

# Photo Degradation of Industrial Dye Using ZnO as Photo Catalyst

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**ABSTRACT:** In this study, the potential of a common semiconductor, ZnO, has been explored as an effective photocatalyst for the photodegradation of model dye: Methylene Blue, a commonly used textile dye. Using advanced oxidation processes (AOPs), ZnO appears to be a suitable alternative to TiO<sub>2</sub> for water treatment. The experiments were carried out by irradiating the aqueous solution of dye containing photocatalysts with UV light. Here, a detailed investigation of the effects of process parameters like catalyst loading, initial dye concentration, presence of hydrogen peroxide and pH on the extent of photodegradation have been presented. Hence, it may be a viable technique for the safe disposal of textile wastewater into the water streams.

**KEYWORDS:** Photocatalysis; Textile wastewater; UV irradiation; ZnO-photocatalyst; Methylene Blue; Advanced oxidation processes.

## I. INTRODUCTION

Textile dyes are an abundant source of colored organic compounds, from where a large quantity of wastewater containing dyestuffs with intensive color and toxicity can be introduced into the aquatic systems, creates severe environmental pollution problems due to their negative impact on photosynthetic activity [1]. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete color removal and degradation of organics and dyes [2, 3]. And most importantly, these methods are not destructive but only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced which calls for further treatment [4-6].

Thus, new treatment methods are necessary for the removal of persistent dye chemicals or converting them into harmless compounds in water. In recent years an alternative to conventional methods, is “advanced oxidation processes” (AOPs), based on the generation of very reactive species such as hydroxyl radicals, that oxidizes a broad range of organic pollutants quickly and non-selectively [7, 8]. Amongst them, top priority goes to semiconductor assisted photocatalytic degradation.

Semiconductors have the electronic structure, which is characterized by a filled valence band, and an empty conduction band [9]. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron-hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl or super oxide radicals [10]. Although, TiO<sub>2</sub> in the anatase form has been used for many environmental applications, ZnO (3.2 eV) is a suitable alternative to TiO<sub>2</sub> so far as band gap energy is concerned.

Though sunlight is abundantly available energy source, but UV irradiation is high energy source for degradation of organics present in the effluents. In photocatalytic process, electron-hole recombination is a major problem to

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circumvent. In photocatalysis, UV irradiation source stands up among other sources to avoid this problem. So it was decided to continue this study in the presence of UV irradiation.

The purpose of the present work is to investigate the potential of ZnO as a photocatalyst under UV radiation for the oxidation of textile dyes in aqueous solutions. Effects of parameters like catalyst-loading, initial dye concentration, pH and the addition of H<sub>2</sub>O<sub>2</sub> on the rate of degradation were investigated. These are the major variables governing the efficiency of the process. An irradiation time of 1h was used. Both the removal of color and the reduction of concentration of the solution were monitored.

## II. EXPERIMENTAL

### 1. Materials

#### 1.1. Dyes

The model dye was Methylene Blue, commercial sample, which contains inorganic salts and organic formulating agents, was used without further purification.

Methylene Blue: formula weight 319.86;  $\lambda_{\max}$  664 nm.

The dye structure in azo tautomeric form is shown in Fig. 1.

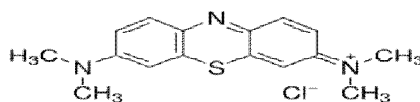


Fig. 1. Methylene Blue dye structure

#### 1.2. Photocatalysts

The ZnO catalyst was a GR grade material of 99% purity (Merck Specialties Private Limited, India) and was used without any further treatment.

### 2. Instruments

Photochemical degradation was carried out in a UV chamber equipped with UV tube of 8W having wavelength 365 nm. Constant stirring of solution was insured by using magnetic stirrers.

The spectra were taken with UV-vis spectrophotometer (Optizen 3220UV); pH meter was used to adjust the pH of the solution.

### 3. Irradiation experiments

To 100 ml of dye solution, photocatalyst was added and suspension was subjected to irradiation. Prior to the runs, dye solutions were stirred in the dark for 20 min after the addition of the catalyst to allow the physical adsorption of dye molecules on catalyst particles to reach the equilibrium. Then the experiments were carried out under UV light. The aqueous suspension was magnetically stirred throughout the experiment. At different time intervals 6ml samples of suspension were withdrawn with the help of a syringe. Then the concentration of dye in each degraded sample was determined with a spectrophotometer at  $\lambda_{\max}$ =664nm. The decolorization efficiency (%) has been calculated as:

$$\text{efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where  $C_0$  is the initial concentration of dye and  $C$  is the concentration of dye after photoirradiation. Similar experiments were carried out by varying the pH of the solution (pH 2.5–9.7), concentration of dye (0.01-0.05mM) and catalyst loading (0.25–2.0 g/l).

The pH of the solution was adjusted initially by adding required amount of NaOH (for higher pH value) or C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> (for lower pH value) for exploring the effect of the pH, otherwise the experiments were carried at the original pH of the solution. Distilled, deionized water was used for all solutions. Photodecolorization was initiated by turning on the UV lamp.

## III. RESULTS AND DISCUSSION

### [1] Effect of Photocatalyst Loading

It should be examined to what extent the dyes are 'photolyzed' if no UV was used. In other words, it is important to estimate the contribution of UV in the overall PCD. Experiment in dark was carried out for the dye without UV for this purpose. It is also interesting to determine the minimum amount of catalyst required to decolorize the maximum

amount of dye at a particular experimental condition. For this, experiments were carried out varying the amount of ZnO photocatalyst for Methylene Blue.

The effect of catalyst loading on degradation of Methylene Blue was investigated by varying the amount of ZnO from 0.25 to 2.00 gL<sup>-1</sup> keeping all other parameters identical and the results are presented in Fig.2. Experiments performed with different concentrations of ZnO showed that with an increased catalyst loading from 0.0025 to 0.01 g in 100 ml in a set of runs dye degradation rate increases, beyond which it shows a significant reduction in dye degradation rate. Thus, the catalyst loading for maximum degradation of Methylene Blue was 0.01 g in 100 ml solution under the experimental conditions.

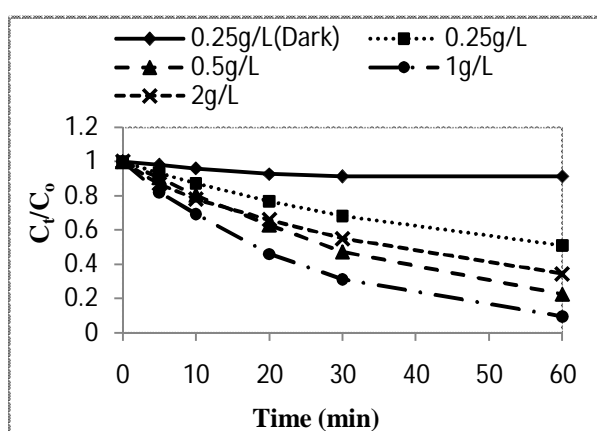


Fig. 2. Effect of ZnO dose on decolorization rate of MB dye. Experimental conditions: [MB]=0.01mM; [ZnO]=0.25g/L to 2.0g/L; Light source=UV; Reaction time=60min

Fig.3 also proves the highest rate constant for 1.0g/L ZnO.

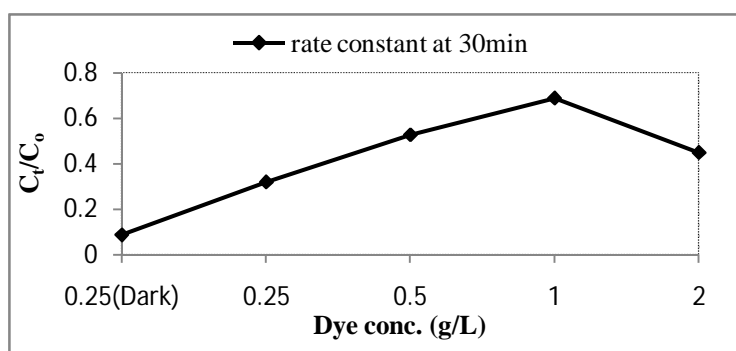


Fig. 3 Rate constant curve showing effect of ZnO concentration on MB decomposition. Experimental conditions: [MB]=0.01mM; [ZnO]=0.25g/L to 2.0g/L; Light source=UV; Reaction time=60min

This observation can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl, and superoxide radicals. When the concentration of ZnO catalyst increased above the limiting value, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Further, at high catalyst loading, it is difficult to maintain the suspension homogenous due to particles agglomeration, which decreases the number of active sites [11-14]. Since the most effective decomposition of Methylene Blue was observed with 1.0g/L of ZnO, the other experiments were performed in this concentration of ZnO.

[2] Effect of Initial Dye Concentration

The influence of initial concentration of MB solution on the photocatalytic degradation is an important aspect of the study. The effect of this parameter on the degree of photodegradation was studied by varying the initial concentration over a range of 0.01mM to 0.05mM. As the concentration of the dye was increased, the rate of photodecolorization decreased indicating for either to increase the catalyst dose or time span for the complete removal.

Fig. 4 depicts the time dependent graphs of decolorization of MB at different concentrations of dye solutions. The possible explanation for this behavior is that as the initial concentration of the dye increases, the solution became more intense colored and the path length of photons entering the solution decreased thereby only fewer photons reached the catalyst surface. And in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration [15]. The same effect was observed by Matthews [16] during the photocatalytic degradation of Methylene blue dye with TiO<sub>2</sub> catalyst.

This suggests that as the initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of ZnO is also constant. So the relative number of free radicals attacking the dye molecules decreases with increasing amount of the catalyst [17]. Hence, at higher concentration, degradation decreases at sufficiently longer distances from the light source or reaction zone due to the retardation of penetration of light. Thus, the rate of degradation decreases with increase in concentration of dyes.

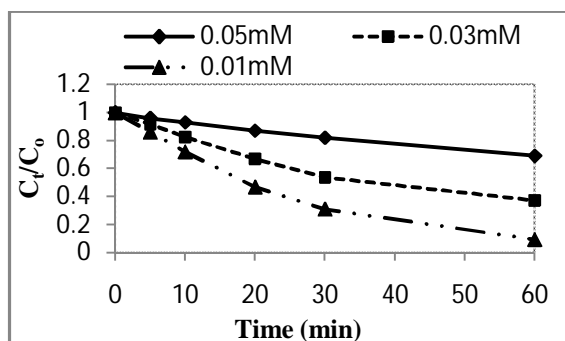


Fig. 4 Effect of initial concentration of MB dye on percentage decolorization. Experimental conditions: [MB]=0.01mM to 0.05mM; [ZnO]=1.0g/L; Light source: UV; Reaction time: 60min

These predictions are in good agreement with the experimental data which is clearly observed from rate constant curve shown in Fig.5. Here decomposition rate is the fastest for 0.01mM MB concentration.

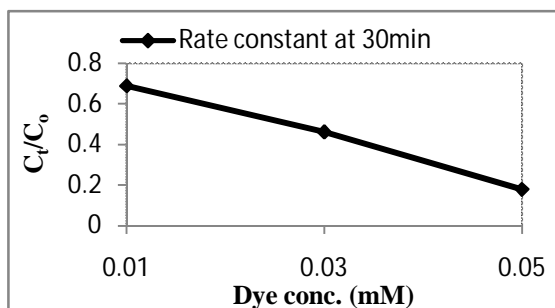


Fig. 5 Rate constant curve showing effect of MB dye concentration on MB decomposition. Experimental conditions: [MB]=0.01mM; [ZnO]=0.25g/L to 2.0g/L; Light source=UV; Reaction time=60min

### [3] Effect of pH

Because of the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surfaces is the pH of the dispersions since it influences the surface-charge-properties of the photocatalysts [18]. Further, industrial effluents may not be neutral. Therefore, the effect of pH on the rate of degradation needs to be considered. In order to investigate the effect of pH on the decolorization kinetics, experiments were conducted at different initial pH values.

In Fig.6 the degree of photodegradation of MB at a fixed reaction time (60 min) is reported in the pH range of 2.5–9.7 in an aqueous ZnO suspension. The results indicated that the degree of photodegradation increased with increasing pH. Similar behavior has also been reported for the photocatalytic efficiency of ZnO for decolorization of azo dyes [19-21]. The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task because of its multiple roles. It is related to the acid base property of the metal oxide surface and can be explained on the basis of zero point charge.

The zero point charge (zpc) for ZnO is  $9.0 \pm 0.3$  [22]. ZnO surface is positively charged below pH 9 and above this pH, surface is negatively charged by adsorbed  $\text{OH}^-$  ions. Below pH 9, active sites on the positively charged catalyst surface are preferentially covered by dye molecules, thus, surface concentration of the dye is relatively high, while those of  $\text{OH}^-$  and hydroxyl radical ( $\bullet\text{OH}$ ) are low. As the catalyst surface was covered by the dye molecules, the absorption of UV radiation on the catalyst surface decreased. Above pH 9 on the other hand, catalyst surface is negatively charged by means of metal-bound  $\text{OH}^-$ , consequently the surface concentration of the dye is low and that of hydroxyl radical is high. The presence of large quantities of  $\text{OH}^-$  ions on the particle surface as well as in the reaction medium favors the formation of  $\text{OH}\bullet$  radical, which is widely accepted as principal oxidizing species responsible for decolorization process at neutral or high pH levels and results in enhancement of the efficiency of the process [21].

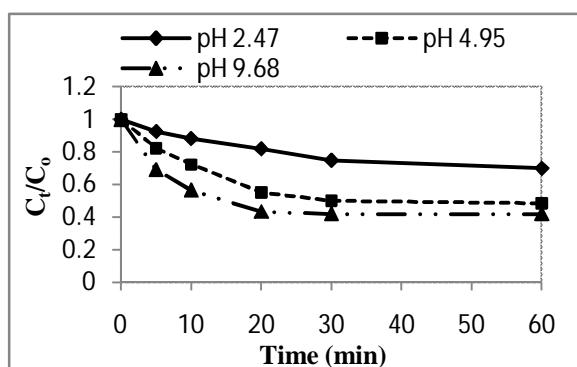


Fig. 6 Effect of pH on decolorization of dye. Experimental conditions: [MB]=0.01mM; [ZnO]=1.0g/L; pH=2.5-9.7; Light source: UV; Reaction time=60min

### [4] Effect of the Presence of Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )

It was experimented that the rate of decolorization rises by increasing the initial dosage of  $\text{H}_2\text{O}_2$  up to a “critical” value at which it is maximum and beyond which it is inhibited. When increasing quantities of  $\text{H}_2\text{O}_2$  are added to the solution, more hydroxyl radicals are available for dye oxidation, the fraction of light absorbed by the photo-decomposition increases, and, consequently, so does its photolysis rate. If additional of  $\text{H}_2\text{O}_2$  is used,  $\text{H}_2\text{O}_2$  acts as scavenger of highly reactive  $\text{OH}$  free radicals to form oxygen and peroxy radicals which are much less reactive. As a consequence, there should be a favorable hydrogen peroxide concentration for the effective removal of dyes, and the critical amount was 2ml  $\text{H}_2\text{O}_2$ , also reported by other researchers for various commercial dyes [23-26].

The presence of  $\text{H}_2\text{O}_2$  also affects the degradation rate of MB using ZnO as catalyst as shown in Fig.7. This prediction is in good agreement with the experimental data.

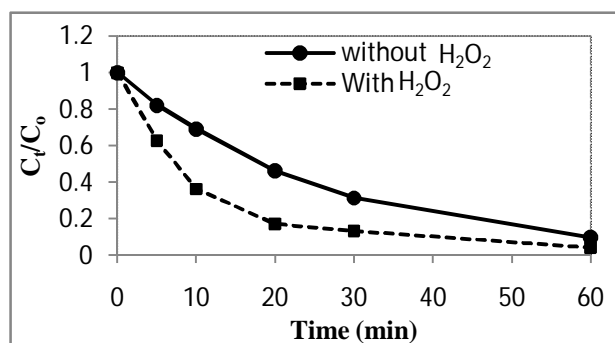


Fig. 7 Effect of H<sub>2</sub>O<sub>2</sub> presence in MB decomposition using ZnO as catalyst. Experimental conditions: [MB]=0.01mM; [ZnO]=1.0g/L; H<sub>2</sub>O<sub>2</sub>=2ml; Light source=UV; Reaction time: 30min

#### IV. CONCLUSION

In this study, photocatalytic decolourization of an azoreactive textile dye, Methylene Blue, has been investigated using ZnO powder catalyst. Effective degradation of MB is possible by photocatalysis in the presence of ZnO and UV light. The PCD efficiency has been generally, found to increase with increase in catalyst loading up to a limiting value, decrease in initial concentration, increase in pH, and in the presence of UV light. The proper addition of hydrogen peroxide could improve the photodegradation rate. We also learned that optimal amount of photocatalyst was 1.0g/L, with dye concentration of 0.01mM. ZnO gives better results in basic solution. The complete removal of color, after selection of desired operational parameters, could be achieved in a relatively short time of about 60 min. Therefore, this simple technology of PCD of the colored effluents has the potential to improve the quality of the wastewater from textile and other industries. The economy may be further improved using certain modifications.

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