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# Study on $TiO_2$-mediated photocatalytic degradation of methylene blue

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**Abstract**

The degradation (oxidation) of methylene blue assisted by $TiO_2$ photocatalysis (with an irradiation wavelength of 365 nm) was investigated in aqueous suspension. The rate constants for this heterogeneous photocatalysis were evaluated as a function of the concentration of the dye, the amount of $TiO_2$ and the pH. The reaction is found to conform to a Langmuir adsorption isotherm and the rate vs. pH profile exhibits a linear increase with pH in acidic solutions with a maximum at around pH 6.9.

*Keywords:* $TiO_2$; Photocatalysis; Methylene blue

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## 1. Introduction

Photocatalysis has been an area of rapidly growing interest over the last 10 years [1]. The photocatalytic degradation of organic compounds is an important branch of the broader subject of photocatalysis. Semiconductor particles are ideal photocatalysts for this reaction. The photocatalysts commonly used are $TiO_2$, ZnO, $WO_3$, CdS, ZnS, $SrTiO_3$ and $Fe_2O_3$, with $TiO_2$ being frequently reported as the most active in organic degradation experiments. In water treatment processes involving semiconductors, non-toxicity and insolubility, both in the dark and on illumination, are important considerations. Titanium dioxide satisfies these requirements. Moreover, it is extremely stable in aqueous suspensions with a diminishing rate of photocorrosion [1]. The use of semiconductor particles as photocatalysts for the initiation of redox chemical reactions continues to be an active area of investigation [2]. In the early literature on this subject [3,4], the emphasis has been mainly on solar energy conversion via the photodecomposition of water or the photoreduction of carbon dioxide. Attempts have also been made to photofix nitrogen with semiconductor catalysts. The photooxidation of benzenes and haloaromatics [5] and phenol [6] assisted by $TiO_2$ has been reported. Dyes pose a potential environmental hazard since their manufacturing produces and involves a variety of organic chemicals, some of which have been shown to be carcinogenic [7]. In this regard, some attempts have been made to study the photocatalytic oxidation of methylene blue on thin films of $TiO_2$ [8] and in aqueous $TiO_2$ suspension using simulated and natural solar energy [9]. However, the lack of a systematic study on the nature of the photocatalytic degradation of methylene blue in aqueous $TiO_2$ suspension as a function of the concentration of methylene blue ([MB]), the amount of $TiO_2$ and the pH prompted this investigation. This study represents part of our investigation on the $TiO_2$-mediated photodestruction of dyes.

## 2. Experimental details

Methylene blue, NaOH, $HClO_4$ and all other chemicals were of AnalaR grade. Water, distilled from a Kilburn still, was redistilled over alkaline permanganate in an all-glass vessel and used for solution preparation. The titanium dioxide ($TiO_2$) photocatalyst was Degussa P-25. This material is mainly anatase, and has a Brunauer–Emmett–Teller (BET) surface area of 50 $m^2\,g^{-1}$ and a mean particle size of 30 nm. Irradiations were performed with a 125 W medium pressure Hg lamp (Mysore Lamps, India). Aqueous suspensions of $TiO_2$

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containing methylene blue in a polymerization tube, with an inlet for $O_2$ and under constant magnetic stirring, were irradiated for different intervals of time. All the experiments were carried out in the presence of $O_2$ as a scavenger for $e_{cb}^-$. The pH of the solutions was adjusted with a Toshniwal CL-46 pH meter. The progress of the reaction was followed by monitoring the disappearance of the dye at 655 nm. The amount of dye decomposed with respect to time was estimated. The rate constants ($k$, $s^{-1}$) were evaluated from the plots of log(Absorbance)$_{655}$ vs. irradiation time, and the rates of decomposition of methylene blue were calculated by multiplying the rate constants by the appropriate initial dye concentrations, $[MB]_0$.

## 3. Results and discussion

### 3.1. Factors influencing the decomposition efficiency of $TiO_2$

### 3.1.1. Effect of initial concentration of methylene blue

It was observed that the plot of log(Absorbance)$_{655}$ vs. time of irradiation at different initial $[MB]_0$ values yielded a straight line (Fig. 1); the slope gave the rate constant ($k$, $s^{-1}$). These values are reported in Table 1. Experiments carried out with various initial concentrations of methylene blue ($6.6 \times 10^{-6}$ to $3.6 \times 10^{-5}$ mol $dm^{-3}$) at the natural pH of the solution showed that the rate of degradation of methylene blue (rate $= k(s^{-1}) \times [MB]_0$) increased with an increase in $[MB]_0$ initially and remained almost constant beyond a certain level (Fig. 2), indicative of Langmuir kinetics. This is confirmed by the linear plots of 1/rate vs. $1/[MB]_0$ with an intercept on the ordinate (Fig. 3), in agreement with the equation

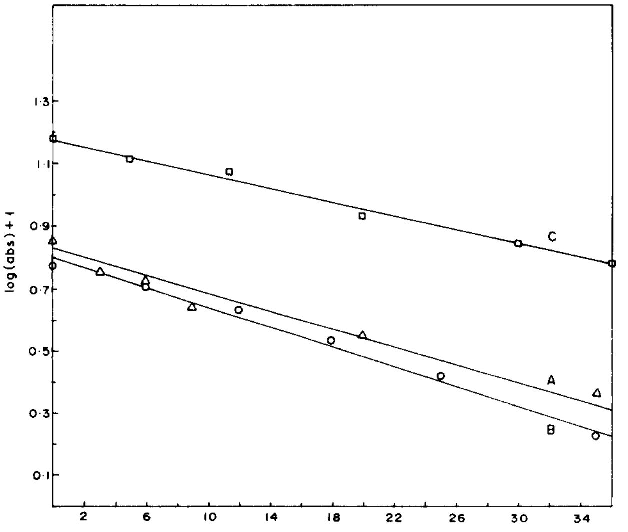

Fig. 1. Influence of $[MB^+]$ on the photocatalytic degradation rate (0.05 g $TiO_2$, pH 3.0): A, $[MB^+] = 6.6 \times 10^{-6}$ mol $dm^{-3}$; B, $[MB^+] = 1.0 \times 10^{-5}$ mol $dm^{-3}$; C, $[MB^+] = 2.0 \times 10^{-5}$ mol $dm^{-3}$.

Table 1
Dependence of the photocatalytic degradation rate on [MB] (pH 3.00; weight of $TiO_2 = 0.05$ g per 75 ml)

| $[MB] \times 10^6$ (mol $dm^{-3}$) | Rate $\times 10^9$ (mol $dm^{-3}$ $s^{-1}$) |
|---|---|
| 6.6 | 3.17 |
| 8.0 | 4.85 |
| 10.0 | 5.67 |
| 12.0 | 6.06 |
| 20.0 | 9.80 |
| 30.0 | 11.80 |
| 33.6 | 11.85 |
| 36.0 | 11.78 |

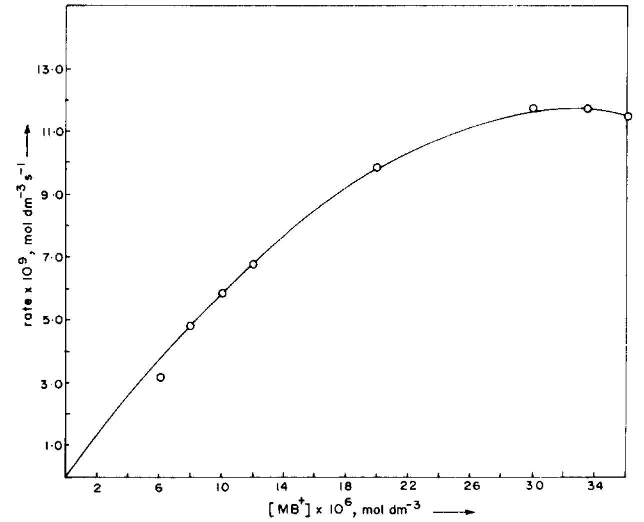

Fig. 2. Rate vs. $[MB^+]$ (0.05 g $TiO_2$, pH 3.2). $[MB^+] \times 10^6$ (mol $dm^{-3}$)/rate $\times 10^9$ (mol $dm^{-3}$ $s^{-1}$): 6.6/3.17; 8.0/4.85; 10.0/5.67; 12.0/6.06; 20.0/9.80; 30.0/11.80; 33.6/11.85; 36.0/11.78.

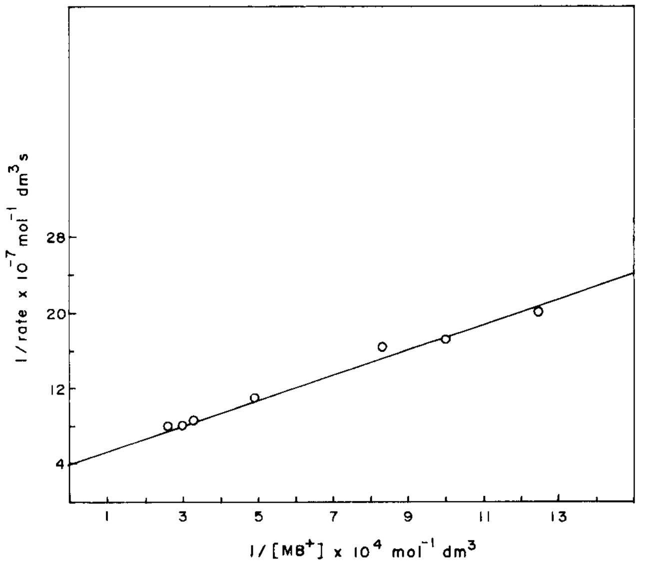

Fig. 3. Langmuir adsorption isotherm (0.05 g $TiO_2$, pH 3.2). Rate$^{-1} \times 10^{-7}$ ($mol^{-1}$ $dm^3$ s)/$[MB^+]^{-1} \times 10^4$ ($mol^{-1}$ $dm^3$): 20.60/12.50; 17.60/10.00; 16.50/8.30; 8.54/3.30; 8.43/2.97; 8.48/2.77.

$$\text{rate}=\frac{k'K[\text{MB}]_0}{1+K[\text{MB}]_0}$$

Hence

$$/\text{rate}=\frac{1}{k'K[\text{MB}]_0}+\frac{1}{k'}$$

where $k'$ is a proportionality constant and $K$ is the equilibrium constant. The values of $k'$ and $K$ obtained from the intercept and slope of this plot are $3.36\times10^{-8}$ mol dm$^{-3}$ s$^{-1}$ and $1.79\times10^{4}$ dm$^{3}$ mol$^{-1}$ respectively. Band gap irradiation of the semiconductor $TiO_2$ leads to the generation of valence band holes and conduction band electrons [10]. Due to the presence of $O_2$ in the reaction solution, the scavenging of $e_{cb}^-$ is envisaged as [11]

$$TiO_2 \xrightarrow{h\nu/365\ \text{nm}} h_{vb}^+ + e_{cb}^- \quad (1)$$

$$O_2 + e_{cb}^- \longrightarrow O_2^- \quad (2)$$

Hence it is clear that the recombination of $h_{vb}^+$ and $e_{cb}^-$ is prevented, enabling $h_{vb}^+$ to oxidize the dye molecule. Furthermore, the $OH^{\cdot}$ and $O_2^-$ produced (steps 3 and 6), being powerful oxidants [12,13], can also oxidatively degrade the dye.

The mechanistic scheme leading to the degradation of the dye is shown below

$$h_s^+ + H_2O \longrightarrow OH_{ad} + H_{aq}^+ \quad (3)$$

$$h_s^+ + \text{dye} \longrightarrow \text{products} \quad (4)$$

$$OH_{ad} + \text{dye} \longrightarrow \text{products} \quad (5)$$

$$e_s + O_2 \longrightarrow O_2^-(aq) \quad (6)$$

$$e_s^- + O_2 + H_2O \longrightarrow HO_2(aq) + OH^-(aq) \quad (7)$$

$$O_2^- + \text{dye} \longrightarrow \text{products} \quad (8)$$

Carbon dioxide, nitrate ions and ammonium ions are formed as products in the reaction, indicating the mineralization of the dye by illuminated $TiO_2$.

### 3.1.2. *Effect of amount of catalyst*

The effect of varying the amount of catalyst $TiO_2$ was studied. Experiments performed with various amounts of catalyst powder (0.003–0.05 g per 75 ml) at constant $[\text{MB}]_0$ ($1\times10^{-5}$ mol dm$^{-3}$) showed the following behaviour: the rate increased with an increase in the amount of catalyst and remained almost constant above a certain level (Fig. 4, Table 2). This can be explained as follows. As the amount of catalyst is increased, the number of photons absorbed and the number of dye molecules adsorbed are increased owing to an increase in the number of $TiO_2$ particles. The density of particles in the area of illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules available are not sufficient for adsorption by the increased number of $TiO_2$ particles, i.e. although more area is available, for a constant $[\text{dye}]_0$, the number of substrate molecules present in the solution is the same. Hence the additional catalyst powder is not involved in catalyst activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit.

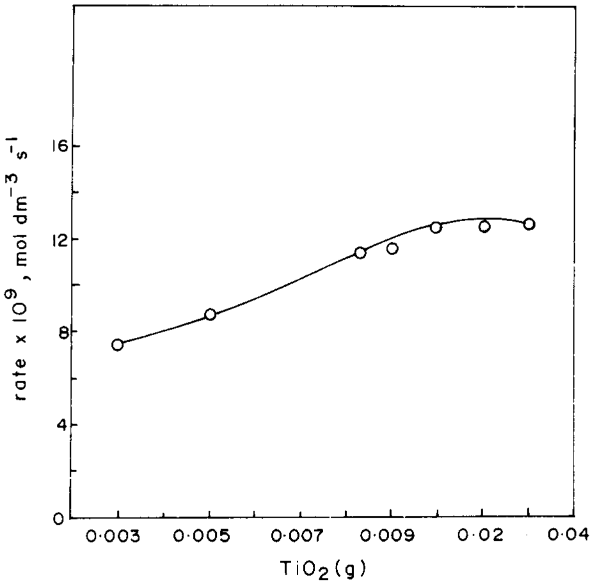

Fig. 4. Dependence of the photocatalytic degradation rate on the amount of $TiO_2$ ($[\text{MB}^+]=1\times10^{-5}$ mol dm$^{-3}$, pH 2.6). $TiO_2$ (g)/rate$\times10^9$ (mol dm$^{-3}$ s$^{-1}$): 0.003/7.25; 0.005/8.57; 0.008/11.83; 0.010/12.58; 0.020/12.20; 0.030/12.90.

Table 2
Dependence of the photocatalytic degradation rate on the amount of $TiO_2$ (pH 3.00; $[\text{MB}]=1\times10^{-5}$ mol dm$^{-3}$)

| Weight of $TiO_2$ (g) per 75 ml | Rate$\times10^9$ (mol dm$^{-3}$ s$^{-1}$) |
|---|---|
| 0.003 | 7.25 |
| 0.005 | 8.57 |
| 0.008 | 11.83 |
| 0.010 | 12.58 |
| 0.020 | 12.20 |
| 0.030 | 12.90 |

### 3.1.3. *Effect of pH*

The role of the pH on the rate of photocatalytic degradation was studied in the pH range 3–8. It was observed that the rate increased with an increase in pH, exhibiting a maximum around pH 6.9–8.0 (Fig. 5, Table 3). This is indicative of the significant role of the surface property of the photocatalyst $TiO_2$; the acid–base property of the metal oxide surface has a considerable influence on the photocatalytic activity with varying pH. The pH effect can be explained on the basis of the zero point of charge of $TiO_2$. The adsorption of $H_2O$ molecules at surface metal sites is followed by the dissociation of OH groups leading to a coverage [14] with chemically equivalent metal hy-

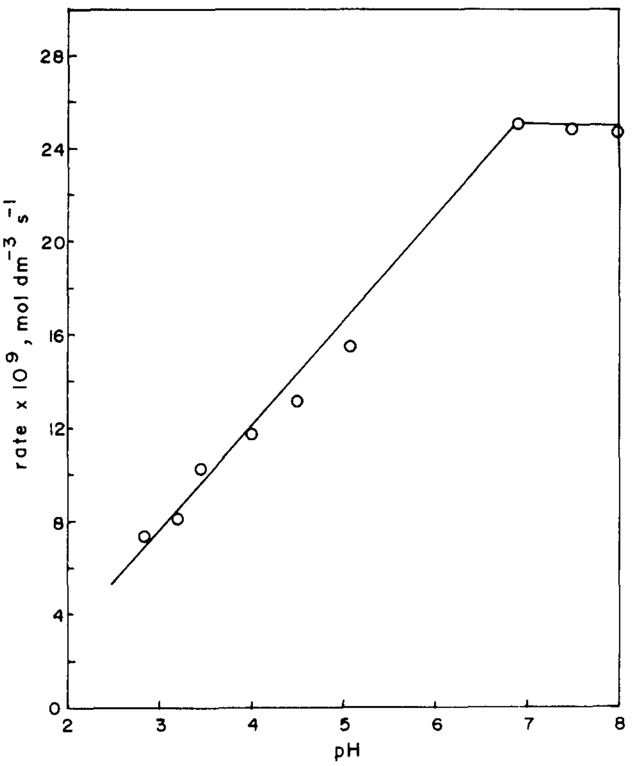

Fig. 5. Effect of pH on the photocatalytic degradation rate of methylene blue (0.01 g $TiO_2$, $[MB^+]=1\times10^{-5}$ mol $dm^{-3}$). pH/rate$\times10^9$ (mol $dm^{-3}$ $s^{-1}$): 2.8/7.4; 3.2/8.0; 3.4/10.0; 4.0/11.6; 4.5/13.0; 5.1/15.2; 6.9/25.0; 7.5/24.8; 8.0/24.3.

Table 3

Effect of pH on the photocatalytic degradation rate (weight of $TiO_2=0.02$ g per 75 ml; $[MB]=1\times10^{-5}$ mol $dm^{-3}$)

| pH | Rate$\times10^9$ (mol $dm^{-3}$ $s^{-1}$) |
|---|---|
| 2.8 | 7.4 |
| 3.2 | 8.0 |
| 3.4 | 10.0 |
| 4.0 | 11.6 |
| 4.5 | 13.0 |
| 5.1 | 15.2 |
| 6.9 | 25.0 |
| 7.5 | 24.8 |
| 8.0 | 24.3 |

droxyl groups (M-OH). Due to the amphoteric behaviour of most metal hydroxides, the following two equilibria must be considered

$$\text{M-OH}+\text{H}^+ \longrightarrow \text{M-OH}_2{}^+ \qquad K_1$$

$$\text{M-OH} \longrightarrow \text{M-O}^- + \text{H}^+ \qquad K_2$$

The zero point of charge ($pH_{zpc}$) of metal oxide particles is defined as the pH at which the concentrations of protonated and deprotonated surface groups are equal

$$pH_{zpc}=\frac{1}{2}(pK_1+pK_2)$$

$pH_{zpc}$ values have been determined for a wide variety of metal oxide particles [1]. As a consequence of this amphoteric behaviour, the metal oxide surface is predominantly positively charged below $pH_{zpc}$ and negatively charged above. The $pH_{zpc}$ of $TiO_2$ is 3.5–6.7. In an earlier study, the effect of pH on the $TiO_2$-assisted photocatalytic degradation of trichloroacetate anion and chloroethylammonium cation was explained on the basis of the $pH_{zpc}$ of $TiO_2$ [11]. With the latter, a maximum rate was observed at around pH 7. In the present study also, a maximum rate occurred around pH 7. Considering the positive charge on the organic molecules, chloroethylammonium cation and methylene blue ($MB^+$), the effect of pH on the photocatalytic degradation of $MB^+$ can be rationalized on the basis of the electrostatic adsorption model where cations are more readily accommodated at negative sites on $TiO_2$. Indeed, the observation of a pH effect on the photocatalytic degradation of chloromethylammonium cation has been explained using this electrostatic model, and computer simulations of this surface charge model with a modified Guoy–Chapman–Stern (GCS) approach have been successfully applied to fit the results [1]. Recently, Meisel and coworkers [15] have studied the charge transfer from viologen radical ions formed in homogeneous solution to ferric oxide particles as a function of pH. They observed a rapid electron injection from methyl viologen radical cations ($MV^{\cdot+}$) above the $pH_{zpc}$ of the material, while the anionic species ($ZV^{\cdot-}$) transferred electrons efficiently only at low pH. Based on the GCS model, a reasonable fit of the experimental data was obtained in the pH range studied. The above examples illustrate that a detailed knowledge of the surface chemistry of semiconductor particles is extremely important to predict and understand their photocatalytic activity.

An important issue of most concern in the photocatalysed mineralization of organic substrates is whether the initial oxidation of the organic substrate occurs on the photocatalyst surface or in solution [16]. In the $TiO_2$-photocatalysed oxidation of acetate, an increase in rate with an increase in pH was observed [17]. It was inferred that, since in alkaline media little adsorption of acetate takes place on the negatively charged $TiO_2$ surface, the hydroxyl radical must diffuse away from the surface of the photocatalyst to oxidize acetate in solution. By contrast, the suppression of the degradation rate of trichloroacetate when $TiO_2$ bears a negative charge seems to support the surface location of the process [18]. Similarly, the degradation of pentachlorophenol was found to proceed at a sustained rate in alkaline medium [19]. In the present study, the observed increase in the rate of the photocatalytic degradation of methylene blue ($MB^+$) with an increase in pH seems to support the surface location of the process.

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