

# Photocatalytic degradation investigation of dicofol

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**Photocatalytic degradation of dicofol was investigated on TiO<sub>2</sub> nano particles (TiO<sub>2</sub>-NPs) under UV light irradiation. It was shown that dicofol could be completely degraded into inorganic chloride ion under the condition of 0.25 mg/mL TiO<sub>2</sub>-NPs, 2 h irradiation of 400 W high pressure mercury lamp with a wavelength of 365 nm and air at a rate of 100 mL/min. The effects of the experimental conditions, including the amount of TiO<sub>2</sub>-NPs, irradiation time and the intensity of light, were studied. The apparent photodegradation rate constant was 0.167/min under the optimal condition. The photocatalytic degradation mechanism of dicofol was also discussed.**

nano TiO<sub>2</sub>, photocatalytic degradation, dicofol

Dicofol is a type of pesticide synthesized from DDT, and has proved their immense value in a wide variety of insecticidal application for tea and vegetable<sup>[1-3]</sup>. Same as other organochlorine pesticides, dicofol shows its acute and residual toxicity in the environment. Chen<sup>[4]</sup> reported that residual dicofol with 5 mg/kg could be found on the processed tea which was manufactured two weeks later after being sprayed with dicofol. During the tea manufacture process, as Sood's report<sup>[5]</sup>, dicofol kept its furthest loss of 52.0 % and 63.4 % in the initial processes of withering, rolling, fermentation and at last stage of drying for black tea and green tea, respectively. Due to the chemical properties of dicofol, it has been identified that dicofol is regarded as a potential "endocrine disrupting compound" since it would cause animal toxicosis, cancer, estrogenic effects, ect.<sup>[6,7]</sup>

As the wide usage of dicofol and its residual toxicity in the environment, there have been growing interests in studying the degradation of dicofol to reduce its pollution. Some reports for the efficient degradation, such as microbial degradation<sup>[8]</sup> and mechanochemical destruction<sup>[9]</sup>, have been published. Generally, in the microbial degradation, only a special kind of microorganism could

be applied to degrading an objective pesticide. In addition, the cultivation and purification of the microorganism were time-consuming, and it would take several days for the full degradation of the pesticides. In Hall's report<sup>[9]</sup>, an organochlorine pesticide, such as DDT, could be mechanochemically destroyed after a 12 h milling with calcium oxide in the argon atmosphere, and no volatile organic material was detected by a conventional GC/MS procedure. Although the above-mentioned methods were available to degrade organochlorine pesticides, they possessed some limitations such as time-consuming or high manipulation cost. Hence, the rapid, easy-to-operate, and low cost degradation methods should be highlighted.

In recent decades, many reports on the photodegradation of organic substances appeared on relative journals. Oxides as PtO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> and its composite were selected and utilized for the degradation. Some considerations were focused on the photocatalytic process based

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on anatase TiO<sub>2</sub> since it operated with low energy photons ( $\lambda < 388$  nm), and required no expensive catalysts. Photodegradation of polychlorinated herbicide “paraquat” was carried out in aqueous solution under UV irradiation<sup>[10]</sup>. PtO<sub>2</sub>/TiO<sub>2</sub> was used as a photocatalyst for the degradations of 4-chlorophenol in aqueous suspension<sup>[11]</sup>. Moreover, 2,3,6-trichlorobenzoic acid was converted to chloride under TiO<sub>2</sub>/UV system<sup>[12]</sup>. Recently, Hu<sup>[13]</sup> utilized TiO<sub>2</sub>-coated side-glowing optical fiber to break down wastewater. All the results indicated that photocatalytic degradation in the presence of TiO<sub>2</sub> is an effective way to degrade dicofol.

In this paper, we report a study of photocatalytic degradation of dicofol on TiO<sub>2</sub>-NPs under UV light irradiation. The effects of the experimental conditions, including the amount of TiO<sub>2</sub>, irradiation time and the intensity of light, were also studied. Finally, the photocatalytic degradation mechanism of dicofol is also discussed.

## 1 Experiment

### 1.1 Characterization and measurement

A home-made ion chromatography (conductance detector, Metrohm 732; anion exchange column, YSA8-81611; electrolyte suppressor, DZS-1A; flow pump, Shimadzu LC-10AtI) was used to detect the content of chloride ion with a current of  $60 \times 10^{-3}$  A for suppressor. Na<sub>2</sub>CO<sub>3</sub> of  $5.7 \times 10^{-3}$  mol/L and NaHCO<sub>3</sub> of  $4.8 \times 10^{-3}$  mol/L were used as gradient elution at a flow rate of 1.2 mL/min. The retention time of chloride ion was 3.12 min. Mercury lamps with 400 W and 16 W were employed as irradiation sources at a wavelength of 365 nm.

Hexane was used to extract degradation products, and the organic phase was collected and concentrated. Identification of degradation intermediates to propose mechanical pathways of dicofol was performed using a GC (Agilent 6890)-MS (5973) equipped with a DB-5 column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). Electron impact positive (EI<sup>+</sup>) ionization model with 70 eV was applied to the GC-MS analysis. The temperature program was selected as: injector temperature 280 °C, an initial oven temperature 100 °C heating to 270 °C at a rate of 10 °C/min and interface temperature 290 °C. A scanning mode with 50 to 500 msu was operated

### 1.2 Photodegradation

As shown in Figure 1, a cooling system with flowing

water was used to keep the reactor temperature at  $20 \pm 1$  °C. The distance between the lamp and the TiO<sub>2</sub> suspension was kept at 10 cm. An amount of dicofol dissolved in acetone was injected into reactor. After solvent was evaporated, TiO<sub>2</sub> powder was added to get suspension with concentration of 0.25 mg/mL and flow air bubble of 100 mL/min. To make a full adsorption of dicofol on TiO<sub>2</sub> nano particles, air flow was bubbled into suspension for 5 min before photocatalysis. After irradiation for different time, samples were filtered through a 0.45  $\mu$ m filter to remove TiO<sub>2</sub> particles. Filtered liquor was extracted by hexane and the aqueous phase was injected into ion chromatography to detect the concentration of chloride ions, whose change indicated the degradation degree of dicofol.

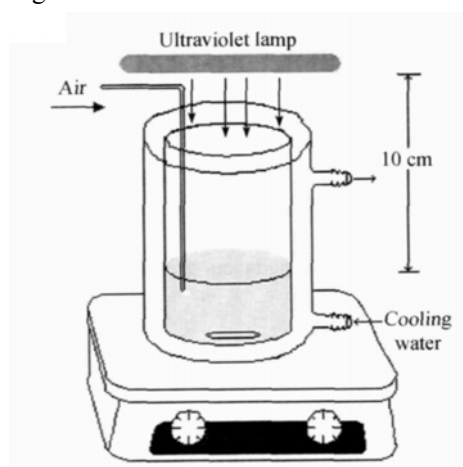


Figure 1 Setup for photocatalytic reaction experiment.

### 1.3 Computational details

Full geometry optimizations of dicofol were carried out by the B3LYP method with 6-31G(d) basis set. Vibrational frequency analyses were employed to assess the nature of optimized structures. An initial position for a possible  $\cdot$ OH radical attack was estimated from calculations of frontier electron density, whereas the point of adsorption of dicofol was judged from partial charges<sup>[14-16]</sup>. All calculations were performed using the Gaussian 03 program.

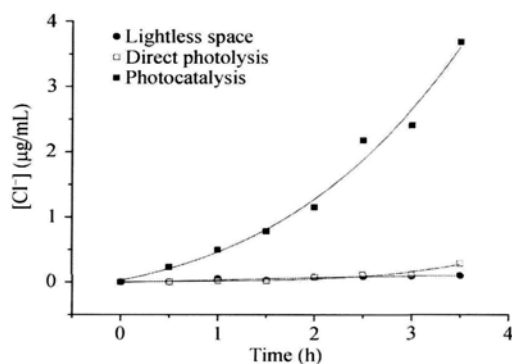
## 2 Results and discussion

### 2.1 Photocatalytic degradation of dicofol

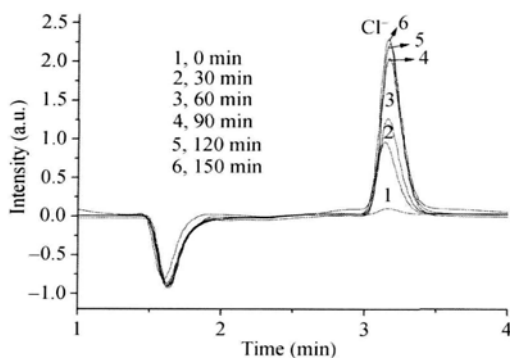
Generally, TiO<sub>2</sub> presents its photocatalytic activity in a wide range of wavelength due to its impurity and crystal defect on the surface, under the maximum effective

wavelength of 387 nm<sup>[17]</sup>. Therefore, mercury lamp with 365 nm was employed as irradiation source in this study. The concentration of chloride ion was taken as an indicator for the study of the effect of irradiation time under different conditions of direct photolysis and photocatalytic degradation, and a lightless space. The results shown in Figure 2 suggest that degradation degree obviously was increased with the increase of the irradiation time under photocatalysis (16 W,  $\lambda$  365 nm), while no obvious content change of chloride ion is observed in the lightless space under the same condition. Furthermore, it was experimentally verified that direct photolysis of the substrate was very slow under UV irradiation alone. As displayed in Figure 3, the results demonstrated that dicofol was degraded completely in 2 h under UV irradiation of 400 W with the addition of nano TiO<sub>2</sub> particles.

The kinetic of dicofol degradation under 400 W irradiation follows an apparent first-order degradation curve.



**Figure 2** Effect of irradiation time on the chloride ion production. Concentration of nano TiO<sub>2</sub>, 0.25 mg/mL; dicofol, 10 μg/mL; air flow rate, 100 mL/min; UV lamp, 16 W.



**Figure 3** Ion chromatographic curves of chloride ion under different irradiation time. Experimental conditions are the same as shown in Figure 2, UV lamp, 400 W.

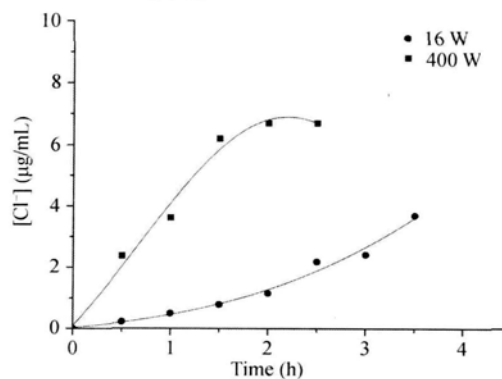
According to formula (1),  $C_0$  and  $C$  represent the original and residual concentration of dicofol.  $C_0$  could be determined until adsorption equilibrium on TiO<sub>2</sub> surface is achieved.  $t$  is the illumination time and  $k$  is apparent photodegradation rate constant.

$$\ln(C_0/C) = kt. \quad (1)^{[18]}$$

To construct relative curve regarding  $\ln(C_0/C)$  as vertical axis and  $t$  as horizontal axis, the result shows that it fits first-order linear transforms. Hence apparent photodegradation rate constant  $k$  is 0.167/min, which is higher than that of organophosphorus insecticides over aqueous TiO<sub>2</sub> suspension in the report<sup>[18]</sup>.

## 2.2 Effect of irradiation source

The effect of irradiation intensity was studied using mercury lamps with a power of 16 W and 400 W as irradiation source. Based on the experimental results as shown in Figure 4, the irradiation intensity played an important role in the photocatalytic degradation of dicofol. According to analytical results, the obvious increase of chloride ion produced in the process of photocatalysis under a 400 W mercury lamp irradiation was observed, whereas the increase was not so obvious under a 16 W mercury lamp application. Apparently, the above results revealed that the photocatalytic degradation of dicofol over aqueous TiO<sub>2</sub> suspension was greatly enhanced by the higher power UV lamp.

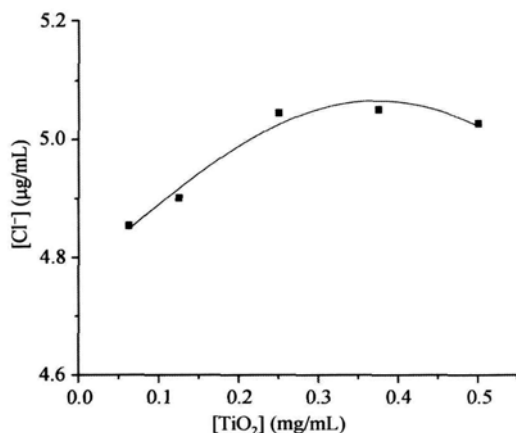


**Figure 4** Relationship between light intensity and concentration change of chloride ion as a function of irradiation time. Experimental conditions are the same as shown in Figure 2.

## 2.3 Effect of TiO<sub>2</sub> concentration

The concentration of TiO<sub>2</sub> played an important role for the generation amount of Cl<sup>-</sup>. Figure 5 displays the relationship between amount of Cl<sup>-</sup> and TiO<sub>2</sub>, ranging from 0.06 to 0.50 mg/mL, while 1 h of irradiation time was selected. Correspondingly, a higher concentration of TiO<sub>2</sub> caused a more production of Cl<sup>-</sup>. Experimental

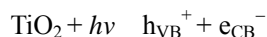
results indicated that the suspension with 0.38 mg/mL TiO<sub>2</sub>, presented the highest photocatalytic conversion. However, the content of Cl<sup>-</sup> decreased contrarily when the concentration of TiO<sub>2</sub> suspension was over 0.50 mg/mL. Previous research reported that TiO<sub>2</sub> took two roles including the photocatalyst and ultraviolet absorber as anti-photooxidation to cause the so-called “shading effect”<sup>[19]</sup>. The influence of “shading effect” was enhanced in the higher concentration of TiO<sub>2</sub><sup>[20,21]</sup>, which caused a slight decrease of the amount of Cl<sup>-</sup> contrarily.



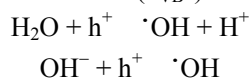
**Figure 5** Photocatalytic degradation of dicofol as a function of concentration of TiO<sub>2</sub>. Experimental conditions are the same as shown in Figure 2, UV lamp, 400 W; irradiation time, 1 h.

#### 2.4 Photocatalytic mechanism

It is well established that conductive band electrons ( $e_{CB}^-$ ) and valence band holes ( $h_{VB}^+$ ) are generated when TiO<sub>2</sub> is irradiated with light energy greater than its band gap energy<sup>[17]</sup>, which caused a series of photocatalytic degradation. The degradation pathways of organic compounds on illuminated TiO<sub>2</sub> surface generally involved a series of electron or hole transfer reactions<sup>[22]</sup>.



In the aqueous TiO<sub>2</sub> system, hydroxyl radical ( $\cdot OH$ ) could be generated by a pathway of the reaction between H<sub>2</sub>O and valence band holes ( $h_{VB}^+$ ).

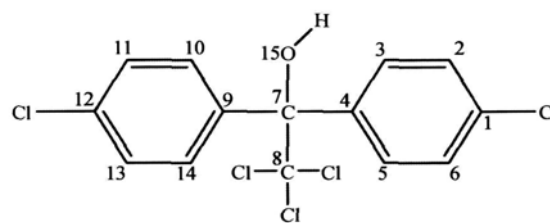


Active hydroxyl radical ( $\cdot OH$ ) could react with dicofol to produce chloride ion and less toxic compound that contains less chlorine content.

Based on the identification results of GC-MS, some intermediate products formed during photocatalysis process were bis(4-chlorophenyl) methanone (compound 2 in Scheme 2), 4-chlorophenyl-4'-hydroxyphenyl

methanone (compound 3 in Scheme 2), 4-chlorophenyl phenyl methanone (compound 4 in Scheme 2), diphenyl methanone (compound 5 in Scheme 2) and other compounds.

Frontier electron densities and point charges of carbon and oxygen atom in dicofol were calculated using Gaussian 03 program (Scheme 1). As summarized in Table 1, the results indicated that the most negative point charges were located on oxygen atom O<sup>15</sup> of -0.744. Hence we could expect that dicofol could be adsorbed on TiO<sub>2</sub> surface through hydroxyl group at natural pH.

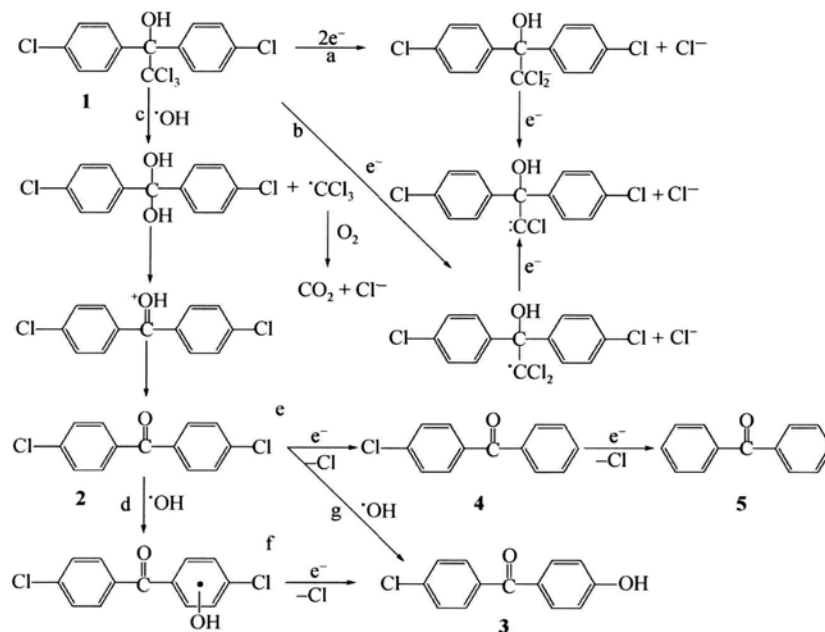


**Scheme 1** Chemical structure with the atom numbers used in the molecular orbital calculation.

**Table 1** Calculated partial charge and frontier electron density derived from B3LYP/6-31G(d) method

Atom	Frontier electron density	Partial charge
C <sup>1</sup>	0.186	-0.005
C <sup>2</sup>	0.063	-0.242
C <sup>3</sup>	0.068	-0.196
C <sup>4</sup>	0.194	-0.078
C <sup>5</sup>	0.077	-0.195
C <sup>6</sup>	0.031	-0.241
C <sup>7</sup>	0.039	0.243
C <sup>8</sup>	0.317	-0.109
C <sup>9</sup>	0.206	-0.060
C <sup>10</sup>	0.041	-0.240
C <sup>11</sup>	0.041	-0.240
C <sup>12</sup>	0.191	-0.007
C <sup>13</sup>	0.086	-0.240
C <sup>14</sup>	0.053	-0.219
O <sup>15</sup>	-	-0.744

Pathways of degradation for dicofol are shown in Scheme 2 based on the results of GC-MS and calculation. According to frontier electron density theory, the calculation of frontier electron density was interesting. The primary position for hydroxyl radical ( $\cdot OH$ ) attacked the atoms with the largest electron density, which presented the highest reactivity<sup>[14-16]</sup>. In dicofol, C<sub>8</sub> is the atom bearing the high electron density (0.317), a cleavage by hydroxyl radical attack was expected (pathway 2c) to form bis(4-chlorophenyl) methanone



Scheme 2 Pathways of degradation of dicofol.

and  $-\text{CCl}_3$ , which reacted with oxygen to generate  $\text{Cl}^-$  and  $\text{CO}_2$ . As a more stable intermediate compound, bis(4-chlorophenyl) methanone presented a similar distribution of electron density on benzene ring as dicofol. A new attack occurred in  $\text{C}_1$  and  $\text{C}_{12}$  causing the formation of 4-chlorophenyl-4'-hydroxyphenyl methanone after dechlorination followed by a hydroxylation (pathway 2g).

Theoretically, some attacks appear on  $\text{C}_4$  and  $\text{C}_9$  to cause a rupture, but under our experiments these attacks were not observed due to the steric of  $-\text{CCl}_3$  which prevented hydroxyl radical attack.

Moreover, besides the oxidation caused by attack of hydroxyl radical, the reductive dechlorination through CB electron transfer was the only feasible initial pathway for dicofol destroying<sup>[22]</sup>. As shown in 2a or 2b, the intermediate compounds and chloride ions were reduced via a one- or two-electron transfer. Furthermore, diphenyl methanone was produced with the continuous

electron transfer (pathway 2e and 2f).

### 3 Conclusions

This study demonstrated an effective and convenient method for the photocatalytic degradation of dicofol under  $\text{TiO}_2$  aqueous suspension with UV irradiation. Dicofol could be completely degraded within 2 h under the selected conditions and the apparent photodegradation rate constant was 0.167/min. The reaction mechanism of  $\text{TiO}_2$  photocatalytic degradation included an attack by peroxide or hydroxyl radical and electron transfer was presented. The radicals were generated on the illuminated nano- $\text{TiO}_2$  surface by the reactions between band electrons ( $e_{\text{CB}}^-$ ) or valence band holes ( $h_{\text{VB}}^+$ ) and  $\text{H}_2\text{O}$ . In addition, a simple and rapid analytical approach for chloric anion, a final degradation product of dicofol, could be considered and developed, by which dicofol could be determined indirectly.

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