



Rapid Visible Light Photo Catalytic Degradation of Eosin Y, Congo Red and Methyl Orange with $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ and MoO_3

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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 Eosin Y, Congo red and Methyl orange in presence of H_2O_2 under visible light irradiation. Photo catalytic studies on 100 ml aqueous dye solutions with 100 mg of dispersed catalyst showed degradation of 96.6% of 20 ppm Eosin Y, 100% degradation of 10ppm of Congo red and 97.4% degradation of 10 ppm of Methyl Orange in 120 min, 45 min and 45 min respectively under visible light irradiation.

Keywords: $\text{Fe}_2(\text{MoO}_4)_3$, Eosin-Y, Congo Red, Methyl Orange, Photo catalytic degradation, Combustion synthesis.

INTRODUCTION

Environmental pollution due to synthetic organic dyes has become a major ecological concern because when released into the environment, these dyes not only impart intense color to water sources but also damage living organisms by stopping reoxygenation capacity of water, block sun light penetration and disturb the natural growth ability of aquatic life. Common methods such as adsorption, ultra filtration and reverse osmosis proposed for remediation of hazardous waste water effluents are non destructive and transfer pollutants from one phase to another causing secondary pollution. Likewise, chlorination and ozonation are also relatively inefficient and are not cost effective. In recent years, degradation of dyes making use of heterogeneous photo catalysis has been widely investigated for the oxidative remediation of organic pollutants. In this process, a photo excitable solid catalyst is continuously irradiated with U.V/ Visible radiation of energy greater than the band gap of the semiconductor to generate electron/hole pairs which migrate to respective conduction/valance bands. The photo generated holes are extremely oxidizing and photo generated electrons are reducing, both of which facilitate degradation of organic dye structure. The key advantage of this process is its inherent destructive nature without involving mass transfer and can be carried out under ambient conditions leading to complete mineralization of organic carbon into CO_2 . Though TiO_2 is shown to be an effective, photo stable, reusable, inexpensive and non toxic catalyst for advanced oxidative degradation of dyes, its poor photo conversion efficiency in the visible region and

rapid recombination of photo generated electron/hole pairs limit its use as a cost effective photo catalyst. Rate of photo catalytic degradation was further found to be enhanced significantly in presence of external oxidants such as H_2O_2 , ClO_3^- , BrO_3^- and $\text{S}_2\text{O}_8^{2-}$. The beneficial effect of an electron donor was attributed to its ability not only to suppress electron-hole recombination rate by removal of e^- from conduction band of photo catalyst but also to generate $\cdot\text{OH}$ radicals primarily responsible for degradation of organic structure. The authors have recently reported [1, 2] the degradation of Rhodamine B, Methylene blue, Carmine Indigo, Crystal violet and Malachite green with $\text{Fe}_2(\text{MoO}_4)_3$ under visible light irradiation mediated by H_2O_2 . The present paper describes H_2O_2 assisted rapid visible light photo catalytic degradation of Eosin Y, Congo red and methyl orange with $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ and MoO_3 .

MATERIALS AND METHODS

Synthesis of Catalyst: $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ and MoO_3 of AR Quality were starting materials; 6.83g $\text{Fe}(\text{NO}_3)_3$ and 7.3004g MoO_3 (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 MoO_3 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 ($\lambda = 1.54059 \text{ \AA}$), 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 BaSO_4 was taken as reference for the reflectance spectra. Micro structural investigation of the sample was performed on the powdered sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

Photo catalytic activity: Photo catalytic activity of $\text{Fe}_2(\text{MoO}_4)_3 + \text{MoO}_3$ was evaluated in terms of degradation of Eosin Y, Congo red and Methyl orange under visible light irradiation using 400 W metal halide lamp as a light source for irradiation. UV radiation below 350nm is eliminated by surrounding the sample with a water jacket. 100 mg of the catalyst powder was added into 100mL Eosin Y aqueous solution (20 mg L^{-1}) 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 light emanating from the source; 5ml aliquots were pipetted at periodic intervals and filtered through 0.45 micron Millipore filters to remove the suspended particles. Extent of decolorization was followed from the corresponding absorption spectrum. The same procedure was adopted for Congo red (10 mg L^{-1}) and Methyl orange (10 mg L^{-1}) indicators. All the experiments were conducted under ambient conditions.

RESULTS AND DISCUSSION

XRD pattern of the powder obtained from the mixture of Ferric nitrate, Molybdenum oxide and glycine mixed in water and calcined at 400°C is shown in fig. 1. The observed peaks could be indexed to $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ (JCPDS File No 83-1701) and MoO_3 (JCPDS File No 76-1003). Absence of peaks due to Fe_2O_3 and other phases of Fe-Mo-oxides indicated that the sample obtained consists of $\text{Fe}_2\text{Mo}_3\text{O}_{12} + \text{MoO}_3$. Microstructures as studied by SEM did not indicate any characteristic texture and the particle size is in the μm region as given in ref [1].

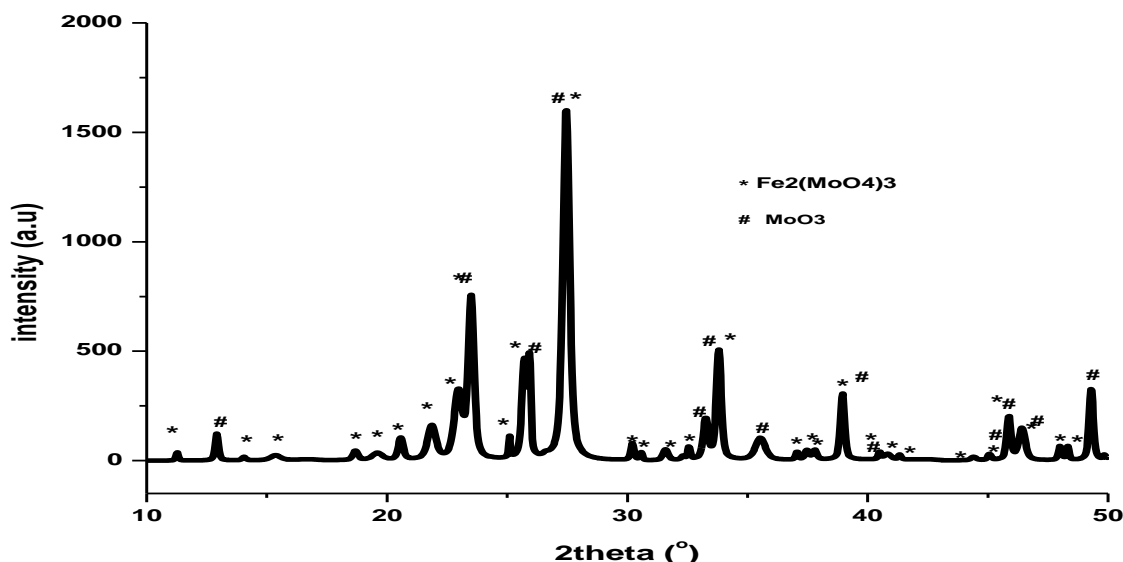


Fig 1. XRD pattern of powder obtained from mixture of Ferric nitrate, Molybdenum oxide and Glycine in water dried at 100°C and calcinated at 400°C for 4 h.

Eosin Y (EY) is an acidic heterocyclic dye used in prints and dye industries. And its remediation from industrial waste water is necessary since it is a health hazard. Photo catalytic degradation of EY has been studied with TiO_2 and ZnO [3, 4], N and Os co- doped TiO_2 [5], (Ba, Sr) TiO_3 [6], N-doped TiO_2 [7], Ag im. $(\text{WO}_4)_2$ [8], Ag-impregnated TiO_2 [9], Nb_2O_5 [10], transition metals doped ZnS [11], PbS -sensitized TiO_2 [12], hexacyanoferrate [13], and Photo-Fenton process [14]. Present paper is the first report on $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ as photo catalyst for the degradation of EY under visible light irradiation. Fig. 2(a) depicts temporal evolution of spectral changes of EY in presence of $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ and H_2O_2 as a function of irradiation time. EY shows a characteristic absorption at $\lambda_{\text{max}}=520\text{nm}$ and the peak intensity decreases with progressive irradiation. Extent of degradation as calculated from lowering in absorption corresponds to 96.6% for 120 min of irradiation. Addition of H_2O_2 to TiO_2 photo catalyst has been reported to show beneficial effect in terms of increasing $\cdot\text{OH}$ concentration and suppressing electron-hole recombination [15]. Therefore, in order to understand the effect of H_2O_2 in the present system, variation of percentage of degradation defined as $(C-C_0) / C_0 \times 100$ as a function of irradiation time is plotted separately for dye solution, dye solution + H_2O_2 , dye solution + catalyst and dye solution + catalyst + H_2O_2 as shown in Fig. 2(b). C and C_0 refer to concentration of dye at time 't' and initial concentration respectively. From the figure, it can be seen that either catalyst or H_2O_2 is not effective in causing degradation beyond 30%, but the combination of H_2O_2 + catalyst is synergistic in leading to a degradation of 96.6% in 120 min.

Congo red is benzene based anionic diazodye toxic to many organisms and a suspected mutagen and carcinogen. Its structural stability makes it less prone to biodegradation. Photo catalytic degradation of Congo red has been studied with TiO_2 [16-21], SnO_2 [22], poly oxo tungstate – anatase composite [23], TiO_2 – pillered clay [24], ZnO [25], ZrO_2 [26], TiO_2 – Fe_3O_4 nano composite [27], Fe_2O_3 [28] and NiS [29] photo catalysts under U.V. irradiation except for [23]. Fig. 3(a) depicts temporal evolution of spectral variations of Congo Red (CR) in presence of $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ and H_2O_2 as a function of irradiation time. CR showed characteristic absorption at $\lambda_{\text{max}}=500\text{nm}$ and the peak intensity decreased with irradiation time and 100% degradation is observed for 45 min of irradiation. Variation of % degradation as function of irradiation time for dye solution, dye solution + H_2O_2 , dye solution + catalyst and dye solution + catalyst + H_2O_2 separately are depicted in fig 3(b).

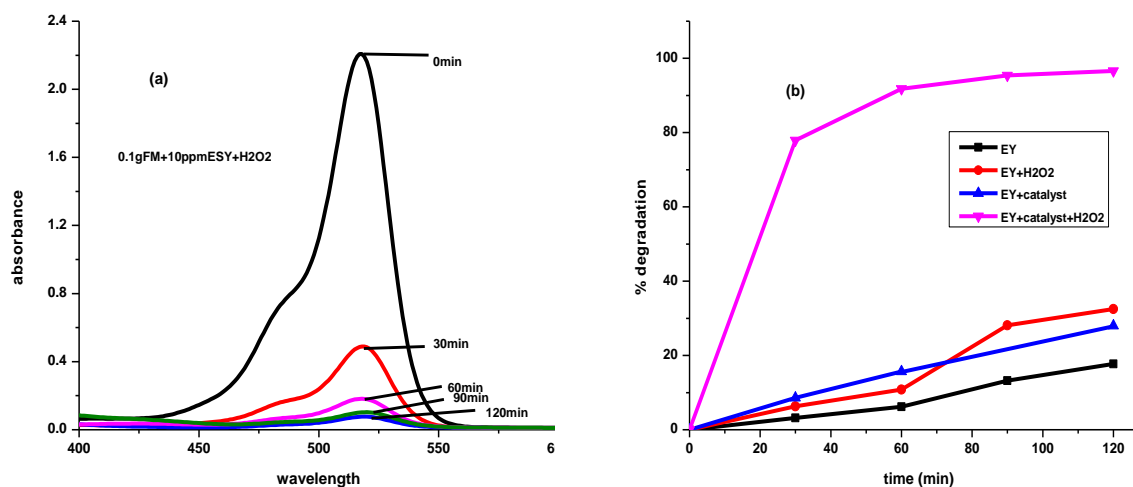


Fig 2 (a) Temporal evolution of spectral changes of dye aqueous solutions in presence of photo catalyst and H₂O₂ as a function of irradiation time for EY. **(b)** Variation of % degradation as a function of irradiation time for aqueous solution of dye (i), dye + H₂O₂ (ii), dye + Fe₂Mo₃O₁₂ catalyst (iii) and dye + H₂O₂ + Fe₂Mo₃O₁₂ for EY.

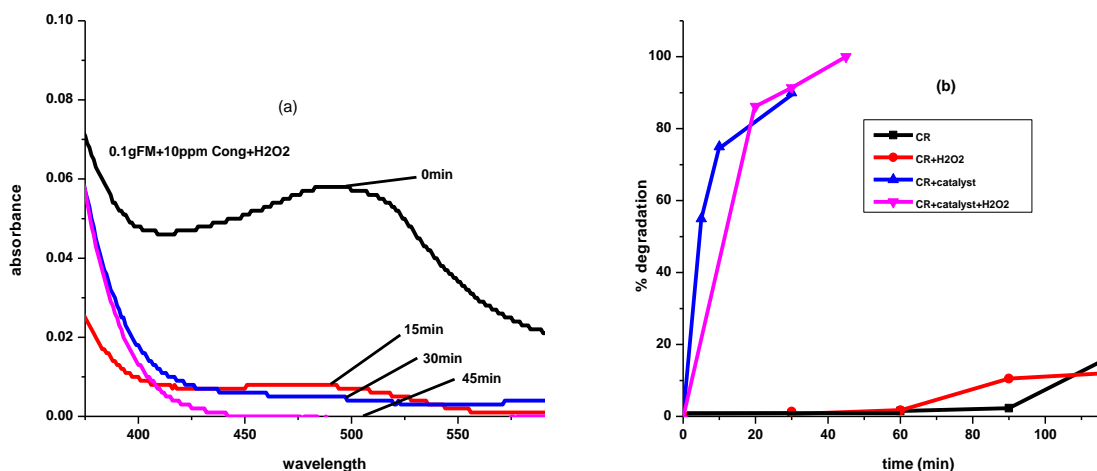


Fig 3 (a) Temporal evolution of spectral changes of dye aqueous solutions in presence of photo catalyst and H₂O₂ as a function of irradiation time for CR. **(b)** Variation of % degradation as a function of irradiation time for aqueous solution of dye (i), dye + H₂O₂ (ii), dye + Fe₂Mo₃O₁₂ catalyst (iii) and dye + H₂O₂ + Fe₂Mo₃O₁₂ for CR.

From the figure, it can be seen that presence of H₂O₂ alone did not show any noticeable degradation but catalyst alone is effective in causing a degradation of about 90% with 30 minutes of irradiation indicating

significant photosensitization. Nevertheless, the combination of catalyst + H_2O_2 showed a complete degradation of 100% for 45 min of irradiation.

Methyl orange (MO) is an azodye used as colorant in textile, paper and leather industries and is known to be toxic, mutagenic carcinogenic and not readily bio degradable. Degradation of methyl orange has been reported with $\alpha\text{-Fe}_2\text{O}_3$ [30], Ag-ZnO [31], Er^{3+} : $\text{YAlO}_3/\text{TiO}_2$ [32], Cr doped ZnS [33], ZnO/Zn stannate [34], phosphotungstic acid [35], nano ZnO [36, 37], metallophorphyrins – TiO_2 [38], BiOBr [39], $\text{TiO}_2/\text{TiO}_2$ mesh [40], CdIn_2S_4 [41], Ag/N- TiO_2 [42], ZnO- TiO_2 [43], Ag doped TiO_2 [44], CuO doped ZnO [45], SnO_2 [46], TiO_2 [47, 48] Sb_2S_3 [49] and SrTiO_3 [50]. Most of the above reported studies have been carried out under U.V irradiation. Fig. 4(a) depicts temporal variation of spectral changes of methyl orange (MO) in presence of H_2O_2 and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ as a function of irradiation time under visible light. MO shows a characteristic absorption at $\lambda_{\text{max}} = 460\text{nm}$ and the peak intensity vanished with irradiation of 45 min indicating 100% decolourization. Variations of % degradation as function of irradiation time for MO, MO + H_2O_2 , MO + catalyst and MO + catalyst + H_2O_2 separately are given in Fig 4(b).

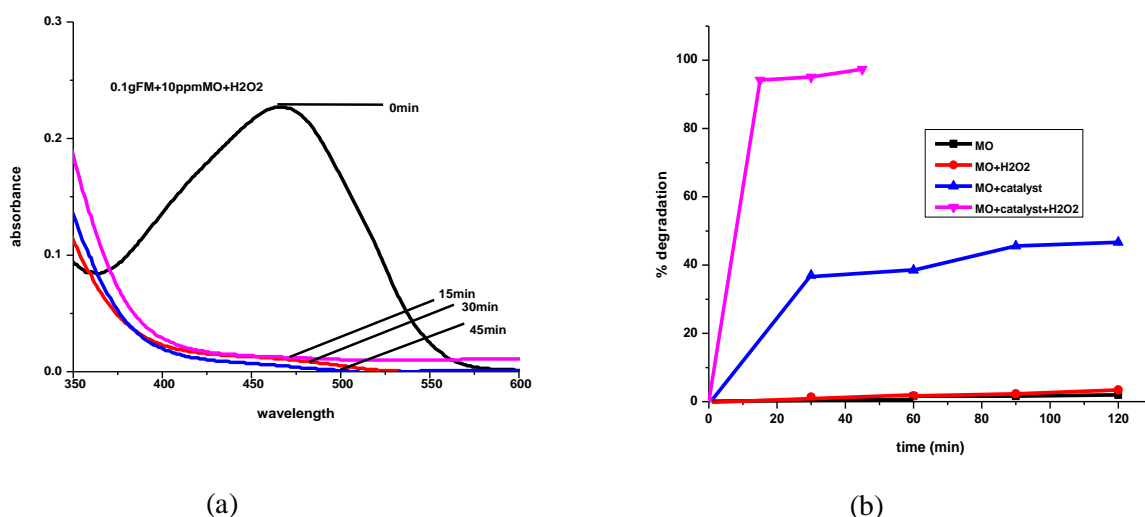


Fig 4 (a) Temporal evolution of spectral changes of dye aqueous solutions in presence of photo catalyst and H_2O_2 as a function of irradiation time for MO. **(b)** Variation of % degradation as a function of irradiation time for aqueous solution of dye (i), dye + H_2O_2 (ii), dye + $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ catalyst (iii) and dye + H_2O_2 + $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ for MO.

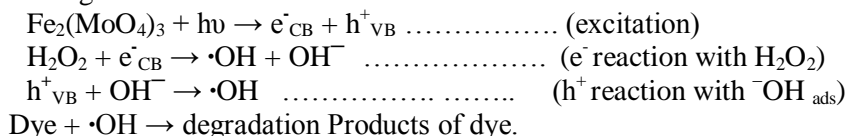
From the figure it is apparent that H_2O_2 alone has no effect on the bleaching of MO while catalyst alone showed some degradation to an extent of 46% for 120 min of irradiation. But, combination of H_2O_2 and catalyst together showed a synergistic effect causing a degradation of 97.4% for only 45 min of irradiation. Rate constants derived from $\ln C/C_0$ vs time of the photo degradation steps of dye alone, dye + H_2O_2 , dye + catalyst and dye + catalyst + H_2O_2 for EY, CR and MO dyes are given in table 1. The magnitudes of rate constants reinforce the synergistic effect of catalyst and H_2O_2 in photo degradation process.

Table 1. Rate constants for different photo degradation systems with EY, CR and MO under visible light irradiation.

Photo degradation of the system	Eosin Y	Congo red	Methyl orange
Dye only	3.0×10^{-5}	2.0×10^{-5}	-
Dye + H_2O_2	7.0×10^{-5}	2.0×10^{-5}	-

Dye+Catalyst	5.0×10^{-5}	5.4×10^{-3}	8.0×10^{-5}
Dye+catalyst+H ₂ O ₂	5.3×10^{-4}	6.5×10^{-3}	3.8×10^{-3}

Based on the observations discussed above, possible mechanism for degradation in the case of EY, CR and MO dyes is suggested as given below:



Extent of degradation might have also been enhanced due to H₂O₂ since it can also generate peroxo complex species $\text{MoO}_2(\text{O}_2)^{2-}$ which participate in the dye degradation through formation of reactive $\cdot\text{O}_2$ (singlet) as was reported by S.H. Tian et al [51] for the degradation of Acid orange II with Fe₂Mo₃O₁₂ photo catalyst. Enhanced degradation in the present study for EY, CR and MO dyes with Fe₂Mo₃O₁₂ is therefore ascribed to the synergistic effect of catalyst and H₂O₂ as well as to the possible formation of a heterojunction between MoO₃ and Fe₂Mo₃O₁₂.

APPLICATIONS

In this study prepared sample showed excellent photo catalytic activity for the degradation of Eosin Y, Congo red and Methyl orange in presence of H₂O₂ under visible light irradiation.

CONCLUSIONS

Fe₂Mo₃O₁₂ with excess MoO₃ prepared by combustion method showed a synergistic effect in the photo catalytic degradation of Eosin Y, Congo red and Methyl orange dyes in presence of H₂O₂. Dye aqueous solutions of 20ppm Eosin Y, 10ppm Congo red and 10ppm Methyl Orange showed bleaching of 96.6%, 100% and 97.4% for 120 min, 45 min and 45 min respectively. Enhanced photo catalytic activity is attributed to presence of H₂O₂ and MoO₃, which facilitate generation of more $\cdot\text{OH}$ free radicals and form a possible heterojunction with Fe₂Mo₃O₁₂ respectively.

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