



# Studies on Photo Catalytic Degradation of Methylene Green Using Nanoscale ZnO in the Presence of Visible and Solar Light Radiations

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## Abstract

Heterogenous photocatalytic oxidation is an effective method to remove low concentrations of organic dyes. The present work incorporates the study of efficiency of ZnO for photocatalytic degradation of Methylene Green dye. The disappearance of the dye has been monitored spectrophotometrically, followed pseudo-first order kinetics, according to Langmuir-Hinshelwood model. Effect of some factors such as catalyst dose, concentration of salt and pH etc., on degradation of the dye was examined. 97% of dye was degraded by the ZnO upon exposure to solar and visible light irradiation for 80 min. The reduction in COD values and increase in CO<sub>2</sub> values indicates the complete mineralization of Methylene Green dye.

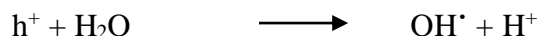
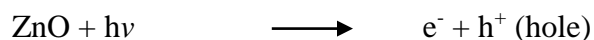
**Key words:** Advanced oxidation technologies (AOTs), Destruction of organic dyes, Hydrogen peroxide and hydroxyl radical

## Introduction

Color dye effluents from chemical & textile industries are sources of toxic matter that induce a lot of damage to the environment. Different methods such as precipitation, air stripping, flocculation, adsorption, reverse osmosis, ultra filtration etc. have been used for removal of them.

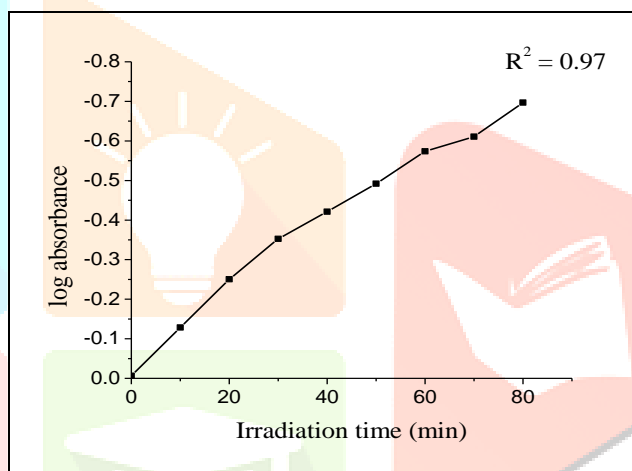
Nanostructured semiconductors are a potential candidate for the mineralization of toxic organic compounds, hazardous inorganic constituent<sup>1</sup>, and bacteria disinfection owing to its strong oxidizing ability, i.e., hydroxyl radical. Numerous metal oxides such as zinc oxide (ZnO), titanium dioxide (TiO<sub>2</sub>), strontium titanate (SrTiO<sub>3</sub>), tungsten oxide (WO<sub>3</sub>), silver nanoparticle, and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) are turned to be potential photocatalysts. ZnO has appeared to be a prominent catalyst as far as water detoxification is concerned; on accounting that, it produces H<sub>2</sub>O<sub>2</sub> more efficiently and shows high reaction and mineralization rates. In addition, it was reported that ZnO showed high surface reactivity due to its higher number of active sites. ZnO has been proven as a superior photocatalyst compared to commercial TiO<sub>2</sub> due to its higher initial rates of activities and absorption efficacy of solar radiations. As a result, ZnO has been widely used in the treatment of wastewater owing to its excellent chemical and physical properties<sup>1,2</sup>.

Semiconductor generates electron-hole pair on excitation which may be used either for reduction or oxidation of the dye<sup>3</sup>.



### Kinetic analysis of Methylene Green (MG)

The photocatalytic degradation of methylene green dye followed pseudo first order kinetics. The detection was realized at 600 nm. The absorbance of methylene green dye decreased with an increase in irradiation time. The plot of log absorbance *versus* time followed pseudo first order kinetics with correlation co-efficient of 0.98, rate constant of  $3.18 \times 10^{-4} \text{ s}^{-1}$  and half life time of  $2.17 \times 10^3 \text{ s}$  (Fig. 1).



**Fig. 1: Pseudo first order kinetics:**  $[\text{MG}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $\text{pH} = 11.0$ ,  $\text{ZnO} = 200 \text{ mg/100 mL}$ , Light intensity =  $27 \times 10^3 \text{ lux}$ , Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

Both ZnO and visible light source were necessary for the photodegradation reaction to occur. A control experiment was conducted by irradiating the dye methylene green under only visible light, in the presence of ZnO, with and without visible irradiation over a period of 80 min. No degradation was observed in the presence of only visible light. However, in the presence of ZnO without irradiation, a slight decrease in absorbance was observed which may be due the adsorption of the dye on to the surface of ZnO. However, on irradiating the dye with ZnO in aqueous slurry about 97 % of the dye got decolorised within 80 min.

### Experimental Method

The photocatalysis of dye was carried out in a solar and visible reactor in the presence of ZnO in media of different pH (4 to 12) with a maximum irradiation time of 1.5 h at room temperature. The reaction mixture (100 mL) was vigorously stirred during irradiation. The starting reaction mixture was kept 30 min conditioned in the dark under stirring to equilibrate. Samples of reaction mixtures (3 mL) were withdrawn, centrifuged and the absorption at 640 nm determined by spectrophotometer.

## Result and Discussions

### Effect of catalyst loading:

Use of excess catalyst is a waste and it also hinder the rate of degradation of organic compounds therefore, the choice of catalyst amount is important. The effect of catalyst loading on MB is given in table 1. The rate of degradation of the MB dye increased from  $1.23 \times 10^{-4} \text{ s}^{-1}$  to  $3.18 \times 10^{-4} \text{ s}^{-1}$  with the increase in amount of ZnO from 50 mg/100 mL to 200 mg/100 mL. Further increase in amount of ZnO from 200 mg/100 mL to 300 mg/100 mL resulted in decreased in rate constant from  $3.18 \times 10^{-4} \text{ s}^{-1}$  to  $1.76 \times 10^{-4} \text{ s}^{-1}$  of photocatalytic reaction. Rate constant has been found to be maximal at 200 mg/100 mL of ZnO amount. This observation indicated that beyond the optimum catalyst concentration, other factors affect the degradation of dyes. It is clear that the rate of degradation did not increase linearly with the increase in the amount of the catalyst in the reactor, and that a limiting rate was achieved when high amounts of ZnO are used. This could be explained on the fact that when low amount of ZnO was used, the rate of reaction on the ZnO surface area was limited and the reaction rate was proportional to the amount of ZnO particles. The attainment of limiting value and further decreased in the reaction rate with increase in the amount of catalyst might be due to (i) aggregation of ZnO particles at high concentrations causing decrease in the number of surface active sites and (ii) increase in opacity and light scattering of ZnO particles at high concentration leading to decrease in the passage of irradiation through the sample<sup>4,5</sup>.

**Table 1: Effect of catalyst loading:** [MG] =  $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ , pH = 11.0, Light intensity =  $27 \times 10^3 \text{ lux}$ , Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

ZnO 200 mg / 100mL	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
50	1.23	5.63
100	1.89	3.66
150	2.56	2.70
200	3.18	2.17
250	2.11	3.28
300	1.76	3.93

### Effect of substrate concentration:

It was important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the substrate concentration. It was noted that the degradation rate increased from  $1.05 \times 10^{-4} \text{ s}^{-1}$  to  $3.18 \times 10^{-4} \text{ s}^{-1}$  with the increase of dye concentration (from  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  to  $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ ). This increase was due to fact more dye

molecules were available in photoactive volume for the photo degradation process. Further increase of the dye concentration led to a decrease in the degradation rate might be due to the fact that the color of the irradiating mixture became more and more intense which prevented the penetration of light to the surface of the catalyst (Table 2). Hence, the generation of relative amount of  $\cdot\text{OH}$  radicals on the surface of the catalyst did not increase.<sup>6</sup>

**Table 2: Effect of substrate concentration:** ZnO = 200 mg/100 mL, pH = 11.0, Light intensity =  $24 \times 10^3$  lux, Temperature =  $30 \pm 0.3$  °C.

[MG] $\times 10^{-5}$ mol dm <sup>-3</sup>	k $\times 10^{-4}$ s <sup>-1</sup>	t <sub>1/2</sub> $\times 10^3$ s
1.0	1.05	6.60
2.0	1.79	3.87
3.0	2.21	3.13
4.0	3.18	2.17
5.0	2.91	2.38
6.0	2.30	2.70
7.0	1.64	4.22
8.0	1.31	5.29

### Effect of Temperature:

The influence of temperature was studied in the range 30-55°C. Rate constant was found to be increased from  $3.18 \times 10^{-4}$  s<sup>-1</sup> to  $3.70 \times 10^{-4}$  s<sup>-1</sup> with increase in temperature from 30-38°C (Table 3). Further increase in temperature reduced the rate constant. Increased temperature tends to reduce electron-hole recombination; however, an increase in temperature also decreases the solubility of oxygen in water<sup>7</sup>. The two above mentioned conflicting factors have been equipoise at 38°C.

**Table 3: Effect of temperature:**  $[MG] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $\text{pH} = 11.0$ ,  $\text{ZnO} = 200 \text{ mg/ 100 mL}$ ,  $\text{Light intensity} = 27 \times 10^3 \text{ lux}$ .

Temperature ( $^{\circ}\text{C}$ )	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
30	3.18	2.17
35	3.30	2.10
40	3.70	1.87
45	3.27	2.11
50	3.11	2.22
55	2.89	2.39

#### Effect of pH:

The interpretation of pH effect on photocatalytic degradation process was a very difficult task since it had multiple roles. Because of the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surface was the pH of the dispersions, since it influenced the surface charge properties of the photo catalyst. Therefore the role of initial pH on the degradation efficiency of MG was investigated in the pH range 5 to 13 (Table 4). The degradation efficiency increased from  $1.50 \times 10^{-4} \text{ s}^{-1}$  to  $3.18 \times 10^{-4} \text{ s}^{-1}$  with increase in pH from 5.0 to 11.0. At high pH values adsorb  $\text{OH}^-$  ions on the surface of the photocatalyst particles act as efficient traps for the photogenerated holes. On further increasing the pH value, the rate constant decreased up to  $2.13 \times 10^{-4} \text{ s}^{-1}$ . On increasing the pH above 5, the increased in reaction rate may be due to the preferential adsorption of  $\text{H}^+$  ions on the photocatalyst surface as compared to the cationic dye molecule. In the high basic medium, the rate of degradation was found to decrease due to competition between the  $\text{OH}^-$  groups to attach to the active site of catalyst. The rate of attachment of  $\text{OH}^-$  groups thus decreases with a resultant decrease in formation of  $\cdot\text{OH}$  free radicals decreased. The formation of  $\cdot\text{OH}$  radical in acidic medium was deferent from the basic medium<sup>8,9</sup>.

**Table 4: Effect of pH:** [MG] =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup>, ZnO = 200 mg/100 mL, Light intensity =  $27 \times 10^3$  lux, Temperature =  $30 \pm 0.3$  °C.

pH	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
5	1.50	4.62
6	1.65	4.20
7	1.88	3.68
8	2.32	2.98
9	2.54	2.72
10	2.90	2.38
11	3.18	2.17
12	2.80	2.47
13	2.13	3.25

**Effect of light intensity:**

Light intensity plays an important role in activating the suspended photocatalysts. The influence of light intensity on the rate of degradation has been examined at constant dye concentration ( $4.0 \times 10^{-5}$  mol dm<sup>-3</sup>) and catalyst loading (200 mg/100 mL). The rate constant values found to be increased from  $1.90 \times 10^{-4} \text{ s}^{-1}$  to  $4.66 \times 10^{-4} \text{ s}^{-1}$  on increasing light intensity from  $12 \times 10^3$  lux to  $56 \times 10^3$  lux (Table 5). This is because at higher intensity electron hole separation competes with electron hole recombination and results high reaction rate<sup>(10,11)</sup>.

**Table 5: Effect of light intensity:** [MG] =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup>, pH = 11.0, ZnO = 200 mg/100 mL, Temperature =  $30 \pm 0.3$  °C.

Light intensity $\times 10^3 \text{ lux}$	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
12	1.90	3.64
20	2.64	2.62
27	3.18	2.17
38	3.80	1.82
46	4.20	1.65
56	4.66	1.48

**Effect of NaCl and Na<sub>2</sub>CO<sub>3</sub>:**

The wastewater from dyeing operations normally contains considerable amount of carbonate ions and chloride ions as sodium carbonate and NaCl are the common auxiliary chemical used in textile processing operations for adjusting the pH of the dye bath. The photocatalytic degradation rate decreased with the increase in Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions concentration from  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> to  $11.0 \times 10^{-4}$  mol dm<sup>-3</sup> (Table 6). The cause of inhibition was due to the ability of these ions to act as hydroxyl radical ( $\cdot\text{OH}$ ) scavengers<sup>12,13</sup>.

**Table 6: Effect of salt:** [MG] =  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>, pH = 11.0, ZnO = 200 mg/100 mL, Light intensity =  $27 \times 10^3$  lux, Temperature =  $30 \pm 0.3$  °C

[Salt] × 10 <sup>-5</sup> mol dm <sup>-3</sup>	NaCl		Na <sub>2</sub> CO <sub>3</sub>	
	k × 10 <sup>-4</sup> s <sup>-1</sup>	t <sub>1/2</sub> × 10 <sup>3</sup> s	k × 10 <sup>-4</sup> s <sup>-1</sup>	t <sub>1/2</sub> × 10 <sup>3</sup> s
0.0	3.18	2.17	3.18	2.17
1.0	2.89	2.39	2.98	3.32
3.0	2.55	2.71	2.57	2.69
5.0	2.31	3.0	2.35	2.94
7.0	2.13	3.25	1.89	3.66
9.0	1.80	3.85	1.70	4.07
11.0	1.62	4.27	1.44	4.81

**Chemical oxygen demand (COD) and free CO<sub>2</sub> measurement during photo degradation process:**

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO<sub>2</sub> and water. In the present work results of chemical oxygen demand were taken as one of the parameter to judge the feasibility of the photochemical process for the degradation of Direct Blue dye solution. The open reflux method was applied for COD determination and the treated solution showed a significant decrease in the COD value of the initial color solution from 400 to 1 mg/100mL while there was an increased in CO<sub>2</sub> values and inorganic ions. A decrease in pH and increase in conductivity of solution was observed with increase in the extent of degradation (Table 7).

**Table 7: COD and free CO<sub>2</sub> measurement during photodegradation process:**

[MG] =  $5 \times 10^{-5}$  mol, ZnO = 200 mg/100 ml, pH = 11.0, Light intensity =  $27 \times 10^3$  lux, Temperature =  $30 \pm 0.3$  °C.

Time (h)	COD (mg/L)	CO <sub>2</sub> (mg/L)	Efficiency (%)	NO <sub>3</sub> <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	Conductivity (mS/cm)
0	440	6	0	0	0	0.101
1	330	22.2	25	3	2.0	0.112
2	261	51	40	4.7	5.0	0.132
3	210	67.5	52	8.0	7.5	0.154
4	145	90.5	67	15.0	11.4	0.161
5	77	119	82	24.1	18.0	0.190
6	34	165	92	27.0	23.0	0.245
7	5	212	98	31.1	28.2	0.298

### Kinetics of Photocatalytic degradation of dyes MG:

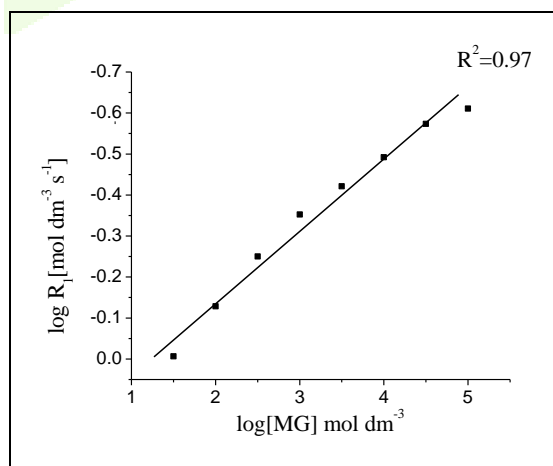
Langmuir-Hinshelwood theory is the most commonly used kinetic model for describing photocatalytic behaviors. As the degradation process proceeds with the illumination of many unstable intermediate species which finally mineralized into inorganic ions and CO<sub>2</sub>. The degradation process is very complex in nature. Therefore, degradation process is considered under the two parallel branches of photocatalysis (R<sub>1</sub>) and photolysis (R<sub>2</sub>).

$$R = R_1 + R_2$$

Where, R, R<sub>1</sub> and R<sub>2</sub> are the net degradation, photocatalysis and photolysis respectively.

But, under chosen experimental condition, photolysis has no effect on degradation process.

The rate constant for degradation of MG (Fig. 2) has been found to be  $6.6 \times 10^{-3}$  (mol dm<sup>-3</sup>) s<sup>-1</sup>.

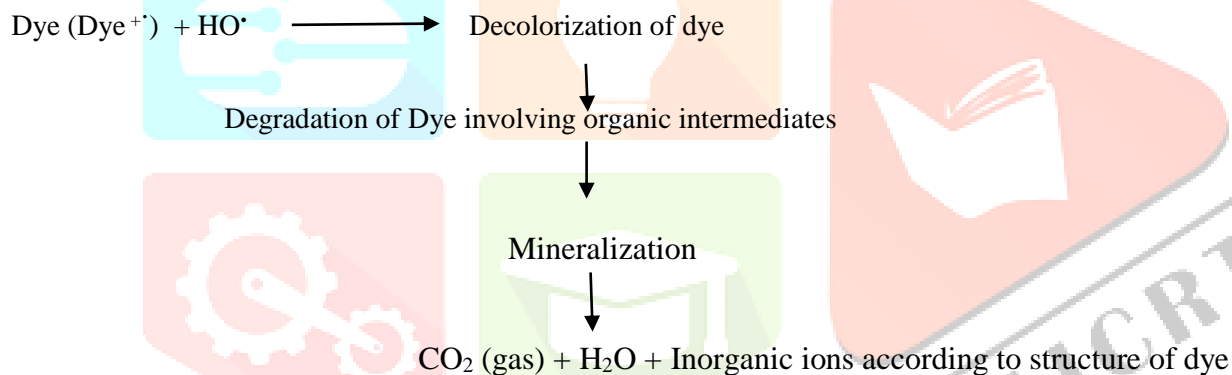


**Fig. 2: The variation of MG degradation rate versus its concentration for photocatalysis: ZnO = 200 mg/100 mL, lux, pH = 11.0, Light intensity =  $27 \times 10^3$ , Temperature =  $30 \pm 0.3$  °C.**



**Photocatalytic degradation mechanism:**

A mechanism of a chemical reaction is a mental model envisaged on the sound basis of experimental findings and mathematical modeling. Numerous mechanisms have been proposed by various workers for many different photocatalytic systems. A pertinent mechanism helps in optimizing most possible reaction conditions. Difference in substrate, nature of photocatalyst and type of radiation / light source lead to a pertinent mechanism. When ZnO the photocatalyst under investigation was illuminated with visible radiation, generation of electron/hole pairs with free electrons produced in the nearby free conduction band leaving positive holes in valence band. The holes at ZnO valence band can oxidize adsorbed water molecules or hydroxide radicals to produce hydroxyl radicals, a very strong oxidizing agent to the dye under investigation. The electron may in the conduction band react with adsorbed oxygen on the surface and the dye molecule. Moreover, they can react with deliquescent oxygen and water in suspended liquid and produce perhydroxyl radicals ( $\text{HO}_2^\cdot$ ) with high chemical activity. There is parallel phenomenon operative. The dye molecules are well known to act as a sensitizer; therefore, on absorption of visible light they transfer photogenerated electrons from the dye molecule to semiconductor<sup>14</sup>. The mechanism of semiconductor photocatalysis is of very complex nature. Dye molecules interact with  $\text{O}_2^\cdot$ ,  $\cdot\text{OH}_2$ , or  $\text{OH}^\cdot$  species to generate intermediates ultimately lead to the formation of degradation products. Hydroxyl radical ( $\text{OH}^\cdot$ ) being very strong oxidizing agent (standard oxidation potential 2.8 eV) mineralizes dye to end product<sup>(15,16)</sup>.



As the degradation process proceeds with the illumination of many unstable intermediate species which finally mineralized into inorganic ions and  $\text{CO}_2$ . The value of COD and  $\text{CO}_2$  also confirmed the complete mineralization of dye. For reactions conducted under different experimental conditions, variations in other factors, such as catalysts load, pH, and light intensity will also be taken into consideration. Additional terms must be added into the solution for the general Langmuir-Hinshelwood model to represent these variations. Additionally, in the Langmuir-Hinshelwood model the reaction is assumed to be a single-step reaction, which is not true for the case in reality.

**Conclusion:**

We have shown that degradation using visible and solar light in conjunction with ZnO is a very promising and implementable for the degradation of organic matter for wastewater treatment in small or large scale. It was observed that pH, catalyst concentration and electron scavengers ( $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$ ) all significantly affect the photocatalytic degradation of Methylene Green. The results of the study indicate that ZnO is very effective in enhancing the photocatalytic degradation of the dye Methylene Green. The best reaction dosage of ZnO catalysts is about 200

mg/100 mL. Study of results of the degradation rate of Methylene Green under investigation revealed that the degradation rate was function of pH of the system. The degradation rate is much faster at pH 11.

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