

# Photocatalytic Degradation of Methylene Green In Aqueous Suspension of ZnO Using Visible Irradiation

Dr. Hitendra Singh Tomar<sup>1</sup>, Sonam Dawar<sup>2</sup>

<sup>1</sup>Govt. Polytechnic College, Agar Malwa (M.P)

<sup>2</sup>School of Studies in Chemistry and Biochemistry, Vikram University, Ujjain,

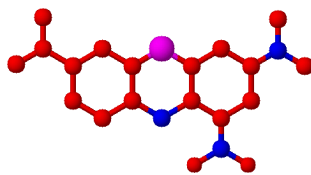
## Abstract:

A study of photocatalytic degradation of the methylene green dye has been carried out in aqueous heterogeneous medium using ZnO as photo-catalyst in a batch reactor. The disappearance of the dye was monitored by spectrophotometric method and found that it follows pseudo-first order kinetics generally according to the Langmuir-Hinshelwood model. The total degradation of dye was studied using chemical oxygen demand (COD) method. The addition of an optimal amount of hydrogen peroxide and potassium persulphate increase the degradation rate while NaCl and Na<sub>2</sub>CO<sub>3</sub> decrease the rate of degradation. The effect of addition of cationic and anionic surfactants has also been investigated. Bubbling of nitrogen in the reaction solution decreases the reaction rate. ZnO has been found experimentally to be a highly efficient photo catalyst for the degradation of methylene green dye.

**Keywords:** methylene green, Photocatalytic degradation, ZnO, Mineralization

## 1. INTRODUCTION

Dye pollutants are major source of environmental concern. The release of wastewater containing dye in the ecosystem is a dramatic source of aesthetic pollution and perturbations in aquatic life. [1, 2] Most of the organic dyes are not easily degradable by standard methods reported such as adsorption on activated carbon, ultra-filtration, reverse osmosis, coagulation, ion exchange and oxidation with peroxide etc. [3-5] Recently, the efficiency of advanced oxidation processes (AOP) for the degradation of recalcitrant compounds has been extensively used. The key advantage of this degradation method is that it can be carried out under ambient conditions and lead to complete mineralization of organic compounds. In pursuit of a better method for the detoxification of colored wastewater, heterogeneous photocatalysis stands uppermost. Many researchers have been attempting the photocatalytic degradation of dyes [6-8] using various photocatalysts, mainly with TiO<sub>2</sub>/UV system but absorption of only small range of solar energy, it is essential to shift the absorption threshold towards the visible region. Keeping this in mind we have undertaken the ZnO assisted photocatalytic degradation of acridine yellow in the visible light. Acridine yellow is a water-soluble dye. It is used widely in coloration of leather and paper etc. Structure of Methylene green is shown in **Figure 1**.



**Figure 1:** Methylene Green

## 2. EXPERIMENTAL PROCEDURE

All the chemicals used were of AR grade. Solutions were prepared by dissolving the desired amount of compound in distilled water. The photocatalytic reaction was carried out in a batch reactor with dimension of 7.5 × 6.0cm provided with a water circulation arrangement in order to maintain the temperature in the range of 25-30°C. The irradiation was carried out using a 500W halogen lamp. In all cases during the photolysis experiments, the slurry composed of the dye solution and catalyst was placed in the reactor and stirred magnetically with simultaneous exposure to visible light. The samples were withdrawn at periodic intervals from the reactor to assess the extent of decolourisation and degradation. Digital lux meter (Lutron LX-101) was used to measure the intensity of light. The pH was constantly monitored using pH meter. Absorbance of reaction mixture at different time intervals was measured at 490nm using UV-Vis spectrophotometer (Systronic 106). The chemical oxygen demand (COD) was measured by the closed reflux method using potassium dichromate as the oxidant under acidic condition. The amount of unreacted oxidant was determined by titration with ferrous ammonium sulphate using feroin indicator. [9]

The photodegradation efficiency for each sample was calculated from the following expression:

$$\eta = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (1)$$

Where,  $\eta$  is photodegradation efficiency;  $\text{COD}_0$  and  $\text{COD}_t$  are COD of dye solution before irradiation and after irradiation for time  $t$  respectively.

## 3. RESULT AND DISCUSSION

### A. Effect of dye concentration

The graphical depiction of photo catalytic degradation of  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  dye solution containing 250 mg ZnO is in (table-1). The change in concentration of the dye in the solution is plotted as a function of irradiation time. It is seen that 95% of the initial concentration of the dye was removed after 140minutes hrs irradiation and complete decolourisation was observed with 150 minutes irradiation time.

**Table-1: Effect of irradiation period**

S.No.	Irradiation Period (min)	COD ( $\text{mg dm}^{-3}$ ) %	Degradation (%)
1	0	100	0
2	30	82	18
3	60	54	46
4	90	46	54
5	120	26	74
6	150	00	100

[MG] =  $2.0 \times 10^{-5}$  mol dm<sup>-3</sup> Amount of ZnO = 200mg/50ml

In contrast negligible decrease in the concentration of dye was observed by irradiation in the absence of ZnO or in the presence of ZnO without light source (Fig.[MG] - 2). The effect of initial concentration of the solute in the photocatalytic degradation rate is described by pseudo first order kinetics. This is rationalized in terms of the Langmuir-Hinshelwood model modified to accommodate reactions occurring at a solid-liquid interface as

$$r_0 = \frac{-dc}{dt} = \frac{k_r KC_0}{(1 + KC_0)} \quad (1)$$

Where r is the rate of disappearance of the dye and C is the initial concentration of the dye. K represents the equilibrium constant for adsorption of the dye on ZnO particles and k<sub>r</sub> represents The limiting rate of the reaction at maximum coverage under the experimental conditions. The integrated form

$$t = \frac{1}{Kk_r} \ln \frac{C_0}{C} + \frac{(C_0 - C)}{k_r} \quad (2)$$

Where t is the time in minutes required for the initial concentration of dye C<sub>0</sub> to become C. At low concentration of the dye the second term in equation (2) is negligible compared to the first term. On neglecting the second term the final form of the equation is

$$\ln \frac{C_0}{C} = tKk_r = k't \quad (3)$$

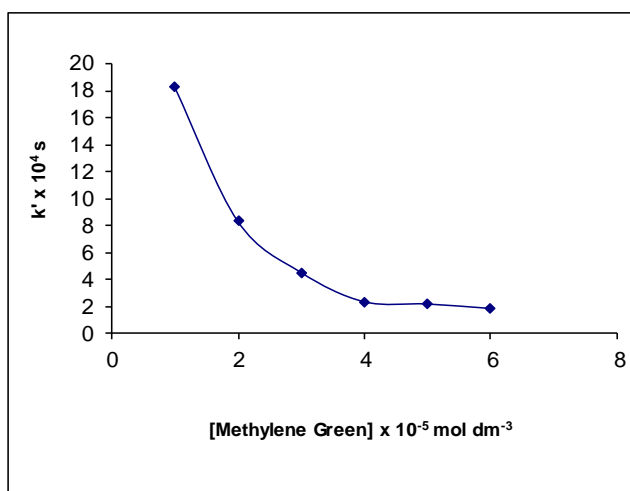
Where k' is the apparent rate constant of the photocatalytic degradation.

$$t_{1/2} = \frac{0.693}{k'} \quad (4)$$

The decrease of k' values with increase in initial concentration of the dye can be ascribed to the decrease in the path length of photons entering the solution due to impermeability of the dye solution. At low concentration the reverse effect observed, there by increasing the number of photon absorption by the catalyst. This decreasing phenomenon can further be explained in terms of the increase in requirement of catalyst surface for the increased concentration of the dye. But here the irradiation time and amountt of catalyst has been kept constant. Hence the relative numbers of O<sub>2</sub><sup>•</sup> and OH<sup>•</sup> radicals formed on the surface of ZnO are also constant. As a result the relative number of O<sub>2</sub><sup>•</sup>& OH<sup>•</sup> attacking the dye molecule decreases with increasing initial concentration of the dye. Hence, the rate of degradation decreases considerably with increase in concentration of the dye. The plot of C<sub>0</sub> versus t<sub>1/2</sub> should yield a straight line of which the slope is 1/k' and the intercept is 0.693/k<sub>r</sub>K. The k<sub>r</sub> and K values were calculated from the slope of the straight line and the intercept respectively. The product of k<sub>r</sub>K = 18.3 x 10<sup>4</sup> s represents the apparent rate constant k' for low initial concentration of the dye and is in agreement with the values obtained from equation 3 (Fig.[MG] - 3).

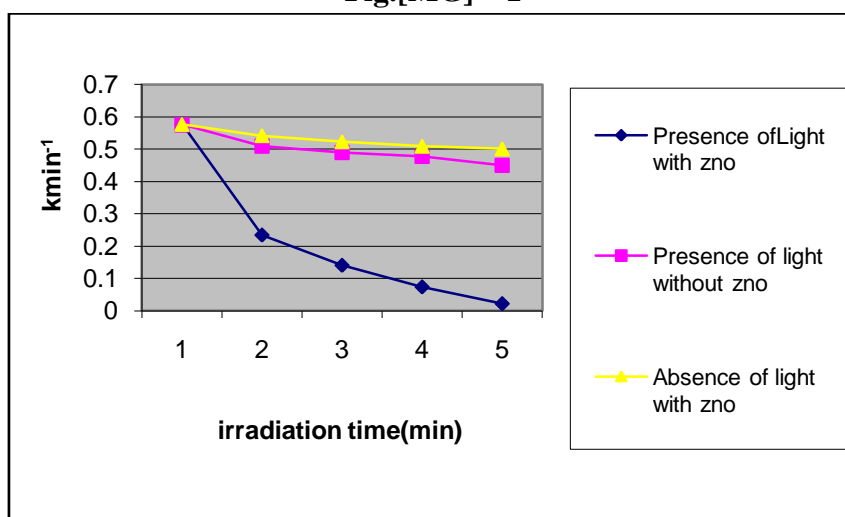
**Table-2:** Effect of dye concentration

S.No.	[AY] x 10 <sup>-5</sup> mol dm <sup>-3</sup>	t <sub>1/2</sub> x 10 <sup>-3</sup> s <sup>-1</sup>	k' x 10 <sup>-4</sup> s
1	1.0	0.36	18.3
2	2.0	0.79	8.32
3	3.0	1.53	4.51
4	4.0	2.97	2.23
5	5.0	3.19	2.16
6	6.0	3.78	1.83



Light intensity=17.5x10<sup>3</sup>lux , Amount of ZnO = 200 mg

**Fig.[MG] – 1**



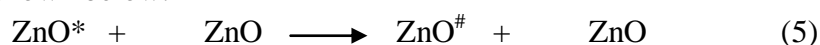
**B. Effect of ZnO loading**

The effect of change in the amount of photocatalyst was performed in the range of 200-600mg/50ml of the dye solution (Table -3). For the dye concentration of 2.0 x 10<sup>-5</sup> mol dm<sup>-3</sup> the change in the ZnO amount from 200-300mg/50ml has increased the apparent rate constant from 8.66 x 10<sup>4</sup> s to 10.6 x 10<sup>4</sup> s and decreased the t<sub>1/2</sub> value from .79 x 10<sup>3</sup> s to .60 x 10<sup>3</sup> s.

**Table-3:** Effect of ZnO Loading

S. No.	Amount of ZnO(mg)	$k' \times 10^4 \text{ s}$	$t_{1/2} \times 10^{-3} \text{ s}^{-1}$
1	200	8.66	0.79
2	300	10.6	0.60
3	400	8.83	0.78
4	500	5.16	1.33
5	600	5.00	1.38

Experimental studies have revealed that the catalyst loading of 300mg/50ml as the optimal dose for the degradation of  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  dye in 1.00 hrs irradiation. Further increase in the amount of ZnO to 600mg, has decreased the  $k'$  value and increased  $t_{1/2}$  values. These observations can be rationalised in terms of availability of active sites on ZnO surface and the penetration of photoactivating light into the suspension. Owing to an increase in the number of ZnO particle as the concentration of catalyst increased the availability of active sites increases but the light penetration and hence the photoactivated volume of the suspension shrinks. The trade off between these two effects is that at low solute concentration, when there are excess active sites, the balance between the opposing effects is evenly poised and change in the amount of ZnO makes little difference to the reaction rate. At high solute concentration availability of excess active sites outweighs the diminishing photoactivated volume and substantially high  $k'$  value is obtained at increase in ZnO concentration. The increased amount of ZnO increase the quantity of photons absorbed as well. Further increase in catalyst concentration beyond 300mg/50ml may result in deactivation of activated molecules due to collision with ground state molecules as shown below.



**ZnO\*** : ZnO with active species adsorbed on its surface

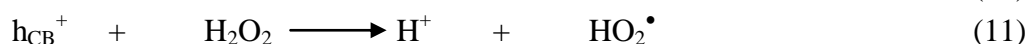
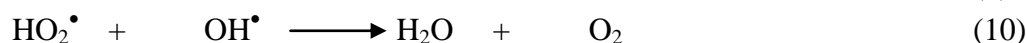
**ZnO<sup>#</sup>** : deactivated form of ZnO\* shielding by ZnO may also take place.

### C. Effect of H<sub>2</sub>O<sub>2</sub>

The decolorization of the dye solution found to be severely affected by the addition of hydrogen peroxide. On adding H<sub>2</sub>O<sub>2</sub> in the concentration range from  $2.0 \times 10^{-3}$  to  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ , rate constant values first increases but after reaching a maxima a fall in the  $k'$  values was found. The initial increase in the reaction rate on addition of H<sub>2</sub>O<sub>2</sub> can be attributed to the formation of OH<sup>•</sup> radicals responsible for the photocatalytic oxidation and it inhibits the electron-hole recombination as well. The oxidizing power of hydrogen radical is 2.05 times more than chlorine, 1.58 times more than H<sub>2</sub>O<sub>2</sub> & 1.35 times more than ozone [16,17]. H<sub>2</sub>O<sub>2</sub> increases the rate of hydroxyl radical formation through three ways: Firstly, it could act as an alternative electron acceptor to oxygen (equation-7), which might restrain the bulk composite of the photo-excited electrons and holes. This should consequently increase the rate of photocatalytic process. Secondly, the reduction of H<sub>2</sub>O<sub>2</sub> at the conductance band would also produce hydroxyl radicals. Even if H<sub>2</sub>O<sub>2</sub> was not reduced at the conductance band it could accept an electron from superoxide again producing hydroxyl radicals (equation-6). Thirdly, the self- decomposition by illumination would also produce hydroxyl radicals (equation-8):



At high concentration, the hydrogen peroxide adsorbed on the photocatalytic surface could effectively scavenge not only the photocatalytic surface formed  $\cdot OH$  radicals (equation 9 and 10) but also the photo-generated holes ( $h_{CB}^+$ ) (equation-11) and thus inhibit the major pathway for heterogeneous generation of  $\cdot OH$  radicals:

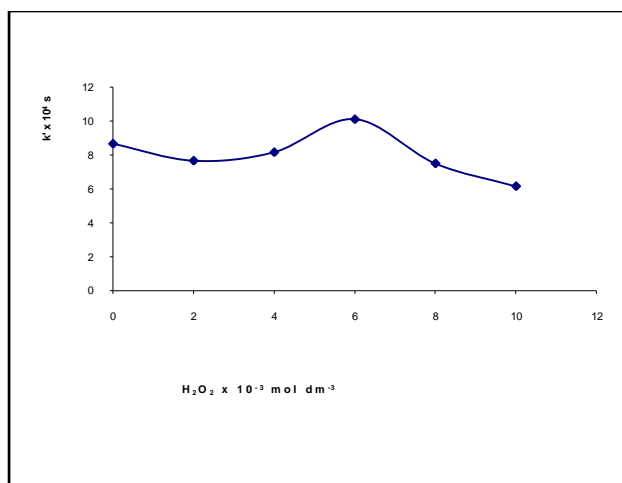


It is worth mentioning here that  $HO_2\cdot$  radicals are less reactive than  $OH\cdot$ , therefore, have negligible contribution in the dye degradation.

**Table 4:** Effect of Effect of hydrogen per oxide

Concentration of $k' \times 10^4$ s	$t_{1/2} \times 10^{-3} s^{-1}$	$[H_2O_2] \times 10^{-4} mol$ $dm^{-3}$
8.66	0.79	0.0
7.66	0.90	2.0
8.16	0.84	4.0
10.1	0.67	6.0
7.50	0.92	8.0
6.16	1.12	10

Initial concentration of Dye =  $2.0 \times 10^{-5} mol dm^{-3}$       Amount of ZnO = 200 mg  
Intensity of light =  $17.5 \times 10^3 lux$



#### D. Effect of irradiation time

Table-1 present the % degradation of the dye at different irradiation period at optimum catalyst loading and dye concentration. Under the experimental condition complete degradation of the dye occurred within 150min of irradiation. The photocatalytic degradation of the dye takes place on the surface of ZnO where  $\cdot OH$  and  $O_2\cdot$  radicals are trapped in the holes of reactive species. Oxygen and water are essential for photocatalytic degradation. The  $\cdot OH$  radicals are strong enough to break the bonds in the

dye molecules adsorbed on the surface of ZnO. When the intensity of light and concentration of dye are constant, the number of  $\cdot\text{OH}$  and  $\text{O}_2\cdot^-$  radicals increase with increase in irradiation period and hence the dye molecules are completely degraded into smaller fragments.

### E. Effect of pH

pH of  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  aqueous dye solution was 6.23. At this pH,  $k'$  value was found to be  $8.66 \times 10^4 \text{ s}$  and corresponding  $t_{1/2}$  value was  $0.79 \times 10^3 \text{ s}$  for an irradiation period of 1 hr (Table-5). pH can be one of the most important parameters for the photocatalytic process and it was of influence on the photooxidation of MG. The presence of the solid-electrolyte interface i.e. the electrical double layer, are modified as the pH of the medium changes and, consequently, the effectiveness of the adsorption-desorption process and spectrum of the photogenerated electron-hole pairs also substantially affected.

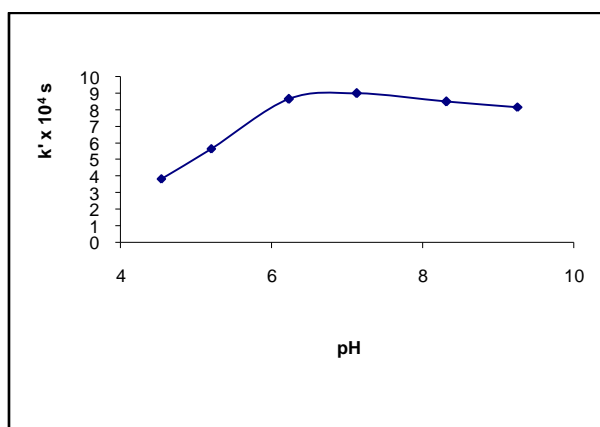
In (Fig. [MG]–6), the initial reaction rate values of the photooxidation of MG are shown in the pH range from 4.5 – 9.2. For the alteration of pH in the acid and alkaline area 5M  $\text{H}_2\text{SO}_4$  and 5M NaOH solutions respectively have been used. At pH values beyond that range a vigorous change of the adsorption spectrum of MG was observed, thus preventing comparison of the results.

For ZnO system a sharper increase is observed as pH is increased from 4 to 8. At pH 8 the maximum initial rate is achieved and increasing further the pH values the photodegradation rate of MG decreases. The low initial reaction rates at acidic or at alkali pH values due to dissolution and photodissolution of ZnO. The semiconductor oxide present an amphoteric behaviour. At acidic pH, ZnO can react with acids to produce the corresponding salt and at alkaline pH, it can react with a base to form complexes like  $[\text{Zn}(\text{OH})_4]^{2-}$ .

**Table 5:** Effect of pH on photodegradation

pH ( $\text{min}^{-1}$ )	$k' \times 10^4 \text{ s}$	$t_{1/2} \times 10^{-3} \text{ s}^{-1}$
4.54	3.83	1.80
5.20	5.66	0.60
6.23	8.66	0.79
7.13	9.00	0.77
8.32	8.50	0.81
9.26	8.16	0.84

Initial concentration of dye =  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ , Amount of ZnO = 200 mg, Intensity of light =  $17.5 \times 10^3 \text{ lux}$



### F. Effect of persulphate ion

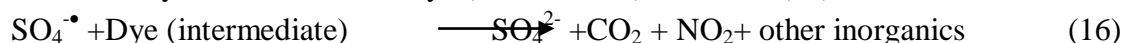
The effect of persulphate ion (electron scavenger) on the photocatalytic degradation was investigated by varying its concentration from  $1.0 \times 10^{-6}$  to  $2.0 \times 10^{-5}$  mol dm<sup>-3</sup> (Table-6). Rate constant values were found to increase with increasing amount of persulphate ion and attained an optimum value for  $5.0 \times 10^{-6}$  mol dm<sup>-3</sup>. The increase in  $k'$  values may be due to the formation of  $\text{SO}_4^{\cdot-}$  as



The sulphate radical anion ( $\text{SO}_4^{\cdot-}$ ) thus formed is a sufficiently strong oxidant ( $E^\circ = 2.6\text{eV}$ ) and may act in following three possible ways with organic compounds (i) by abstracting a hydrogen atom from saturated carbon, (ii) by adding to unsaturated or aromatic carbon and (iii) by removing one electron from the carboxylate anions and from certain neutral molecules. In addition, it can trap the photogenerated electron and/or generate hydroxyl radicals.



The hydroxyl radical and sulphate radical anion being powerful oxidants degrade the dye molecule at a faster rate. The  $\text{SO}_4^{\cdot-}$  has the unique nature of attacking the dye molecule at various positions and hence the fragmentation of the dye molecules is rapid.

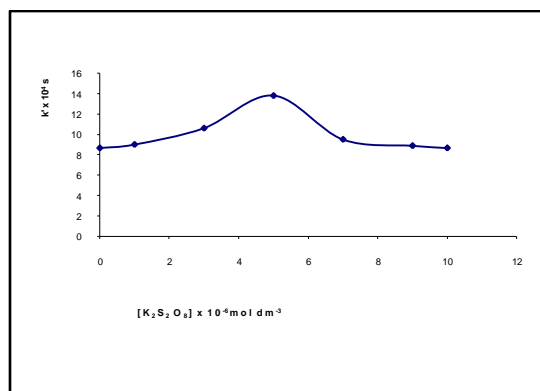


Further increase in persulphate concentration has decreased the degradation rate owing to the adsorption of sulphate ions formed during the reaction on the surface of ZnO deactivating a section of the catalyst.

**Table 6: Effect of Potassium Persulphate**

$[\text{K}_2\text{S}_2\text{O}_8] \times 10^{-6}$ mol dm <sup>-3</sup>	$k' \times 10^4$ s	$t_{1/2} \times 10^{-3}$ s <sup>-1</sup>
0	8.66	0.79
1.0	9.00	0.76
3.0	10.6	0.60
5.0	13.8	0.49
7.0	9.50	0.72
9.0	8.88	0.78
10.0	8.66	0.79

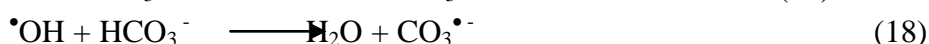
Initial concentration of Dye =  $2.0 \times 10^{-5}$  mol dm<sup>-3</sup>, Amount of ZnO = 200 mg, Intensity of light =  $17.5 \times 10^3$  lux





### G. Effect of sodium carbonate

For the fixing of dye on the fabrics and fastness of the colour sodium carbonate is often used. Consequently, the wastewater from the dyeing operation contains substantial amount of carbonate ions. Hence, it is important to study the effect of carbonate ions in the photodegradation efficiency. Experiments were performed with sodium carbonate in the range  $4.0 \times 10^{-6}$  to  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup>. It is observed that k' value gradually decreases with increasing amount of carbonate ion (Table-7). The decrease in the rate of degradation in the presence of carbonate ion is due to the hydroxyl scavenging property of carbonate ions as evident from the following reactions:

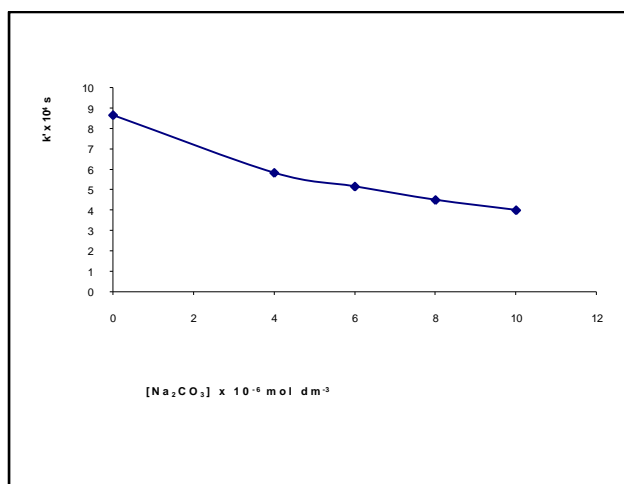


Hence, auxiliary chemicals like sodium carbonate may hinder the photocatalytic degradation of dyes.

**Table 7:** Effect of Sodium carbonate

[Na <sub>2</sub> CO <sub>3</sub> ] x 10 <sup>-6</sup> mol dm <sup>-3</sup>	k' x 10 <sup>4</sup> s	t <sub>1/2</sub> x 10 <sup>-3</sup> s <sup>-1</sup>
0	8.66	0.79
4.0	5.83	1.14
6.0	5.16	1.33
8.0	4.50	1.53
1.0	4.00	1.72

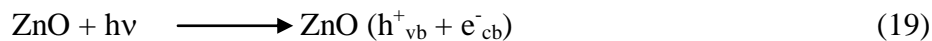
Initial concentration of Dye =  $2.0 \times 10^{-5}$  mol dm<sup>-3</sup>, Amount of ZnO = 200 mg,  
Intensity of light =  $17.5 \times 10^3$  lux



### H. Effect of sodium chloride

The photocatalytic degradation efficiency was considerably decreased upon the addition of inert salts like sodium chloride, sodium sulphate and sodium phosphate. Hence, the effect of chloride ions on the photocatalytic degradation was studied. Photodegradation studies were carried out with sodium chloride in the range  $3.0 \times 10^{-6}$  to  $10 \times 10^{-6}$  mol dm<sup>-3</sup> keeping dye solution concentration of  $2.0 \times 10^{-5}$  mol dm<sup>-3</sup>. k' value of the degradation process decreases gradually with increase in the amount of chloride ions (

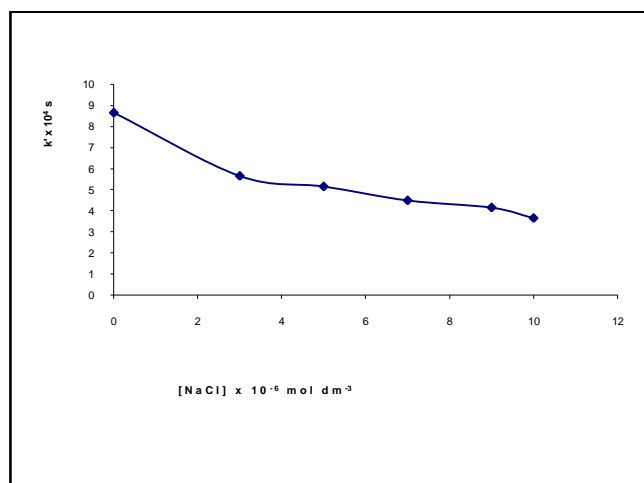
Table-8). The decrease in the % degradation of the dye in the presence of chloride ions is due to the hole scavenging properties of these ions as shown in the following reaction sequence. This is a typical example for competitive inhibition.



**Table 8:** Effect of Sodium chloride

[NaCl] x 10 <sup>-5</sup> mol dm <sup>-3</sup>	k' x 10 <sup>4</sup> s	t <sub>1/2</sub> x 10 <sup>-3</sup> s <sup>-1</sup>
0	8.66	0.79
3.0	5.66	1.20
5.0	5.16	1.32
7.0	4.50	1.50
9.0	4.16	1.62
10	3.66	1.86

Initial concentration of Dye = 2.0x10<sup>-5</sup> mol dm<sup>-3</sup>, Amount of ZnO = 200 mg, Intensity of light = 17.5x10<sup>3</sup> lux



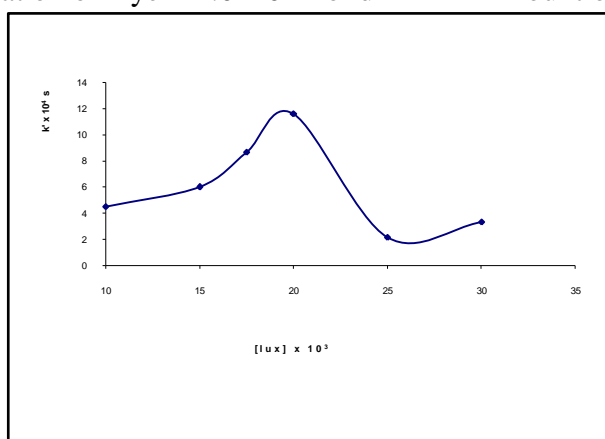
### I. Effect of the light Intensity

The influence of light intensity on the rate of degradation has been examined at constant dye concentration (2.0 x 10<sup>-5</sup> mol dm<sup>-3</sup>) and catalyst loading (200mg/50ml). It is evident that the rate of decolourization and photodegradation increases with increasing light intensity (Table-9), because the visible radiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is independent on light intensity. The rate of degradation increases (Fig.[MG] -10) with increased radiation on the catalyst surface resulting in more hydroxyl radicals.

**Table 9:** Effect of Light Intensity

Light Intensity x 10 <sup>3</sup> lux	k' x 10 <sup>4</sup> s	t <sub>1/2</sub> x 10 <sup>-3</sup> s <sup>-1</sup>
10.0	4.50	1.53
15.0	6.00	1.15
17.5	8.66	0.73
20.0	11.6	0.59
25.0	2.16	0.31
30.0	3.33	0.20

Initial concentration of Dye = 2.0x10<sup>-5</sup> mol dm<sup>-3</sup> Amount of ZnO = 200 mg



### J. Effect of other photocatalysts

Experiments were performed with other photocatalysts as well (Table-10). Generally, semiconductors having large band gaps are good photocatalysts. It has already been reported that semiconductors such as ZnO and TiO<sub>2</sub> have band gaps larger than 3 eV show strong photocatalytic activity. The conduction and valence band potentials of both ZnO and TiO<sub>2</sub> are larger than the corresponding redox potentials of H<sup>+</sup>/H<sub>2</sub> and H<sub>2</sub>O/O<sub>2</sub> and the photogenerated electron and hole can be separated efficiently. CdS with smaller band gaps show less activity since its conduction band is much lower than that of ZnO and TiO<sub>2</sub>. Electron (CB) in these semiconductors rapidly falls into the hole thus showing reduced activity.

**Table10:** Effect of other photocatalysts

Photocatalyst	k' x 10 <sup>4</sup> s	Band gap (eV)
ZnO	8.66	3.2
TiO <sub>2</sub>	7.66	3.1
CdS	5.50	2.3

Initial concentration of Dye = 2.0x10<sup>-5</sup> mol dm<sup>-3</sup>, Amount of catalyst = 200 mg, Light intensity = 17.5x10<sup>3</sup> lux

### K. Effect of bubbling of nitrogen

The effect of bubbling of nitrogen through the aqueous suspension of the dye on the reaction rate constants has been studied. It is observed that photodegradation is severely retarded by bubbling of pure nitrogen because the dissolved oxygen in the solution plays an important role by trapping the conduction band electrons forming superoxide ions ( $O_2^{\bullet-}$ ) and thus preventing the electron-hole recombination



and at same time  $H_2O_2$  is formed from  $O_2^{\bullet-}$

### L. Photodegradation products

When ZnO is irradiated in the presence of an aqueous solution the  $\bullet OH$  radicals formed on the illuminated semiconductor surface, are strong oxidizing agents with an oxidation potential of 2.8 eV. They can easily attack the adsorbed dye molecule or those in the vicinity of the surface of the catalyst, thus leading to their complete mineralization. The photocatalytic degradation of methylene green certainly involves various chemical and photocatalytic stages and a few intermediates. The evolution of  $CO_2$  during the degradation is the evidence of total destruction of dye in the aqueous medium. During the experiment the generation of  $CO_2$  was identified by titrimetric method, and the decrease in pH indicates the formation of some mineral acid. The destruction of the dye has been confirmed by the COD method. The absence of any aromatic moiety has been further supported by the UV spectrum.

**Table 11:** Concentration of photodegradation product

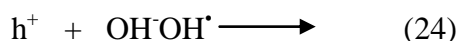
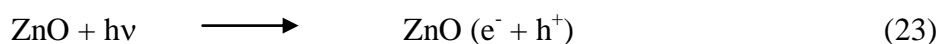
Time(min.)	$CO_2(mg\ dm^{-3})$
0	9.2
30	13.5
60	21.0
90	35.1
120	35.6
150	35.7

Initial concentration of Dye =  $2.0 \times 10^{-5} mol\ dm^{-3}$ , Amount of ZnO = 200 mg, Intensity of light =  $17.5 \times 10^3\ lux$

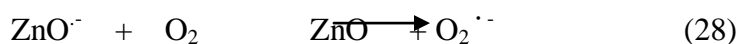
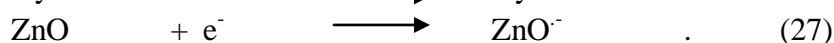
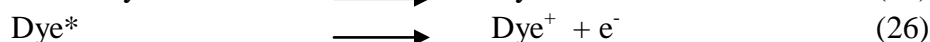
### M. Mechanism

It is a well established fact that by the irradiation on an aqueous ZnO suspension with light energy greater than the band gap energy of the semiconductor ( $h\nu > E_g = 3.2eV$ ) conduction band electrons ( $e^-$ ) and valence band holes ( $h^+$ ) are generated. A fraction of the photogenerated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons act as powerful oxidants, respectively. The photogenerated electrons react with the adsorbed molecular  $O_2$  on the ZnO particle sites, reducing it to a superoxide radical anion  $O_2^{\bullet-}$ , while the photogenerated holes can oxidize either the dye molecule directly or the  $OH^-$  ions and the  $H_2O$  molecules adsorbed the ZnO surface to  $\bullet OH$  radicals. The  $\bullet OH$  radicals formed on the illuminated semiconductor surface are quite strong oxidizing agents with a standard electrode potential of 2.8 V.

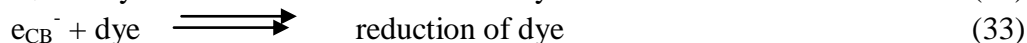
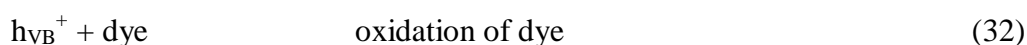
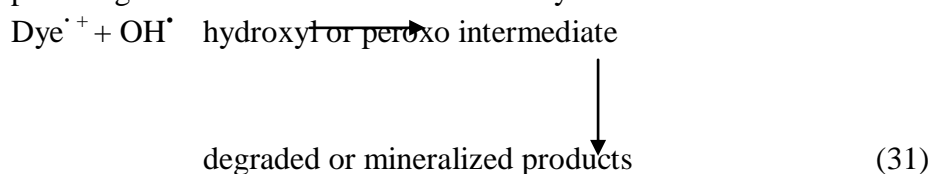
These can easily attack the adsorbed organic molecule or those located close to the surface of the catalyst, thus leading finally to their complete mineralization. In photocatalytic oxidation process, the generation of hydroxyl radicals takes places in two possible ways. Semiconductor ZnO, upon absorption of a photon of suitable energy can act as a photocatalytic substrate by producing electron-hole pair by the excitement of electrons from valence band to conduction band. The photogenerated holes that are able to migrate to the hydroxylated surface can create the highly reactive and short-lived hydroxyl radical  $\cdot\text{OH}$  [22-26].



In second way, the dye molecules act as a sensitizer by the absorption of visible light, and the transfer of photogenerated electrons from the dye molecule to semiconductor has been reported to be very effective. The various steps of overall mechanism envisioned are:



The equation (25) depicts the absorption of light by the dye molecule ( $\text{Dye}^*$ ). This excited dye ( $\text{Dye}^*$ ) injects an electron to the conduction band of ZnO in equation (27), where it is scavenged by  $\text{O}_2$  to form active oxygen molecule as shown in equation (28). Further active oxygen molecule formed in equation (29) subsequently reacts with  $\text{H}_2\text{O}$  to generate  $\text{OH}^\cdot$  radicals. These active radicals drive the photodegradation or mineralization of the dye molecule.



#### 4. CONCLUSION

1. Result obtained in this study demonstrates that photoassisted ZnO mediated degradation of dyes in combination with  $\text{H}_2\text{O}_2$  and per sulfate ion is an effective treatment technology.
2. The presence of inorganic salts and sodium carbonate hinders the photocatalytic degradation of dyes.
3. Complete mineralization of the dyes may be possible in a short irradiation period if the concentration of the dyes, catalyst loading, pH, amount of  $\text{H}_2\text{O}_2$  and persulphate are optimised properly.
4. Simple and easy to handle method for the treatment of colored pollutants wastewater.
5. The proposed mechanism will help to understand the intricacies of degradation process.

## 5. REFERENCES

1. C. Galindo, P. Jacques and A. Kalt, Photooxidation of the phenylazonaphthol AO20 on TiO<sub>2</sub>: kinetic and mechanistic investigation, *Chemosphere*, 45 (2001)997.
2. J.M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, *Catal. Today*, 53 (1999) 2111.
3. U.PaggaandK.Taeger,*WaterRes.*,28(1994)1051.
4. O.Krik,*EncyclopediaofChemicalTechnology.4thed.*, 8 (1993) 753.
5. C.A.K. Gouvea, F. Wypych, S.G. Moraes, N. Duran, N. Nagata and P. Peralta-Zamora, Semiconductorassisted photocatalytic degradation of reactive dyes in aqueous solution, *Chemosphere*, 40 (2000) 433.
6. C. Galindo, P. Jacques and A. Kalt, Photochemical and photocatalytic degradation of an indigo dye: a case study of acid blue 74(AB74), *J. Photochem. Photobiol. A: Chem.*, 141(2001) 47–56.
7. Z. Sun, Y. Chen, Q. Ke, Y. Yang and J. Yuan, *J. Photochem. Photobiol.A:Chem.*,149(2002)169–174.
8. T. Sauer, G.C. Neto, H.J. Jose and R.F.P.M. Moreira, *J. Photochem. Photobiol. A: Chem.*, 149 (2002) 147–154.
9. APHA, *Standard Methods for the Examination of Water and Wastewater*, American Water Works Association, New York, 1989.
10. N. Serpone and E. Pelizzetti, *Photocatalysis: Fundamentals and Applications*, John Wiley Sons, Inc.,New York, 1989, pp. 603–634.
11. R.W. Matthews, *J. Phys. Chem.*, 91 (1987) 3328–3333.
12. R.J. Davis, J.L.Gainer, G. Neal and I. Wenwu, *Wat. Environ. Res.*, 66(1) (1994) 50–53.
13. R.W. Matthews, Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide, *Catalysis*, 111 (1988) 264–272.
14. L.C. Chen and T.C. Chou, Characterization and photocatalytic activity of K<sup>+</sup>-doped TiO<sub>2</sub> photocatalysis, *J. Mol. Catal.*, 85 (1993) 201.
15. A.I. Ekabi and N. Serpone, *J. Phys. Chem.*, 92 (1988)5726.
16. M. Fujihira, Y. Satoh and T. Osa, *Bull. Chem. Soc.Japan*, 55 (1982) 666–671.
17. K. Harada, J. Hisanaga and K. Tanaka, *Water Res.*,11 (1990) 415.
18. D. Robert, B. Dongui and J.V. Weber, *J. Photochem. Photobiol. A: Chem.*,87(2003)261–266.
19. N. Daneshvar, D. Salari and A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO<sub>2</sub>, *J. Photochem. Photobiol. A: Chem.*,162(2004) 317–322.
20. S. Sakthivel, B. Neppolian, M.V. Shankar, B.Arabindoo, M. Palanichamy and V. Murugesan, Solar photocatalytic degradation of azo dyes: comparison of photocatalytic efficiency of ZnO and TiO<sub>2</sub>. *Sol. Energy Mater. Sol. Cells*, 77(2003) 65– 82.
21. I. Poulivos, A. Avranas, E. Rekliti and A. Zouboulis, Photocatalytic oxidation of auramine O in the presence of semiconductor oxides, *J. Chem. Technol. Biotechnol.*, 75 (2000) 205.
22. E. Evgenidou, K. Fytianos and I. Poulivos, Photocatalytic oxidation of dimethoate in aqueous solution. *J. Photochem. Photobiol. A: Chem.*,175 (2005) 29–38.
23. A.B. Prevot, M. Vincenti, A. Bianciotto and E. Pramauro, *Appl. Catal. B: Environ.*, 22 (1999) 149–158.

24. I. Poulios and I. Tsachpinis, Photodegradation of textile reactive black 5 in the presence of semiconducting oxides, *J. Chem. Technol. Biotechnol.*, 74 (1999) 349–357.
25. C. Vinodogopal, L. Fisher, S. Hotchandani, A.K. Chattopadhyay and P.K. Kamat, *J. Phys. Chem.*, 100 (1996) 8436.
26. C. Vinodogopal, S. Hotchandani, A.K. Chattopadhyay and P.K. Kamat, *Res. Chem. Intermed.*, 23(3) (1997)219.
27. F.J. Beltran, G. Overjero and B. Acedo, *Water Res.*,27(6) (1993) 1013.
28. D. Bockelmann, M. Lindner and D. Bahnemann, *Fine Particles: Science and Technology*, Kluwer Academic Publishers, The Netherlands, 1996.
29. G. Kyriacou, K. Tzaouanas and I. Poulios, *J. Environ. Sci. Health A*, 32(4) (1997) 963.
30. M. Zhao, S. Chen and Y. Tao, *J. Chem. Technol. Biotechnol.*, 64 (1995) 339.
31. E. Evgenidou, K. Fytianos and I. Poulios, Semiconductor- sensitized photodegradation of dichlorovos in water using TiO<sub>2</sub> and ZnO as catalysts, *Appl. Catal. B*, 59 (2005) 81–89.
32. C. Galindo, P. Jacques and A. Kalt, Photodegradation of aminoazobenzene acids orange 52 by three advanced oxidation process: UV/TiO<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub> and Vis/TiO<sub>2</sub>, *J. Photochem. Photobiol. A. Chem.*, 141(2001) 47–56.
33. M. Pera-Titus, V.G. Molina, M.A. Banos, J. Gimenez and S. Esplugas, *Appl. Catal. B*, 47 (2004) 219–256.
34. D.F. Ollis, *Catal. Technol.*, 2 (1998) 149.
35. M.A. Behnajady, N. Modirshala and R. Hamzavi, Kinetic study on photocatalytic degradation of C.I. acid yellow 23 by ZnO, *J. Hazard. Mater., B*, 133 (2006) 226–232.