# Photodegradation of visible-light-absorbing organic compounds in the presence of semiconductor catalysts

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#### Abstract

Organic compounds which absorb visible radiation can be oxidatively degraded using semiconductor catalysts by sensitized charge transfer. As a model system, the photodeg-radation of rose bengal in the presence of  $TiO_2$  and ZnO is studied. Evidence is presented which shows that sensitized oxidation leads to mineralization. As a result of concentration quenching the rate of the reaction is found to decrease with an increase in the dye concentration.

# 1. Introduction

The use of semiconductor particles as photocatalysts for the initiation of redox chemical reactions continues to be an active area of investigation [1-8]. In early literature on the subject [9-11], 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 [3]. Unfortunately, the observed quantum yields in the above reactions are considerably below the limits of practical viability. However, one area in which semiconductor photocatalysis may have immediate practical applications is the photo-oxidation of organic contaminants in water [2, 5, 12–15]. The pollution of drinking water supplies by agrochemical and organochloro compounds originating from chlorination is an urgent problem for which remedial measures need to be found. It has been noted that organic contaminants in water can be completely mineralized (*i.e.* converted into  $CO_2$ ,  $H_2O$ ,  $N_2$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $PO_3^{3-}$  etc.) [2, 5, 12–15] by irradiation in the presence of TiO<sub>2</sub>. Unfortunately, the TiO<sub>2</sub> catalyst employed is rather insensitive to solar radiation and artificial light sources are too expensive for large-scale application. We have noted that organic compounds which absorb visible radiation can be photodegraded using n-type semiconductor catalysts via sensitization. Here, the photoexcited contaminant adsorbed on the surface of the catalyst injects electrons into the conduction band, which are utilized in the oxidation of the compound. In principle, it is possible to attach chromophores to the potential agrochemicals without altering the desired activity. Then photodegradation may be achieved using solar radiation in the presence of TiO2. As a model system to illustrate this effect, we have studied the photodegradation of rose bengal using visible radiation in the presence of a semiconductor catalyst and oxygen.

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# 2. Experimental details

The photocatalysts used in the experiment were ZnO (BDH) and TiO<sub>2</sub> (Aldrich). The surface area of the powders was estimated using a Horiba particle size distribution analyser (CAPA 700). Water used for preparing the catalyst suspension was deionized and distilled and was found to be free from organic matter as tested by permanganate decolouration. Rose bengal (Aldrich) was used as received and solution concentrations were estimated spectrophotometrically (Shimadzu UV-300 spectrophotometer) at 549 nm. The structural formula and the absorption spectrum of the dye are shown in Fig. 1. A dye solution containing the catalyst (20 mg ZnO or 8.7 mg TiO<sub>2</sub>, so that the weights are in proportion to the surface area) was ultrasonically agitated to obtain a uniform dispersion. The solution (150 ml) contained in a 250 ml Pyrex beaker was irradiated from the bottom using a solar simulator (Applied Photophysics) provided with a 1 kV metal halide discharge tube. Radiation was passed through Pyrex glass to cut off UV radiation. The solution was kept purged with purified air at a rate of 30 ml min<sup>-1</sup>. At different intervals of irradiation aliquots of solution drawn from the beaker were centrifuged to remove the catalyst and the depletion of the dye was monitored spectrophotometrically. In a separate experiment photolysis was carried out in a flask kept purged with oxygen and the outgoing gas was tested for CO<sub>2</sub> by chromatography. For comparison the dye solution was also irradiated in the absence of the catalyst and the rate of degradation observed. The adsorption isotherms for the dye were obtained by prolonged agitation of the catalyst in dye solutions of varying concentrations, followed by spectrophotometric estimation of the dye remaining in the solution.

# 3. Results and discussion

Light-induced charge transfer at the semiconductor-dye-electrolyte interface is well known in connection with silver halide photography. In 1938 Gurney and Mott [16] suggested that the dye sensitization of silver halides results from the injection of electrons from the excited dye molecules to the conduction band of the silver halide. Subsequently, the dye sensitization of semiconductors was studied by many workers



Fig. 1. Absorption spectrum and structural formula of rose bengal.

and it was established that anodic (cathodic) sensitization occurs when an excited dye molecule adsorbed at the surface of the semiconductor injects electrons (holes) into the conduction (valence) bands [17–20]. The type of sensitization depends on the relative locations of the bands of the semiconductor and the energy levels of the dye. If they are located as shown in Fig. 2(a) an electron excited from the lower (S<sub>0</sub>) to the upper (S<sub>1</sub>) energy level is transferred to the conduction band. When the energy levels are located as shown in Fig. 2(b) an electron from the valence band is transferred to the unoccupied lower level (*i.e.* hole injection into the valence band). Generally n-type (p-type) semiconductors show anodic (cathodic) sensitization. The sensitized degradation of the dye can be explained as follows. Excited dye molecules adsorbed at the surface of the semiconductor particle inject electrons into the conduction band, which are transferred to oxygen molecules, *i.e.* 

$$D + h\nu \longrightarrow D^*$$
 (1)

$$D^* \longrightarrow D^+ + e^- \tag{2}$$

$$e^- + O_2 \longrightarrow O_2^- \tag{3}$$

A dye molecule that has lost an electron (*i.e.*  $D^+$ ) readily reacts with hydroxyl ions undergoing oxidation via the following steps

$$D^+ + OH \longrightarrow D + OH^0 \tag{4}$$

$$D+2OH^0 \longrightarrow H_2O+$$
 oxidation products (5)

The charge transfer cycle is completed by H<sup>+</sup> ions accepting electrons from O<sub>2</sub><sup>-</sup>

$$2\mathbf{H}^+ + 2\mathbf{O}_2^- \longrightarrow \mathbf{H}_2\mathbf{O} + 3/2\mathbf{O}_2 \tag{6}$$

At low concentrations of the dye ([D]) the rate equation governing the degradation of the dye is

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = -k[\mathrm{D}] \tag{7}$$

The constant k depends on the quantity of catalyst used and the intensity of light. It was observed that a plot of  $\ln[D]$  vs. t (Fig. 3) is a straight line for narrow intervals



Electrolyte

Fig. 2. Anodic (a) and cathodic (b) dye sensitization diagrams illustrating the band positions of the semiconductor and the energy levels of the dye.



Fig. 3. Plots of  $\ln[D]$  vs. t for several concentration intervals ([D] is dye concentration): (a)  $TiO_2$  (8.7 mg in 150 ml); (b) ZnO (20 mg in 150 ml).

# TABLE 1

Values of k at different initial concentrations  $[D]_i$  of the dye

$[D]_i \ (\mu \text{mol } l^{-1})$ 24.6	$k(\text{ZnO}) \ (\min^{-1})$ 0.77	$k(\text{TiO}_2) \ (\text{min}^{-1}) \\ 0.22$
7.4	1.53	0.68
1.7	4.3	1.96

of variation of [D]. Figure 3 shows the plots for several concentration intervals of the dye. There is a noticeable increase in the rate constant k with a decrease in [D]. This effect is associated with the concentration quenching of the excited dye molecules adsorbed at the catalyst surface

$$D^* + D^* + D^* + \dots \longrightarrow D + D + D + \dots$$
(8)

*i.e.* the excited dye molecules  $D^*$  interact with each other and dissipate the excitation energy as heat. At higher dye concentrations the quenching is increased as the surface concentration of the dye on the catalyst particle is also increased. When the surface concentration of the dye is high, the probability of the mutual interaction of excited dye molecules is enhanced. Table 1 gives the k values for TiO<sub>2</sub> and ZnO at several initial dye concentrations. It can be seen that the values for ZnO are somewhat higher than those for equivalent surface areas of TiO<sub>2</sub>. The dye adsorption isotherms of TiO<sub>2</sub> and ZnO are compared in Fig. 4. Both isotherms are of the Langmuir type and dye adsorption is stronger in the case of ZnO. A comparatively higher k value for ZnO can be attributed to the stronger dye adsorption. In addition to concentration quenching, the carrier trapping at the dye-semiconductor interface will also reduce the rate of the degradation reaction. A dye-sensitized charge transfer at a semiconductor surface involves only one band (conduction band for n-type) and no minority carriers are



Fig. 4. Dye adsorption isotherms for ZnO (a) and TiO<sub>2</sub> (b) (*n* is the amount of dye adsorbed per unit of solid mass and  $C_i$  is the initial concentration of the dye).

used. Consequently, surface and bulk recombination losses due to defects are not encountered and this is favourable for the photodegradation process.

The detection of carbon dioxide indicates that mineralization is taking place. However, partial oxidative decomposition via reaction (5) cannot be ruled out. If the intermediates do not absorb visible radiation, they will be further degraded by the direct photocatalytic mode.

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