Visible Light Induced Synergistic Degradation of Rhodamine-B, Methylene Blue And Malachite Green By $Fe_2(MoO_4)_3$ And MoO_3

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ABSTRACT

$Fe_2(MoO_4)_3$ with excess MoO_3 has been prepared by combustion method using Ferric nitrate, MoO_3 and glycine. The calcined powder showed a band gap of 2.6 ev as calculated from UVDRS. SEM studies revealed particle size in the μm region. The sample as prepared showed excellent photo catalytic activity for the degradation of Rhodamine- B, Methylene blue and Malachite green in presence of H_2O_2 under visible light irradiation. Photo catalytic studies on 100 ml aqueous solution containing 5ppm indicator with 100 mg of dispersed catalyst indicated degradation of 99.8% of Rhodamine-B, 98% of Methylene blue and 99.6% of Malachite green in 40 min, 30 min and 15 min respectively.

Keywords: $Fe_2(MoO_4)_3$, Rhodamine-B, Methylene Blue, Malachite green, photo catalytic degradation, Combustion synthesis.

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INTRODUCTION

Waste water in textile industry is a major source of environmental pollution since the remnant constituent dyes in the exhaust are not biodegradable, highly toxic and impart persistent colour of high intensity. Several methods have been proposed to decolourise such exhausts and to remove the organic pollutants by way of adsorption, bio-degradation, ozonation, chlorination etc [1]. Recently, heterogeneous photo catalysis has emerged as an alternate method for decontamination of such organic pollutants, in which metal oxide or mixed metal oxide semiconductors are used as photo catalysts. Of the various metal oxides, TiO_2 has been widely studied because of its high catalytic activity, high chemical stability and low cost. Nevertheless, the wide band gap of 3.2 ev associated with anatase precludes its application in the visible region which constitutes around 43% of solar radiation reaching the earth. Though several efforts have been made to bring the absorption of TiO_2 to visible region by way of doping with cations or anions, dye sensitization and formation of hetero structures with narrow band gap materials [2, 3], their industrial application is yet to be realised. Hence, development of suitable non TiO_2 based materials which are active under visible light for use as cost effective photo catalysts is under intensive investigation.

Metal molybdates are an important class of functional materials that are used in photoluminescence, microwave application, sensors and catalysis [4-7]. Of these, Ferric molybdate $Fe_2(MoO_4)_3$ has been reported to exhibit interesting catalytic as well as magnetic properties. It crystallises in two polymorphic

forms - a low temperature monoclinic α-form and a high temperature orthorhombic β form with structural transformation of α to β phases occurring at 518^0c on heating [8]. $Fe_2(MoO_4)_3$ was also reported to function as a catalyst for oxidation of methane to methanol [9], methanol to formaldehyde [10-11] and propene to acrolein [12], but its use as a photo catalyst has not been investigated extensively except for the degradation of Bromo-pyrogallal red [13] Acid orange II [14] and Methylene Blue [15]. In the case of degradation of Bromo-pyrogallal red, $Fe_2(MoO_4)_3$ was synthesised by microwave irradiation, while for Acid Orange II, it was prepared by wet chemical process. Synthesis of $Fe_2(MoO_4)_3$ has also been reported in terms of solid-state reactions [16], coprecipitation [17], sol-gel [18], hydrothermal [19] and mechanochemical [20] methods. The present paper describes the use of $Fe_2(MoO_4)_3$ + MoO_3 as photo catalyst for degradation of Rhodamine-B, Methylene blue and Malachite green under visible light irradiation.

MATERIALS AND METHODS

Synthesis of Catalyst: $Fe(NO_3)_3.9 H_2O$ and MoO_3 of AR Quality were starting materials; 6.83g $Fe(NO_3)_3$ 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 110^0C until it became viscous with liberation of large amounts of brown fumes. The dried mass was then calcined at 400^0C for 4 hrs. 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 $BaSO_4$ 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 $Fe_2(MoO_4)_3$ + MoO_3 was evaluated in terms of degradation of Rhodamine B (RhB), Methylene Blue (MB) and Malachite green (MG) under visible light irradiation from 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 RhB 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 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 decolourisation was followed by recording the corresponding absorption spectrum. The same procedure was adopted for MB and MG indicators. All the experiments were conducted under ambient conditions.

RESULTS AND DISCUSSION

XRD of the resultant powder obtained from the mixture of Ferric nitrate, Molybdenum oxide (Fe: Mo=1:3) and glycine mixed in water and calcined at 400^0C is shown in fig. 1.
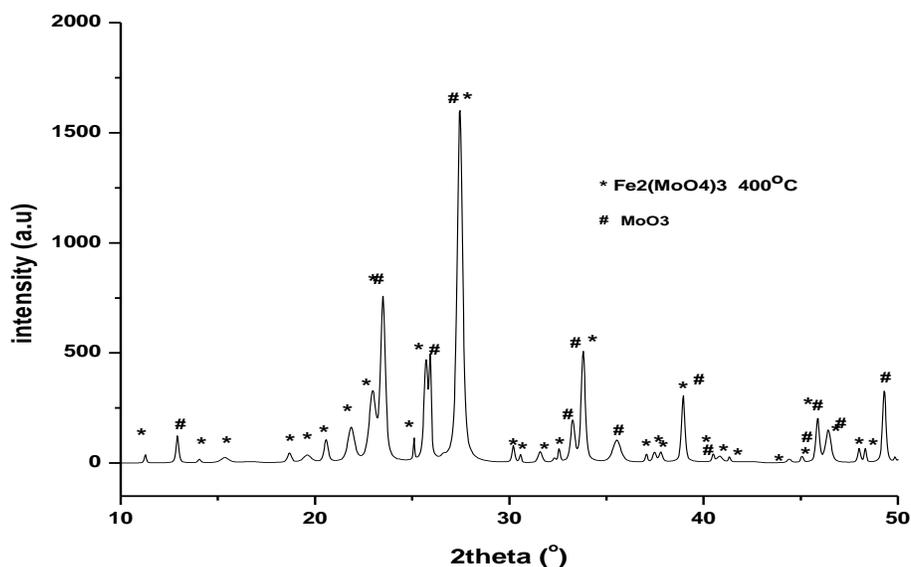
Fig 1. XRD pattern of powder obtained from mixture of Ferric nitrate, Molybdenum oxide and Glycine in water dried at 100^oC and calcinated at 400^oc for 4 h.

The observed peaks could be indexed to $Fe_2(MoO_4)_3$ of JCPDS File no 83-1701 and MoO_3 JCPDS File no 76-1003. Absence of peaks due to Fe_2O_3 indicates that the sample obtained is a mixture of $Fe_2(MoO_4)_3$ + MoO_3.

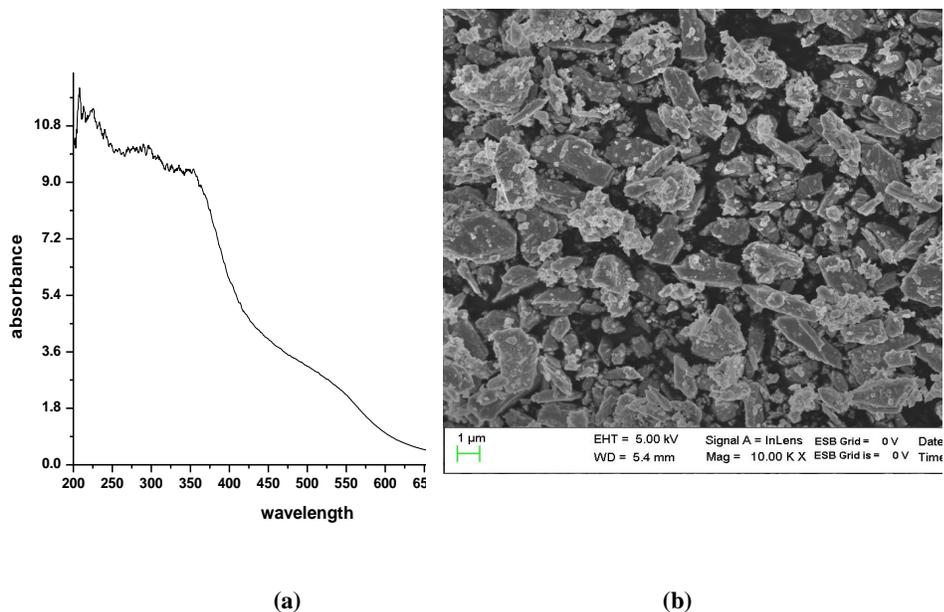(a)   (b)

Fig 2. (a) UV-vis diffuse reflectance spectrum of $Fe_2(MoO_4)_3$ + MoO_3 powder.
(b) SEM image of $Fe_2(MoO_4)_3$ + MoO_3 powder.

Photo absorptivity of the calcined powder was investigated by UVDRS and the corresponding spectrum shown in fig. 2 (a) indicates that $Fe_2(MoO_4)_3$ + MoO_3 powder is having a considerable absorption in the

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visible region with a calculated band gap of 2.6 ev. Scanning electron micrograph of the calcined powder is depicted in fig. 2 (b) from which it can be seen that the particle size is in µm region.
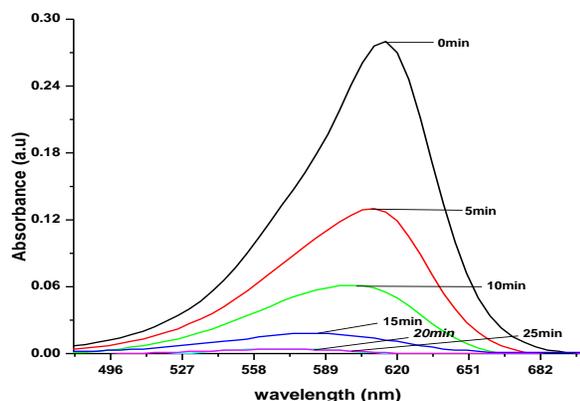
Temporal evolution of spectral changes of Rh B/ MB/ MG aqueous solutions containing 100 mg of dispersed $Fe_2(MoO_4)_3 + MoO_3$ catalyst as a function of exposure time are shown in Fig 4. From the spectral changes it is evident that degradation of Rh-B occurred to an extent of 99.8% in just 40 minutes, while degradation of 98% MB and 99.6% MG occurred in 30 and 15 minutes respectively. Shuanhong Tian et al [15] reported degradation of Acid Orange II and Methylene Blue over $Fe_2(MoO_4)_3$ in the visible region, and indicated that presence of H_2O_2 in the degradation turns it into a Fenton-like reaction for the generation of ·OH radicals. According to these researchers, addition of H_2O_2 to the adsorbed $Fe_2(MoO_4)_3$ catalyst caused 91.3% degradation of Methylene Blue in 30 minutes. In the present study also, the presence of H_2O_2 has been found to be critical in improving the catalytic efficiency of $Fe_2(MoO_4)_3 + MoO_3$ sample. The optimum amount of H_2O_2 in our study is found to be 10 mmoles per 100 ml of aqueous solution containing 5ppm of MB and 98% degradation was obtained in 30 min.
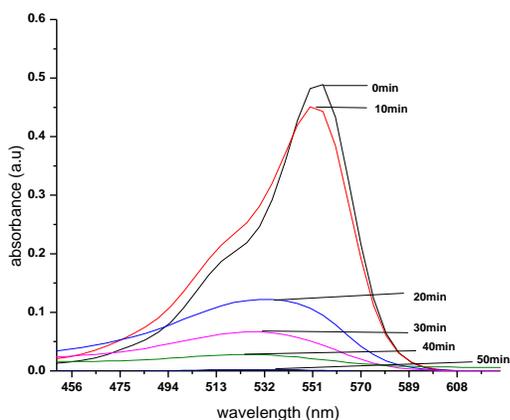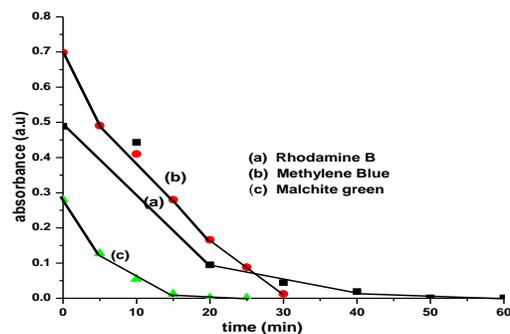

(a)
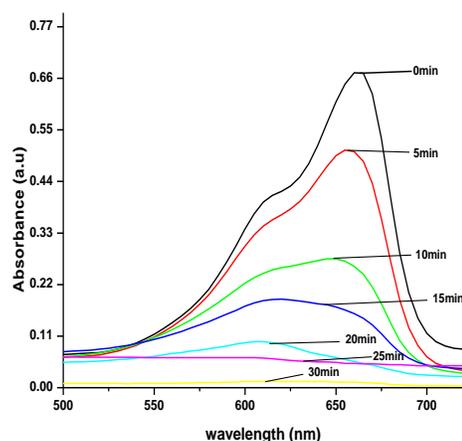
(b)

(c)

(d)

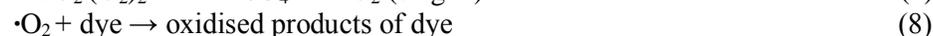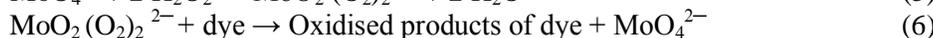**Fig 4.** Temporal evolution of spectral changes of aqueous solutions of (a) Rh-B (b) MB and (c) MG with dispersed Catalyst as a function of exposure time. (d) Variation of Absorbance of RhB, MB and MG aqueous solutions With dispersed catalyst as a function of exposure time.

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Photocatalytic degradation of the dyes under investigation seems to occur as per the following mechanism.

$$Fe_2(MoO_4)_3 + h\upsilon \rightarrow e^-_{CB} + h^+_{VB} \tag{1}$$

$$H_2O_2 + e^-_{CB} \rightarrow \cdot OH + OH^- \tag{2}$$

$$h^+/_{VB} + OH^- \rightarrow \cdot OH \tag{3}$$

$$Dye + \cdot OH \rightarrow \text{Oxidised products of dye} \tag{4}$$

Initial absorption of visible light causes excitation of e^- from valance band (VB) to conduction band (CB) of $Fe_2(MoO_4)_3$. The electron in the conduction band generates $\cdot OH$ free radical from H_2O_2 and the hole in the valence band also forms $\cdot OH$. The $\cdot OH$ radicals will then oxidise the indicator as a result of which intensity of absorption characteristic of the corresponding dye solution rapidly decreases. As per Tian etal [14], molybdenum forms peroxo complex with H_2O_2 which can cause degradation of dye as per the following mechanism.

$$MoO_4^{2-} + 2\,H_2O_2 \rightarrow MoO_2(O_2)_2{}^{2-} + 2\,H_2O \tag{5}$$

$$MoO_2(O_2)_2{}^{2-} + dye \rightarrow \text{Oxidised products of dye} + MoO_4^{2-} \tag{6}$$

$$MoO_2(O_2)_2{}^{2-} \rightarrow MoO_4^{2-} + \cdot O_2 \text{ (singlet)} \tag{7}$$

$$\cdot O_2 + dye \rightarrow \text{oxidised products of dye} \tag{8}$$

In both mechanisms, H_2O_2 is shown to play a significant role in the generation of free radicals that are responsible for the oxidation of dye. Though degradation of Rh-B, MB and MG have been reported in literature using TiO_2, $ZnWO_4$ and $PbWO_4$ irradiation used in these studies is in the U.V region [22-28]. However, the present study describes the successful degradation of these dyes in the visible region. In the absence of $Fe_2(MoO_4)_3 + MoO_3$, the reduction in intensity of the dye solution corresponded to 19.0% of Rh-B, 19.4% of MB and 39.3% of MG for the respective exposure times of 40, 30 and 15 min. This establishes clearly that photo degradation occur predominately as compared to photosensitisation. The enhanced photo catalytic activity due to $Fe_2(MoO_4)_3 + MoO_3$ in the present study is therefore attributed to more crystalline nature of the sample, presence of H_2O_2 and the synergistic interaction between $Fe_2(MoO_4)_3$ and MoO_3.

APPLICATIONS

The sample, $Fe_2(MoO_4)_3$, prepared showed excellent photo catalytic activity for the degradation of Rhodamine- B, Methylene blue and Malachite green in presence of H_2O_2 under visible light irradiation.

CONCLUSIONS

$Fe_2(MoO_4)_3$ with excess MoO_3 has been synthesised by glycine combustion method at 400^0C. The calcined powder showed a significant absorption in the visible region along with a good photo catalytic activity for the degradation of Rh-B, MB and MG dyes under visible light irradiation. The presence of H_2O_2 and MoO_3 enhanced the extent of degradation. Photo catalytic degradation of 100 ml aqueous solutions of Rh-B, MB and MG ($5\,mg\,L^{-1}$) containing 100 mg of the dispersed catalyst occurred in 40, 30 and 15 min respectively.

ACKNOWLEDGMENTS

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