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Photocatalytic degradation of organic contaminants in water with TiO$_2$ supported on polythene films

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Abstract

TiO$_2$ is known to be an excellent photocatalyst for complete mineralization of organic contaminants in water. However, the separation of TiO$_2$ particles creates problems in practical application of the process. It is found that TiO$_2$ can be readily supported on polythene films without inhibiting the photocatalytic activity. As an example, data on photocatalytic degradation of phenol by TiO$_2$ supported on polythene films is presented.

Keywords: Photocatalytic degradation; Organic contaminants; Polythene films

1. Introduction

It is now established that organic contaminants in water can be completely mineralized by irradiation in the presence of oxygen and the photocatalyst TiO$_2$ [1–7]. Light absorbed by the catalyst generates electron-hole pairs that rapidly tunnel into the solution. Holes are accepted by OH$^-$ ions in the solution to generate highly oxidative hydroxyl free radicals (OH^0) which degrade the organic molecules [8]. Electrons are consumed by dissolved oxygen to yield O$_2^-$ and the charge transfer cycle is completed by reaction of O$_2^-$ with H$^+$ ions.

Various classes of potentially hazardous compounds (e.g. chloroaromatic, organophosphorous compounds etc.) have been tested and results confirm the wide applicability of TiO$_2$ based photocatalysis [3,9–12]. However, a practical limitation of the method is separation of the catalyst, once the process is completed. Several authors have shown that the problem can be circumvented by supporting the catalyst on a suitable substrate [13–20]. We have found that polythene film is an effective cheap substrate for binding TiO$_2$ particles. TiO$_2$ can be bound to the surface of polythene films, simply by ironing film sprinkled with TiO$_2$ powder. We found that TiO$_2$ in such films are photocatalytically active. As an example, data on photodegradation of phenol, in the presence of TiO$_2$ coated polythene film, is presented.

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2. Experimental

The anatase form of TiO$_2$ (Aldrich 99.9%) of specific surface area ~ 3.8 m^2 g^{-1} (as measured by Horiba particle size distribution analyzer (CAPA 700)) was coated on polythene film (commercial polythene film, thickness 0.006 cm) by the following method. Cleaned polythene film was laid horizontally on a talbe (preferably on a clean sheet of glass). The film was evenly sprinkled with TiO$_2$ powder at a coverage of $\sim 10 \times 10^{-5}$ g cm^{-2} (powder can be made to spread evenly on the surface of the film by rubbing with cotton wool). A sheet of paper is then placed above the film and ironed (temperature of the iron ~ 74 °C, weight = 1.9 kg, surface area = 155 cm^2). The film is rinsed with sodium hydroxide to remove grease, washed with water to release loosely bound particles of TiO$_2$ and dried. The difference in weights of coated and the bare films gave TiO$_2$ coverage as 8.8×10^{-5} of cm^{-2}.

Photolysis experiments were carried out in a 500 ml water-cooled (26 °C) photochemical reactor (Applied Photophysics) with a cylindrical quartz inner jacket (diameter ~ 5.7 cm). TiO$_2$ coated polythene film (14×15 cm^2) was wrapped around the quartz cylinder. The light source (400 W medium pressure mercury lamp) was mounted at the central axis of the cylinder. Photolysis solution (400 ml of 10^{-3} M phenol) was placed in the annular region (width of 0.65 cm) between the quartz cylinder and the double walled pyrex outer jacket. Solutions were kept purged with oxygen at a bubbling rate of 15 ml min^{-1}. Phenol concentration was estimated

fluorometically at 260 m (Shimadzu RF-5000, Spec-trofluorophotometer). Carbon dioxide in the outgoing gas was monitored by gas chromatography (Shimadzu GC-9AM gas chromatograph, activated charcoal column, thermal conductivity detector).

An experiment was also carried out to examine phenol degradation under solar irradiation, when the catalyst is coated on a polythene film. The phenol solution (initial concentration = 1.2×10^{-5} M) was contained in a cylindrical glass vessel (diameter 12.2 cm, height 6.5 cm). TiO_2 coated circular polythene film (diameter 12 cm) was kept submerged in the solution and exposed to sunlight. The average solar intensity during the period of exposure as measured with an Eko Pyranometer (Model SBP-801) was 0.67 kW m^{-2}.

Results and discussion

Fig. 1 shows the rate of carbon dioxide evolution in the reactor expeirment with TiO_2 coated polythene film, when the initial concentration of phenol in the solution is 10^{-3} mol l^{-1}. For comparison, carbon dioxide evolution from TiO_2 coated polythene film immersed in distilled water and bare polythene film immersed in phenol solution is also presented. In the former case, a detectable but small quantity of carbon dioxide is liberated. This demonstrates that the degradation of polythene by coating TiO_2 on the surface is negligible. Alternatively the source of carbon dioxide in this case
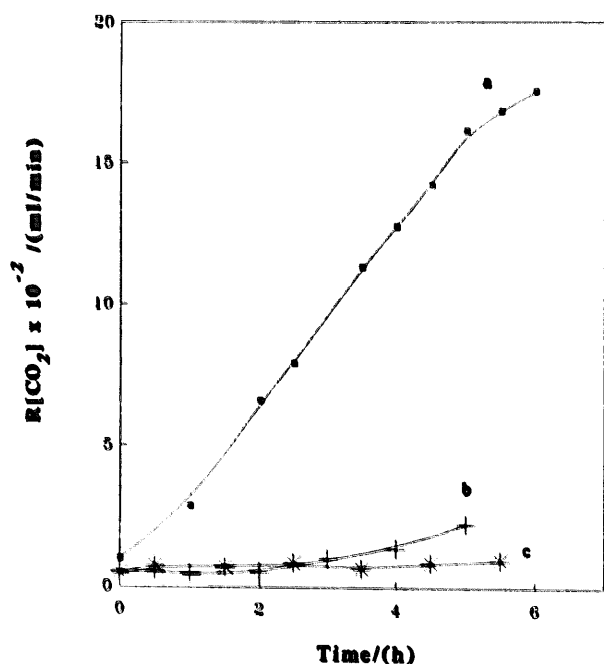
could be impurities present in polythene. The insignificant quantity of carbon dioxide detected in the latter expeirment arise from degradation of phenol by UV light. When fine particles of TiO_2 are embedded internally in polythene films, it has been shown that, polythene undergoes significant photodegradation when irradiated with UV light [21,22]. In the present case, TiO_2 particles are mostly affixed to the surface (Fig. 2), and a major portion of the particle surface is wetted by the solution. Consequently photogenerated holes are preferentially transferred to absorbed OH$^-$ ions on the TiO_2 particles. Thus, photodegradation holes are preferentially transferred to absorbed OH$^-$ ions on the TiO_2 particles. Thus photodegradation of polythene by hole consumption is suppressed. From Fig. 1, the total amount of carbon dioxide evolved from the phenolic solution in 6 h is ~63 ml, whereas complete degradation of phenol via,

$$C_6H_5OH + 28OH \longrightarrow 6CO_2 + 17H_2)$$

should generate a maximum of 54 ml of carbon dioxide. Again from the same figure, TiO_2 coated polythene (in the absence of phenol) yields 8.6 ml of carbon dioxide in 6 h. Clearly extra carbon dioxide originates from the film. Impurities in the film and/or partial degradation of polythene are responsible for this effect. The method we have adopted for deposition of TiO_2 on polythene may result in partial embedding of TiO_2 grains on polythene (i.e. a situation intermediate to that of 1 and 2 of Fig. 2). As visible degradation of polythene was not observed, it is more likely that the source of extra carbon dioxide is impurities in the polythene film. In the present method of TiO_2 deposition, all TiO_2 particles may not become adhered to the external surface. Results obtained are reproducible and improvement of the technique of deposition may be give better results.

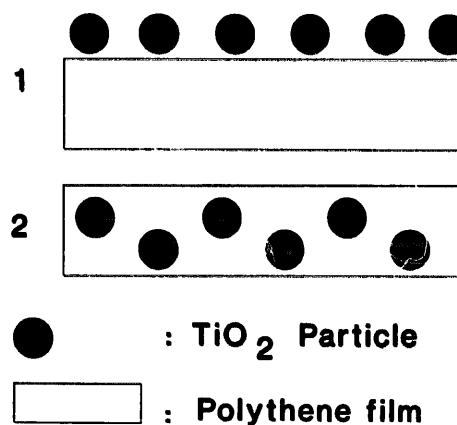Fig. 3 shows the depletion of phenol in the presence of a TiO_2 coated film, when the solution is exposed

Fig. 1. Rate of CO_2 evolution with (light source was 400 W Hg arc lamp). (a) 10^{-3} M phenol solution with TiO_2 coated polythene film. (b) Distilled H_2O with TiO_2 coated polythene film. (c) 10^{-3} phenol solution with bare polythene film.

Fig. 2. (1) TiO_2 particles affixed to the surface of the polythene film. (2) TiO_2 particles embedded in the polythene film.
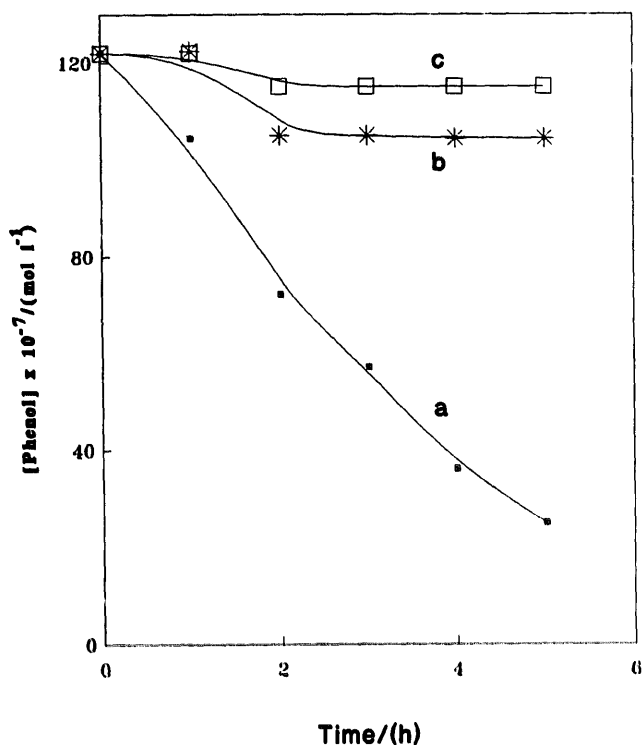
Fig. 3. Depletion of phenol with sunlight. (a) 12×10^{-5} M phenol solution with TiO_2 coated polythene film. (b) 1.2×10^{-5} M phenol solution with TiO_2 coated polythene film in the absence of sunlight. (c) 1.2×10^{-5} M phenol solution with bare TiO_2 film.

to sunlight. (The average solar intensity during the period of exposure are measured with an Elco pyranometer (Model SBP-801) was ~ 0.7 kW m^{-2}). The solution was not aerated by bubbling air or stirred. It is seen that more than 50% phenol has got degraded in ~ 2.5 h. In absence of TiO_2 in the film, depletion of phenol was not observed.

The above investigation shows that TiO_2 supported on the surface of polythene films is photocatalytically active and suitable for mineralization of organic pollutants in water. The support materials (commercial polythene film) are cheap and the coating procedure is simple. Furthermore, the catalyst coated polythene films can be kept submerged just below the surface of ponds, pools and even running water.

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