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Photodegradation of 3,4-dichloropropionamide in aqueous TiO_2 suspensions

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Abstract

Results of the photodegradation of 3,4-DPA in the presence of TiO_2 are discussed. 100% destruction of an aqueous solution of 3,4-DPA (265 ppm) occurred within 5 h when illuminated with a medium pressure lamp ($\lambda \approx 365$ nm) in the presence of TiO_2. During the photodegradation of 3,4-DPA, formation of Cl^-, H^+, NO_3^- and CO_2 were observed. Application of solar energy instead of artificial illumination also gave successful results.

Keywords: Pesticides; Photodegradation; Semiconductors

1. Introduction

Pesticides are widely used in agriculture although their use may create environmental hazards. During the last few years the amounts of pesticides used have increased rapidly. In certain countries, farmers apply pesticides in more than recommended amounts. These pesticides can affect man and other organisms. Non-persistent pesticides decompose quite rapidly in the natural environment and do not create many problems. Persistent pesticides have caused concern because they are quite stable in the natural environment. Most of these persistent pesticides are highly toxic to many animals and plants. Chlorinated hydrocarbons fall into the latter category. The toxicity of organochlorine compounds is related to their chlorine content.

3,4-Dichloropropionamide (3,4-DPA) is widely used in paddy cultivation as a post-emergence selective herbicide to control weeds with broad leaves. LD_{50} of 3,4-DPA for rats is 1285 mg tech kg^{-1} and for man it can cause depression of the central nervous system and irritation of eyes, nose, skin etc. [1].

Organic pollutants can be degraded photochemically by using semiconductors such as TiO_2, ZnO or Fe_2O_3 [2–4]. Heterogeneous photocatalytic degradation of 3,4-DPA is described herein. The effect of various parameters on the photodegradation of 3,4-DPA is also discussed and mechanism for this degradation process is proposed.

2. Experimental details

2.1. Materials

TiO_2 (anatase) was purchased from Aldrich. All solutions were prepared using distilled deionized water. Standard solutions of anions (Cl^-, NO_3^-) were made from respective ANALAR grade sodium salts and diluted to appropriate strengths immediately before use.

2.2. Photoreactor and light source

A photochemical reactor (model RQ 125, Photochemical reactors Ltd, UK) and a medium pressure mercury lamp (λ = mainly 365–366 nm) were used. A Pyrex glass thimble was used to cut-off light having $\lambda < 300$ nm. The temperature of the system was kept at room temperature by circulating water. Dioxygen was bubbled at a flaw rate of 23 cm^3 min^{-1} through the inlet of the photochemical reactor.

2.3. Procedure

An aqueous solution of 3,4-DPA was ultrasonically agitated with a known amount of TiO_2 for 2 h in the dark and then transferred into the photochemical reactor. Illumination was carried out using the medium pressure mercury lamp while bubbling dioxygen (23 cm^3 min^{-1}) through the solution. Samples were taken out at different time intervals and were immediately centrifuged to remove TiO_2. These sam-

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ples were used for analyses. Unless specified, all the reactions conducted in the photochemical reactor were carried out using 200 cm^3 of aqueous solutions of 3,4-DPA (265 ppm) containing TiO_2 (100 mg dm^{-3}). The initial pH values of 7 and 9 were adjusted by using pH = 7 buffer (a mixture of Na_2HPO_4 and $KHPO_4$) or NaOH.

Experiments under sunlight were carried out in glass troughs containing 500 cm^3 of aqueous solutions of 3,4-DPA (265 ppm) with or without TiO_2 (100 mg dm^{-3}). These experiments were carried out on sunny days between 9.00 a.m and 4.00 p.m.

2.4. Analyses

Concentrations of 3,4-DPA were measured by high performance liquid chromatography (HPLC). The HPLC apparatus (JASCO) was fitted with a SIL C18-5 column and a variable wavelength UV detector. The wavelength used for detection was 254 nm and retention time was 8.3 min. The mobile phase was 20% H_2O and 80% CH_3OH. Cl^- and NO_3^- concentrations were measured by using ion-selective electrodes attached to an ion meter (Horiba). The pH was measured by a pH meter (Horiba).

CO_2 was swept out of the reactor by a flow of O_2 and was allowed to bubble through three consecutive solutions of $Ba(OH)_2$. Weight of the $BaCO_3$ precipitated was measured.

3. Results and discussion

3.1. Photodegradation of 3,4-DPA

3.1.1. Decrease in concentration of 3,4-DPA

Fig. 1 shows the destruction of 3,4-DPA from an aqueous solution of 3,4-DPA which had an initial concentration of 127 ppm in the presence of 100 mg dm^{-3} TiO_2, and almost 100% destruction occurred after irradiating for 4–5 h. The half-life ($t_{1/2}$) of this photodegradation process is about 100 min.

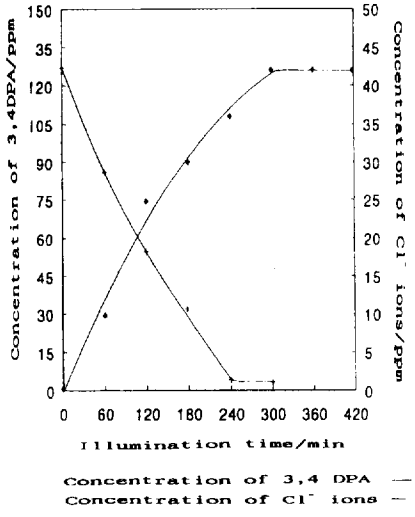


Fig. 1. Destruction of 3,4-DPA and formation of Cl^- ions in the presence of 100 mg dm^{-3} TiO_2.

3.1.2. Products of photodegradation of 3,4-DPA

Formation of Cl^-, CO_2, NO_3^- and a decrease in pH were observed.

3.1.3. Formation of Cl^- ions

Fig. 1 indicates that the formation of Cl^- ions increases with time. 100% stoichiometric amount is obtained after irradiating for 5 h. in the presence of TiO_2. As the toxicity of organochlorine compounds are related to chlorine content, dechlorination of 3,4-DPA by this method is important for detoxification.

3.1.4. Mineralization of organic C to CO_2

As Fig. 2 indicates complete oxidation of organic C to CO_2 was not observed to result from illumination of a 265 ppm aqueous solution of 3,4-DPA in the presence of TiO_2 (100 mg dm^{-3}) for 32 h. However under the same conditions 100% destruction and dechlorination of 3,4-DPA were observed within 5 h. This indicates that photodegradation of 3,4-DPA occurs through intermediates. Formation of compounds containing carbonyl group were observed during the reaction.

3.1.5. Formation of NO_3^- ions

When a 265 ppm solution of 3,4-DPA was illuminated in the presence of TiO_2 (100 mg dm^{-3}) for 6 h, 75% formation of NO_3^- was observed (Fig. 3).

3.1.6. Change in pH during the photodegradation

During the photodegradation of 3,4-DPA pH decreases (Fig. 4). This is due to the formation of acidic products such as HCl and HNO_3.

3.2. Effect of various parameters on the degradation of 3,4-DPA

Degradation of 3,4-DPA does not occur in the absence of light.

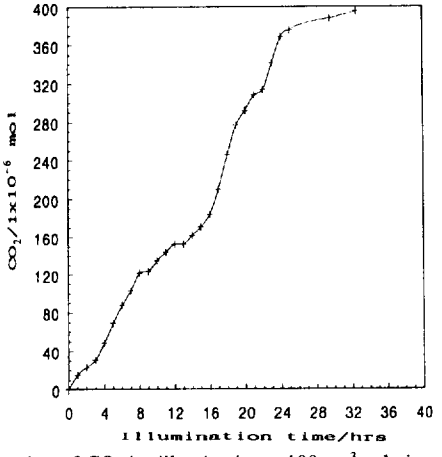


Fig. 2. Formation of CO_2 by illuminating a 100 cm^3 solution of 3,4-DPA (265 ppm) in the presence of TiO_2 (100 mg dm^{-3}).

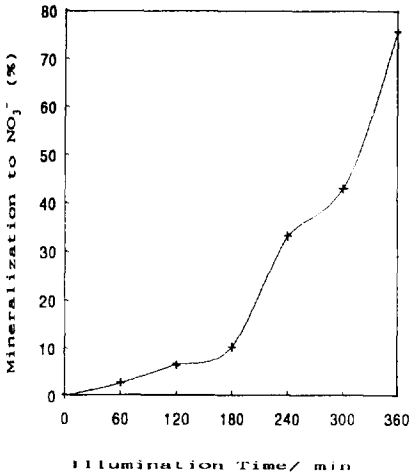


Fig. 3. Formation of NO_3^- during irradiation of 3,4-DPA (265 ppm, 100 mg dm^{-3} TiO_2).

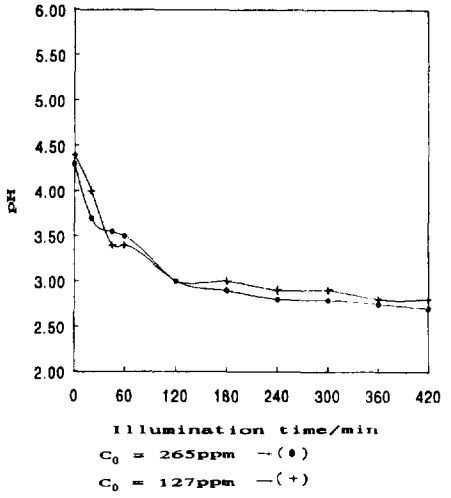


Fig. 4. Change in pH of 3,4-DPA during its photodegradation (100 mg dm^{-3} TiO_2).

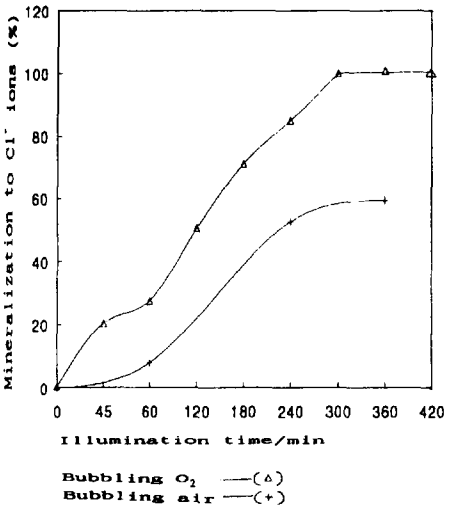


Fig. 5. Effect of O_2 on the dechlorination of 3,4-DPA (TiO_2 100 mg dm^{-3}).

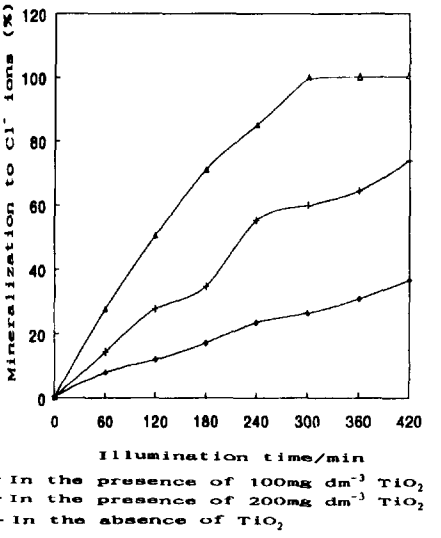


Fig. 6. Effect of TiO_2 on the dechlorination of 3,4-DPA (265 ppm).

3.2.1. *Effect of oxygen*

When a 265 ppm aqueous solution of 3,4-DPA was irradiated in the presence of TiO_2 (100 mg dm^{-3}) in a dioxygen atmosphere 100% dechlorination occurred after irradiation for 6 h. However, under similar conditions air caused only 60% dechlorination (Fig. 5). This shows the requirement of dioxygen for photodegradation of 3,4-DPA in the presence of TiO_2.

3.2.2. *Effect of amount of TiO_2*

When a 265 ppm aqueous solution of 3,4-DPA was irradiated in the presence of 100 mg dm^{-3} of TiO_2 100% dechlorination of 3,4-DPA was observed within 5 h. However as the concentration of TiO_2 increases dechlorination decreases (Fig. 6). This is due to the shielding of incident light by TiO_2 particles. Dechlorination is quite slow in the absence of TiO_2.

3.2.3. *Effect of initial concentration of 3,4-DPA*

3.2.3.1. *Effect on destruction of 3,4-DPA*

The effect of initial concentration on the photodegradation of 3,4-DPA was studied. In the presence of 100 mg dm^{-3} TiO_2, when 127 ppm and 265 ppm 3,4-DPA solutions were taken as initial concentrations, half-lives were $t_{1/2} \approx 100$ min and 105 min respectively. Within the experimental errors this difference is not significant. Therefore, $t_{1/2}$ is independent of the initial concentrations considered herein.

3.2.3.2. *Effect on dechlorination of 3,4-DPA*

When the initial concentrations of 3,4-DPA were 127 ppm and 265 ppm, 100% dechlorination occurred within 5 h of illumination in the presence of 100 mg dm^{-3} TiO_2.

3.2.4. *Effect of initial pH*

3.2.4.1. *Effect on degradation of 3,4-DPA*

When a solution of 3,4-DPA (265 ppm) having an initial pH of 4.3 (normal pH of the pesticide) was illuminated in the presence of TiO_2 (100 mg dm^{-3}), 100% degradation of

3,4-DPA occurred in 5 h. Under the same conditions, however, if the initial pH was 9 or 7, degradation of 3,4-DPA was 75% and 60% respectively. The $t_{1/2}$ for the destruction of 3,4-DPA at initial pH of 7 was twice as that of at pH 4.3. Higher activity in acidic and basic media may be due to the possible hydrolysis of 3,4-DPA in acidic and basic media.

3.2.4.2. Effect on dechlorination of 3,4-DPA

Under the same experimental conditions as described in Section 3.2.4.1, 100% dechlorination occurred in 5 h, when the initial pH was 4.3. However, when the initial pH was 9 or 7, dechlorination during that period was 70% and 40% respectively.

3.3. Application of solar energy instead of artificial light for the photodegradation of 3,4-DPA

The application of artificial light source for the degradation of 3,4-DPA is not applicable to the natural environment. To solve this problem solar experiments were carried out.

3.3.1. Destruction of 3,4-DPA under solar exposure

Under solar illumination for 7 h, the destruction of 3,4-DPA was higher (60%) in the presence of TiO_2 (100 mg dm^{-3}) than in the absence of TiO_2 (33%). The slower activity compared with that of artificial illumination is due to the absorption of a small fraction of solar energy by TiO_2.

3.3.2. Dechlorination of 3,4-DPA under solar exposure

When irradiated by solar energy for 7 h in the absence of TiO_2 dechlorination of 3,4-DPA was very low ($\approx 30\%$). However in the presence of TiO_2 (100 mg dm^{-3}) solar irradiation caused approximately 70% of dechlorination. As the toxicity of organochlorine compounds is related to the amount of chlorine present in them, the presence of TiO_2 is essential when detoxification of 3,4-DPA is carried out under solar exposure.

3.3.3. Change in pH of 3,4-DPA under solar exposure

In the presence of TiO_2, the pH decreased from 4.3 to 2.8 owing to the formation of HCl and HNO_3 by the degradation of 3,4-DPA. However, in the absence of TiO_2 the change in pH under solar exposer was very low (from 4.3 to 4.1).

3.4. Mechanism of photodegradation of 3,4-DPA

When a semiconductor is illuminated with light having $\lambda >$ band gap energy, electrons and holes are formed in the conduction and valence band respectively. The band gap energy for TiO_2 is 3.2 eV, $\lambda = 390$ nm [5].

$$TiO \xrightarrow{h\nu} e^-_{(cb)} + h^+_{(vb)} + TiO_2$$

Some of these charged particles migrate to the interface between TiO_2 particles and H_2O. Organic molecules adsorb on to the surface of TiO_2. Therefore oxidation–reduction reactions can take place [6,7].

$$e^- + O_2 \rightarrow O_2^-$$

These O_2^- ions are unstable and reactive [5].

$$O_2^- + H_2O \rightarrow HOO^{\bullet} + OH^-$$

$$O_2^- + H^+ \rightarrow HOO^{\bullet}$$

The latter occurs specially in acidic medium.

Peroxide radicals thus formed oxidize 3,4-DPA and other intermediate products [5].

$$h^+ + OH \rightarrow OH^{\bullet}$$

$$h^+ + H_2O \rightarrow OH^{\bullet} + H^+$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

$$H_2O_2 \rightarrow H\text{–}O\text{–}O^- + H^+$$

HOO^- is a good oxidizing agent and can oxidize 3,4-DPA and intermediate products.

As the time increases, concentration of intermediate products increases. Then, competition between intermediates and 3,4-DPA for the reactive sites of TiO_2 increases. As a result rate of photodegradation of 3,4-DPA decreases as the time increases (Fig. 1).

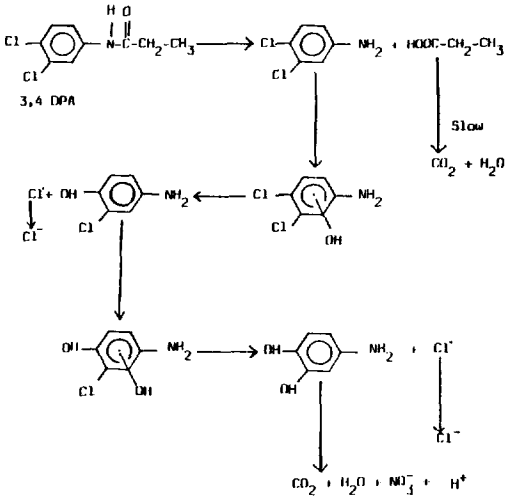
The photodegradation of 3,4-DPA may consists of several steps. Therefore it is difficult to propose a complete mechanism from the present data.

$HOO^{\bullet}$ and $HO^{\bullet}$ may attack aromatic ring and chloride groups of 3,4-DPA. After the addition of $OH^{\bullet}$ to the aromatic group, the ring opens. Dechlorination may occur by replacement of Cl by $OH^{\bullet}$ radicals.

$$Cl + OH^{\bullet} \rightarrow Cl^{\bullet} + OH$$

$$Cl^{\bullet} + e_{(cb)} \rightarrow Cl^-$$

Finally CO_2, NO_3^-, Cl^-, H^+ and H_2O are formed via the formation of intermediates (Scheme 1).



Scheme 1.

The overall reaction may be

$$2C_9H_9ONCl_2 + 23O_2 \rightarrow 18CO_2 + 6H_2O + 2HNO_3 + 4HCl$$

4. Conclusions

3,4-DPA can be completely degraded and dechlorinated by illuminating with artificial light ($\lambda \approx 365$ nm) in the presence of TiO_2. Acidic medium is suitable for this reaction. Presence of oxygen and amount of TiO_2 present are important. Solar energy may also be used instead of artificial illumination.

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