

# Photocatalytic degradation of methyl green dye using $\text{TiO}_2$ under visible light irradiation

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## Abstract

Inordinate population growth and advanced technological development at one hand bettered the life of human and on the other hand it is greatly damaging the environment. Paper, rubber, cosmetics, leather, ink, dyeing, plastic and textile industries use colour for dyeing their products and thus use a huge amount of water which results in the production of dye containing wastewater with hazardous effects on the environment. The treatment of coloured wastewater containing hazardous dyes is one of the growing needs of the present time. Advanced oxidation processes are eco-friendly methods of destroying organic pollutants by using semiconductor and visible light. In the present work the study of hazardous synthetic dyes especially used in textile industries has been carried out. Dyes used in textile industry are highly toxic, stable, soluble in water and non biodegradable and have adverse impacts on the living organisms and human beings. The degradation kinetics was studied under different conditions such as substrate and photo catalyst concentration, reaction pH, addition of oxidants and temperature. The degradation rates proved to be strongly influenced by these parameters. The results indicated that photo catalytic reaction was enhanced in alkaline medium. The photo catalyst  $\text{TiO}_2$  was found to be more efficient for the degradation of methyl green dye. COD removal was measured at regular intervals to quantify the mineralization of methyl green dye

**Key Word:** Development, environment, wastewater, dyes, semiconductor, photocatalyst.

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## INTRODUCTION

Textile dyes and other industrial dyestuffs constitute one of the largest group of organic compounds that represent an increasing environmental danger, About 1-20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents,<sup>1,2</sup> for the treatment of dye containing wastewater, traditional methods such as flocculation carbon adsorption, reverse osmosis and activated sludge process has difficulties in the complete destruction of dye pollutants<sup>3</sup> and has the further disadvantage of potentially oxidation-reduction reactions, The oxidative degradation of an organic pollutant is attributed at the positive role where adsorbed water or hydroxyl groups are oxidized to hydroxyl

radicals ( $\text{OH}\cdot$ ), which then react with the pollutant molecule<sup>4</sup>. Thus leading finally to their complete mineralization. In the present work the photo catalytic degradation in aqueous solution of the Methyl Green dye was investigated. This group of dyes is the oldest known synthetic groups. Most basic dyes of this series are beautiful, crystalline compounds with a reflex, the color in solution. They are of brilliant color due to the resonance of unsymmetrical triphenylcarbonium ions and cover a range of shades from blue, including violet and green. To optimize the kinetic of the degradation process, several parameters were studied.

## Experimental

Methyl Green was obtained from Loba Chemie. Photo catalyst  $\text{TiO}_2$  was obtained from the S.D. Fine Company. All Solutions were prepared in doubly distilled water. Photo catalytic experiments were carried out with 50 ml of dye solution ( $3.8 \times 10^{-5} \text{ mol dm}^{-3}$ ) using 300mg of  $\text{TiO}_2$  photo catalytic under exposure to visible irradiation in specially designed double-walled slurry type batch reactor vessel made up of Pyrex glass (7.5 cm height, 6 cm diameter) surrounded by thermostatic water circulation arrangement to keep the temperature in the range of  $30 \pm 0.3^\circ\text{C}$ . Irradiation was carried out using 500 w halogen lamp surrounded by aluminum reflector to avoid irradiation loss. During photo catalytic experiments after

stirring for 10 min slurry composed of dye solution and catalyst was placed in dark for ½ h in order to establish equilibrium between adsorption and desorption phenomenon of dye molecule on photo catalyst surface. Then slurry containing aqueous dye solution and TiO<sub>2</sub> was stirred magnetically to ensure complete suspension of catalyst particle while exposing to visible light. At specific time intervals aliquot (3 ml) was withdrawn and centrifuges for 2 min at 3500 rpm to remove TiO<sub>2</sub> particle from aliquot to assess extent of decolourisation photo metrically. Changes in absorption spectra were recorded at 480 nm on double beam UV-Vis, spectrophotometer (Systronic Model No. 166) Intensity of visible radiation was measured by a digital luxmeter (Lutron LX 101). pH of solution was measured using a digital pH meter. COD and CO<sub>2</sub> estimation were performed. Performance efficiency was calculated as  $\% \text{ Efficiency} = \frac{c_0 - c_t}{c_0} \times 100$ . Where C and C<sub>0</sub> are initial and final dye lument ration

## RESULTS AND DISCUSSION

An aliquot was taken from the reaction mixture at regular time interval and the absorbance was measured spectra photo metrically at max value of 630 nm. The absorbance of the solution was found to decrease with increasing time. Which indicates that the concentration of Methyl Green dye decreased with increasing time of exposure.

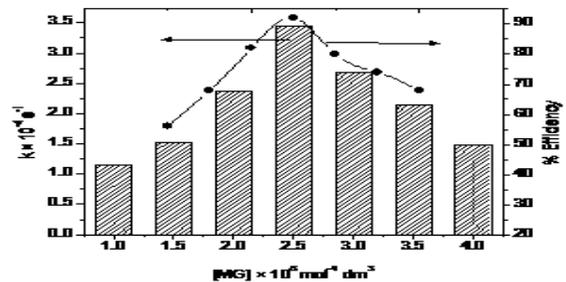
### Effect of initial dye concentration variation

It is important both from a mechanistic and from an application point of view to study the dependence of the photocatalytic reaction rate on the substrate concentration. The effect of initial concentration of the dye on the rate of degradation was performed by varying the initial dye concentration from  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  to  $4.0 \times 10^{-5} \text{ mol dm}^{-3}$ . The photocatalytic degradation rate initially increased from  $1.15 \times 10^{-4} \text{ s}^{-1}$  to  $3.45 \times 10^{-4} \text{ s}^{-1}$ . Further increase of dye concentration led to a decrease in the degradation rate. The rate of degradation related to the probability of  $\cdot\text{OH}$  radicals formation on the catalyst surface and the probability of  $\cdot\text{OH}$  radicals reacting with dye molecules. As the initial concentration of the dye increased the probability of reaction between dye molecules and oxidizing species also increase, led to an enhancement in the decolorization rate. On the contrary, the degradation efficiency of the dye decreased as the dye concentration increased further. The presumed reason might be that at high dye concentrations the generation of  $\cdot\text{OH}$  radicals on the surface of catalyst got reduced since the active sites were covered by dye ions and that reduced the efficiency of the catalytic reaction<sup>(5,6)</sup>.

**Table 1:** Effect of initial dye concentration variation

TiO<sub>2</sub> = 100 mg/ 100 mL, pH = 10.0, Light intensity =  $20 \times 10^3 \text{ lux}$ ,  
Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

[MG] × 10 <sup>5</sup> mol <sup>-1</sup> dm <sup>3</sup>	k × 10 <sup>-4</sup> s <sup>-1</sup>	t <sub>1/2</sub> × 10 <sup>3</sup> s
1.0	1.15	6.02
1.5	1.53	4.52
2.0	2.37	2.92
2.5	3.45	2.00
3.0	2.68	2.58
3.5	2.14	3.23
4.0	1.49	4.65



**Figure 1:** Effect of initial dye concentration variation

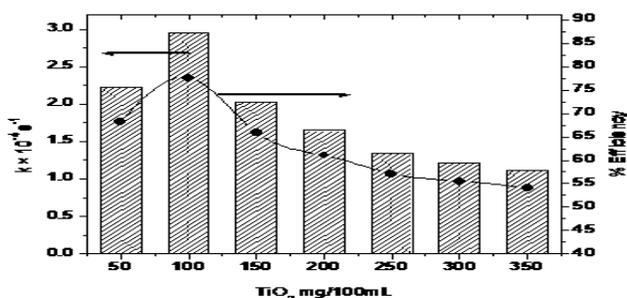
### Effect of amount of catalyst variation

The effect of TiO<sub>2</sub> loading on the photodegradation rate of the methyl green dye has been examined by varying its amount from 50 mg/L to 350 mg/L. It was observed that above a certain level of concentration the reaction rate values decreased and became independent of the catalyst concentration. The photocatalytic degradation rate initially increased from  $2.22 \times 10^{-4} \text{ s}^{-1}$  to  $2.95 \times 10^{-4} \text{ s}^{-1}$  with the increase in catalyst loading from 50 mg/100 mL to 100 mg/ 100 mL above this loading, due to increase in turbidity of the solution light transmission reduced through the solution. While below this level, it could be assumed that the catalyst surface and absorption of light by the catalyst were the limiting factors<sup>7</sup>. The enhancement of the removal rate was due to the increase in the amount of catalyst weight which increased the number of dye molecules adsorbed and the increase in the density of particles in the area of illumination. Thus higher amount of the catalyst might not be useful both in view of possible aggregation as well as reduced irradiation field due to increase in light scattering. The catalyst amount has both positive and negative impact on the photodecomposition rate. Furthermore, rate might decreased as a result in surface area available for light harvesting occasioned by agglomeration at high solid concentration<sup>8</sup>.

**Table 2:** Effect of amount of catalyst variation

[MG] =  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> pH = 10.0 TiO<sub>2</sub> = 100 mg /100 mL, Light intensity =  $20 \times 10^3$  lux Temperature =  $30 \pm 0.3$  °C.

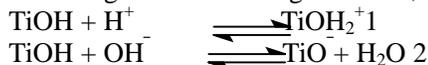
TiO <sub>2</sub> mg/100mL	k × 10 <sup>-4</sup> s <sup>-1</sup>	t <sub>1/2</sub> × 10 <sup>3</sup> s
50	2.22	3.12
100	2.95	2.34
150	2.03	3.41
200	1.65	4.20
250	1.34	5.17
300	1.22	5.68
350	1.11	6.24



**Figure 2:** Effect of amount of catalyst variation

### Effect of solution pH

The photocatalytic reactions were conducted at different pH values from 2 to 14. The results obtained are shown graphically in Fig.3 indicated that photocatalytic reaction was enhanced in alkaline medium because strong adsorption of the dye on the TiO<sub>2</sub> particles due to electrostatic attraction between of the negatively charged TiO<sub>2</sub> with cationic dye. Optimal pH was observed at about 10 with rate constant  $3.37 \times 10^{-4}$  s<sup>-1</sup>. On further increasing the pH value the rate constant values decreased up to  $1.61 \times 10^{-4}$  s<sup>-1</sup>. At high pH values the hydroxyl radicals were rapidly scavenged and they did not have the opportunity to react with dye molecules. The interpretation of pH effects on the efficiency of dye photodegradation process is complex because of multiple roles. First, is related to the ionization state of the surface according to the following reactions,



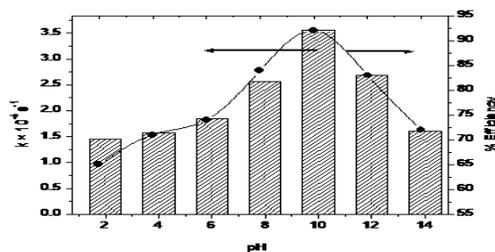
Change in pH could thus influenced the adsorption of dye molecules onto the TiO<sub>2</sub> surface, an important step for the photocatalytic oxidation to take place. Acid-base properties of the metal oxide surface could have considerable implications upon their photocatalytic activity. The point of zero charge (pzc) of the TiO<sub>2</sub> is at pH 6.8. Thus, the TiO<sub>2</sub> surface is positively charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8). Hydroxyl radicals

could be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the main oxidation species at low pH whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels. In alkaline solution generation of <sup>•</sup>OH radicals is enhanced, thus the efficiency of the process got logically enhanced. The TiO<sub>2</sub> particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption would be reduced. Hence, pH plays an important role both in the characteristics of textile waters and in the reaction mechanism that can contribute to dye degradation, namely hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conduction band<sup>9,10</sup>.

**Table 3:** Effect of solution pH

[MG] =  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup>, TiO<sub>2</sub> = 100 mg/ 100 mL, Light intensity =  $20 \times 10^3$  lux, Temperature =  $30 \pm 0.3$  °C.

pH	k × 10 <sup>-4</sup> s <sup>-1</sup>	t <sub>1/2</sub> × 10 <sup>3</sup> s
2	1.45	4.77
4	1.57	4.41
6	1.84	3.76
8	2.57	2.69
10	3.55	1.95
12	2.69	2.57
14	1.61	4.30



**Figure 3:** Effect of solution pH

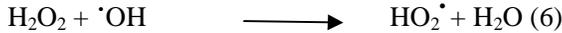
### Effect of H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

It was observed that H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> addition was beneficial to facilitate for the photo oxidation of the dye. The reactive radical intermediates SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH formed from these oxidants by reactions with the photogenerated electrons known exert a dual function as strong oxidant themselves and as electron scavengers, thus inhibiting the electron-hole recombination at the semiconductor surface<sup>(1)</sup>. The photocatalytic degradation rate increased as the concentration of H<sub>2</sub>O<sub>2</sub> increased from  $3.56 \times 10^{-4}$  s<sup>-1</sup> to  $5.37 \times 10^{-4}$  s<sup>-1</sup> and it reached the optimum at  $5.37 \times 10^{-4}$  s<sup>-1</sup>. After this the rate started decreasing as the concentration of the H<sub>2</sub>O<sub>2</sub> increased. H<sub>2</sub>O<sub>2</sub> has two functions in the process of photocatalytic degradation. It can accept a photo generated electron from the conduction band and

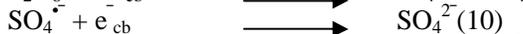
thus promoted the charge separation and it also forms  $\cdot\text{OH}$  radicals.



Excess  $\text{H}_2\text{O}_2$  might act as a hole or an  $\cdot\text{OH}$  scavenger and form peroxocompounds, which are detrimental to the photocatalytic action. This is an explanation for the need of an optimal concentration of  $\text{H}_2\text{O}_2$  for the maximum effect.



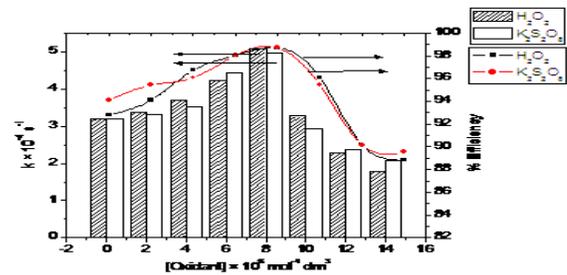
$\text{K}_2\text{S}_2\text{O}_8$  could also trap the photogenerated conduction band electron resulted in the formation of sulphateradical anion ( $\text{SO}_4^{\cdot-}$ ), a strong oxidizing agent (standard oxidation potential = 2.6 eV), which could participate in degradation process. With increase in  $\text{K}_2\text{S}_2\text{O}_8$  concentration from  $2.0 \times 10^{-6} \text{ mol dm}^{-3}$  to  $8.0 \times 10^{-6} \text{ mol dm}^{-3}$ , rate constant values increased from  $3.49 \times 10^{-4} \text{ s}^{-1}$  to  $5.25 \times 10^{-4} \text{ s}^{-1}$ . At optimal concentration of  $\text{K}_2\text{S}_2\text{O}_8$ , a rate constant value has been found to be  $5.25 \times 10^{-4} \text{ s}^{-1}$ . After this the rate started decreasing as the concentration increased. A possible explanation of this behavior might be the light absorption from dye molecule led to the photosensitization of the molecule, which is accompanied by the excitation of an electron from the lower to the upper energy level. Following this, the excited dye molecules injected electrons to the  $\text{S}_2\text{O}_8^{2-}$ . The resulted  $\text{SO}_4^{\cdot-}$  radicals, strong oxidizing agents, attack the chromophore group in dye leading to the decolorization of the solution. The decrease in rate constant values above optimum concentration might be due to adsorption of sulphate ions formed during the reaction on surface of catalyst deactivating a section of photocatalyst.



**Table 4:** Effect of  $\text{H}_2\text{O}_2$  and  $\text{K}_2\text{S}_2\text{O}_8$

[MG] =  $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ , pH = 10.0  $\text{TiO}_2$  = 100 mg / 100 mL, Light intensity =  $20 \times 10^3 \text{ lux}$ , Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

[Oxidant] $\times 10^6 \text{ mol}^{-1} \text{ dm}^3$	$\text{H}_2\text{O}_2$		$\text{K}_2\text{S}_2\text{O}_8$	
	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}^{-1}$	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}^{-1}$
0.0	3.37	2.05	3.37	2.05
2.0	3.56	1.94	3.49	1.98
4.0	3.91	1.77	3.72	1.86
6.0	4.45	1.55	4.68	1.48
8.0	5.37	1.29	5.25	1.32
10.0	3.45	2.00	3.10	2.23
12.0	2.41	2.87	2.49	2.78
14.0	1.88	3.68	2.18	3.17



**Figure 4:** Effect Of Oxidant  $\text{H}_2\text{O}_2$  And  $\text{K}_2\text{S}_2\text{O}_8$

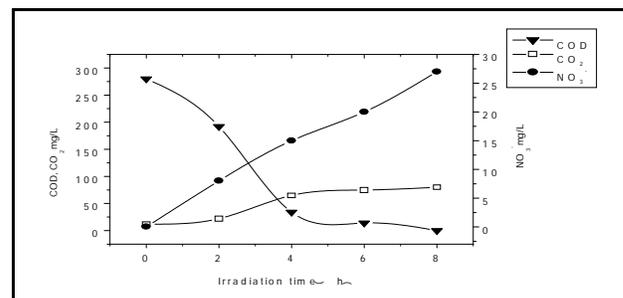
### COD and $\text{CO}_2$ measurements during mineralization process

Chemical oxygen demand (COD) values are related to the total concentration of organics in the solutions using this criterion, the mineralization of methyl green has been investigated under  $\text{TiO}_2/\text{Vis}$  process and COD and  $\text{CO}_2$  measurements have been carried out. The COD of the dye solution was estimated before and after treatment. The reduction in the COD values of the treated dye solution indicated the mineralization of dye molecules along with color removal<sup>(39)</sup>. COD values decreased slower than the discoloration of the solution because dyes are not directly mineralized, but transformed into intermediate byproducts. These byproducts might submit other cycles of degradation to complete mineralization. COD and  $\text{CO}_2$  measurement were carried out to analyze the extent of mineralization of the organic molecule. After 8 hours of irradiation COD values decreased from 280 mg/L to 0 mg/L and  $\text{CO}_2$  values increase from 12 mg/L to 80 mg/L.

**Table 5:** COD and  $\text{CO}_2$  measurements during photodegradation process

[MG] =  $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $\text{TiO}_2$  = 100 mg/100 mL, pH = 10.0 Light intensity =  $20 \times 10^3 \text{ lux}$ , Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

Irradiation time (h)	COD (mg/L)	$\text{CO}_2$ (mg/L)	Efficiency (%)	$\text{NO}_3^-$ (mg/L)	pH
0	280	12	0	0	10.0
2	192	22	31	8	8.50
4	34	65	87	15	6.57
6	14	75	95	20	3.90
8	0	80	100	27	3.10



## CONCLUSION

Photo assisted mineralization of Methyl Green can be effectively carried out utilizing  $\text{TiO}_2$  with visible light. Amount of catalyst, solution pH have been found to be Vital parameter. The presence of inorganic salts such as sodium carbonate and sodium chloride hinders the photo catalytic degradation of textile dyes. Synergetic of  $\text{H}_2\text{O}_2$  and  $\text{K}_2\text{S}_2\text{O}_8$  has also been investigated. The reduction in COD of the effluent suggested that the dye molecules were completely mineralized.

## ACKNOWLEDGEMENT

Authors acknowledgment the support and Laboratory facilities provides by Chemistry Department Govt. S.B.N. P.G. College, Barwani M.P. (India)

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Source of Support: None Declared  
Conflict of Interest: None Declared