Photocatalytic mineralization of paraquat dissolved in water by TiO$_2$ supported on polythene and polypropylene films

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Abstract

Paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) is extensively used as a weedicide and the resulting water contamination is a potential health hazard. It is found that paraquat can be mineralized to CO_2, NH_3, HCl and small quantities of NO_2^-/NO_3^- by solar or artificial irradiation of contaminated water in the presence of TiO$_2$-coated polythene or polypropylene films.

Keywords: Photocatalytic mineralization; Paraquat; Polythene films; Polypropylene films

1. Introduction

Complete mineralization of organic compounds dissolved in water using TiO$_2$ as a photocatalyst has attracted much attention as a promising method of depolluting contaminated water [1–6]. A large number of potentially hazardous compounds used as agrochemicals, insecticides, etc. have been tested in laboratory experiments and results confirm the wide applicability of TiO$_2$-based oxidative photodegradation of organic water contaminants. However, the separation of the dispersed catalyst is a technical problem and several authors have suggested that this can be circumvented by supporting the catalyst on a suitable substrate [7–11].

In an earlier paper [12] we showed that TiO$_2$ affixed to the surface of polythene films is photocatalytically active and as a model the photodegradation of phenol was studied. The present paper describes the photodegradation of paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride), a commonly used weedicide, using polythene or polypropylene films on which TiO$_2$ is supported. This method avoids the need for separation of the catalyst. The rate of photodegradation is slightly lower than that for TiO$_2$ suspension, possibly because of complete embedding of some TiO$_2$ grains within the polymer.

2. Experimental details

TiO$_2$ (Aldrich 99.9%, specific surface area as measured by a Horiba APA 700 particle size distribution analyser about 3.8 m^2 g^{-1}, mainly of anatase form but contaminated with rutile) was coated on polythene (thickness about 0.006 cm) and polypropylene (thickness about 0.005 cm) films by the following method. A sheet of paper (thickness about 0.01 cm) was laid on the surface of a hotplate (surface temperature about 80 °C) and the film was stretched above the sheet of paper. TiO$_2$ was sprinkled on the surface of the film and rubbed with cotton wool. The coated film was rinsed with NaOH to remove grease and washed with water to release the loosely bound particles. Alternatively TiO$_2$ may be coated on polythene and polypropylene by ironing a film evenly spread with TiO$_2$ powder. The difference in weight between the coated and bare films gave the TiO$_2$ coverage as 8.8×10^{-5} g cm^{-2} for polythene and 3.1×10^{-5} g cm^{-2} for polypropylene. In the above processes TiO$_2$ particles become affixed to the surface of the film and embedding of particles inside the plastic material is minimal. Embedded particles are not photocatalytically active and lead to some degradation of the film [12]. Photolysis experiments were carried out in a 500 ml water-cooled (26 °C) photochemical reactor (Applied Photophysics) with a cylindrical quartz inner jacket (diameter about 5.7 cm). The TiO$_2$-coated film was wrapped around the quartz cylinder. The light source (400 W medium pressure mercury lamp of photon flux about 5×10^{19} photons s^{-1}) was mounted on the central axis of the cylinder. Paraquat solution (400 ml containing 50 ppm paraquat) was placed in the annular region (width about 0.65 cm) between the quartz cylinder and the double-walled Pyrex outer jacket. Solutions were kept purged with oxygen at a rate 15 ml min^{-1} and the paraquat concentration in the solution was estimated colorimetrically by the dithionite method [13]. Carbon diox-

ide in the outgoing gas was monitored by gas chromatography (Shimadzu GC 9AM gas chromatograph, activated charcoal column, thermal conductivity detector). The other degradation products NH_4^+ and NO_3^-/NO_2^- were estimated by indophenol blue and cadmium column reduction methods [14] respectively.

Experiments were also conducted to examine paraquat degradation under solar irradiation when the catalyst is coated on polythene and polypropylene films (film area 100 cm²). Samples of paraquat solution (initial concentration 50 ppm) contained in a cylindrical glass vessel (diameter 12.2 cm, height 6.5 cm) were exposed to sunlight (the average solar intensity during the period of exposure as measured by an Eko Model SBP-801 pyranometer was about 6.80 kW m⁻²).

3. Results and discussion

Fig. 1 shows the rate of carbon dioxide evolution ($R(CO_2)$) in the reactor experiment when the initial concentration of paraquat was 50 ppm. $R(CO_2)$ initially increases and then begins to decrease when the degradation is nearly complete. The total amounts of CO_2 evolved in the experiments with the polythene and polypropylene films are 24.6 ± 0.4 and 25.2 ± 0.4 ml respectively. The stoichiometry of paraquat degradation according to the schematic equation

$$C_{12}\ddot{H}_{14}Cl_2N_2 + nOH \longrightarrow 12CO_2 + \text{other products}$$

$$(NH_4^+, NO_3^-/NO_2^-, H_2O, HCl) \quad (1)$$

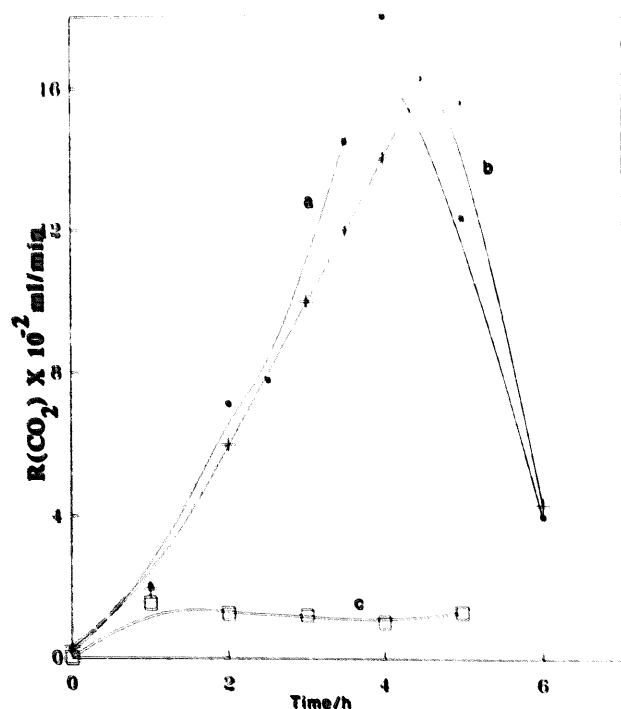requires the generation of about 20.6 ml of CO_2. The source of the slight excess of CO_2 is presumably the impurities in

Fig. 1. Rate of carbon dioxide evolution ($R(CO_2)$) vs. time: a, TiO₂-coated polythene film; b, TiO₂-coated polypropylene film; c, polythene film without TiO₂.
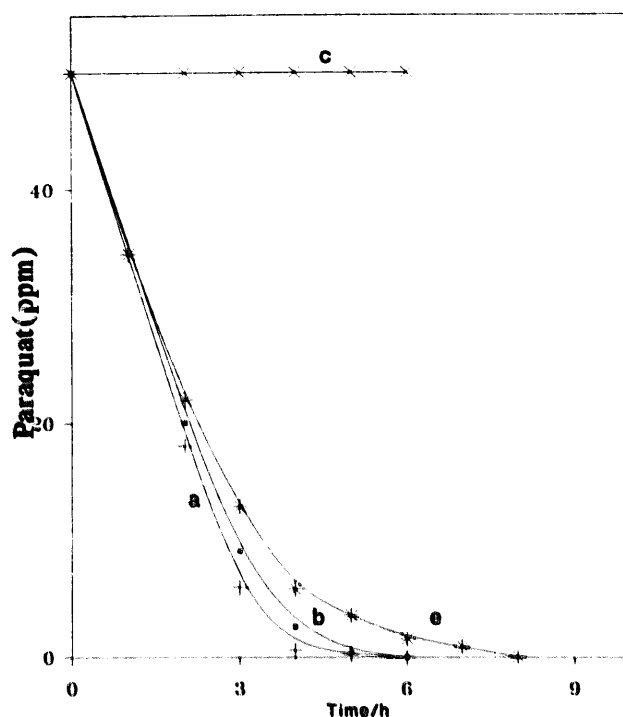

Fig. 2. Depletion of paraquat in solution: a, TiO₂-coated polythene film in reactor experiment; b, TiO₂-coated polypropylene film in reactor experiment; c, polythene film without TiO₂ in reactor experiment; e, TiO₂-coated polythene film in sunlight.

the film. When a TiO₂-coated film immersed in distilled water is irradiated, CO_2 approximately equivalent to the excess is liberated. Fig. 2 indicates the depletion of paraquat in the solution under the same experimental conditions.

The main degradation product originating from nitrogen in paraquat is ammonia. The time development of ammonia during photolysis is shown in Fig. 3. Small but detectable amounts of nitrite and barely detectable quantities of nitrate were also observed (Fig. 4). Perhaps the primary degradation product originating from nitrogen in paraquat is ammonia and NO_2^-/NO_3^- are oxidation products of ammonia. It is known that in the presence of oxygen, ammonia in aqueous solution is photo-oxidized to NO_2^-/NO_3^- by UV light; TiO_2 enhances the rate of oxidation [15]. The stoichiometry of paraquat degradation requires the generation of 1.7×10^{-4} mol NH_3. The yield of ammonia obtained after 6 h irradiation is about 1×10^{-4} mol. this is expected as some ammonia is eliminated during purging. It was found that paraquat is also completely mineralized when the catalyst-coated film submerged in the solution is exposed to sunlight. The depletion of paraquat in the solution and the generation of ammonia are presented respectively in Fig. 2, curve e and Fig. 3, curve b. In experiments with UV lamps and sunlight the optimum photocatalytic activity occurs when the TiO_2 coverage is approximately 8.8×10^{-5} g cm⁻² for polythene and 3.1×10^{-5} g cm⁻² for polypropylene. Thus a significantly lower coverage is sufficient in the case of polypropylene. Polythene softens at lower temperatures compared with polypropylene; consequently, in the process of coating, more
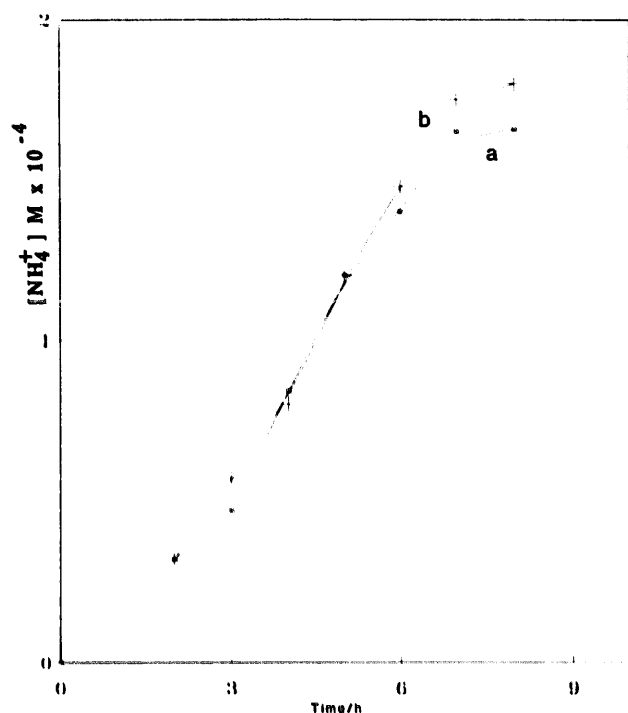
Fig. 3. Time development of ammonia in photolysis solution: a, experiment with UV lamps and TiO_2-coated polythene film; b, experiment with sunlight and TiO_2-coated polythene film.

particles become embedded inside the plastic in the case of polythene. This is also supported by the observation that when TiO_2 is coated on polythene at lower temperatures, higher activity is obtained for lower surface coverage of TiO_2. Embedded particles are photocatalytically inactive as they are not wetted by the solution. Adsorption of the contaminant [16] on the TiO_2 surface is an essential requirement for its catalytic photodegradation; partially embedded TiO_2 particles retain the ability to adsorb species in the solution and activation energies needed for oxidative degradation remain unaltered [17]. In the above experiments the initial paraquat concentration was 50 ppm as paraquat contamination under field conditions is not expected to exceed this value. Paraquat in concentrations higher than 50 ppm is also photodegraded by the catalyst-coated films.

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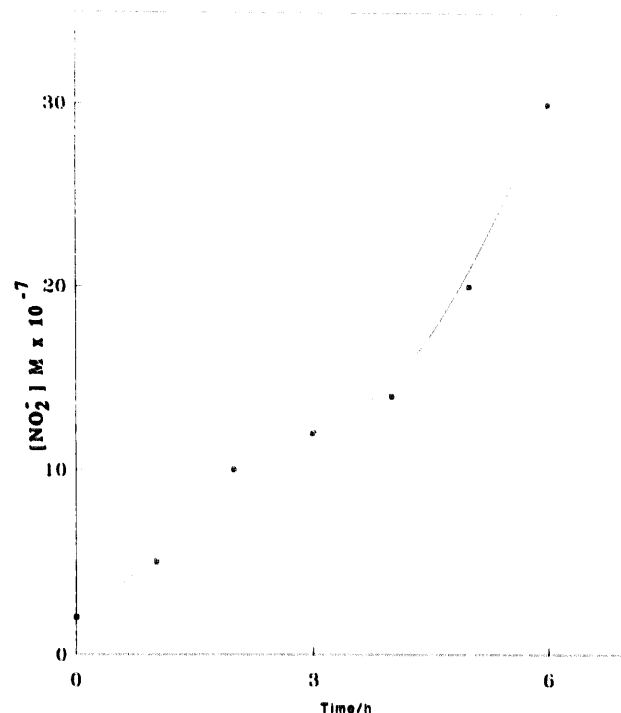[1] M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello and N. Serpone, *Chemosphere, 14* (1985) 195.

Fig. 4. Production of nitrite in photolysis solution in experiment with TiO_2-coated polythene film.

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