



## H<sub>2</sub>O<sub>2</sub>-Assisted Rapid Visible light Degradation of Carmine Indigo, Crystal Violet and Eosin-Y with MoO<sub>3</sub> Modified Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>

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Bi<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> with excess of MoO<sub>3</sub> has been prepared by the combustion method using bismuth nitrate, MoO<sub>3</sub> and glycine. The calcined powder showed a band gap of 2.9 eV based on UV-visible diffuse reflectance spectrum. SEM studies revealed particle size in the μm region. The sample as prepared showed excellent photo catalytic activity for the degradation of carmine indigo, crystal violet and Eosin Y in presence of H<sub>2</sub>O<sub>2</sub> under visible light irradiation. Degradation of 20 ppm carmine indigo, 5 ppm crystal violet and 20 ppm Eosin Y aqueous solutions containing 100 mg of dispersed catalyst occurred in 40, 70 and 90 min, respectively. Times taken for degradation of these dyes in the present study are considerably less compared to earlier reports.

**Keywords:** Bi<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, Carmine indigo, Crystal violet, Eosin Y, Photo catalytic degradation, Combustion synthesis.

### INTRODUCTION

Synthetic organic compounds used in dyeing, printing, textile, photography and cosmetics are generally less biodegradable and their presence in industrial effluents is extremely hazardous due to their potential carcinogenic nature. Removal of these toxic pollutants which also render intense colour to aquatic environment is a prime ecological concern. Though several methods like adsorption, ozonation, chlorination, reverse osmosis, ultra filtration have been proposed for the removal of toxic organic pollutants, these methods are either uneconomical or involve technical complications. Recently, advanced oxidation process using semi conductor metal oxides/ mixed metal oxides has been found to be more efficient for mitigation of air pollution, water disinfection, water purification and hazardous waste water remediation. In this regard, TiO<sub>2</sub> has been widely studied because of its high catalytic activity, low cost, facile synthesis and good thermal and chemical stability. But, due to its absorption only in the UV region, use of TiO<sub>2</sub> is not cost effective. Several researchers tried to shift the absorption of TiO<sub>2</sub> into visible region by selective anion/cation doping, dye sensitization and formation of heterostructures with materials of suitable band potential. Alternatively, a number of non-TiO<sub>2</sub> based substances like ZnWO<sub>4</sub>, BiVO<sub>4</sub>, LaFeO<sub>3</sub>, BiFeO<sub>3</sub>, Bi<sub>2</sub>WO<sub>6</sub>, Bi<sub>2</sub>MoO<sub>6</sub> and Fe<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> have also emerged as potential photocatalysts for oxidative degradation of organic pollutants under visible light irradiation.

The main advantage of such heterogeneous photo catalytic process is that it can break down many organic substances directly into CO<sub>2</sub>, H<sub>2</sub>O and mineral salts without formation of any toxic intermediates.

Among the dyes in commercial use, carmine indigo, Crystal violet and Eosin-Y are used extensively for several applications. For instance, carmine indigo is used as textile colouring agent, additive in pharmaceutical tablets and capsules, in confectionery items and for medical diagnostic purposes<sup>1</sup>. But, carmine indigo is also regarded as highly toxic that may cause skin and eye irritations, tumours at the site of application and lead to gastro intestinal irritations when administered intravenously<sup>2</sup>. A good number of methods like electrochemical coagulation<sup>3</sup>, plasma decomposition<sup>4</sup>, microbial decolourization<sup>5</sup>, intense ultrasonic treatment<sup>6</sup>, Biosorption<sup>7</sup>, photo catalytic degradation using TiO<sub>2</sub><sup>8</sup>, TiO<sub>2</sub> impregnated active carbon<sup>9</sup>, TiO<sub>2</sub> coated non-woven fibers<sup>2</sup>, rubber sheet impregnated with TiO<sub>2</sub><sup>10</sup>, Ag-doped TiO<sub>2</sub><sup>11</sup>, N-doped TiO<sub>2</sub><sup>1</sup>, Aluminum phosphate coated TiO<sub>2</sub><sup>12</sup>, nano TiO<sub>2</sub><sup>13</sup>, natural rutile<sup>14</sup>, ZnO<sup>15</sup>, Fe-doped ZnO<sup>16</sup>, Bi<sub>2</sub>MoO<sub>6</sub><sup>17</sup>, α-Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub><sup>18</sup> and Sm<sub>2</sub>FeTaO<sub>7</sub><sup>19</sup> have been reported for the removal of carmine indigo. The irradiation times reported for degradation of carmine indigo under U.V irradiation varied from 30 to 300 min. in case of TiO<sub>2</sub> based catalysts<sup>1,2,7-14</sup> and from 200-600 min. in case of non-TiO<sub>2</sub> based catalysts<sup>15-19</sup>. Similarly, crystal violet a triaryl methane dye is used in paper, leather, textile, ball point pen industries as well as for cell viability arrays in

biochemistry and it is also considered to be carcinogenic. Photo degradation of crystal violet has been reported using ZnO<sup>20-23</sup>, iron oxide<sup>24</sup>, barium-strontium titanate<sup>25</sup>, nano TiO<sub>2</sub><sup>26-28</sup>, V-doped TiO<sub>2</sub><sup>29</sup>, Ni-containing polytungstometalate<sup>30</sup>, Sm<sub>2</sub>InTaO<sub>7</sub><sup>31</sup>, TiO<sub>2</sub> doped Bi<sub>2</sub>O<sub>3</sub><sup>32</sup>, Bi<sub>2</sub>WO<sub>6</sub><sup>33</sup>, ZnS<sup>34</sup> and Fenton-like systems<sup>35</sup>. Degradation times reported for crystal violet in the above methods ranged from 180-360 min under solar radiation and 30-90 min under UV radiation. Eosin-Y an acidic xanthene dye is used in dyeing, printing, leather, printing-ink industries as well as in fluorescent pigments. It is carcinogenic and promotes mould growth. Photo catalytic degradation of Eosin-Y has been studied by different investigators with TiO<sub>2</sub> and ZnO<sup>36,37</sup>, N and Os codoped TiO<sub>2</sub><sup>38</sup>, (Ba, Sr) TiO<sub>3</sub><sup>39</sup>, N-doped TiO<sub>2</sub><sup>40</sup>, Ag In (WO<sub>4</sub>)<sub>2</sub><sup>41</sup>, Ag-impregnated TiO<sub>2</sub><sup>42</sup>, Nb<sub>2</sub>O<sub>5</sub><sup>43</sup>, transitions metal doped ZnS<sup>44</sup>, PbS-modified TiO<sub>2</sub><sup>45</sup>, hexacyano ferrate<sup>46</sup> and photo fenton process<sup>47</sup>. From literature review<sup>18</sup>, it can be seen that except for extensive studies on Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> as a photocatalyst for the degradation of organic dyes have not been reported. The present paper describes H<sub>2</sub>O<sub>2</sub>-assisted rapid degradation of carmine indigo, crystal violet and Eosin-Y under visible light irradiation with MoO<sub>3</sub> modified Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>. Carmine indigo, Crystal violet and Eosin-Y are chosen because they belong to different classes of dyes and contain different chromophores.

## EXPERIMENTAL

**Synthesis of photocatalyst:** Bi(NO<sub>3</sub>)<sub>3</sub>.5 H<sub>2</sub>O and MoO<sub>3</sub> of AR quality were starting materials, 5.40307 g Bi(NO<sub>3</sub>)<sub>3</sub> and 4.80992 g MoO<sub>3</sub> (Bi: Mo = 1:3) were added to 50 mL of water under constant stirring followed by the addition of 0.50171 g of glycine. The precursor solution containing dispersed MoO<sub>3</sub> 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 and used for phase identification.

Phase purity of the calcined and washed powder was investigated with X-ray diffractometer (PAN alytical-X' Pert PRO, Japan) at room temperature, using Nickel filtered CuK<sub>α</sub> radiation ( $\lambda = 1.54059 \text{ \AA}$ ), with a scan rate of 2° min<sup>-1</sup>. 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<sub>4</sub> 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).

**Photocatalytic studies:** Photocatalytic activity of Bi<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> was evaluated in terms of degradation of carmine indigo, crystal violet and Eosin-Y under visible light irradiation from 400 W metal halide lamp as a light source for irradiation. UV radiation below 350 nm is eliminated by surrounding the sample with a water jacket. 100 mg of the catalyst powder was added into 100 mL carmine indigo aqueous solution (20 mg/L) and the suspension was magnetically stirred for 0.5 h in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye. The suspension was then exposed to light emanating from the source; 5 mL aliquots were pipetted at periodic time intervals and filtered through 0.45 micron

Millipore filters to remove the suspended powder. Progress of decolourization was followed by recording the corresponding absorption spectrum. The same procedure has been adopted for (5 mg/L) crystal violet and (20 mg/L) Eosin-Y indicators. All the experiments were conducted under ambient conditions.

## RESULTS AND DISCUSSION

Fig. 1 depicts XRD pattern of the mixture of Bi-nitrate, MoO<sub>3</sub> and glycine mixed in water, dried and calcined at 400 °C for 4 h. All the observed peaks could be indexed to Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> and MoO<sub>3</sub> of JCPDS file numbers 70-1396 and 76-1003, respectively. Absence of peaks due to Bi<sub>2</sub>O<sub>3</sub> and other phases of Bi and Mo -oxides indicates complete formation of Bi<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> existing with excess MoO<sub>3</sub> present. Scanning electron micrograph of the calcined powder shown in Fig. 2 indicated no characteristic texture and showed the particle size in  $\mu\text{m}$  region. Temporal evolution of spectral changes of carmine indigo dye aqueous solution in presence of H<sub>2</sub>O<sub>2</sub> and photocatalyst as a function of irradiation time are shown in Fig. 3(a). Carmine indigo showed characteristic absorption at  $\lambda_{\text{max}} = 610 \text{ nm}$  and complete bleaching is observed for 40 min of irradiation. Variation of  $(C-C_0)/C_0 \times 100$  as a function of irradiation time for dye solution, dye solution + H<sub>2</sub>O<sub>2</sub>, dye solution + catalyst and dye solution + H<sub>2</sub>O<sub>2</sub> + catalyst are shown in Fig. 3(b). Aqueous solution of dye in presence of catalyst alone did not show any significant change in intensity whereas dye aqueous solution in presence of H<sub>2</sub>O<sub>2</sub> showed gradual decrease in absorption intensity even up to 200 min. of irradiation. But, dye aqueous solution in presence of H<sub>2</sub>O<sub>2</sub> and catalyst showed a complete bleaching in 40 min. These results indicate that bleaching of the dye is rapid in presence of catalyst + H<sub>2</sub>O<sub>2</sub> and the degradation time is less compared to previous reports with TiO<sub>2</sub> and other non-TiO<sub>2</sub> photocatalysts. Temporal evolution of spectral changes of crystal violet dye aqueous solution, in presence of H<sub>2</sub>O<sub>2</sub> and catalyst as a function of irradiation time are shown in Fig. 4(a). Aqueous solution of crystal violet showed a characteristic absorption at  $\lambda_{\text{max}} = 550 \text{ nm}$  and complete bleaching of dye is observed for 70 min of irradiation. Variation of  $(C-C_0)/C_0 \times 100$  as a function of irradiation time for dye solution, dye solution + H<sub>2</sub>O<sub>2</sub>, dye solution + catalyst and dye solution + H<sub>2</sub>O<sub>2</sub> + catalyst are shown in Fig. 4(b). Dye solution + catalyst did not show any decrease in absorption intensity while in presence of H<sub>2</sub>O<sub>2</sub>, the dye solution showed a significant decrease in intensity with irradiation up to 200 min. But, dye solution + H<sub>2</sub>O<sub>2</sub> + catalyst showed a synergistic effect in that 70 min irradiation rendered it completely bleached. Decolourization of crystal violet is more rapid in the present study compared to earlier literature reports. Temporal evolution of aqueous solution of Eosin-Y dye in presence of H<sub>2</sub>O<sub>2</sub> and Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> as a function of irradiation time are shown in Fig. 5(a). Eosin Y showed a characteristic absorption at  $\lambda_{\text{max}} = 519 \text{ nm}$  and 98 % bleaching of dye occurred in 90 min. Variation of  $(C-C_0)/C_0 \times 100$  as a function of irradiation time for Eosin-Y aqueous solution, Eosin-Y solution + H<sub>2</sub>O<sub>2</sub>, Eosin-Y solution + catalyst and Eosin-Y solution + catalyst + H<sub>2</sub>O<sub>2</sub> are shown in Fig. 5(b). Dye solution alone and dye solution + H<sub>2</sub>O<sub>2</sub> and dye solution + catalyst showed a small degradation for 120 min of irradiation. But, dye solution + catalyst + H<sub>2</sub>O<sub>2</sub>

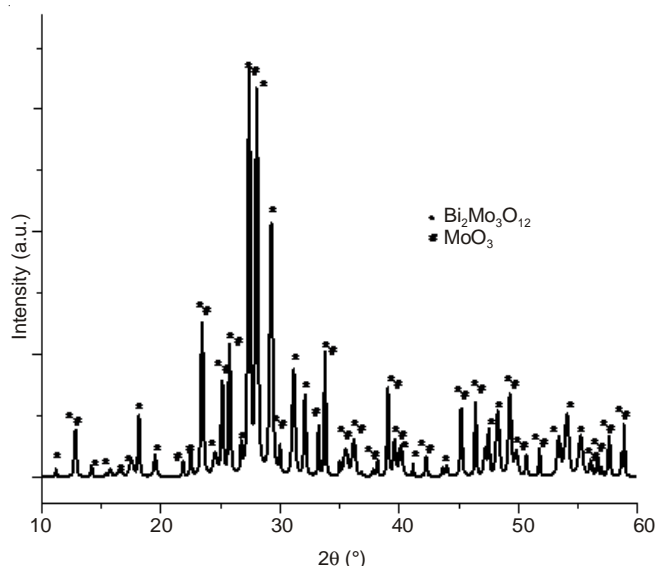
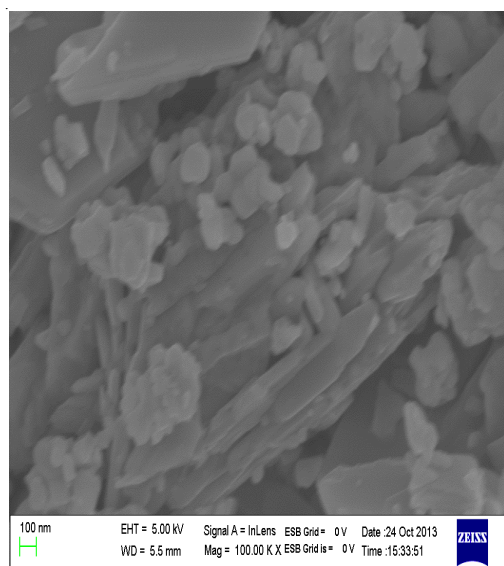


Fig. 1. XRD pattern of powder obtained from mixture of Bismuth nitrate, Molybdenum oxide and glycine in water, dried at 100 °C and calcinated at 400 °C for 4 h

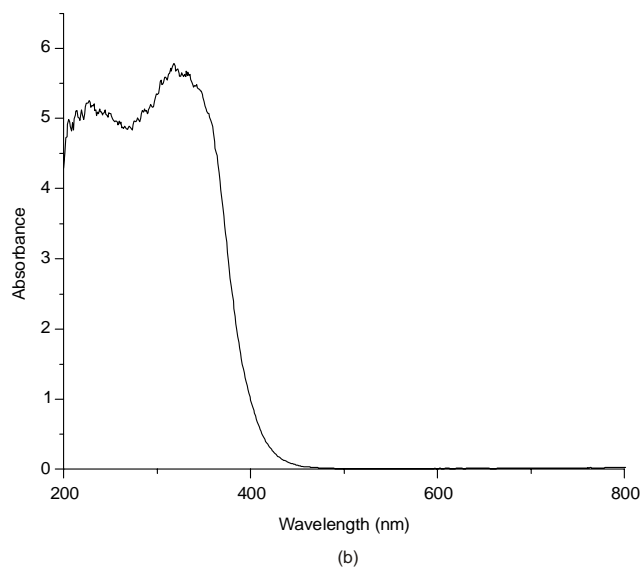
showed significant bleaching of 97 % for the same irradiation time of 120 min.

Two different degradation mechanisms have been reported<sup>48,49</sup> for the photocatalytic degradation of crystal violet: (i) successive N-demethylation of the dye with a simultaneous blue shift in absorption maximum yielding seven intermediates and (ii) direct cleavage of the conjugated chromophore structure without any blue shift. Since no shift in  $\lambda_{\max}$  is noticed in the present study, the second mechanism seems to be operative in the degradation. Addition of  $\text{H}_2\text{O}_2$  seems to improve its photocatalytic degradation efficiency by facilitating - (i) removal of electron in the conduction band of the catalyst and thereby suppressing the electron-hole recombination (ii) increasing the  $\cdot\text{OH}$  free radical concentration enhancing oxidative degradation of the dye and (iii) generating other radicals capable of degradation of aromatic structure of the dye.

Possible reaction scheme for the degradation of carmine indigo, crystal violet and Eosin-Y dyes in the present case is suggested below.



(a)



(b)

Fig. 2. (a) SEM image of  $\text{Bi}_2(\text{MoO}_4)_3 + \text{MoO}_3$  calcined powder; (b) UV-visible diffuse reflectance spectrum of  $\text{Bi}_2(\text{MoO}_4)_3 + \text{MoO}_3$  powder

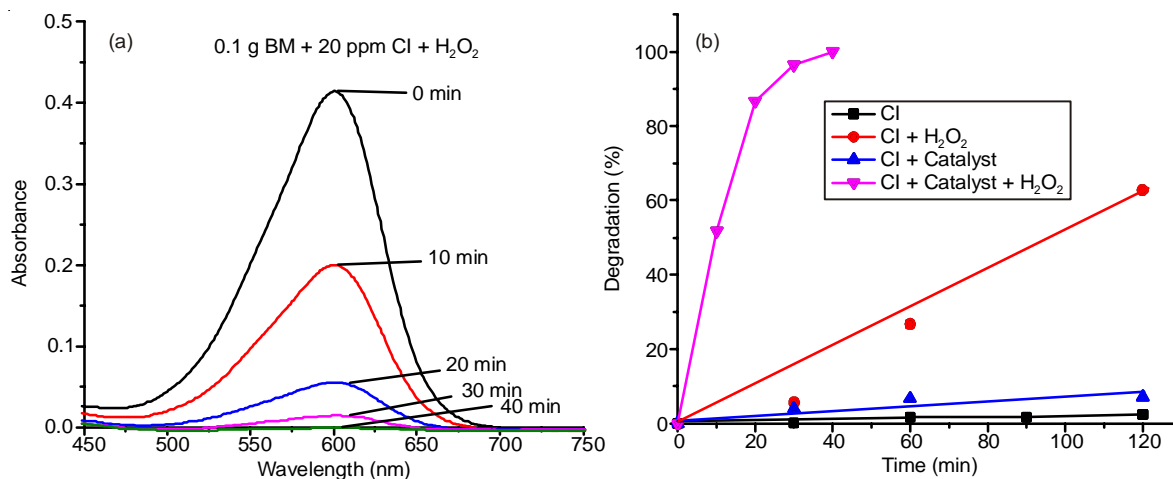


Fig. 3. (a) Temporal evolution of spectral changes of carmine indigo aqueous solution in presence of photo catalyst and  $\text{H}_2\text{O}_2$  as a function of irradiation time; (b) Variation of  $(C-C_0)/C_0 \times 100$  as a function of irradiation time for aqueous solution of carmine indigo (i),  $\text{Cl} + \text{H}_2\text{O}_2$  (ii),  $\text{Cl} + \text{Bi}_2\text{Mo}_3\text{O}_{12}$  (iii) and  $\text{Cl} + \text{H}_2\text{O}_2 + \text{Bi}_2\text{Mo}_3\text{O}_{12}$

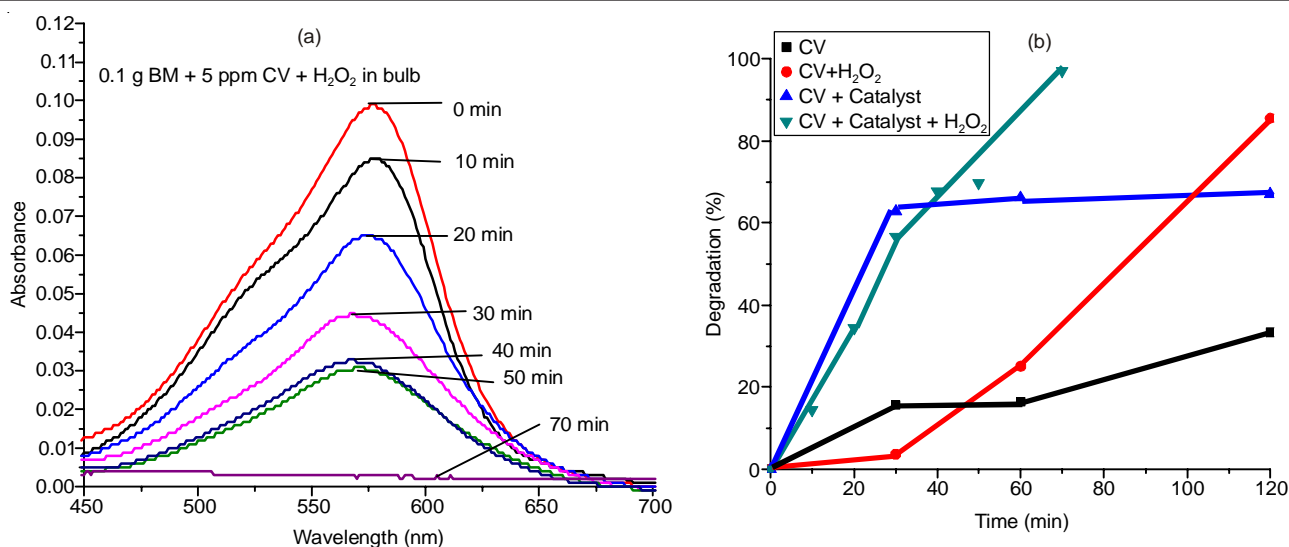


Fig. 4. (a) Temporal evolution of spectral changes of crystal violet aqueous solution in presence of photocatalyst and H<sub>2</sub>O<sub>2</sub> as a function of irradiation time; (b) variation of  $(C-C_0)/C_0 \times 100$  as a function of irradiation time for aqueous solution of crystal violet (i), crystal violet + H<sub>2</sub>O<sub>2</sub> (ii), crystal violet + Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> (iii) and crystal violet + H<sub>2</sub>O<sub>2</sub> + Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>

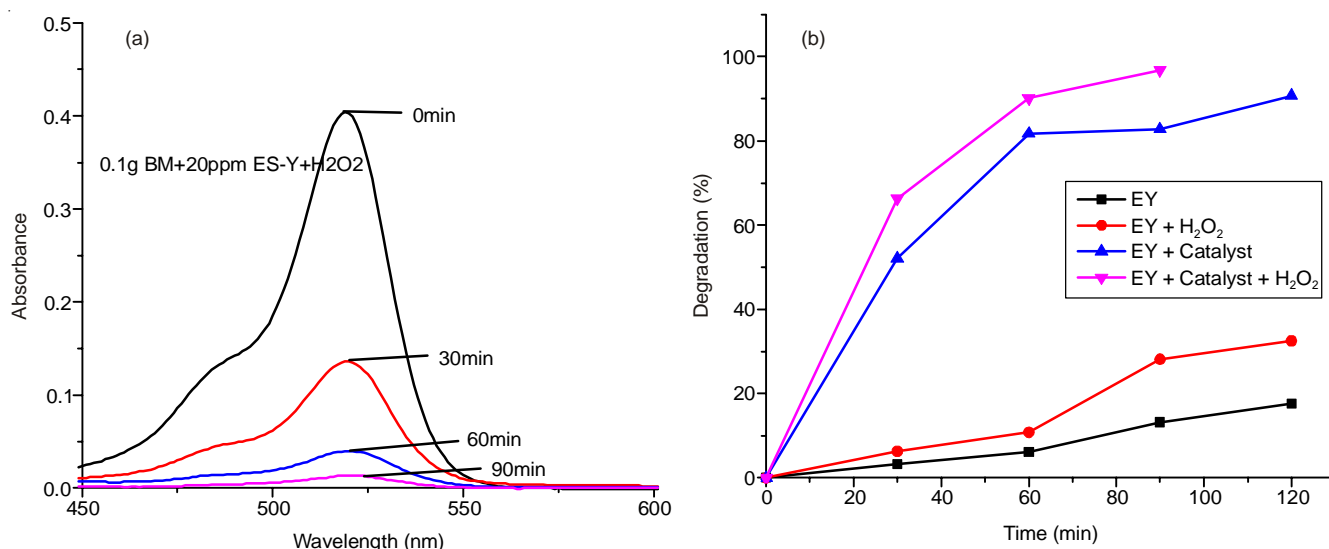


Fig. 5. (a) Temporal evolution of spectral changes of EY aqueous solution in presence of photocatalyst and H<sub>2</sub>O<sub>2</sub> as a function of irradiation time; (b) Variation of  $(C-C_0)/C_0 \times 100$  as a function of irradiation time for aqueous solution of EY (i), EY + H<sub>2</sub>O<sub>2</sub> (ii), EY + Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> (iii) and EY + H<sub>2</sub>O<sub>2</sub> + Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>

(CB-conduction band and VB-valance band of Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>)

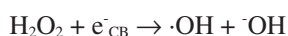
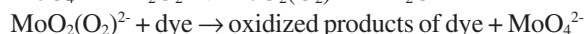
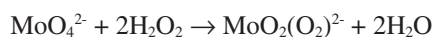


Photo catalytic efficiency might have also been enhanced further due to possible formation of MoO<sub>2</sub>(O<sub>2</sub>)<sup>2-</sup> which can also cause degradation of dye as follows.



In the above processes, H<sub>2</sub>O<sub>2</sub> helps generate either ·OH free radicals or ·O<sub>2</sub> singlet both of which are useful for rapid degradation of carmine indigo, crystal violet and Eosin-Y dyes. The enhanced rate of degradation in the present study is therefore ascribed to two factors- (i) synergistic effect of H<sub>2</sub>O<sub>2</sub> and Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> and (ii) possible formation of a hetrojunction between Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> and excess MoO<sub>3</sub> present.

## Conclusion

Bi<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> with excess MoO<sub>3</sub> has been synthesized by glycine combustion method at 400 °C. The calcined powder showed a significant absorption in the region of 300-400 nm and showed a good photocatalytic activity for the degradation of carmine indigo, crystal violet and Eosin-Y under visible light irradiation in presence of H<sub>2</sub>O<sub>2</sub>. Degradation of 20 ppm carmine indigo, 5 ppm crystal violet and 20 ppm Eosin Y in 100 mL aqueous solution each containing 100 mg of the dispersed catalyst occurred in 40, 70 and 120 min, respectively. The observed photodegradation times of carmine indigo, crystal violet and Eosin-Y in the present study are considerably less compared to previous reports.

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