

## Visible Light Induced Photodegradation of Organic Pollutants on Dye Adsorbed TiO<sub>2</sub> Surface

Debabrata Chatterjee

Chemistry Group, Central Mechanical Engineering Research Institute,  
Durgapur-713209, India

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### Abstract

Visible light assisted degradation of a organics in air-equilibrated aqueous mixtures has been achieved using Safranin-O adsorbed TiO<sub>2</sub> semiconductor particulate system. At ambient conditions over 50-75% degradation of organics has been observed on illuminating the reacting system with a 150W xenon lamp. A mechanism involving excitation of surface adsorbed dye, followed by charge injection into the TiO<sub>2</sub> conduction band and formation of reactive  $\cdot\text{O}_2^-/\cdot\text{HO}_2$  radicals is proposed for the degradation of organics to carbon dioxide.

*Key words* : Photodegradation, Dye sensitization, TiO<sub>2</sub> semiconductor, organics, visible light, Safranin-O

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### 1. Introduction

Photosensitized degradation of colored contaminants in waste water on semiconductor surface is of current importance. [1-5]. Although semi-conducting TiO<sub>2</sub> in presence of UV radiation has become the benchmark photo-catalyst for degradation of myriad of a water bound pollutants as documented in the literature [6-10], the vital drawback of TiO<sub>2</sub> semiconductor is that it absorbs a small portion of solar spectrum in the UV region (band gap energy of TiO<sub>2</sub> is 3.0 to 3.2eV). Hence, the photo-catalytic process has the disadvantage that it can not harvests maximum solar energy by utilizing visible light.

Very recently we had explored that the dye sensitization technique for degradation of colorants in visible light illuminated dye modified TiO<sub>2</sub> dispersion could also be workable for degradation of *colorless* water bound pollutants like aromatics, halocarbons and surfactants [11-14]. We have selected a number of organic pollutants viz. halocarbons, phenols, surfactants, pesticide etc. for this study. In the present paper we report the prospect of Safranin-O adsorbed TiO<sub>2</sub> towards decomposition of pesticide in some common pollutants obtainable in

industrial effluent in presence visible light and air.

### 2. Experimental

#### 2.1 Materials and methods

Adsorption of dye samples on to the surface of TiO<sub>2</sub> semiconductor (obtained from Fluka) and characterization of surface adsorbed dyes were carried by following the procedure reported earlier [11-14]. The concentration of adsorbed dye determined spectrophotometrically (by measuring the difference in absorbance of free dye and that in the supernatant liquid obtained after filtration) was found to be 519  $\mu\text{equivalent/gm}$  for Safranin-O. All other chemicals used were of A.R. grade and doubly-distilled water was used throughout the experiment. Spectral (UV-visible) measurements were carried out with a GBC Cintra 10 spectrophotometer. Fluorescence measurements were performed in the Chemistry Department, Burdwan University using a Hitachi F-4010 spectrofluorometer.

#### 2.2. Photo-degradation of pollutants

In a typical photo-catalysis experiment aqueous suspension (50ml) containing 100mg of surface modified photo-catalyst designated as TiO<sub>2</sub>-D and 0.1mmol of pollutant (designated as P hereafter) were taken in a

flat-surfaced glass reactor. The pre-aerated reaction mixture was illuminated with a 150W xenon lamp (Oriental Instruments) under continuous magnetic stirring. Oxygen was replenished by opening the photoreactor to the atmosphere when the reaction mixture was sampled after an appropriate interval of irradiation time. The pH of reacting system was adjusted at 5.0 (NaOH). Extent of pollutant degradation was estimated spectrophotometrically. Production of CO<sub>2</sub> was demonstrated by the precipitation of BaCO<sub>3</sub> in Ba(OH)<sub>2</sub> solution. The evolved CO<sub>2</sub> was flushed with oxygen through alkali (KOH) scrubber and estimated by titration against acid (HCl).

### 3. Results and discussion

Spectra of the Sfranine-O adsorbed on to the surface of the TiO<sub>2</sub> recorded in the solid state revealed no appreciable difference in the spectral features ( $\lambda_{\max}^{\text{Abs}} = 519\text{nm}$  and  $\lambda_{\max}^{\text{Em}} = 595\text{nm}$ ) that has been noticed for free dye in the aqueous solutions. Charge transfer and relevant photophysical properties of surface adsorbed Sfranine-O is available in a recent report [15].

A series of blank experiments revealed that nearly 8-12% of the initial concentration of the pollutants found to be adsorbed on to the surface of the TiO<sub>2</sub> catalyst in the dark under experimental conditions. No appreciable photo-degradation of organics was observed by illumination of unmodified TiO<sub>2</sub> with visible light. Dye molecules were found to be non-interacting with the pollutant molecules in dark as there was no change in the spectral pattern of dyes observed after 8 hrs of stirring the aqueous solution of dyes in presence of pollutant each in dark. Results of photo-degradation of pollutants with dye modified TiO<sub>2</sub> are summarized in Table 1. Failure of noticing any appreciable photo-degradation of any above pollutants after prolonged (8h) illumination either with dye adsorbed TiO<sub>2</sub>-D system in absence of oxygen or with dye adsorbed onto non-conducting material

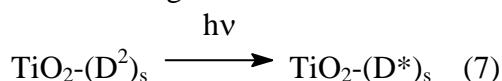
alumina (Al<sub>2</sub>O<sub>3</sub>-D) in place of TiO<sub>2</sub>-D provides good evidences that the described

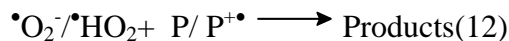
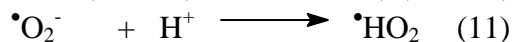
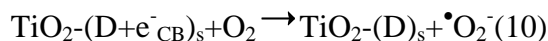
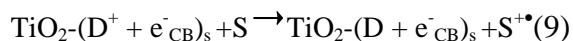
**Table-1** Results of TiO<sub>2</sub>-Sufarine-O catalyzed photo degradation of pollutants in water

P <sup>a</sup>	Degradation of P(%) <sup>b</sup>	<sup>c</sup> CO <sub>2</sub> (mmol)
Phenol	68	3.5
Chlorophenol	60	2.9
Trichloroethylene	77	0.98
1,2-Dichloroethane	70	1.1
Triton X 100	57 <sup>c</sup>	1.37
DBS <sup>d</sup>	61	0.94
CPC	49	0.03
Atrazine <sup>e</sup>	64	0.35

<sup>a</sup>initial concentration of pollutant is 1mmol, <sup>b</sup> based on pollutant concentration, <sup>c</sup>CO<sub>2</sub> produced in the reacting system after 5 h of reaction, <sup>d</sup> initial concentration of pollutant is 0.04 mmol, <sup>e</sup> initial concentration of pollutant is 0.0687mmol

photo-degradation is a semi-conducting TiO<sub>2</sub>-mediated phenomenon and oxygen is essential for an effective photo-degradation process. We had reported earlier [12] that the reduction of conduction band of the TiO<sub>2</sub> semiconductor takes place through photo-excitation of surface adsorbed thionine and eosin Y and <sup>•</sup>O<sub>2</sub>/<sup>•</sup>HO<sub>2</sub> species is produced through scavenging of conduction band electrons by oxygen molecules. Formation of <sup>•</sup>O<sub>2</sub> radical has been evidenced by using a chemiluminescent probe, luminol [16]. Based on the present experimental results and considering the earlier reports [11-14], a working mechanism of photo catalytic degradation of pollutant is typically shown in the following scheme.





( $h\nu$  = visible light ; D = safranin-O ; P = pollutant)

### Scheme-1

The presence of oxygen is profoundly related to the effective photo degradation of organics. In absence of oxygen the extent of photo degradation of any pollutants was found to be negligible, which necessarily indicates that the rapid scavenging of the conduction band electron by the dioxygen is very important for an effective photo degradation process as the reduced oxygen species press forward the degradation of organics [16]. Repeated attacks of  $\bullet\text{O}_2^- / \bullet\text{HO}_2$  radicals to pollutant species (P/P $^{\bullet+}$ ) in the reacting system essentially lead the degradation of organic molecules ultimately to carbon dioxide in a secondary autocatalytic dark reaction. As discussed in the previous reports that the surface adsorbed dyes are vulnerable towards the  $\bullet\text{O}_2^- / \bullet\text{HO}_2$  radicals attack in absence of pollutant and suffer slow photodegradation [12-14]. However, in presence of pollutants instead of self-degradation of surface adsorbed sensitizer dyes, pollutants undergo decomposition as observed experimentally (Table 1) in the present case. The results in Table 1 are in compliance to the fact that under specified reaction conditions the concentration of pollutants is highly in excess over the concentration of surface adsorbed dyes. As a result interaction of pollutants molecules with  $\bullet\text{O}_2^- / \bullet\text{HO}_2$  radicals would be kinetically more viable than with immobilized dye molecules.

### Conclusion

The results demonstrate the capability of the present catalytic system towards degradation of pesticide using visible light by generating highly reactive  $\bullet\text{O}_2^- / \bullet\text{HO}_2$  radical species. Repeated attack of these radical species on to

organic pollutant molecules results in their ultimate decomposition to carbon dioxide.

### Acknowledgment

We gratefully acknowledge the financial support (No.15/6/99-(ST)) obtained from MNES, Govt. of India and partial financial support from RSC (RSC research grant/2003). We are thankful to Dr. G.P.Sinha, Director of this institute for his encouragement. We are also thankful to Dr. A.K.Mukherjee, Dept. of Chemistry, Burdwan University for useful suggestions and extending help in fluorescence measurements.

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