TITANIUM DIOXIDE CATALYSED PHOTO-OXIDATION OF METHYL VIOLET

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Summary

The photodegradation of methyl violet in an oxygen-purged aqueous solution containing TiO_2 was studied. The effective rate constants for complete mineralization were determined as a function of pH, temperature and the concentration of the catalyst.

1. Introduction

The use of semiconductor particle dispersions as photocatalysts has received much attention during the past few years [1 - 6]. Although a vast majority of reports on this subject deals with photocleavage of water, the quantum efficiencies achieved are too small to be viable as practical systems [1-6]. The situation regarding photoreduction of dinitrogen and carbon dioxide with semiconductor photocatalysts is the same [7 - 10]. However, one area in which semiconductor photocatalysis could have immediate practical impact is photo-oxidation of contaminants in water [11 - 14]. The contamination of drinking water supplies by agrochemicals [15, 16] and organochlorine compounds resulting from chlorination [17] is a problem of much concern. Recently it has been noted that organic compounds can be completely mineralized (*i.e.*, converted to CO_2 , H_2O , N_2 and Cl^- in the case of organochlorine compounds) when an oxygen-purged suspension of TiO_2 is irradiated with UV light [11 - 13]. Most of the above studies reported in the literature were conducted with substances that could contaminate drinking water in the real situations [11-13] (e.g., chloroaromatics). It is difficult to make such measurements because of the complications involved in the continuous estimation of the low concentrations of contaminants during the process of photolysis. As a simple system free from this difficulty, we studied the photo-oxidation of an oxygen-purged methyl violet solution

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in the presence of TiO_2 . Since accurate spectrophotometric determination of this dye is extremely simple, the variation in the reaction rate with the quantity of catalyst, the temperature and the pH can be monitored easily.

2. Experimental details

The anatase form of titanium dioxide (Aldrich 99.9%) was used in all experiments without any treatment. The particle size distribution was ascertained with a particle size counter (Horiba Capa-700). The average particle size was found to be 0.65 μ m, and the size distribution is presented in Fig. 1. The water used for making the TiO₂ suspension was double distilled and free from organic matter when tested by discolouration of permanganate. Recrystallized methyl violet was used and estimated spectrophotometrically (Shimadzu UV-300) at 580 nm. The structural formula of methyl violet and its absorption spectrum are shown in Fig. 2. In all experiments the initial dye concentration was 5×10^{-5} M.





Fig. 2. (a) Structural formula of methyl violet; (b) absorption spectrum of methyl violet.

The photolysis experiments were carried out in a double-walled borosilicate glass photochemical reactor of volume 350 ml (Applied Photophysics) thermostatted by circulating water. The light source was a 450 W medium pressure mercury lamp mounted at the central axis of the reactor (filters were not used to cut off emissions in the visible region, *i.e.* 546 and 579 nm). Purified air passed successively through wash bottles containing chromic acid, NaOH and water (to remove organic matter, carbon dioxide and the spray) was bubbled through the suspension at a rate of 650 ml min⁻¹. The temperature of the reaction mixture was varied by changing the temperature of the circulating water. To examine CO₂ production, an experiment was also conducted by purging the solution with pure O₂ (*i.e.*, free from CO_2) and the outgoing gas was tested for carbon dioxide using $Ba(OH)_2$. In all experiments, the dye concentrations at different time intervals were determined by taking aliquots and centrifuging them to remove the TiO_2 particles. The pH of the solutions were adjusted with NaOH (AnalaR).

3. Results and discussion

At the low concentrations of the dye used in the present experiment, detection and reliable estimation of the intermediate products of photooxidation were not possible. The overall reaction can be written as

$$D + O_2 \xrightarrow{\text{TiO}_2/h\nu} CO_2 + H_2O + HCl + N_2$$
(1)

where D denotes the dye. If the O_2 concentration remains constant (*i.e.* when the purging is rapid and at the rate of bubbling used in this experiment air and pure O_2 gave the same result, indicating that the dissolved O_2 concentration remained constant), the dye concentration will decrease with time according to

$$[D] = [D] \exp(-kt) \tag{2}$$

where k is the rate constant. The above relation is found to be valid to a high degree of approximation when the photolysis is carried out with dye solutions of low concentration (*i.e.* 10 - 4 mol l^{-1}). As expected the plots of [D] vs. t give straight lines (Fig. 3). At a given temperature and pH, k is found to



Fig. 3. Plot of $\ln[D]$ vs. time (catalyst concentration, 0.33 g l⁻¹; pH 6.5).

depend on the amount of catalyst used. Initially k increases with an increase in the quantity of catalyst and then begins to decrease (Table 1). This can be understood because the molecules that participate in the reaction are the species adsorbed onto the TiO₂ particles, and their number is increased by increasing the amount of catalyst employed. However, when the concentration of catalyst is excessively large, more particles (with adsorbed dye) remain screened from the light owing to the cut-off by the suspension. The combination of these two effects gives rise to an optimum catalyst concentration which is dependent on the intensity of the light and the geometry of the reactor.

The initial step in a photo-oxidation process of this type is believed to be the formation of free hydroxyl radicals [11 - 14] via hole transfer from the valence band of the semiconductor to OH⁻ ions, and the electrons from the conduction band are transferred to oxygen, *i.e.*

$$\begin{array}{ccc} OH^- + h^+ \longrightarrow OH & O_2 + e^- \longrightarrow O_2^- \\ \uparrow & \uparrow & \uparrow \\ VB \ TiO_2 & CB \ TiO_2 \end{array} \tag{3}$$

The hydroxyl free radicals oxidize organic matter and the electrons from O_2^- are donated to H⁺ ions, *i.e.*

$$2OH + D \longrightarrow H_2O + oxidation \text{ products}$$
(4)

 $2H^+ + 2O_2^- \longrightarrow H_2O + \frac{3}{2}O_2$

Actually reactions (3) and (4) could proceed via several steps with the formation of other intermediate species. It is clear that reaction (3) is favoured by an increase in pH. As expected, the rate constant is found to increase on increase in pH (Fig. 4).

When the temperature is increased, the reaction rate (Fig. 5 and Table 2) gradually increases and then decreases. Thermodynamically, a higher

TABLE 1

Rate constant for different concentrations c of catalyst (temperature, 2.5 °C; estimated error in the measurement k, $\pm 0.001 \text{ min}^{-1}$)

$\begin{array}{c|c} C (g l^{-1}) & k (min^{-1}) \\ \hline 0.17 & 0.019 \\ 0.33 & 0.020 \\ 0.67 & 0.021 \\ 1.67 & 0.016 \end{array}$

TABLE 2

Values of the rate constant at different temperatures (concentration of catalyst, 0.33 g l^{-1})

<i>T</i> (°C)	$k \ (\min^{-1})$
25	0.020
40	0.022
60	0.033
70	0.020



Fig. 4. Plot of [D] vs. time for photolysis experiments at different pHs. The numbers indicated near each curve are the pH values.



Fig. 5. Plot of [D] vs. time at different temperatures.

temperature favours the degradation of the dye molecules; however, the adsorption of the dye onto the catalyst decreases as the temperature is increased. The above observation is a consequence of the presence of these two opposing factors. Direct degradation of the dye upon irradiation (*i.e.*, the absence of TiO_2 in the solution) was found to be small compared with catalytic photodegradation. In the presence of a dye, TiO_2 particles can be sensitized to visible radiation by injection of electrons into the conduction band [18]. When visible light free from UV was used (100 W tungsten filament lamp) the rate of degradation was found to be negligible, indicating that the sensitized decomposition is insignificant. The above study clearly demonstrates that organic contaminants in water present at low concentrations can be completely oxidized by photocatalysis with TiO₂.

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