

Titanium oxide (TiO₂) assisted photocatalytic degradation of methylene blue

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Abstract: The aqueous solution of methylene blue (MB) has been subjected to photocatalytic degradation by UV radiation in presence of TiO₂ photo-catalyst containing different concentrations of H₂O₂. The experiments conducted at different dye concentrations (12 and 20 ppm), catalyst loading, pH and H₂O₂ dosage (1-10 ml l⁻¹), revealed that the degradation rate is strongly influenced by respective experimental parameters. However the influence of catalyst alone is not predominant in degradation. The decolorization of dye proceed to near completeness when H₂O₂ is used. The best degradation results are observed at 0.1 wt% of catalyst loading at pH 2 for TiO₂/UV system. It has been found that the optimum concentration of H₂O₂ for 12 ppm and 20 ppm amount of the dye was 2ml l⁻¹ for UV/H₂O₂ system. The kinetic of degradation of the dye followed the pseudo first order rate. The degradation studies using TiO₂/UV/H₂O₂ system, indicates enhancement in the degradation rate of the dye compared to that of UV/H₂O₂ system alone.

Key words: Methylene blue, TiO₂, Photocatalytic, Discoloration

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Introduction

A variety of hazardous pollutants are discharged into the aquatic bodies from several industrial streams (Ganesh and Boardman, 1994; Yadav *et al.*, 2007). Dye from textile industries and other commercial dyestuffs have been a focus of environmental remediation in the last few years (Ganesh and Boardman, 1994; Weber and Adams, 1995; Mathur and Bhatnagar, 2007). Conventional methods for the abatement of water pollution from dye and textile industries like adsorption, absorption, incineration and biodegradation were found to be ineffective and expensive. Moreover, they pose secondary disposal problems and associated increase in time and cost of operation (Hoffmann *et al.*, 1995; Marye and Dulay, 1993; Lewis, 1993; Legrini *et al.*, 1993; Prashant, 1993; Pant *et al.*, 2008; Laowansiri *et al.*, 2008).

Recent development in the realm of chemical water treatment techniques has lead to the improvement in oxidative degradation by photochemical methods. Photo-catalytic oxidation is cost effective and capable of degrading any complex organic chemicals when compared to other purification techniques. The formation of transient hydroxyl radicals (OH⁻) during photooxidation are highly reactive than any oxidation agent. The photodegradation are generally classified into two categories such as homogeneous and heterogeneous processes. Homogeneous processes occur in presence of UV light in conjunction with an oxidants such as ozone and hydrogen peroxide. Heterogeneous processes occur in presence of oxidants and solid photocatalyst. Photocatalytic degradations are very sensitive to pH, catalyst dosage, type of effluent, effluent concentration and the charges between the effluent and the catalyst (Madhu *et al.*, 2007). In the present study methylene blue is degraded under homogeneous and heterogeneous conditions.

Semiconductor photocatalysis has become more appealing than the conventional oxidation methods. Semiconductors are inexpensive, nontoxic and capable of extended use without substantial loss of photocatalytic activity. Semiconductor may be easily recovered by filtration and centrifugation. TiO₂ was chosen as Photocatalyst, which is a white solid and insoluble in water. TiO₂ occurs in three forms, anatase, rutile and brookite. Anatase form of TiO₂ was considered as the best photocatalyst.

In the present study, an attempt is made to investigate the degradation kinetics of methylene blue in presence of UV light using TiO₂ catalyst. The effect of dye concentration, pH, amount of catalyst and addition of oxidants like H₂O₂ have been examined. The dye concentration 12 and 20 ppm is selected to simulate the industrial waste based on the studies of Jun *et al.* (2007). Suitable kinetic models have been proposed for the degradation studies.

Materials and Methods

Titanium (IV) oxide (TiO₂) anatase (Sigma Aldrich, Germany) having mean particle size less than 44µm has been used as catalyst. Methylene blue (C₁₆H₁₈ClN₃SCl) which was obtained from Qualigens Fine Chemicals (India). Its chemical structure makes it to fall under a group of azin dyes as shown in Fig. 1. λ_{max} for the dye is 664.8 wavelength. A medium pressure UV lamp of 25W with an average wave length of 365 nm procured from Philips was used as an irradiation source. All the chemicals used to prepare the buffer solutions, hydrogen peroxide (H₂O₂) solution (30% stabilized for synthesis) and CH₃COCH₃ were procured from Ranbaxy Chemicals (India). Potable water (pH=7.9, DO=7.5 ppm, Total alkalinity=360 mg l⁻¹ of CaCO₃, Turbidity 10 NTU) was used for the preparation of dye solutions.

Kinetic model to predict rate constant for the reaction: The reaction rate for photocatalytic reactions are independent of hydroxyl concentration (Guettai *et al.*, 2005). Therefore a pseudo first-order kinetic model was used to fit the experimental data

$$\frac{-dC_{MB}}{dt} = kC_{MB}C_{OH^*} \quad \dots\dots\dots(1)$$

where C_{MB} represents the dye concentration, ppm; C_{OH^*} represents the hydroxyl radical concentration, ppm;

By the pseudo-stationary hypothesis (*i.e.* the C_{OH^*} can be considered to be a constant in the presence of excess H_2O_2), the rate expression (1) can be simplified to fit an equation following the first order kinetics,

$$\frac{-dC_{MB}}{dt} = kC_{MB} \quad \dots\dots\dots(2)$$

Integrating the above equation; from ' C_{MB0} ' to ' C_{MB} ' on the left hand side, and '0' to 't' on the right;

$$\int_{C_{MB0}}^{C_{MB}} -dC_{MB} = k \int_0^t dt$$

$$\ln(C_{MB0}/C_{MB}) = kt \quad \dots\dots\dots(3)$$

where C_{MB0} represents the initial dye concentration in ppm, K is Pseudo first order rate constant (min^{-1}), T is time interval (min), C_{MB} represents the final dye concentration in ppm.

Experimental procedure for degradation studies: A 100 ml substrate solutions of 12 and 20 ppm was prepared in water. TiO_2 was prepared with varying concentration (0.025 to 0.15 wt % of TiO_2 substrate solutions of 12 and 20 ppm) was added to the solution and the mixture was transferred to the reaction vessel. Reaction temperature was maintained at room temperature at $27^\circ\text{C} \pm 3^\circ\text{C}$ for all the experimental trials. It has been planned to study the degradation studies under atmospheric conditions (1 atm Pressure). The aliquots were withdrawn from the reaction mixture at regular intervals and were centrifuged before analyzing the dye concentration (Madhu *et al.*, 2006). The concentration of dye was measured using UV spectrophotometer (Systronics-117). The pH of the solutions was adjusted with an Inlab pH meter. Experiments were conducted under different pH conditions. Further degradation studies were carried out for UV/ TiO_2 , UV/ H_2O_2 , UV/ H_2O_2/TiO_2 systems.

Results and Discussion

Effect of catalyst: In order to determine optimal amount of photo catalyst to affect oxidation, experiments were carried out without and with catalyst loadings (0.025 to 0.15 wt %) at pH 7 at 27°C under atmospheric pressure condition. No degradation was observed without catalyst loading and oxidant dosage. The percentage of unreacted MB as a function of irradiation time at pH 7

is shown in Fig. 2. It was found that after 2 hr the extent of color degradation in presence of catalyst, at a loading of 0.1 wt% gave a better performance than other catalyst loadings when studied under constant pH conditions. The rate has increased from 0.025% to 0.1 wt % catalysts loading. Further increase in catalyst loading decreased the rate of discoloration. Fig. 3 represents % MB degraded with variation of catalyst loading after 120 min, where 0.1 wt % shows better degradation. Therefore 0.1 wt% catalyst loading is considered to be an optimal value. This phenomenon may be explained as, with an increase in catalyst loading the light penetration through the solution becomes difficult. Increase in catalyst concentration decreases photo absorption which in turn reduces the dye adsorption onto the catalyst surface thus reducing the reaction rates (Zhu *et al.*, 2000; Epling and Lin, 2002; Madhu *et al.*, 2006; Madhu *et al.*, 2007). Fig. 4 shows the degradation of MB is higher for 0.1 wt% catalyst loading after 120 min exposure to UV irradiation under constant stirring conditions. Optimal concentration of the catalyst depends on working condition and the incident radiation reflux (Chen and Ray, 1999; Assabane *et al.*, 2000; Zhu *et al.*, 2000).

Effect of pH: According to literature (Hoffmann *et al.*, 1995; Marye and Dulay, 1993; Lewis, 1993; Legrini *et al.*, 1993; Prashant, 1993) pH value is by far the major factor influencing the rate of the photocatalytic process. For these reasons the experiments were carried out to find the optimal pH of reaction mixture for decomposition of MB. The examined range of pH was from 2 to 8 by varying weight of catalyst (0.025, 0.05 and 0.10 wt %). The results are shown in Fig. 4, 5 and 6. It is noticed that the best results are obtained in acidic solutions after 2 hours of irradiation) best degradation results were obtained at pH 2).

This is an indicative of the significant role of the photocatalyst TiO_2 . The acid base property of the metal oxide has a considerable influence on the photocatalytic activity with varying pH. The pH effect can be explained on the basis of the zero point of charge of TiO_2 . The adsorption of H_2O molecules at surface metal sites is followed by the dissociation of the OH groups leading to the coverage with chemically equivalent metal hydroxides (MOH). Due to the amphoteric behavior the following to equilibrium must be considered.

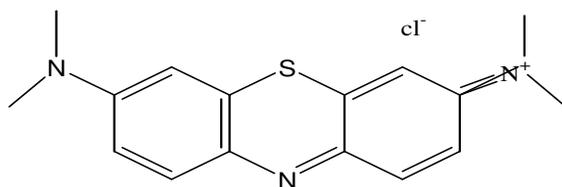


Fig. 1: Structure of methylene blue (MB)

Table - 1: Pseudo-first-order rate constants at different H₂O₂ dosages, R² values for 12 ppm initial dye concentration

H ₂ O ₂ dosage (ml ⁻¹)	K (min ⁻¹)	R ²
1	0.0490	0.892
2	0.0530	0.896
3	0.0478	0.961
5	0.0448	0.981
6	0.0428	0.960
8	0.0411	0.955
10	0.0390	0.980

Table - 2: Pseudo-first-order rate constants at different H₂O₂ dosages, R² values for 20 ppm initial dye concentration

H ₂ O ₂ dosage (ml ⁻¹)	K (min ⁻¹)	R ²
1	0.0293	0.964
2	0.0423	0.977
3	0.0342	0.985
5	0.0273	0.926
6	0.0244	0.933
8	0.0174	0.968

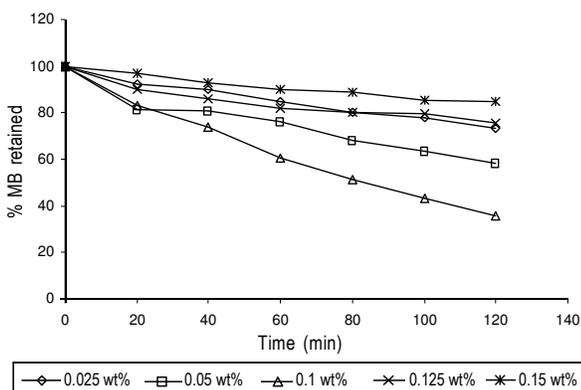


Fig. 2: Concentration of MB retained versus time at 7 pH and at temperature of 27°C at effluent concentration of 12 ppm

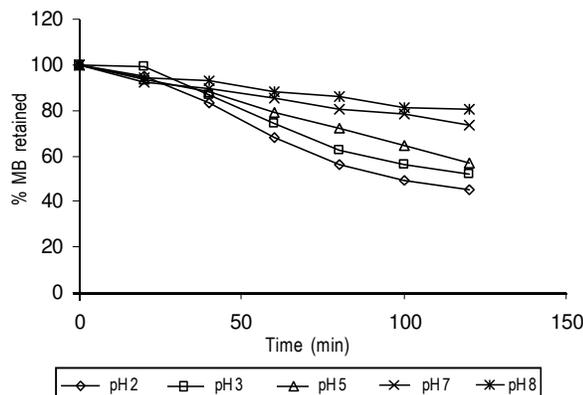


Fig. 4: % of MB retained versus time for different pH of the substrate solution at 0.025 wt% catalyst loading at 12 ppm dye concentration

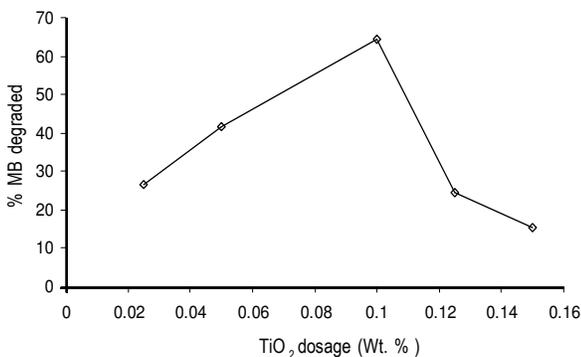


Fig. 3: % of MB degraded versus weight % of catalyst loading after 120 minutes at pH 7 for 12 ppm dye concentration

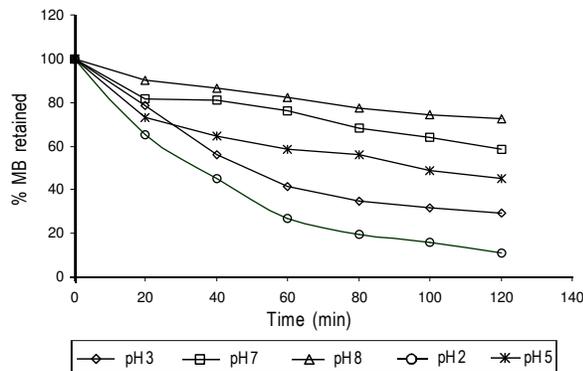


Fig. 5: % of MB retained versus time for different pH of the substrate solution at 0.05 wt% catalyst loading at 12 ppm dye concentration

pH changes can thus influence the adsorption of molecules onto the TiO₂ surface, an important step for the photo-oxidation to take place. For the TiO₂ sample used zero point charge (pH zc) is around 5.8 to 6.8 (Madhu *et al.*, 2006). As a consequence of this amphoteric behavior the metal oxide surface is predominantly positively charged below pH zc and negatively charged above. So when pH is less than 6 a strong adsorption of negatively charged MB on the TiO₂ particles occurs as a result of the attraction of the positively charged TiO₂ with the negatively charged dye. In this case, the highest degradation rate was achieved at pH 2.

In alkaline solutions the MB molecules are negatively charged and their adsorption is also affected by an increase in the density of TiO groups on the semiconductor surface. Thus due to columbic repulsion substrate is scarcely adsorbed. At high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with the dyes.

In real interpretation of pH effects on the efficiency of dye photo degradation process is very difficult because three possible reaction mechanisms can contribute to dye degradation, namely

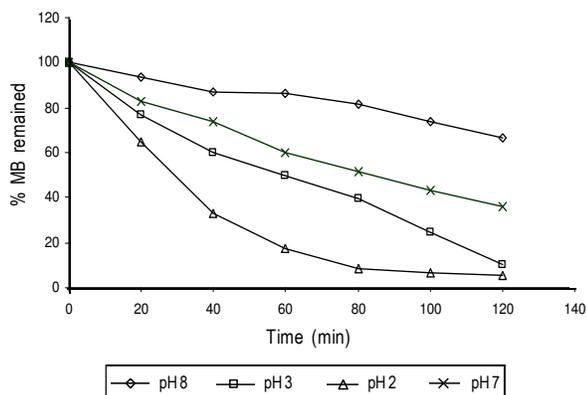


Fig. 6: % of MB retained versus time for different pH of the substrate solution at 0.05 wt% catalyst loading at 12 ppm dye concentration

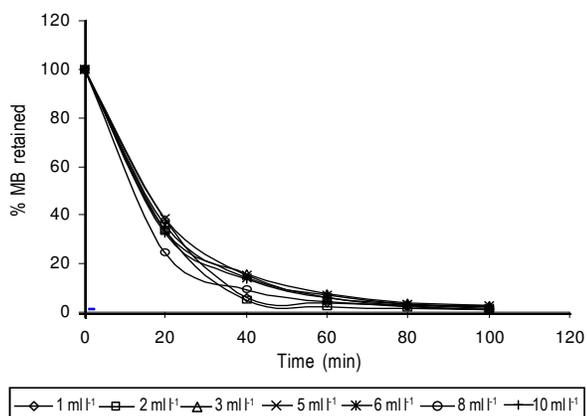


Fig. 7: Concentration of MB remained versus time with different H₂O₂ dosages for 12 ppm initial dye concentration for 7 pH substrate solution

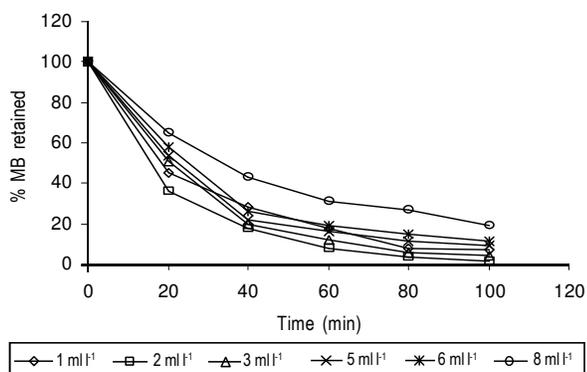


Fig. 8: Concentration of MB remained versus time with different H₂O₂ dosages for 20 ppm initial dye concentration for 7 pH substrate solution

hydroxyl attack, direct oxidation by the oxidation with positive hole and direct reduction by the electron in the conduction band. It appears that the effect of pH on the degradation of pollutants is variable and controversial. Since the major oxidative species at low pH, is considered to be the positive hole whereas at high or neutral

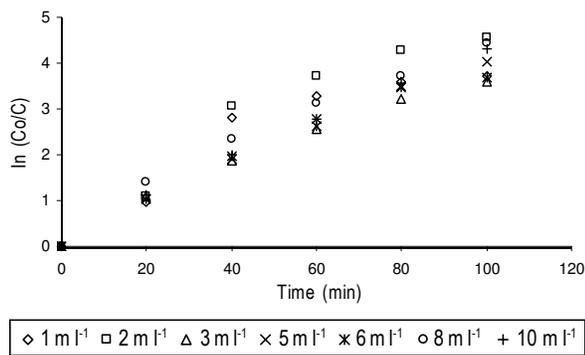


Fig. 9: Kinetic regime graph for the degradation of MB using H₂O₂/UV for 12 ppm initial dye concentration

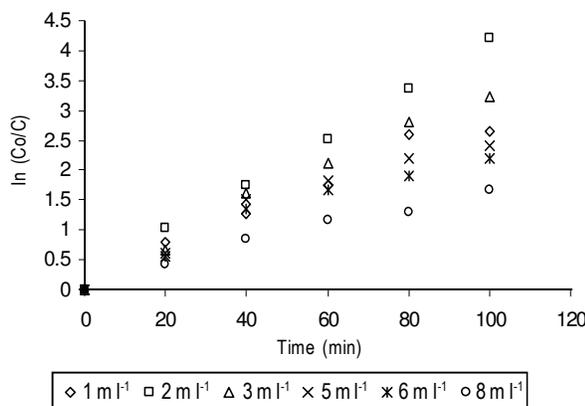


Fig. 10: Kinetic regime graph for the degradation of MB using H₂O₂/UV for 20 ppm initial dye concentration

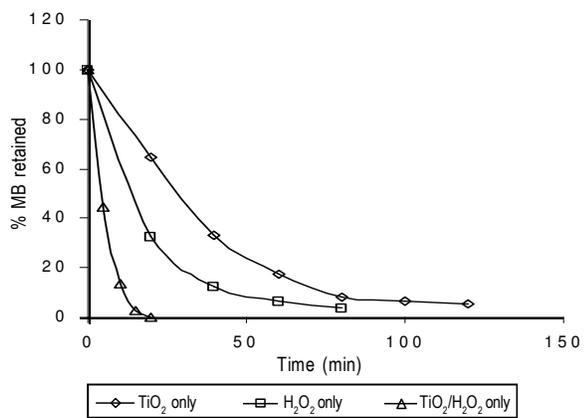


Fig. 11: Concentration of MB retained versus time with and without photo catalyst and H₂O₂ at 12 ppm initial dye concentration and pH 2

pH the hydroxyl radicals are considered to be the predominant species.

Effect of H₂O₂: Oxidants such as H₂O₂ had major effect on degradation rates (Guettai and Amar, 2005; Madhu et al., 2007). Therefore discoloration tests were carried out for varying H₂O₂

doses in 12 and 20 ppm MB solution prepared using pH 7 water and the results (% MB retained as function of time) were plotted as shown in Fig. 7 and 8. The degradation rate increased from 1 ml⁻¹ to 2 ml⁻¹ of H₂O₂. Further increase in H₂O₂ loading reduced the degradation rates. Higher concentration of H₂O₂ rendered reaction solution acidic resulting in reduced rates, while higher rates are obtained in alkaline media. Bubbles were evolved from the photolysis of H₂O₂ (Tanja *et al.*, 2002) or CO₂ produced from the complete mineralization of MB (Arslan *et al.*, 2000; Galindo *et al.*, 2000). The production of the bubbles increased with the increase of H₂O₂. Higher concentration of H₂O₂ liberated more of hydroxyl free radicals, which caused the dye discoloration. However, increase in the H₂O₂ concentration beyond certain limits (critical concentration) does not increase the reaction rates as it tends to act as a hydroxyl radical scavenger instead of a free radical generator (Baxendale and Wilson, 1957; Guettai and Amar, 2005). Fig. 7 infers that 2ml⁻¹ can be considered to be an optimum value of H₂O₂ loading for the discoloration in the presence of UV. The degradation rate data obtained for different substrate concentration were plotted using pseudo first order kinetic model as shown in Fig. 9 and 10. The fairness of the fit is indicated by the fact that linear regression (R²) values are always greater than 0.89. Therefore the model is in good agreement with the experimental data. The values of the first order rate constant are indicated in the Table 1 and 2 for 12 and 20 ppm initial dye concentration. The value of k is maximum (0.053 min⁻¹ for 12 ppm and 0.0423 min⁻¹ for 20 ppm initial dye concentration.) at H₂O₂ dosage of 2ml⁻¹. From the results it can be interpreted that the rate of degradation decreases with increase in dye concentration, which results in the light scattering effect, in turn reducing the light penetration to the catalyst substrate interface.

Degradation using H₂O₂/ UV / sTiO₂: Discoloration tests were further carried out using 0.1% catalyst loading at 2ml⁻¹ H₂O₂ dosage. The results are shown in the Fig. 11. It is observed that the combination of 2 ml⁻¹ of H₂O₂ and 0.1 wt% TiO₂ gives better degradation as compared to 0.1 wt% TiO₂ and 2ml H₂O₂ alone at pH 2 for 12 ppm MB concentration. It has been concluded that 0.1% catalyst loading at 2 ml⁻¹ H₂O₂ represents the optimum condition for photo degradation of MB which is as shown in Fig. 11. There has been an enhancement in the rate of degradation with addition of catalyst and oxidant and there is a consequent reduction in time to decolorize the solution.

Heterogeneous photocatalysis has proved to be very effective in the removal of toxic pollutants from the industrial wastewaters owing to its ability to convert them into innocuous end products such as CO₂, H₂O *etc.* In order to study the optimum conditions for catalyst loading; comparative studies were carried out by varying the pH of the solution. Acidic medium gives better degradation compared to neutral or alkaline medium for all catalyst loadings. For H₂O₂/UV system, the reaction rate increases up to a critical value (2ml⁻¹) and then decreases as H₂O₂ added beyond

the critical value begins to act as a scavenger for the hydroxyl radicals. The degradation kinetics of MB with H₂O₂ (which represents a homogenous system) follows a pseudo-first-order kinetics. Presence of the catalyst in UV/H₂O₂ system resulted in increased degradation as compared in its absence.

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