



## Visible Light Induced Photocatalytic Degradation of Toluidine Blue-O by using Molybdenum Doped Titanium Dioxide

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### ABSTRACT

Environmental pollution is a big problem, which we all are facing today. Out of which, water pollution is a major problem. Different technologies of advanced oxidation processes are playing important role in solving this problem. Photocatalysis, which is an important part of advanced oxidation process, is considered as a promising technology for waste water treatment. In the present investigation, the photocatalytic degradation of toluidine blue-O (TB) has been studied using molybdenum doped titanium dioxide. The progress of the reaction was observed spectrophotometrically. The conditions for optimum degradation rate of the dye were achieved. It was observed that degradation of the dye follows pseudo-first order kinetics.

**Key words:** Molybdenum doped titanium dioxide, Photocatalytic degradation, Toluidine blue-O

### INTRODUCTION

Ever increasing environmental pollution is a big challenge for chemists, which is generated in its various facets due to increasing population, transportation and industrialization. Many of the industries discharge their effluents without proper treatment to the nearby water resources, which pollute water. If this situation is not controlled timely, there will be scarcity of potable water. Researchers have developed a number of methods for the treatment of waste waters, but these are associated with one or the other demerits. In this context, photocatalysis has emerged as an alternate way of treating waste waters/effluents. This method is better due to its green chemical. In this technology variety of semiconductors are being used as photocatalysts in the present of light. In solid acid catalysis, small amount of a dopant metal usually improves the catalytic activity. Developing a visible light responsive photocatalyst is of great use for practical applications.

TiO<sub>2</sub> is one of the most popular photocatalyst because of its advantages of stability, activity and low cost. Attempts have been made time to time to enhance the activity of this semiconductors by applying different methods. Ameta and co-workers [1-5] have made a significant contribution in the field of photocatalysis and reported a number of systems. Li et al. [6] studied the alkaline earth metal ion doping of TiO<sub>2</sub> and their photocatalytic properties. Munusamy et al. [7] studied the photocatalytic effect of TiO<sub>2</sub> on degradation of brilliant green. Narayanan et al. [8] carried out photodegradation of methyl orange over zirconia doped TiO<sub>2</sub> using solar energy. Sahu and Parida [9] prepared Au/TiO<sub>2</sub> catalyst and used it for the degradation of various azo dyes such as methylene blue, methyl orange, reactive blue-4, and eosin-B under solar irradiation. Ranjit and Viswanathan [10] have prepared iron doped TiO<sub>2</sub> from sol-gel and coprecipitation method and used it for the removal of 2-chlorophenol.

Kim et al. [11] reported photodecomposition of 2-chlorophenol using nano sized Mn-incorporated TiO<sub>2</sub> powders prepared by a solvothermal method. Riaz et al. [12] carried out photodegradation of orange II under visible light using Cu-Ni doped TiO<sub>2</sub> prepared by precipitation method whereas Ramirez et al. [13] studied the solar assisted degradation of acid orange 7 (AO 7) textile dye in aqueous solutions by Ce-doped TiO<sub>2</sub>. Safari et al. [14] reported that the photocatalytic activity of iron-doped TiO<sub>2</sub> was found more than pure TiO<sub>2</sub>. A series of vanadium-doped TiO<sub>2</sub> photocatalysts were synthesized by two modified sol-gel methods by Wu and Chen [15]. V-doped TiO<sub>2</sub> showed a red-shift in the UV-Vis spectra and had higher activity in photodegradation of dyes under visible light than pure TiO<sub>2</sub>. Zhu et al. [16] synthesized Fe doped TiO<sub>2</sub> by hydrothermal method, which showed better photocatalytic activity for the degradation of dye in aqueous solution under UV and visible light as compared to pure TiO<sub>2</sub>, while

Rupa et al. [17] synthesized nanoparticles of photodeposited TiO<sub>2</sub> (1% Ag) particles and used for degradation of reactive yellow-17. In the present work, an attempt has been made to enhance the performance of titania by doping it with molybdenum.

## EXPERIMENTAL

### Materials and Methods

Toluidine blue-O (sd fine-Chem) and titanium tetraisopropoxide (Spectrochem), hydrochloric acid (Himedia), sodium hydroxide (Himedia), 2-propanol (Himedia) used in the present investigation were used, as received. The chemical formula of toluidine blue-O is C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>SCl and its molar mass is 270.374 g/mol. Its  $\lambda_{\max}$  is 660 nm. The structure of the dye is shown in Fig. 1.

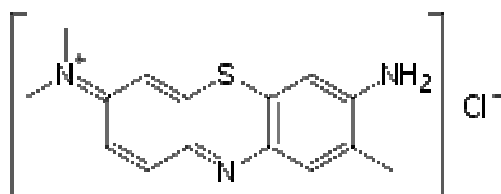


Fig. 1 Chemical structure of toluidine blue-O

### Preparation of Mo doped- TiO<sub>2</sub> supported on Zeolite

The supported photocatalyst was prepared by sol-gel method. TiO<sub>2</sub> (sol) was synthesized by the controlled hydrolysis of titanium isopropoxide in presence of ethanol and nitric acid at 4°C with vigorous stirring for 10-11 hours. In this solution, salt of molybdenum was added as dopant. After stirring, the solution was stored in an ice bath for 3 days with occasional shaking. The solvent was then finally removed by rotatory evaporation at 35°C. The dried solid was heated in an oven and calcined at 450°C for 20-30 min. Finally, the supported TiO<sub>2</sub> photocatalyst was obtained by slurring the above prepared solid powder with the zeolite (in the form of molecular sieves) in the ratio of 1: 2.

A stock solution of toluidine blue-O ( $1.0 \times 10^{-3}$  M) was prepared in doubly distilled water. Irradiation was carried out keeping whole assembly exposed to a 200 W tungsten lamp (Philips, light intensity = 60.0 mWcm<sup>-2</sup>). This intensity of light at various distances from the lamp was measured with the help of solarimeter (Model CEL 201). The pH of the solution was measured by a digital pH meter of Systronics (Model 335). The desired pH of the solution was adjusted by the addition of previously standardized hydrochloric acid and sodium hydroxide solutions.

The progress of photocatalytic reaction was followed by taking optical density at regular time intervals using an UV-Vis spectrophotometer (Systronics Model 106). Controlled experiments were also carried out to confirm that reaction is neither photochemical nor thermal but it is photocatalytic in nature. 0.0270 g of toluidine blue-O was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was  $1.0 \times 10^{-3}$  M. It was used as a stock solution. This stock solution was further diluted. The optical density of methylene blue solution was determined with the help of a spectrophotometer at  $\lambda_{\max} = 660$  nm. The dye solution was placed in equal amounts in four beakers.

The first beaker containing toluidine blue-O solution was kept in dark, the second beaker containing the dye solution was exposed to light, the third beaker containing the dye solution and 0.14 g of Mo doped-TiO<sub>2</sub> was kept in dark, and the fourth beaker containing the dye solution and 0.14 g of Mo doped-TiO<sub>2</sub> was exposed to light. After keeping these beakers for 3-4 hours, the optical density of the solution in each beaker was measured with the help of spectrophotometer. It was found that the optical density of solutions of first three beakers remained almost constant, while the solution of fourth beaker had a decrease in initial value of optical density. From this observation, it is clear that this reaction requires presence of both; the light as well as semiconductor Mo doped-TiO<sub>2</sub>. Hence, this reaction is a photocatalytic reaction in nature.

A solution of  $2.60 \times 10^{-5}$  M of toluidine blue-O was prepared in doubly distilled water and 0.14 g of Mo doped-TiO<sub>2</sub> was added to it. The pH of the reaction mixture was adjusted to 8.5 and then this solution was exposed to a 200 W tungsten lamp at 60.0 mWcm<sup>-2</sup>.

A decrease was observed in the optical density of toluidine blue-O solution with increasing time of exposure. The photocatalytic degradation of the dye was studied at  $\lambda_{\max} = 660$  nm. The plot of  $1 + \log$  O. D. versus time was found linear, which indicates that the photocatalytic degradation of methylene blue follows pseudo-first order kinetics. The rate constant for this reaction was determined with the help of the rate equation i.e. Rate constant (k) = 2.303 × Slope.

## RESULT AND DISCUSSION

A typical run is presented in Table 1 and it is graphically represented in Figure 2.

**Table -1 A Typical Run** pH = 8.5, [Toluidine Blue-O] =  $2.60 \times 10^{-5}$  M; Mo doped-TiO<sub>2</sub> = 0.14 g, Light Intensity = 60.0 mWcm<sup>-2</sup>  
Rate Constant, k =  $2.06 \times 10^{-4}$  sec<sup>-1</sup> (For Pure TiO<sub>2</sub>); k =  $3.07 \times 10^{-4}$  sec<sup>-1</sup> (For Mo doped-TiO<sub>2</sub>)

Time (min.)	PURE TiO <sub>2</sub>		Mo DOPED-TiO <sub>2</sub>	
	Optical Density (O. D.)	1 + log O. D.	Optical Density (O. D.)	1 + log O. D.
0	0.277	0.4425	0.277	0.4425
5	0.263	0.4199	0.253	0.4031
10	0.245	0.3892	0.229	0.3598
15	0.230	0.3617	0.209	0.3201
20	0.216	0.3345	0.191	0.2810
25	0.204	0.3096	0.174	0.2405
30	0.192	0.2833	0.158	0.1987
35	0.180	0.2553	0.145	0.1614
40	0.169	0.2279	0.132	0.1206
45	0.158	0.1987	0.120	0.0792
50	0.149	0.1732	0.109	0.0374

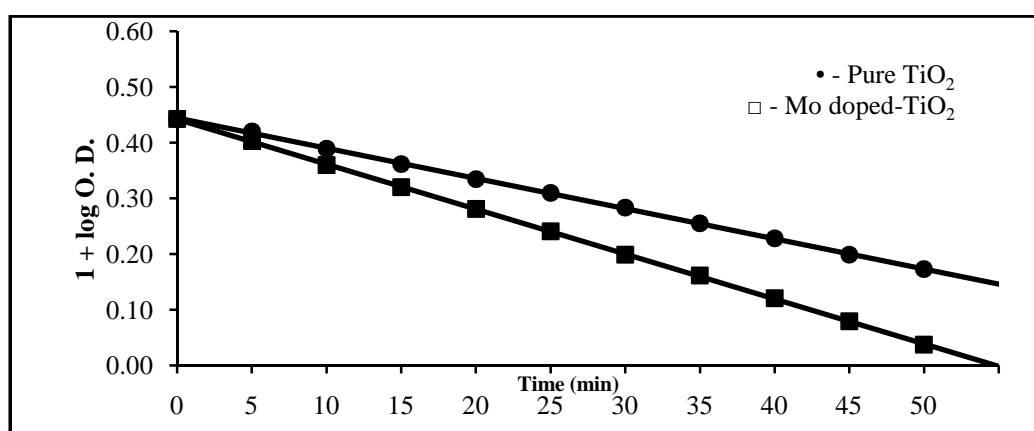


Fig. 2 A Typical Run

### Effect of pH

The pH of the solution is likely to affect the degradation of toluidine blue-O dye and therefore, the rate of degradation of the dye was studied in the pH range 7.0-10.0. The observation showed negligible degradation of the dye in the acidic region and therefore, this region was not studied. The observations are reported in Table 2. It has been observed that the rate of photocatalytic degradation of toluidine blue-O was increased as pH was increased from 7.0 to 8.5 and it got an optimum value at pH 8.5. On further increasing the pH, the rate of the reaction was decreased. This behavior may be explained on the basis that when pH was increased from 7.0 to 8.5, attraction between cationic dye molecules and hydroxyl ions increases and accordingly the rate of photocatalytic degradation of the dye increases. Above pH 8.5, a decrease in the rate of photocatalytic degradation of the dye was observed, which may be due to the fact that cationic form of toluidine blue-O converts in its neutral form, which faces less attraction towards the negatively charged semiconductor surface. Hence, the rate was decreased.

**Table 2 - Effect of pH**  
[Toluidine blue-O] =  $2.60 \times 10^{-5}$  M, Mo doped-TiO<sub>2</sub> = 0.14 g, Light Intensity = 60.0 mWcm<sup>-2</sup>

pH	Rate constant $\times 10^4$ (sec <sup>-1</sup> )
7.0	1.70
7.5	2.11
8.0	2.54
<b>8.5</b>	<b>3.07</b>
9.0	2.84
9.5	2.47
10.0	2.38

### Effect of Toluidine Blue-O Concentration

The effect of dye concentration was also observed by taking concentrations of the dye from  $2.0 \times 10^{-5}$  to  $3.0 \times 10^{-5}$  M. The results are tabulated in Table 3. The rate of photocatalytic degradation of dye was found to increase on increasing the concentration up to  $2.6 \times 10^{-5}$  M. It may be due to the fact that as the concentration of the dye was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with increase in the concentration of the dye further due to dye itself will start acting as a filter for the incident irradiation.

**Table -3 Effect of Toluidine Blue-O Concentration**  
**pH = 8.5, Mo Doped-TiO<sub>2</sub> = 0.14 g, Light Intensity = 60.0 mWcm<sup>-2</sup>**

[Toluidine blue-O] × 10 <sup>5</sup> M	Rate constant × 10 <sup>4</sup> (sec <sup>-1</sup> )
2.0	1.61
2.1	1.74
2.2	1.87
2.3	1.94
2.4	2.37
2.5	2.76
<b>2.6</b>	<b>3.07</b>
2.7	2.54
2.8	2.20
2.9	1.90
3.0	1.66

#### Effect of amount of Mo doped-TiO<sub>2</sub>

The amount of semiconductor also affects the degradation rate of the dye and therefore, different amount of semiconductor was taken. The results are tabulated in Table 4. It was observed that the rate of reaction was increased with increasing the amount of Mo doped-TiO<sub>2</sub> upto 0.14 g. Beyond 0.14 g, the rate of reaction become virtually constant. This behavior may be explained on the fact that as the amount of semiconductor was increased, the exposed surface area of the semiconductor also increases. However, after this limiting value (0.14 g), increase only the thickness of the semiconductor layer and not the exposed surface area. This was also confirmed by using reaction vessels of different dimensions. It was observed that the point of saturation shifted to a higher value for vessels of larger capacities while it shifted of lower value for vessels of smaller capacities.

**Table 4 - Effect of amount of Mo doped-TiO<sub>2</sub>**  
**pH = 8.5, [Toluidine blue-O] = 2.60 × 10<sup>-5</sup> M, Light Intensity = 60.0 mWcm<sup>-2</sup>**

Amount of Mo doped-TiO <sub>2</sub> (g)	Rate constant × 10 <sup>4</sup> (sec <sup>-1</sup> )
0.02	1.28
0.04	1.50
0.06	1.63
0.08	1.83
0.10	2.20
0.12	2.64
<b>0.14</b>	<b>3.07</b>
0.16	3.07
0.18	3.06
0.20	3.06

#### Effect of Light Intensity

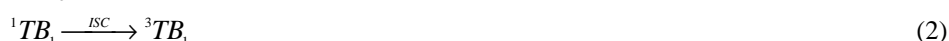
The effect of light intensity was observed by varying intensity of light. For this purpose, the distance between the light sources and the dye solution was varied. The results are tabulated in Table 5. It was observed that the rate of reaction was increased with increasing light intensity (upto 60.0 mWcm<sup>-2</sup>) due to fact that the number of photons striking per unit area of the semiconductor also increase. However, at higher light intensities, some thermal side reactions may also start and hence, the rate of photocatalytic degradation was decreased on increasing the intensity of light further.

**Table -5 Effect of Light Intensity**  
**pH = 8.5, [Toluidine blue-O] = 2.60 × 10<sup>-5</sup> M, Mo doped-TiO<sub>2</sub> = 0.14 g**

Light intensity (mWcm <sup>-2</sup> )	Rate constant × 10 <sup>4</sup> (sec <sup>-1</sup> )
20	1.29
30	1.56
40	2.06
50	2.61
<b>60</b>	<b>3.07</b>
70	2.88

#### Mechanism

A tentative mechanism for photocatalytic degradation of toluidine blue-O is proposed on the basis of observations and it is given below –



Toluidine blue-O (TB) dye absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state. On the other hand, the semiconducting Mo doped-TiO<sub>2</sub> (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band, thus, leaving behind a hole. This hole abstracts an electron from <sup>-</sup>OH ions to generate <sup>•</sup>OH radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of <sup>•</sup>OH radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers (2-propanol), where the rate of degradation was drastically reduced.

### CONCLUSION

In the present investigation, it has been observed that the photocatalytic activity of titania was enhanced due to its doping with molybdenum. The rate constant for dye degradation using pure titania and Mo-doped TiO<sub>2</sub> confirmed these results, where the rate constant was almost 1.5 times in the case of modified titania in compare to pure titania. The metal doping of semiconductors will explore the use of modified semiconductors for their various applications. The technology of photocatalysis is now being used.

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