

# Photocatalytic degradation of organochlorine compounds using $\text{TiO}_2$ supported on fiberglass cloth

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**Abstract**—The feasibility of photocatalytic degradation of organochlorine compounds using  $\text{TiO}_2$  supported on fiberglass cloth as a photocatalyst was studied. The results showed that  $2.0 \times 10^{-4} \text{ mol/dm}^3$  of dichloroethylene, trichloroethylene and tetrachloroethylene can be completely photocatalytically degraded within a short time under illumination with a 375W medium pressure mercury lamp. The effects of parameters such as illumination time, initial concentration of organochlorine compounds, amount of air flow and concentration of  $\text{H}_2\text{O}_2$  on the photocatalytic degradation were investigated. The  $\text{TiO}_2$  supported on the fiberglass was not easily detached and after 500h illumination there was no significant loss of photocatalytic activity of  $\text{TiO}_2$ . The possible mechanisms of photocatalytic degradation were discussed.

**Keywords:** photocatalytic degradation; organochlorine compounds;  $\text{TiO}_2$  thin films; fiberglass.

## 1 Introduction

Organochlorine compounds are widely used in various industries, and have been reported to contaminate running water, rivers, lakes and even underground water. Some of them have been known to be carcinogenic. In recent years, photocatalytic degradation of organochlorine compounds using oxygenated aqueous semiconductor powder dispersions have been studied extensively (Hoffmann, 1995; Ollis, 1991). These reports were satisfactory. But it was evident that in any waste water treatment process filtration and resuspension should be avoided if possible. Recently we have supported  $\text{TiO}_2$  on a glass external surface and a glass internal surface by sonication, respectively (Zhao, 1995; Chen, 1995a). Both systems proved to be both stable and efficacious catalysts for photodegradation of organic pollutants.

In this paper, we described using  $\text{TiO}_2$  supported on fiberglass cloth as a photocatalyst photocatalytic degradation of organochlorine compounds. The effects of parameters on the photocatalytic degradation were investigated. The possible mechanisms of photocatalytic degradation were discussed.

## 2 Experimental

### 2.1 Materials

Organochlorine compounds used in the experiments were dichloroethylene ( $\text{C}_2\text{H}_2\text{Cl}_2$ ), trichloroethylene ( $\text{C}_2\text{HCl}_3$ ) and tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ ) and they were reagent grade, and other reagents were analytically pure grade.

### 2.2 Photoreactor and procedure

Experiments were carried out in a quartz photochemical reactor (Chen, 1995a). A schematic diagram of the photochemical reactor is shown in Fig.1. The cylindrical annular-type reactor consisted of three parts. The first part was an empty chamber in which a 375W medium pressure

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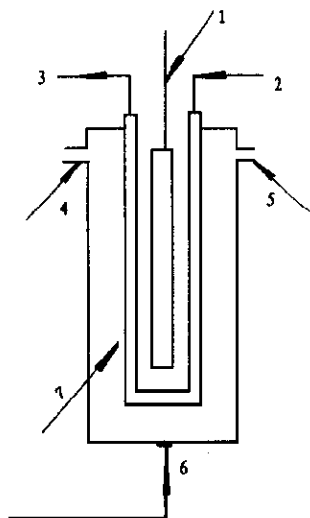


Fig. 1 Schematic diagram of photochemical reactor (1) lamp; (2) water-cooling inlet; (3) water-cooling outlet; (4) vent; (5) in-out sampling; (6) gas entry; (7) reaction chamber

mercury lamp was hung. The second part was an inside thimble. Running water was passed through the thimble to cool the reaction solution. Owing to the continuous cooling, the temperature of the reaction solution was maintained at approximately 30°C. The third part was an outside thimble. At the start of the experiment the fiberglass cloth supported TiO<sub>2</sub> was wrapped between the inside thimble and the outside thimble and the reaction solution (Volume, 400 ml) was put in the reaction chamber. Air was introduced into the reaction solution through the gas entry at the base of the reactor. All experiments were performed at an initial pH of 7.0, air flow was 0.02 m<sup>3</sup>/h, except for experiments where air flow was varied. After illumination, samples (volume of each sample was 5 cm<sup>3</sup>) were taken intermittently for analysis.

### 2.3 Analysis

The concentration of organochlorine compounds was determined by a gas chromatography equipped with an electron capture detector. The concentration of Cl<sup>-</sup> was determined by ion-exchange chromatography.

The photodegradation efficiency of the organochlorine compounds was calculated from the following expression:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

where,  $\eta$  is photodegradation efficiency;  $C_0$  is initial concentration of organochlorine compounds;  $C_t$  is the concentration of organochlorine compounds after  $t$  illumination.

### 2.4 Preparation method of TiO<sub>2</sub> supported on fiberglass cloth

TiO<sub>2</sub> supported on fiberglass cloth using sol-gel impregnation. The full details of the preparation method of TiO<sub>2</sub> supported on fiberglass cloth were described in an earlier paper (Chen, 1996). It was known from weighing that the amount of TiO<sub>2</sub> supported on the fiberglass was 2.2g. From analysis of X-ray powder diffraction patterns it can be seen that supported TiO<sub>2</sub> was mostly in the anatase form, and from SEM observation, the average diameter of the particles was about 5μm.

## 3 Results and discussion

### 3.1 Effect of illumination time

The relationship between the photodegradation efficiency of organochlorine compounds and the illumination time is shown in Table 1. It is clear that the photodegradation efficiency increased with increasing illumination time. With an initial concentration of  $2.0 \times 10^{-4}$  mol/dm<sup>3</sup> dichloroethylene and trichloroethylene can be completely photocatalytically degraded after 30 min illumination, with the same concentration of the organochlorine compounds, the photodegradation efficiency decreased as follows:

Dichloroethylene > Trichloroethylene > Tetrachloroethylene. It is clear that the photodegradation efficiency was related to the number of chlorine contained.

Table 1 Effect of illumination time

	Illumination time, min						
	0	5	10	15	20	30	60
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> , %	0	78.6	95.9	100			
C <sub>2</sub> HCl <sub>3</sub> , %	0	49.1	69.3	81.9	92.2	100	
C <sub>2</sub> Cl <sub>4</sub> , %	0	21.0	42.3	56.8	67.0	80.1	96.2

Note: Initial concentration  $C_0 = 2.0 \times 10^{-4}$  mol/dm<sup>3</sup>

The photocatalytic degradation reaction of the organochlorine compounds follows first-order kinetics. The apparent rate constants for the degradation of dichloroethylene, trichloroethylene and tetrachloroethylene were 0.313 min<sup>-1</sup>, 0.123 min<sup>-1</sup> and 0.054 min<sup>-1</sup>, respectively.

The results also showed that Cl<sup>-</sup> can be quantitative recovered with the progress of photocatalytic degradation of the organochlorine compounds.

The mechanisms of photocatalytic degradation of organic pollutants have been described previously (Hoffmann, 1995; Chen, 1995b). It was considered that hydroxy radicals and superoxide ions are to be the primary oxidizing species, and H<sub>2</sub>O and O<sub>2</sub> are necessary for the photocatalytic degradation. When under UV illumination electron-hole pairs are created on the TiO<sub>2</sub> surface, oxygen adsorbed on the TiO<sub>2</sub> surface prevents the recombination of electron-hole pairs by trapping electrons; superoxide ions are thus formed, <sup>•</sup>OH radicals are formed from holes reacting with either H<sub>2</sub>O or OH<sup>-</sup> adsorbed on the TiO<sub>2</sub> surface, <sup>•</sup>OH and O<sub>2</sub><sup>•-</sup> are also formed from H<sub>2</sub>O<sub>2</sub>.

### 3.2 Effect of initial concentration

From Table 2 it can be seen that the photodegradation efficiency decreased with increasing initial concentration of the organochlorine compounds. With  $2.0 \times 10^{-4}$  mol/dm<sup>3</sup> of C<sub>2</sub>HCl<sub>3</sub> the photodegradation efficiency was 69.3%, and with  $5.0 \times 10^{-4}$  mol/dm<sup>3</sup> of C<sub>2</sub>HCl<sub>3</sub> the photodegradation efficiency was only 48.2% after 10 min illumination.

### 3.3 Effect of H<sub>2</sub>O<sub>2</sub> concentration

Table 3 shows the effect of H<sub>2</sub>O<sub>2</sub> concentration on the photodegradation efficiency. Adding a small amount of H<sub>2</sub>O<sub>2</sub> (up to  $4.0 \times 10^{-3}$  mol/dm<sup>3</sup>) increased the photodegradation efficiency rapidly,

but if the H<sub>2</sub>O<sub>2</sub> concentration was larger than  $4.0 \times 10^{-3}$  mol/dm<sup>3</sup>, the photodegradation efficiency decreased gradually.

Table 2 Effect of initial concentration

	Initial concentration, mol/dm <sup>3</sup>			
	$1.0 \times 10^{-4}$	$2.0 \times 10^{-4}$	$5.0 \times 10^{-4}$	$1.0 \times 10^{-3}$
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> , %	100	95.9	72.2	46.1
C <sub>2</sub> HCl <sub>3</sub> , %	92.7	69.3	48.2	21.6

Note: Illumination time  $t = 10$  min

Table 3 Effect of H<sub>2</sub>O<sub>2</sub> concentration

	H <sub>2</sub> O <sub>2</sub> concentration, $\times 10^{-3}$ mol/dm <sup>3</sup>						
	0	0.5	1	2	4	6	8
C <sub>2</sub> HCl <sub>3</sub> , %	49.1	58.3	66.2	79.2	87.0	84.3	70.9
C <sub>2</sub> Cl <sub>4</sub> , %	21.0	29.6	34.2	38.5	43.2	40.2	36.7

Note: Illumination time  $t = 5$  min

H<sub>2</sub>O<sub>2</sub> was suitable for trapping electrons (Al-Ekabi, 1988; Zhao, 1995), preventing the recombination of electron-hole pairs, thus increasing the chances of the formation of <sup>•</sup>OH and O<sub>2</sub><sup>•-</sup> on the surface of TiO<sub>2</sub>, but when the H<sub>2</sub>O<sub>2</sub> concentration was higher, the amount of <sup>•</sup>OH formed

on the surface of the  $\text{TiO}_2$  increased rapidly. It is our assumption that because the annihilation rates of  $\cdot\text{OH}$  and  $\cdot\text{OH}$  were faster than the reaction rates of  $\cdot\text{OH}$  and organic contaminants ( $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$ ),  $\cdot\text{OH}$  and  $\cdot\text{OH}$  were annihilated before the reaction of  $\cdot\text{OH}$  with organic contaminants, so that the photodegradation efficiency decreased.

### 3.4 Effect of air flow

The data in Table 4 show that without air flow, the photodegradation efficiency was lower and that the photodegradation efficiency increased rapidly with increasing air flow up to  $0.02 \text{ m}^3/\text{h}$ .

Table 4 Effect of air flow

	Amount of air flow, m <sup>3</sup> /h						
	0	0.002	0.005	0.01	0.02	0.03	0.05
C <sub>2</sub> HCl <sub>3</sub> , %	19.1	29.8	39.1	47.0	49.1	49.2	49.3
C <sub>2</sub> Cl <sub>4</sub> , %	7.2	11.5	14.6	19.8	21.0	21.1	21.2

Note: Illumination time  $t = 5 \text{ min}$

The reason for this behaviours was that dissolved oxygen in the solution plays an important role by trapping the conduction band electrons, superoxide ions ( $\text{O}_2^-$ ) were formed and thus delay the electron-hole pairs recombination ( $\text{O}_2 + e^- \rightarrow \text{O}_2^-$ ), and the same time  $\text{H}_2\text{O}_2$  was formed from  $\text{O}_2^-$ , increasing the amount of  $\cdot\text{OH}$  and  $\text{O}_2^-$  (Chen, 1995b; Zhao, 1995). On the other hand, air flow accelerated adsorb and desorb of the organochlorine compounds.

### 3.5 The photocatalytic activity of $\text{TiO}_2$

The results showed that there was no significant loss of photocatalytic activity of  $\text{TiO}_2$  after 500h illumination by a 375W medium pressure mercury lamp, and the  $\text{TiO}_2$  supported on fiberglass cloth was not easily detached, since no  $\text{TiO}_2$  powders were found at the end of the photocatalytic experiments.

## 4 Conclusion

The present studies showed that  $2.0 \times 10^{-4} \text{ mol}/\text{dm}^3$  of the organochlorine compounds can be completely photocatalytically degraded using  $\text{TiO}_2$  supported on the fiberglass cloth within a short illumination time. The addition of a small amount of  $\text{H}_2\text{O}_2$  ( $4.0 \times 10^{-3} \text{ mol}/\text{dm}^3$ ) could increase the photodegradation efficiency significantly. Air flow ( $0.02 \text{ m}^3/\text{h}$ ) was favorable for the photocatalytic degradation of the organochlorine compounds.

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