dye aqueous solution as a function of exposure time under different conditions (a) only dye solution (b) dye solution +H₂O₂ (c) dye solution + Catalyst (d) dye solution + H₂O₂+ Catalyst with (A) illumination under a bulb and (B) under sunlight.

The following mechanism is likely for the degradation of the dye.



Also, H₂O₂ forms peroxy complex MoO₂(O₂)₂²⁻ which is capable of causing degradation of dye as per the following reactions.



The exceedingly rapid degradation of CV and CI in the visible light irradiation, is ascribed to a combination of (i) more crystallinity of the sample as evidenced by sharp peaks in the XRD pattern (ii) the presence of H₂O₂ which generates a fenton like reaction with Fe-based catalyst and (iii) the formation of a hetrojunction between the photocatalyst Fe₂Mo₃O₁₂ and excess MoO₃ present along with the catalyst.

APPLICATIONS

Fe₂Mo₃O₁₂ prepared showed excellent photocatalytic activity for the degradation of crystal violet and carmine indigo in presence of H₂O₂ under either visible light irradiation using a bulb or under direct exposure to sun light.

CONCLUSIONS

Fe₂(MoO₄)₃ with excess MoO₃ prepared by combustion method showed a synergetic effect in the photocatalytic degradation of both crystal violet and carmine indigo dyes. The present study revealed that rapid degradation can be achieved in presence of H₂O₂. The dye aqueous solutions of crystal violet and carmine indigo showed complete bleaching in 30 min and 5min respectively under sun light as compared to 90-360 min and 150-600min reported in literature. The enhanced photocatalytic activity is attributed to more crystallinity of the catalyst, presence of H₂O₂ and MoO₃.

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