

# Degradation of Methylene Blue Dye using A Photochemical Reactor

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## Abstract

This paper describes the basics of photocatalysis using semiconductors like TiO<sub>2</sub> and the application of photocatalytic processes for waste water purification from different industries. The photocatalytic activity of TiO<sub>2</sub> and CuO for the degradation of different substances under UV light irradiation. The higher photocatalytic activity was obtained for TiO<sub>2</sub>. In the present investigation, result indicates that removal of dye methylene blue (MB) has been studied by considering influent concentration, loading of photo catalyst, pH and contact time as operating variables. The percentage removal of dye MB increase with increase in contact time. The optimum contact time was fixed at 120 minutes for TiO<sub>2</sub> and CuO. The results of this study reveal that the dyes could be removed by semiconducting materials assisted photoalytic degradation. The kinetics study of experimental data was analyzed using the pseudo first order kinetics and Pseudo second order model to determine adsorption rate constant.

**Keywords: Photocatalytic, Methylene blue, TiO<sub>2</sub>, dye**

## I. INTRODUCTION

Contaminants from industrial effluents often pose a major environmental problem. Semiconductor photocatalysis is one technique that has great potential to control aqueous organic as well as inorganic contaminants or air pollutants. Advantages over conventional oxidation processes, such as 1. complete mineralization of the pollutants, 2. use of near-UV, 3. no addition of other chemicals, and 4. operation at near room temperature. Among the various oxide semiconductor photocatalysts, TiO<sub>2</sub> is an important photocatalyst due to its strong oxidizing power. In this article the mechanism of the heterogeneous photocatalysis on semiconductors, mainly on TiO<sub>2</sub>, and applications of the methods to water purification are described.

Today more than 10,000 dyes have been incorporated in colour index. In order to remove hazardous materials like dyes, poisonous metals, and toxic organic and inorganic substances from wastewater is very difficult. There are various methods for removal of organic and inorganic compounds from the wastewater as filtration, electrolysis, precipitation, ion exchange and adsorption process. Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small scale industries. Among all the above-mentioned methods, photocatalysis is highly effective and cheap process than the other methods. TiO<sub>2</sub> is an important photocatalyst, because they are most efficient and shows the highest quantum yield. It is safe and inexpensive material, stable to photo corrosion and insoluble in water. In the present investigation, TiO<sub>2</sub> is used as photocatalyst which can remove dyes from the wastewater. A detailed batch study with the TiO<sub>2</sub> has been carried out in the present investigation. The effect of pH, contact time, concentration of photocatalyst, and first order study were also investigated.

## II. MATERIALS AND METHODS

The basic dye used in this study is Methylene blue; it is a heterocyclic aromatic compound. A.R. grade supplied by Research lab, Mumbai. MB in commercial purity was used without further purification. The accurate weighted quantity of the dye was dissolved in double distilled water to prepare the stock solution (500 mg/L) experimentally dilution. Dye concentration was determined by using absorbance value measured before and after the treatment with UV-Visible Spectrophotometer. A TiO<sub>2</sub> was supplied by Research lab.

### A. Analytical Procedure:

The concentration of paracetamol in the samples was monitored by UV-Vis Spectrophotometer-119 (Sysstronics Ltd.). Initially different concentration samples were prepared to make reference chart. Concentrations varied from 5 ppm to 50 ppm. pH meter (Sysstronics Ltd.) was used to measure the pH value of the solution.

### III. PHOTOCATALYTIC STUDY

The removal of the dye was observed by spectrophotometer (Systronic Model 119). The calibration curve of Methylene blue dye was obtained at 665nm. The dye solution was exposed to UV light (125 Watt) by addition of TiO<sub>2</sub> and CuO at a distance 30 cm from the reaction vessel (fig.1). Double distilled water was used throughout the experiment. UV-spectrophotometer in glass cuvette with path length 1.00 cm and the progress of photocatalytic reaction can be observed .the sample separated from the photocatalysts by centrifuging. Samples were withdrawn at different time interval (15min.). To study the effect of important parameters like pH, contact time, initial concentration and photocatalyst dose on the MB dye, A batch experiment were conducted for each experiment. The kinetics was determined by analyzing decolourization of dye from aqueous solution at different time intervals. A batch experiment was conducted for each experiment. The kinetics study was determined by analyzing decolourization of dye from aqueous solution at different time intervals.

### IV. PHOTOCATALYTIC EXPERIMENT

Photooxidation of paracetamol was conducted in a batch process. This unit is configured with an annular cylindrical reactor (Fig. 2) with a quartz tube at the centre of the reactor to house 125W UV light (= 365nm) source, jacket was provide for cooling purpose. Cooling media (water) was circulated by chillier (Lelesil). For each set of experiments, 0.1 g/L solution of paracetamol was prepared. In prepared paracetamol solution TiO<sub>2</sub> catalysts was suspended. This suspension was mixed with a magnetic stirrer for 15 min. This mixture was charge into reactor for photooxidation. Mixture is stirred using magnetic stirrer. (Air can be bubbled for the better stirring but it is optional). Samples were periodically withdrawn, centrifuged and analysed by spectrophotometer.

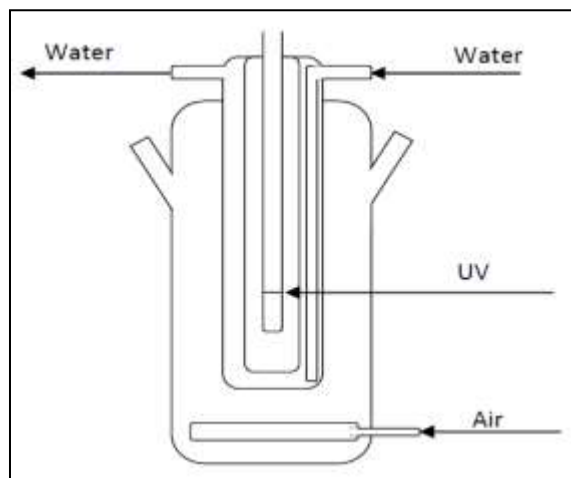


Fig. 1: Photocatalytic reactor

### V. RESULTS AND DISCUSSION

#### A. Effect of pH:

In the study of effect of variation of pH, It was found that as pH of the reaction mixture was raised, the rate of Photocatalytic degradation also increases. About 0.2 gm of photocatalyst were added in the solution in different concentration from 5 mg/L to 30 mg/L . Solutions were irradiation by UV light for given time interval and the percentage of removal was determined. Initial pH was adjusted by adding HCl and NaOH (0.05M). pH where the highest percentage was chosen for the study of photocatalysis. The rate of photocatalytic bleaching of Methylene blue was found increase with increase in pH. Effect of pH on Methylene blue removal. The pH of the dye solution on the percentage of removal of MB was studied by varying the pH. It is one of the most important factor controlling the removal of dye on photocatalysis. The pH increases 4 to 7 the percentage of removal increases from 34.2 to 91.4 % and from 7 to 14 the removal decreases from 91.4 to 77 % show the effect of pH (2-14) on the percentage removal of M.B. The higher percentage removal was obtained at pH 7.0 is 91.4 %, pH 7 was suitable for further study.

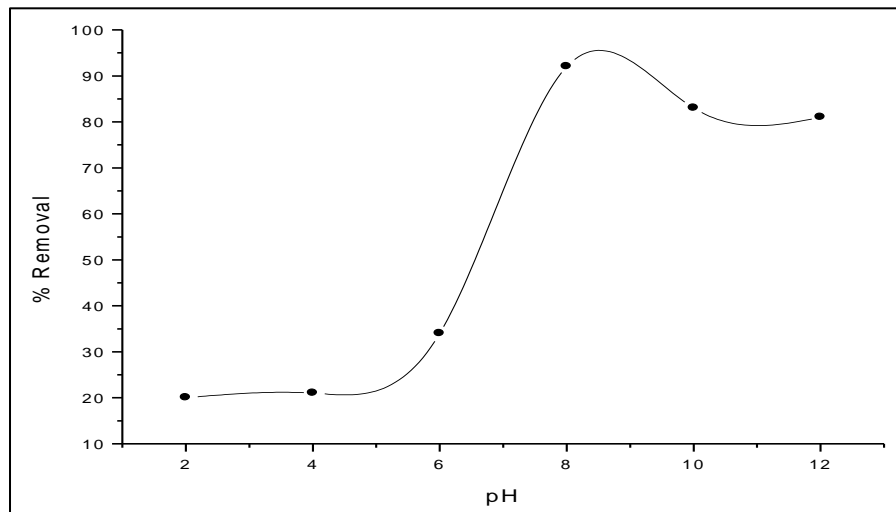


Fig. 2: Effect of pH on degradation of MB

### B. Effect of Concentration and Time:

The percentage of removal is increased with decreasing the initial concentration of Methylene blue. The equilibrium time is taken for the maximum removal of MB by increasing in photocatalyst. The equilibrium time was found to be 180 min for 10 mg/L to 50 mg/L of the MB dye concentration. The removal of the dye is rapid in the initial stage of contact time and gradually decreases with the increasing the time.

Effect of contact time and dye concentration on the removal of Methylene Blue from aqueous solution in presented in by TiO<sub>2</sub>. The experiments were carried out at 1200 rpm 5.0 g/L mass adsorbent at room temperature, pH 7.0 and the dye concentrations of Methylene Blue (10 to 50 mg /L) for different time intervals up to 180 min. The percentage dye removal decreases with increasing the dye concentration. Though the percentage removal decreases with increase in dye concentration and remained nearly constant after equilibrium time. Photocatalytic degradation capacity at equilibrium for MB increased from 15.5 to 80 mg/g for 50 ppm, 20.7 to 95.4 mg/g for 30 ppm, and for 10 ppm it is very high 21.4 to 90 mg/g respectively for TiO<sub>2</sub>.The equilibrium established within 180 min for both photocatalyst for all the concentration studies. The removal efficiency of MB degradation experiments were set up with varying the dose (1.0 mg/L, to 5.0 mg/L) for TiO<sub>2</sub> while keeping initial dye conc. of 40 g/L and temp was 30 +0.1 °C and pH 7.0. The percentage removal was increased and equilibrium time and was decreases with adsorbent dose. The percentage removal increases from 61 to 90 % as the TiO<sub>2</sub> dose was increased from 2.0 to 5.0 g/L at the equilibrium time. Maximum dye was sequestered from the solution within 180 min. after the start of experiment. The rate of reaction increases with increase in amount of TiO<sub>2</sub>.

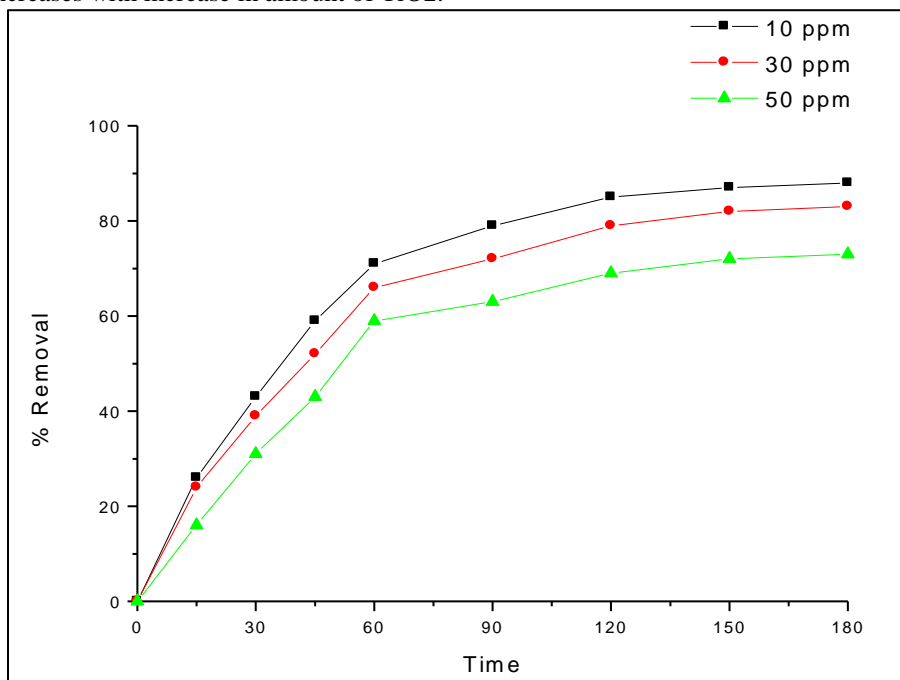


Fig. 3: Effect of concentration of MB

**C. Effect of Photocatalyst Loading:**

In order to examine the effect of Photocatalyst dose on the removal efficiency of MB degradation experiments were set up with varying the dose (1.0 mg/L, to 5.0 mg/L) for TiO<sub>2</sub> while keeping initial dye conc. of 30 g/L and temp was 30 +0.1 °C and pH 7.0. The percentage removal was increased and equilibrium time and was decreases with adsorbent dose. The percentage removal increases from 61 to 90 % as the TiO<sub>2</sub> dose was increased from 2.0 to 5.0 g/L at the equilibrium time. Maximum dye was sequestered from the solution within 180 min. after the start of experiment. The rate of reaction increases with increase in amount of TiO<sub>2</sub>. As the amount of semiconductor increases the exposed surface area of the semiconductor also increases.

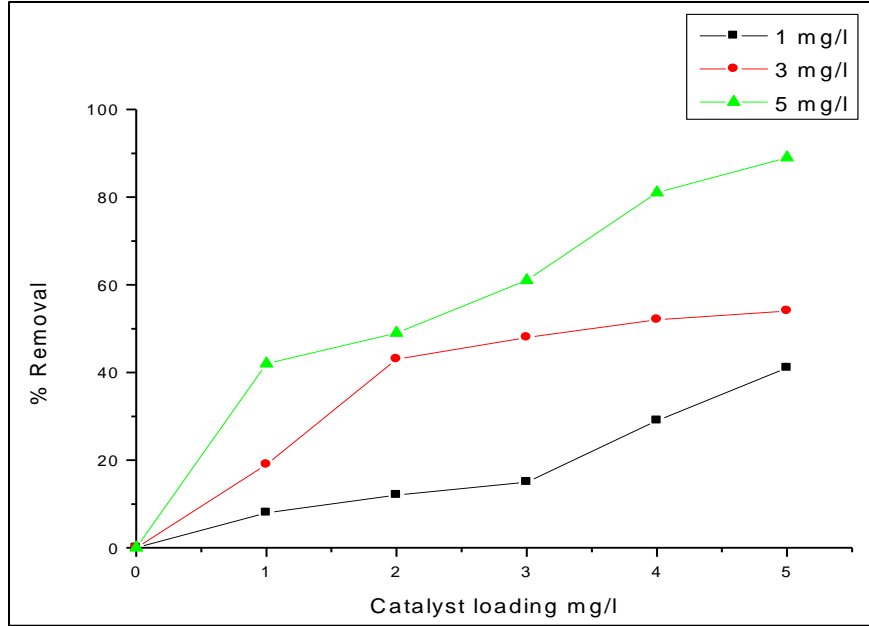


Fig. 4: Effect of photocatalyst loading.

**VI. KINETIC STUDY**

The kinetic study of MB removal by photocatalytic degradation the pseudo first order kinetics models were used to fit in the experimental data,  $\log(q_e - q_t)$  Vs  $t$  was plotted at different concentrations. The photocatalytic degradation of MB with TiO<sub>2</sub> obeys pseudofirst order kinetics at different concentration. for the most initial concentration indicating that this model is less appropriate. The Lagergren first order rate constant ( $K_1$ ) and  $q_e$  cal determined from the model are presented by  $\log(q_e - q_t) = \log q_e - (K_1/2.303)t$ ..... (1) Where  $q_e$  and  $q_t$  are the adsorption capacity in mg/g at equilibrium at the time  $t$  respectively  $K_1$  is the rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ). The first order rate constant  $K_1$  and  $q_e$  for first order equation are determined from the slope and intercept. The coefficient of correlation for the first order kinetic model as not high for all adsorbents and concentration.

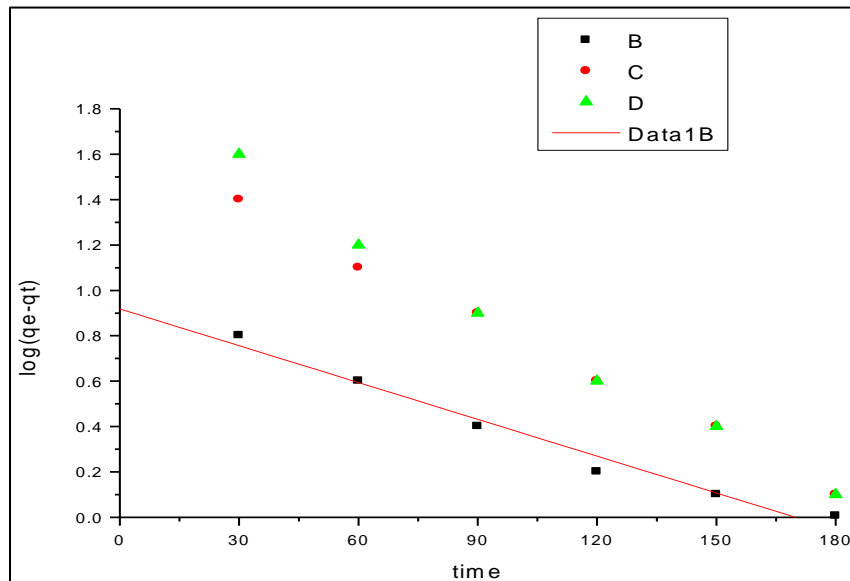


Fig. 5: Pseudo first order kinetics

## VII. CONCLUSION

A wide variety of semiconductors have been examined for their photocatalytic capacity and thus for TiO<sub>2</sub> have been shown to be the most active among the others. TiO<sub>2</sub> was selected as the photocatalyst for this project because it is insoluble under most conditions, Photo stable, nontoxic and has higher photocatalytic efficiency and relatively inexpensive. The photocatalytic oxidation using a semiconducting material TiO<sub>2</sub> with UV light was successively applied for the degradation of dye and metal species. TiO<sub>2</sub> can remove the dye and metal from aqueous solution. The degradation rate was increased significantly by increasing the amount of semiconductor, while on increasing substrate concentration decolourisation decreases. Photocatalytic degradation of Methylene Blue can be achieved by using TiO<sub>2</sub>, (semiconductor). The experimental results indicates that the kinetics of degradation process TiO<sub>2</sub>/UV, fit well with pseudo first order reaction. From this experiment it is possible to obtain decolorized water in a convenient time scale. The rate of degradation of dye is found to be more at 0.5 g/L than the in 1.0 g/L. TiO<sub>2</sub> is more efficient photocatalyst in the removal of Methylene Blue. The Experimental results indicates that the degradation process, TiO<sub>2</sub> /UV, system is very effective compared with different natural and artificial adsorbent available. In this system there is hundred percent of removal of dye is possible in a practical time scale.

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