

## Photodegradation of Commercial Dye, Methylene Blue Using Immobilized TiO<sub>2</sub>

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**Abstract.** Much of the efforts have been devoted to the study of photochemical processes using semiconductor oxides, such as TiO<sub>2</sub>, CdS or ZnO because of their efficiency in the complete mineralization. The development of TiO<sub>2</sub> photocatalyst immobilized on a supporting material would be beneficial since it reduces losses of photocatalyst, avoids the problem of separation and recovery of photocatalyst. Therefore, in the present study, a photocatalytic decolorization system equipped with immobilized TiO<sub>2</sub> was used to remove a commercial dye from aqueous solution. The effectiveness of using immobilized TiO<sub>2</sub> to remove Methylene Blue was investigated under various operational parameters. The percentage of dye removal increased with increasing irradiation time. A higher number of dip coating resulted in a better removal rate and the maximum number of dip coatings that can be applied was twenty. The decrease in the efficiency of the recycled catalyst may be attributed to the deposition of photoinensitive hydroxides on the photocatalysts surface blocking its active site. Due to the ease of usage and good photocatalytic efficiency, the research work done showed its potential application in decolouring organic dyes for pollution prevention.

**Keywords:** Methylene Blue; Dyes; Photocatalyst; TiO<sub>2</sub>; Immobilization

### 1. Introduction

Nowadays pollution in aqueous environment is gaining considerable attention. This pollution problem arises due to the relatively high toxicity of industrial wastewater such as from textile printing industry, tanneries, distilleries, paper and pulp industry. The wastewater from textile industry is rated as one of the most polluting amongst all industrial sectors by considering the volumes discharged and effluent composition [1]. Generally, textile wastewater consists of dyes, pigments and various organic compounds which are stable to light, oxidizing agent, and are resistant to aerobic digestion. The presence of dyes even in trace quantities is highly undesirable as it reduces the light penetration into water thereby decreasing the efficiency of photosynthesis in aquatic plants and resulting in impairment on their growth. Thus, the ecosystem of streams can be seriously affected.

The photodegradation of dyes using photocatalyst is one of the noteworthy treatment processes. This treatment method has generated much interest because of its efficiency in mineralization, especially towards organic pollutants. In the past, most of the studies related to such photodegradation reactions have been carried out using a suspension form [2]. Titanium dioxide (TiO<sub>2</sub>) in anatase form has attracted much attention for its potential application in the decomposition of various environmental pollutants in both gaseous and liquid phases [3], [4]. When TiO<sub>2</sub> is illuminated with light energy greater than the bandgap

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energy ( $\lambda < 380$  nm), it can act as a photocatalyst to mineralize toxic and bioresistant organic compounds from aqueous solution to non-toxic and safer compounds.

However, one of the disadvantages of using  $\text{TiO}_2$  in suspension form would be the post-treatment catalyst recovery stage. Post-treatment catalyst recovery would be undesirable on industrial scale as it would add to the capital and operating costs of the treatment. In order to overcome this problem, efforts have been attempted to immobilize  $\text{TiO}_2$  onto various solid supports [5]-[7].

## 2. Materials and Methods

The  $\text{TiO}_2$  powder P-25 (mainly in anatase form, mean particle size of 30 nm, BET surface area of 50  $\text{m}^2/\text{g}$ ) from Degussa (Frankfurt, Germany) was used as the photocatalyst in this study. The immobilization of  $\text{TiO}_2$  on glass plate was carried out according to the previously reported method [8], [9]. The cationic dye, MB from Sigma-Aldrich was used as the sorbate in this study without further purification. Irradiation experiments of dye solution was carried out by stirring 1500 ml of 5 mg/l dye solution with immobilized  $\text{TiO}_2$  at room temperature ( $25 \pm 2^\circ\text{C}$ ) for 6 hours unless otherwise stated. Aeration was provided by bubbling air into the reaction solution by an air pump to ensure a constant supply of oxygen. UV-irradiation was provided by a UV lamp 100 W, 220 V. For the effect of contact time and initial dye concentration, at predetermined time intervals, approximately 5 ml of the solution was withdrawn from the reservoir. The effect of dip coating was performed by varying the number of dip coating, 5, 10 and 20 times. The effect of light source was studied by using 3 different light sources which are sunlight, UV-lamp and white fluorescent. The concentration of dye in the solution was determined using a Shimadzu 160B double beam UV-vis spectrophotometer. All measurements were made at the wavelength corresponding to maximum absorption,  $\lambda_{\text{max}} = 664$  nm.

## 3. Results and Discussion

### 3.1. Effect of Contact Time and Initial Dye Concentration

The study of the influence of contact time on the removal of MB by photodegradation is shown in Figure 1. It is evident that the percentage of removal increases with increasing irradiation time. This is because more  $\bullet\text{OH}$  radicals will be generated when the exposure time is longer. The generation of  $\bullet\text{OH}$  radicals is crucial in photodegradation process as it oxidizes the organic pollutants to carbon dioxide, water and some simple mineral acids.

It is apparent that there is a decrease of dye degradation as the dye concentration increases. This is might be closely related to the attachment of dye molecules on the surface of the photocatalyst. With increasing dye concentration, more organic substances will be covering the active sites of  $\text{TiO}_2$ . As the intensity of light and irradiation time are constant, so there will be less number of photons reaching the catalyst surface. Less  $\bullet\text{OH}$  radicals will be formed and subsequently the relative number of  $\bullet\text{OH}$  radicals that attack the compound also decreases. Thus, an inhibitive effect in photodegradation is anticipated. Another possible cause for such results is the UV-screening effect of the dye itself. A significant amount of UV may be absorbed at a high dye concentration by the dye molecules rather than the  $\text{TiO}_2$  particles and that reduce the efficiency of the catalytic reaction because the concentrations of OH and  $\text{O}_2$  decrease.

### 3.2. Effect of Number of Dip-coating

The numbers of  $\text{TiO}_2$  dip coating studied were 5, 10 and 20 times. The  $\text{TiO}_2$ - film surface immobilized on the glass plate was kept uniform and the mass of  $\text{TiO}_2$  film with 5, 10 and 20-coating times was 0.3539, 0.9441 and 1.7725 g, respectively. The percentage removal for 5, 10 and 20 coating times are 81.19, 87.29 and 92.53 respectively at 360 minutes (Figure 2). The enhancement of the removal rate is due to the increase in the density of particles in the area of illumination. Since the photodegradation of dye pollutants only takes place on the surface of  $\text{TiO}_2$  particles, the increase of the  $\text{TiO}_2$  loading increased the surface coverage of  $\text{TiO}_2$  on the glass plate, which led to the enhancement of the rate of photodegradation of the dye.

However, there will be increase in turbidity of the solution if it is overloaded with  $\text{TiO}_2$  as this will reduces the light transmission through the solution. While below this level, it is assumed that the catalyst surface and absorption of light by the catalyst are the limiting factors. Therefore, it is not necessarily to be

useful if there is higher amount of the catalyst in view of possible aggregation as well as irradiation field due to increase in light scattering.

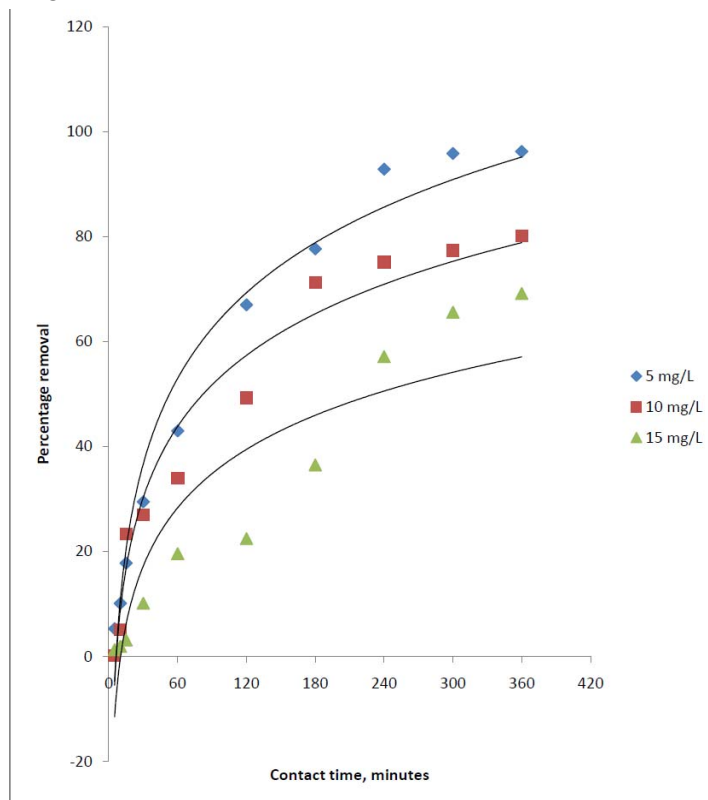


Fig. 1: Effect of contact time and initial dye concentration for the photodegradation of MB

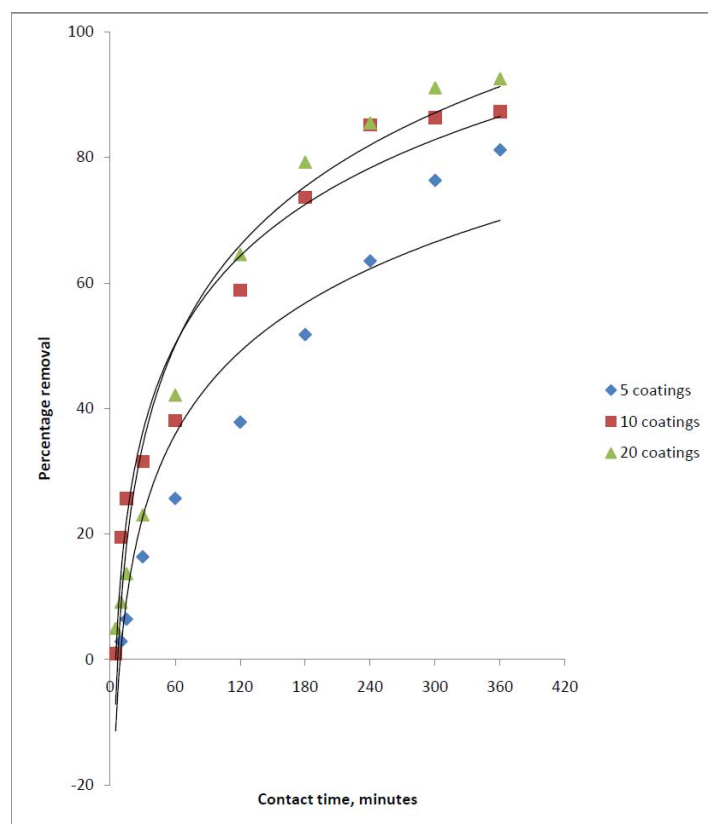


Fig. 2: Effect of number of dip coating for the photodegradation of MB

### 3.3. Effect of Light Sources

Figure 3 shows the effect of light sources in the removal of MB. As shown in the figure, solution exposed to sunlight has the highest percentage removal rate with 90.25 whereas fluorescent light has the

lowest percentage removal rate with only 9.67. For the UV light, the photodegradation was only conducted until 180 minutes. This is because this lamp will be overheated if in use for long period of time. The photocatalytic degradation increased with increasing light intensity because higher light intensity generated more photons which were required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst. The production of electron and hole is a necessity for the reaction with water, hydroxide ion or oxygen to form powerful oxidizing species for the photodegradation process.

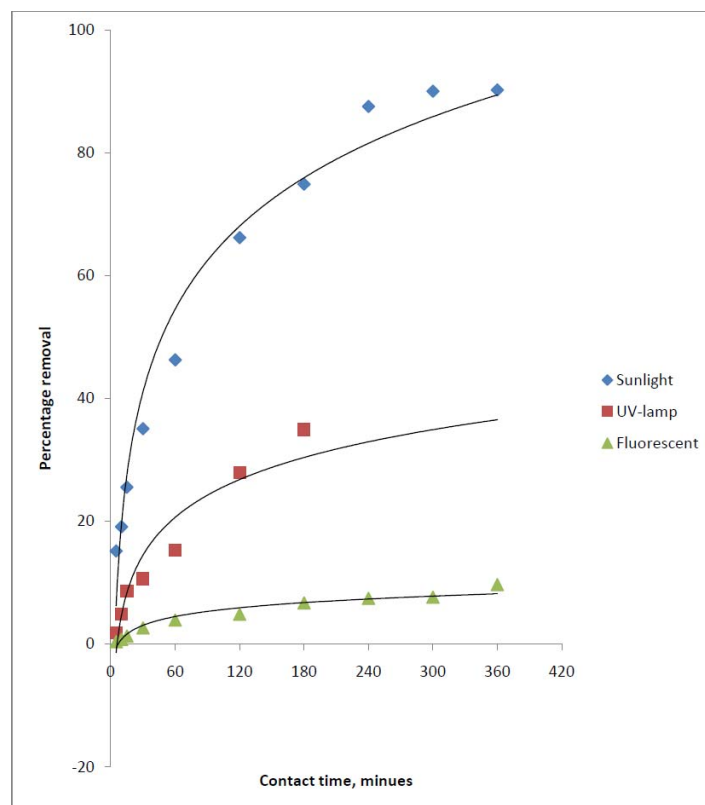


Fig. 3: Effect of light sources for the photodegradation of MB

## 4. Conclusions

From this study, it is evident that the immobilized  $\text{TiO}_2$  is capable in removing MB under the illumination of either UV or sunlight. The results revealed that the  $\text{TiO}_2$  loading plays an important role in determining the photocatalytic decoloring efficiency of MB. Further studies on the intermediates produced in the photodegradation process will be carried out to ensure that no undesirable hazardous compounds were formed before complete mineralization takes place. Finally, the possibility to repetitive usage of  $\text{TiO}_2$  should be explored and concentrated in future study.

## 5. Acknowledgements

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