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PHOTOMINERALIZATION OF CARBOFURAN BY TiO₂-SUPPORTED CATALYST

K. TENNAKONE, C. T. K. TILAKARATNE and I. R. M. KOTTEGODA Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka

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Abstract—Purification of water using TiO_2 as a photocatalyst has attracted a great deal of attention. The technical limitation of using the powder form of TiO_2 is the separation of the catalyst. It has been found that TiO_2 microcystallites can be firmly affixed to the glass plates without any deactivation. As an example, mineralization of carbofuran was tested. Results indicated that total mineralization can be achieved after 15 h of irradiation. This method is a low-cost process and plates can be reused without any deactivation. The major drawback is the requirement of UV irradiation for the water decontamination. © 1997 Elsevier Science Ltd

Key words-photocatalysts, carbofuran, microcrystallites, titanium dioxide, semiconductor photocatalysis

INTRODUCTION

Photocatalytic oxidation of organic contaminants in water such as agrochemicals and industrial waste using TiO₂ continues to be an active area of research with practical applications (Gal et al., 1992; Klopffer, 1992; Muneer and Das, 1992). Photocatalytic activity of TiO₂ results from the generation of highly oxidative holes during illumination with bandgap radiation (Mathews and McEvoy, 1992). The superoxide ion produced via electron acceptance by molecular oxygen could also participate in the oxidation reactions. A technical limitation of this method is the need for separation of the catalyst, which escalates the cost and completely rules out the adoption of this method for the purification of drinking water. This problem can be circumvented by supporting the catalyst in an inert substrate; for purification of drinking water, complete inertness and prevention of leaching are stringent requirements (Mathews, 1992; Fox et al., 1994; Tennakone et al., 1995). Glass possesses the above properties, and it has been found that TiO₂ can be firmly affixed to glass surfaces without deactivation and the supported TiO₂ is photocatalytically active in mineralization of organic compounds dissolved in water. To study the photocatalytic activity of the TiO₂coated glass plates, photocatalytic degradation of carbofuran was studied as an example. Carbofuran is extensively used in Sri Lanka as a soil insecticide having a lethal dose (LD_{50}) of 13 mg kg⁻¹ of body weight. Residues of the substance, even if the quantities are small, may accumulate in the surrounding soil and ground-water, which may be the source of human contact with toxic chemicals. Therefore, complete destruction of carbofuran is

essential, as it is potentially dangerous to living organisms.

EXPERIMENTAL

TiO₂ was coated on glass plates by the following method. One ml of titanium isopropoxide (Aldrich, London, UK) and 5 ml of glacial acetic acid (BDH) were added to 10 ml of propan-2-ol, the mixture being kept stirred. The mixture was then exposed to moist atmosphere of 85% relative humidity. Hydrolysis of titanium isopropoxide produces fine crystallites of TiO₂ and the above procedure prevents their agglomeration. Five ml of the above solution is further diluted with 10 ml of propan-2-ol and ~0.5 ml of this solution was spread on a sheet of commercial soda glass $(7.5 \times 2.5 \times 0.1 \text{ cm}^3)$ heated to a temperature of 125°C. The glass plates were baked at 430°C for 3 min. The loosely bound outer crust was removed after the plates were cooled. This process was repeated several times, until the TiO₂ coverage is ~2.5 × 10⁻⁵ g cm⁻² (gravimetrical analysis).

Photolysis experiments were conducted in a 400-ml water-cooled (26°C) photochemical reactor with a cylindrical quartz inner jacket. TiO2-coated glass plates (total area $7.5 \times 2.5 \text{ cm}^2$) were placed in the carbofuran solution (450 ml of 222 ppm) in the annular region between the two jackets. The light source used was a medium-pressure mercury arc lamp (400 W) fixed at the central axis of the inner jacket (Fig. 1). The light output was about 5×10^{19} photons per second, which is predominantly in the range of 365-366 nm. The solution was purged with oxygen (CO₂-free) at a bubbling rate of 15 ml min⁻¹. Carbon dioxide in the outgoing gas was monitored by a gas chromatograph (Shimadzu GC-9 AM Gas Chromatograph) with an activated charcoal column and a thermal conductivity detector. The other degradation products, ammonia and nitrate/nitrite, were estimated by indophenol blue and cadmium column reduction methods, respectively (Henry, 1969; Gotterman et al., 1978). Spectrophotometric, fluorometric examination of the solution revealed degradation of carbofuran. Chemical oxygen demand (COD) of the solution (which is a measure of the depletion of carbofuran or its partial degradation products) was measured at different time intervals during irradiation (Fresenius *et al.*, 1987). Control experiments were also carried out, i.e. irradiation of the carbofuran solution in the absence of TiO_2 and irradiation of distilled water in the presence of TiO_2 -deposited glass plates.

RESULTS AND DISCUSSION

The absorption spectrum of carbofuran is shown in Fig. 2. Absorption peaks corresponding to carbofuran which appeared at 220 and 280 nm decreased progressively and disappeared completely at ~15-h illumination. The rate of carbon dioxide evolution $(R[CO_2])$ during photolysis and the time evolution of the decrease of the COD value of the solution are presented in Figs 3 and 4, respectively. In agreement with spectrophotometric data, these observations also prove that complete mineralization of carbofuran occurs in about 15 h. The control experiments lead us to confirm the observation that the enhancement in the rate of degradation is a photocatalytic oxidation.

Fluorescence studies (Shimadzu RF-5000 Spectrofluorophotometer) show the formation of an intermediate during photocatalytic degradation of carbofuran (Fig. 5). The emission peak of carbofuran which appears at \sim 450 nm (excitation wavelength 325 nm) decreases with the progress of irradiation and a new peak originating from an unidentified



Fig. 1. Experimental set-up for illumination.



Fig. 2. Absorption spectrum of carbofuran (a) before irradiation and (b) after irradiation.

intermediate begins to appear at ~ 375 nm. Both peaks level off within ~ 15 h, showing that the intermediate is also degraded completely.

The optimum degradation rate $(0.155 \text{ ml min}^{-1} \text{ within 8 h})$ occurred when the coverage of TiO₂ on the surface of the plates was $\sim 2.5 \times 10^{-5} \text{ g cm}^{-2}$. Commercially available TiO₂ powder (Aldrich), when deposited on glass, also showed some activity towards degradation of carbofuran; however, a larger



Fig. 3. Rate of CO₂ formation [R(CO₂)] with irradiation time: (a) TiO₂-coated glass plates/O₂ purging; (b) TiO₂coated glass plates/Ar purging; (c) without TiO₂-coated glass plates/O₂ purging.



Fig. 4. Variation of chemical oxygen demand (COD) value with irradiation time.

coverage is required and the rate of degradation at the optimum coverage is much less than that of crystallites prepared by hydrolysis of titanium isopropoxide. It has been reported (Gratzel and Kalyanasundaran, 1994; Hagfeldt *et al.*, 1995) that TiO_2 particles prepared by this method have linear dimensions in the nanometer range (i.e. 20–50 nm). Fine particles are photocatalytically more active, because of the larger surface area and the readiness with which the photogenerated carriers are tunnelled to the solution interface. The resultant adhered film of TiO₂ (in this study) cannot be removed by merely rinsing with water or boiling in water or even by scratching. The adhesion is probably caused by the electrostatic charge on the TiO₂ particle surface being attracted to the negatively charged surface of the glass. In addition, the film was optically transparent, thermally stable and resistant to aqueous and organic solvents. The X-ray diffraction (XRD) patterns for all the samples showed typical diffraction features owing to the anatase structure (d = 3.52, 1.89 and 2.38). The size of the TiO₂ crystalities determined from XRD using Sherrer's equation was c. 58 nm.

The rate of CO₂ generation (due to the degradation of carbofuran) versus membrane thickness (number of coatings) was studied and the rates are given in Fig. 6. For extremely thin membranes, the degradation rates were low. For these membranes the limiting factor for the low rate is the lack of required amount of the catalyst. When the membrane is thick, the degradation rate decreases again. In thicker membranes, carriers must travel greater distances to catalytic sites where carbofuran is adsorbed, a process that increases the probability of e---h+ recombination prior to reaction. These results indicate the tendency of the photocatalytic rate to increase with film thickness and finally reach a maximum. R[CO₂] values are relatively high for 20 coatings and this film had a thickness of c. 6 μ m. Film thickness was measured by fringe interference techniques.

The effect of pH on the degradation rate was also studied. Optimum photocatalytic activity is seen at pH 6, and at high pH values the degradation rate was relatively low. The stoichiometric equation for



Fig. 5. Fluorescence spectrum of carbofuran (a) before irradiation, and after (b) 4-h irradiation, (c) 8-h irradiation, (d) 10-h irradiation, (e) 12-h irradiation and (f) 18-h irradiation.



Fig. 6. Variation of rate of CO_2 formation $R[CO_2]$ with TiO_2 film thickness (number of coatings).



Fig. 7. Structural formula of carbofuran.

oxidative degradation of carbofuran (the structural formula given in Fig. 7) is

$$C_{12}H_{15}O_3N + nOH^{\bullet} \rightarrow 12CO_2$$

+ other products (NH_4^+, NO_3^-, NO_2^-) (1)

The stoichiometry of equation (1) requires generation of $\sim 120 \text{ ml}$ of CO₂ (at 26°C and atmospheric pressure). The total amount of CO₂ evolved in the experiment (including CO₂ dissolved in the solution) is 110 ml, indicating that almost complete degradation has taken place. At the termination of photolysis (16 h), the solution was found to contain NH_4^+ , NO_3^- and NO_2^- , the equivalent nitrogen content being 8×10^{-4} moles. The nitrogen content of carbofuran used for photolysis is 1×10^{-3} moles. This small discrepancy could be understood as elimination of some ammonia during purging. The above experiment was conducted at a concentration of carbofuran (222 ppm) in solution which is much higher than the expected level of contamination under field conditions (1-2 ppm). Furthermore, only 16.87% of the photon flux (total area of the TiO_2 -coated plates = 7.5×2.5 cm²; area through which the light emanated = 445.17 cm^2) and irradiation for a much shorter duration of time would be sufficient. As an example, total mineralization of a 2-ppm solution usually occurs within 3 h, but it is

possible to achieve this within 30 min when the total photon flux can be used under optimal conditions (i.e. in a specially designed reactor). The efficiency of treatment depends upon the illumination, TiO_2 film thickness, photocatalytic surface area, etc., as well as the substrate concentration. Further experimentation in different light intensities and field trials are essential to check the applicability of the method.

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