



## Research article

Kinetics and mechanism of photolysis and TiO<sub>2</sub> photocatalysis of triclosan

Hyun-Seok Son, Gwangpyo Ko, Kyung-Duk Zoh\*

Institute of Health &amp; Environment, Seoul National University, Seoul 110-799, Republic of Korea

## ARTICLE INFO

## Article history:

Received 23 April 2008

Received in revised form

27 November 2008

Accepted 29 November 2008

Available online 6 December 2008

## Keywords:

TiO<sub>2</sub>

Langmuir–Hinshelwood

Radical scavenger

Dibenzo-dichloro-*p*-dioxinDibenzo-*p*-dioxin

## ABSTRACT

The degradations of triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol), a potent broad-spectrum antimicrobial agent, were compared in TiO<sub>2</sub>-only in the dark condition, photolysis, and TiO<sub>2</sub> photocatalysis with a UV-A lamp. TiO<sub>2</sub> photocatalysis more effectively degraded and mineralized triclosan compared to TiO<sub>2</sub>-only and photolysis conditions. While triclosan removed only 30% by TiO<sub>2</sub>-only condition within 20 min, the triclosan degradation in photolysis and photocatalysis at the same time was 75 and 82%, respectively, and TOC removal was significantly higher in photocatalysis than in photolysis. The data of kinetics showed that triclosan adsorption onto TiO<sub>2</sub> was fitted to Langmuir isotherm, and TiO<sub>2</sub> photocatalysis was fitted to Langmuir–Hinshelwood model ( $b = 27.99 \text{ mM}^{-1}$ ,  $K_{\text{triclosan}} = 9.49 \text{ mM}^{-1}$ ). The neutral range of pH was favorable to photocatalysis due to the charge effect between TiO<sub>2</sub> and triclosan. The addition of 2-propanol, a radical scavenger, significantly reduced the degradation of triclosan both in photolysis and photocatalysis. Dioxin-type intermediates such as dibenzo-dichloro-*p*-dioxin (DCDD), dibenzo-*p*-dioxin were produced in photolysis with and without 2-propanol, and also in photocatalysis with 2-propanol, but these intermediates were not detected in photocatalysis without 2-propanol. This result indicates that the photocatalytic degradation of triclosan is mainly achieved by radicals, and these radicals can further degrade dioxin-type intermediates once they are produced in photocatalysis.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol) is a potent broad-spectrum antimicrobial agent that is included as an additive in many products [1]. Triclosan resistance in bacteria may arise by inhibiting the enzyme enoyl-carrier protein reductase, blocking lipid biosynthesis in *E. coli*, and promoting a mutation in the *FabI* gene [2].

Triclosan in wastewater treatment plant is primarily subjected to biological degradation, sorption to sludge, or discharged to receiving surface water untreated [3,4]. Triclosan discharged to surface water, which has the typical pH between 7 and 9, is resistant to ionization since the pK<sub>a</sub> of triclosan is 7.9–8.1 [5]. Although the adsorption of triclosan onto particulate matter can be expected because of its high octanol–water partition coefficient ( $\log K_{\text{ow}} = 5.4$ ) [6,7], it requires the post-treatment for treated water as well as adsorption process. Since the biological degradation of triclosan has been found to be inefficient [8], an alternative or post-treatment is required after adsorption and biological treatment processes.

Singer et al. [7] reported a significant removal rate (0.03 day<sup>-1</sup>) of triclosan by photolysis in the epilimnion of Greifensee lake in

Switzerland. Since Tixier et al. [9] reported a high quantum yield (0.31) of triclosan for light at 313 nm, therefore photolysis may be main reason of the elimination of triclosan in the lake.

Photolysis can be a promising method to supplement the existing treatment of triclosan in wastewater treatment plants. However, one of the major drawbacks of using photolysis to treat triclosan is the production of harmful intermediates. It was found that the photolysis can produce dioxin- and phenol-type intermediates in the presence or absence of chloride ions, as a result of the structural similarities between triclosan and dioxin compounds [10]. Dioxin and phenol are environmentally important materials because of their high toxicity and potential for bioaccumulation; therefore, preventing their production may be more important than degrading triclosan by photolysis.

Recent research performed in our laboratory [11] showed that dibenzo-dichloro-*p*-dioxin (DCDD) and dibenzo-*p*-dioxin were detected in the photolysis of triclosan at the low light intensity at UV-A condition (maximum wavelength = 365 nm), where OH radical contribution is lower than at UV-C condition (maximum wavelength = 254 nm). However, DCDD and dibenzo-*p*-dioxin were not detected in photolysis of triclosan at UV-C. This result indicates that oxidants such as OH radicals during photolysis are the key factors in preventing the production of dioxin-type intermediates in the photolysis of triclosan. Photocatalytic reaction can be the alternative to maximize production of oxidants such as OH radicals [12–14]. Photocatalysis may completely mineralize a

\* Corresponding author. Tel.: +82 2 745 9104; fax: +82 2 745 9104.  
E-mail address: [zohkd@snu.ac.kr](mailto:zohkd@snu.ac.kr) (K.-D. Zoh).

variety of aliphatic and aromatic compounds under suitable conditions [14,15].

This study investigated the kinetics and degradation mechanism of photocatalysis and photolysis of triclosan. The kinetic experiments of  $\text{TiO}_2$  photocatalysis and photolysis of triclosan were examined, and the results were compared with  $\text{TiO}_2$ -only in the dark condition (blank). 2-Propanol, as a radical scavenger, was added to photolysis and photocatalysis of triclosan to examine effect of OH radical in both processes. Additionally, the relation between the production of dioxin-type intermediates and OH radical was discussed using the qualitative analysis of the intermediates.

## 2. Experimental

### 2.1. Materials and reagent

Triclosan (Merck, solid phase), methanol (J.T. Baker), and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (J.T. Baker),  $\text{CH}_3\text{CHOHCH}_3$  (Aldrich),  $\text{MgSO}_4$  (Aldrich) and  $\text{TiO}_2$  (P-25, Degussa Chemical Co., Germany) were used as received. 1,10-Phenanthroline monohydrate ( $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ ), potassium trioxalatoferate (III) trihydrate ( $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ ), and sodium acetate ( $\text{NaC}_2\text{H}_3$ ) used for the determination of UV intensity were purchased from Aldrich and Fisher, respectively.

### 2.2. Experimental set-up

All experiments were performed in a circulating photo-reactor system, consisting of a ventilation system for temperature control, a reservoir for maintaining constant reaction volume during the experiment, a metering pump (Cole-Parmer) for circulating the reactor contents by  $0.1 \text{ L min}^{-1}$ , and a reactor column connected with flexible Teflon tubing. The reservoir was a 1.5 L glass bottle whose contents were gently stirred during the experiment to maintain uniformity of the suspension. The reactor column consists of a cylindrical piece of quartz which permitted the transmission of UV light with an inside diameter of 5 cm, length of 30 cm, resulting in 150 mL per one reactor column.

The cylindrical photo-reactor was encased in steel that was equipped with two medium-pressure Hg-vapor UV-A lamps (450 W, Ace glass) with the maximum wavelength at 365 nm. The distance between the reactor column and each UV lamp was 10 cm. UV light intensity during the experiments was measured by ferrioxalate actinometry method, which produces one  $\text{Fe}^{2+}$  ion as a function of every  $\text{Fe}^{3+}$  ion lost by light [11,16,17].

Experimental reactions were performed under atmospheric pressure at 293 K. The initial concentration of  $1.73 \times 10^{-2} \text{ mM}$  triclosan was used in every experiment except the experiment investigating the effect of the initial concentration of triclosan. The light intensity used in all photolytic and photocatalytic reactions was  $1.37 \times 10^{-4} \text{ Einstein L}^{-1} \text{ min}^{-1}$ . In adsorption cases and photocatalytic runs,  $0.1 \text{ g L}^{-1}$  of  $\text{TiO}_2$  concentration was used. The concentration of 1.3 mM of 2-propanol, as OH radical scavenger, was used.

All experiments except for adsorption cases were repeated three times. The qualitative analysis by GC/MS was performed to investigate the intermediates of triclosan photolysis and photocatalysis.

### 2.3. Analysis

Triclosan was extracted via solid phase extraction by C-18 solid cartridges (Waters, USA). A 10 mL sample was filtered through the C-18 cartridge, which was then flushed with water. The column was then extracted with 5 mL of methanol, and the  $\text{MgSO}_4$  was added into these extracted samples to remove water. The triclosan concentration in the resulting samples was analyzed by HP 6890 gas

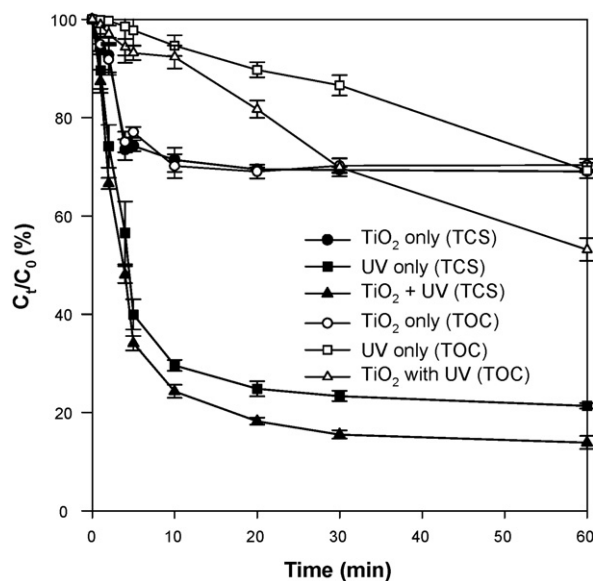


Fig. 1. Comparison of triclosan (TCS) and TOC removal efficiency at  $\text{TiO}_2$ -only (adsorption), photolysis (UV-only), and  $\text{TiO}_2$  photocatalysis.

chromatography and a mass selective detector (Hewlett Packard 5973) (GC/MS) with a 5% phenyl methyl siloxane capillary column (HP 5-MS,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ). The sample ( $2 \mu\text{L}$ ) was injected into the GC at  $250^\circ\text{C}$  with the splitless condition. The mass detector was operated with the electron ionization at 70 eV and the mass scan range at 35–550  $m/z$ . The oven temperature was increased from 70 to  $280^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  and held for 6 min at  $280^\circ\text{C}$ . Helium was used as the carrier gas at a flow rate of  $1.2 \text{ mL min}^{-1}$ .

To measure the mineralization of triclosan, TOC measurement was performed using an ultraviolet persulfate oxidation TOC analyzer with an infrared detector (Phoenix 8000TM, TekMar Dohrmann). A pH meter (Orion, Model 52A) was used to determine the pH of the reaction solution during experiments.

## 3. Results and discussion

### 3.1. Comparison with $\text{TiO}_2$ adsorption, photolysis, and photocatalysis of triclosan

First, we compared the triclosan removal from water with  $\text{TiO}_2$ -only, photolysis, and photocatalysis condition. As shown in Fig. 1, approximately 30% of triclosan was removed from the solution within 20 min with  $\text{TiO}_2$ -only in the dark condition, and the equilibrium during the adsorption reaction was achieved within 10 min. Fig. 1 also showed that TOC reduction in  $\text{TiO}_2$ -only condition is the same as the triclosan removal, indicating that triclosan adsorption onto  $\text{TiO}_2$  is not a chemical reaction, but a physical separation phenomenon.

Fig. 1 also shows that the photolytic and photocatalytic efficiencies of triclosan for the same times were 75 and 82%, respectively. The removal of TOC was significantly higher in photocatalysis than in photolysis, indicating that photocatalysis is more efficient than photolysis in the mineralization of triclosan.

The photolytic and photocatalytic degradation can be achieved by direct reaction with photons produced by UV, and/or by indirect reaction with OH radicals produced by the reaction between  $\text{H}_2\text{O}/\text{OH}^-$  ion and  $\text{TiO}_2$ . Since the light source used in this study is in the UV-A range (365 nm), and OH radical is not known to be effectively produced in photolytic condition at 365 nm compared to 254 nm [18–20]. Therefore, the removal of triclosan in photolysis

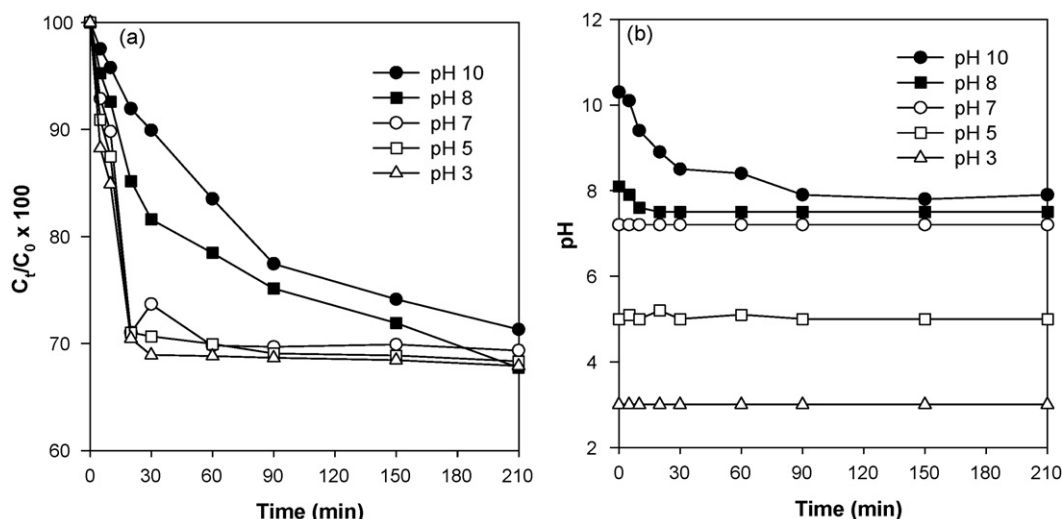


Fig. 2. (a) Effect of initial pH and (b) pH change in the adsorption of triclosan by TiO<sub>2</sub> (the deviation of pH  $\pm 0.3$ ).

is expected to be mostly achieved by photon from UV irradiation. Instead, the generation of OH radical in the photocatalysis of triclosan is expected to be greater than that in the photolysis.

### 3.2. Effect of pH and initial concentration on adsorption

Next, Fig. 2(a) shows that, as the initial pH of the solution containing triclosan decreased, more effective triclosan adsorption by TiO<sub>2</sub> was achieved. This phenomenon can be due to the alteration of electric charges of triclosan and TiO<sub>2</sub> depending on the pH in the solution. The  $p_{zc}$  value of TiO<sub>2</sub> is found at pH 6.25. That is, TiO<sub>2</sub> surface is positively charged in acid media (pH < 6.25), whereas it is negatively charged under alkaline conditions (pH > 6.25) [12]. Also, triclosan can be transformed to triclosan anion in the basic pH (pH > 8) since the  $pK_a$  value of triclosan is between 7.9 and 8.1 [5]. Therefore, the less effective adsorption of triclosan with TiO<sub>2</sub> in basic pH can be achieved compared to neutral and acidic pH due to the repulsive force works between triclosan and TiO<sub>2</sub> catalyst in pH higher than 8.

It was also found that, while no pH change in the solution containing TiO<sub>2</sub> for triclosan adsorption were observed at initial

pH less than 8, the solution pH during adsorption at initial pH 8 and 10 reduced to 7.5 and 7.9 after 30 and 90 min, respectively (Fig. 2(b)). This result implicates that the best condition for the triclosan adsorption can be neutral pH.

In photocatalysis, pH also can affect the reaction of OH radical production from H<sub>2</sub>O/OH<sup>-</sup> and TiO<sub>2</sub>. It is already known that TiO<sub>2</sub>-photocatalytic efficiency was not changed at neutral pH, but significantly decreased in the acidic condition by inhibiting the generation of OH radical [21]. Therefore, considering effect of pH on both TiO<sub>2</sub> adsorption and photocatalysis, the experiments of TiO<sub>2</sub> photocatalysis and photolysis were conducted at neutral pH, and no pH adjustment on the reaction solution was needed.

Fig. 3(a) shows the equilibrium isotherm of triclosan adsorption to TiO<sub>2</sub>. Fig. 3 shows that the higher the initial concentration of triclosan is, the longer the time for adsorption equilibrium was achieved. This adsorption data is consistent with the Langmuir isotherm expressed in Eq. (1) that the activities on the adsorbent surface depend on the concentration of adsorbate [22].

$$\frac{1}{q_e} = \frac{1}{q_{\max} b} \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (1)$$

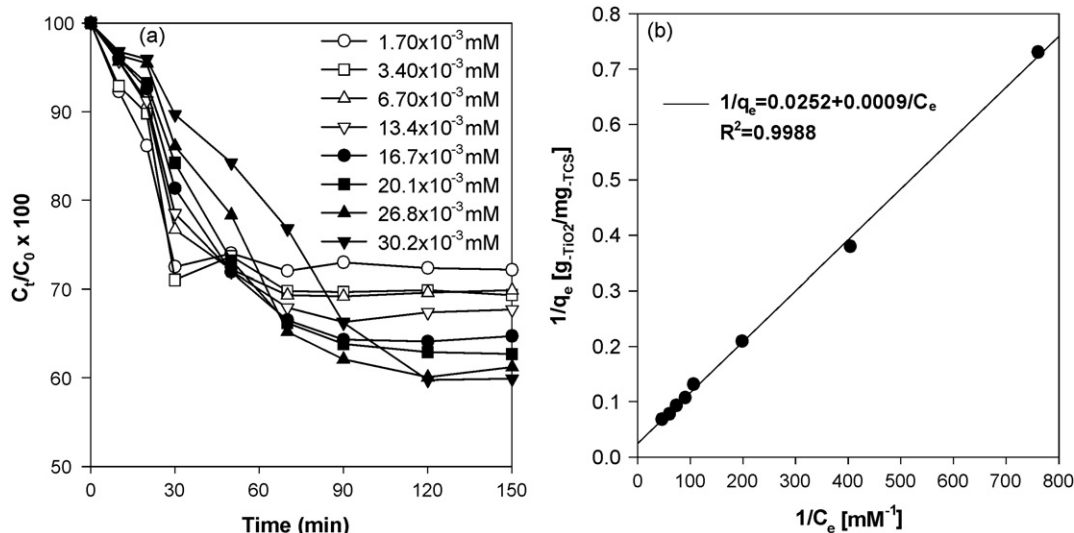


Fig. 3. (a) Effect of triclosan initial concentration in the adsorption of triclosan and (b) Langmuir isotherm plot of triclosan adsorption onto TiO<sub>2</sub> using data of (a) (initial pH 6.5  $\pm 0.3$ ).

**Table 1**

The effect of the initial concentration on the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) at the initial reaction time of 5 min in photocatalytic reaction.

Initial concentration of triclosan (mM)	$k_{\text{obs}}$ ( $\text{min}^{-1}$ )	$R^2$
0.030	$0.167 \pm 0.013$	0.932
0.017	$0.171 \pm 0.012$	0.935
0.010	$0.187 \pm 0.011$	0.957
0.007	$0.202 \pm 0.011$	0.964
0.003	$0.216 \pm 0.010$	0.973

where  $q_e$  (mg-triclosan/g-TiO<sub>2</sub>) is an adsorbed mass of triclosan on TiO<sub>2</sub>,  $C_e$  the equilibrium concentration of triclosan (mM),  $q_{\text{max}}$  (mg-triclosan/g-TiO<sub>2</sub>), and  $b$  ( $\text{mM}^{-1}$ ) is maximum adsorption capacity, and empirical parameter, respectively. Linearity was achieved with  $R^2$  of 0.998 by plotting  $1/C_e$  vs.  $1/q_e$  using Eq. (1) (Fig. 3(b)). The values of  $q_{\text{max}}$  and  $b$  were 39.7 mg/g and  $28.0 \text{ mM}^{-1}$ , respectively.

### 3.3. Effect of initial triclosan concentration and reaction characteristics in photocatalysis

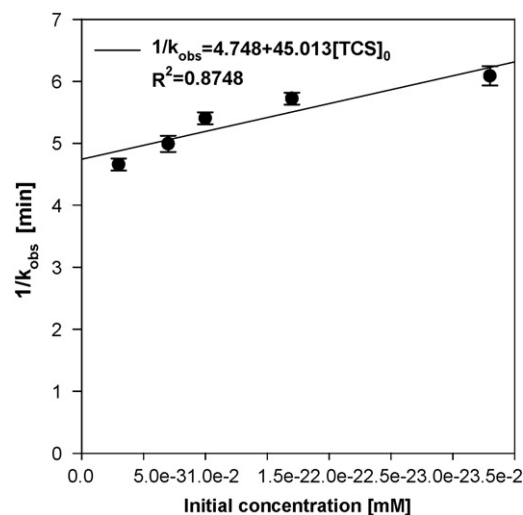
TiO<sub>2</sub>-photocatalytic reaction is known to be the heterogeneous reaction between triclosan and TiO<sub>2</sub>, and the oxidation reaction can be achieved by OH radicals produced from the reaction with TiO<sub>2</sub> and H<sub>2</sub>O under UV irradiation. Table 1 shows that triclosan degradation within first 5 min followed the pseudo-first-order kinetics, and the removal efficiency of triclosan in the photocatalysis decreased as the initial triclosan concentration increased. The result indicates that the photocatalytic reaction rate is dependent on the initial concentration of triclosan.

The Langmuir–Hinshelwood model can be applied to estimate the contribution of adsorption and oxidation in the reaction [23,24]. Eq. (2) shows the equation of the Langmuir–Hinshelwood model;

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_{\text{TCS}}k_{\text{rxn}}} + \frac{[\text{TCS}]_0}{k_{\text{rxn}}} \quad (2)$$

where  $k_{\text{obs}}$  ( $\text{min}^{-1}$ ) is the observed pseudo-first-order constant,  $K_{\text{triclosan}}$  ( $\text{mM}^{-1}$ ) is equilibrium adsorption constants of triclosan on TiO<sub>2</sub>,  $[\text{TCS}]_0$  is the initial concentration of triclosan, and  $k_{\text{rxn}}$  ( $\text{mM min}^{-1}$ ) is the reaction rate between triclosan and OH radicals. This model implicates that the surface reaction rate on TiO<sub>2</sub> is the determining step during the adsorption and desorption procedures in the photocatalysis of triclosan.

As shown in Fig. 4, the data for triclosan photocatalysis was fitted to Eq. (2), and the resulting values of  $k_{\text{rxn}}$  and  $K_{\text{triclosan}}$  obtained were



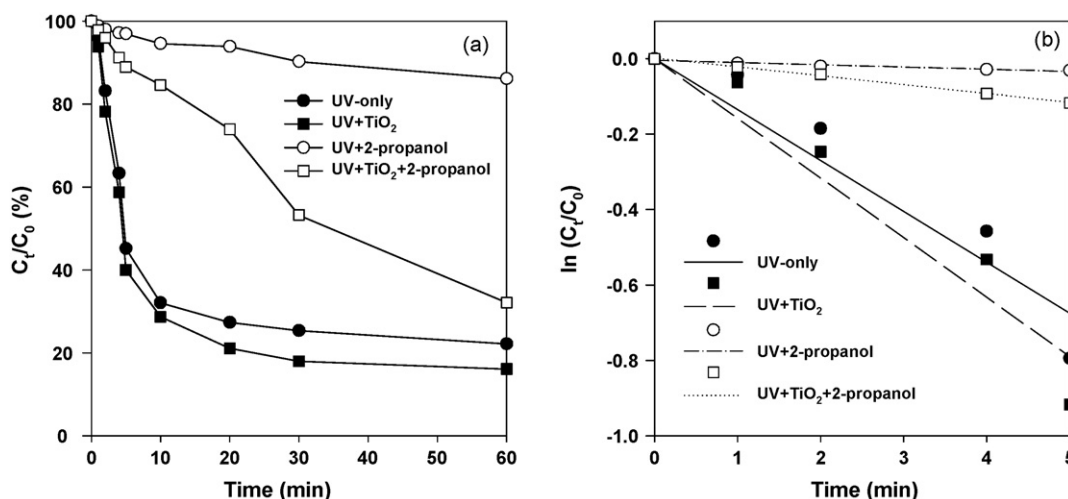
**Fig. 4.** Effect of triclosan (TCS) initial concentration on the degradation rate in photocatalysis by plot of  $[\text{triclosan}]_{\text{initial}}$  vs.  $1/k_{\text{obs}}$  using Langmuir–Hinshelwood model.

$0.022 \text{ mM min}^{-1}$ , and  $9.49 \text{ mM}^{-1}$  with  $R^2$  value of 0.8748, respectively. The  $K_{\text{triclosan}}$  value of  $9.49 \text{ mM}^{-1}$  was less than the value of  $b$  ( $28.0 \text{ mM}^{-1}$ ) obtained from Langmuir isotherm, which mean the ratio of the adsorption rate to the desorption rate of triclosan on TiO<sub>2</sub>. This implicates that the chemical oxidation occurred at the surface of TiO<sub>2</sub> in the photocatalytic reaction, and the occupancy of triclosan on TiO<sub>2</sub> was reduced by the surface reaction. This result is consistent with Ollis's finding on the surface reaction of TiO<sub>2</sub> [25].

### 3.4. Effect of 2-propanol on triclosan photolysis and photocatalysis

In this study, in order to investigate the contribution of OH radical in photolysis and photocatalysis of triclosan, the triclosan degradation rates were compared in the absence and in the presence of 2-propanol, as a radical scavenger [24,26–28], and the results are shown in Fig. 5. Fig. 5 shows that the degradation rate of triclosan was significantly reduced in the photolytic and photocatalytic reaction in the presence of 2-propanol compared with the cases without 2-propanol.

As shown Fig. 5(a), while triclosan was slightly degraded in photolytic reaction with 2-propanol for overall time, photocatalytic



**Fig. 5.** (a) Photolysis and photocatalysis efficiencies of triclosan for 60 min and (b) pseudo-first-order rate plot using data in (a) within 5 min of reaction time ( $[\text{C}_3\text{H}_7\text{OH}] = 1.3 \text{ mM}$ ).

**Table 2**  
Intermediates produced in TiO<sub>2</sub> adsorption, photolysis, and photocatalysis of triclosan.

Treatment method	Dibenzo-dichloro- <i>p</i> -dioxin	Dibenzo- <i>p</i> -dioxin	Dichloro-phenol	Chloro-phenol	Phenol	Benzoic-acid
Photolysis	Detect	Detect	Detect	Detect	Detect	Detect
Photolysis with 2-propanol	Detect	Detect	Detect	Detect	Detect	Detect
Photocatalysis	ND	ND	Detect	Detect	Detect	Detect
Photocatalysis with 2-propanol	Detect	Detect	Detect	Detect	Detect	Detect

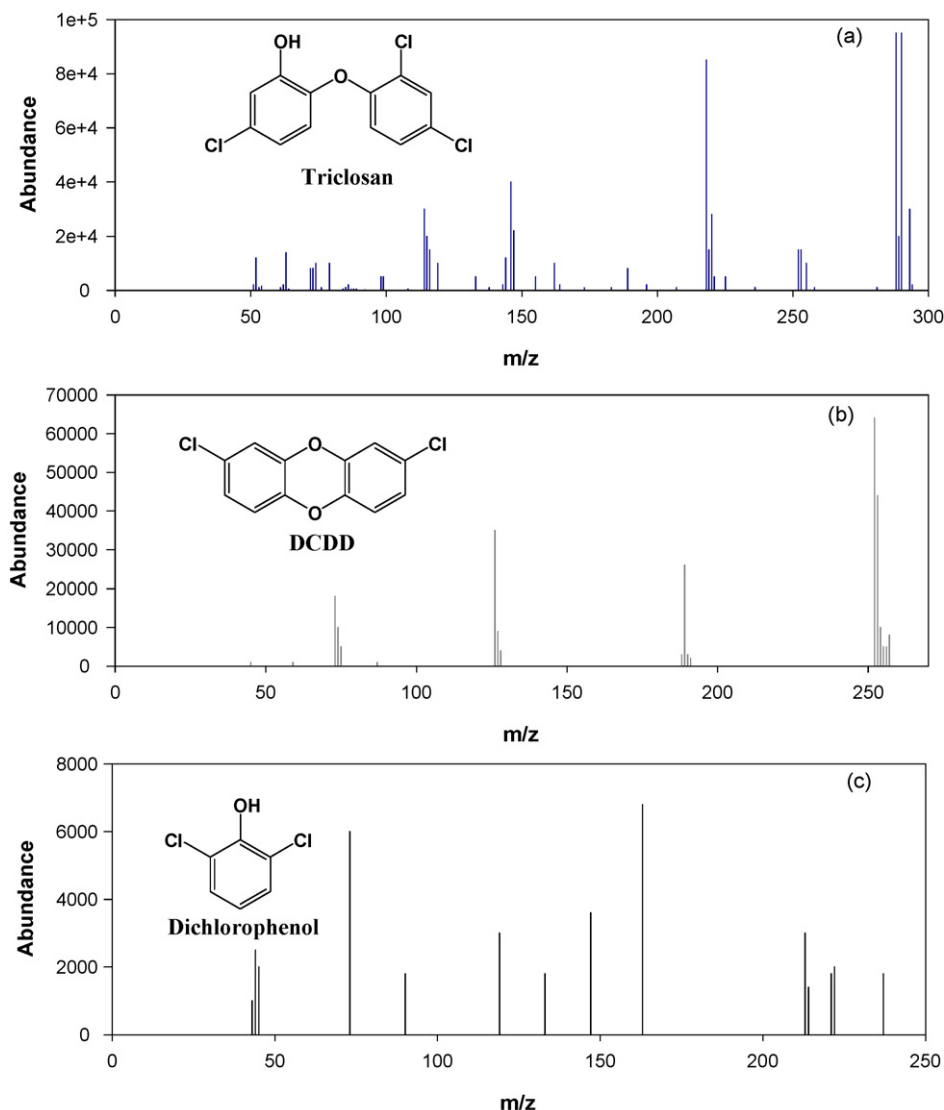
ND = not detect.

degradation rate of triclosan with 2-propanol was accelerated after the lapse of time. It indicates that the effect of 2-propanol on the photocatalytic reaction of triclosan appeared at the initial reaction time. Fig. 5(b) showed the linear regression plot of time vs.  $\ln(C_t/C_0)$  using data presented in Fig. 5(a). It shows that the degradation rate dramatically decreased by adding 2-propanol in both photolytic and photocatalytic conditions. By linear regression using the plot in Fig. 5(b), we found that the pseudo-first-order rate decreased from 0.155 to 0.006 min<sup>-1</sup> in photolysis, and from 0.177 to 0.024 min<sup>-1</sup> in photocatalysis, respectively.

The effect of 2-propanol during the triclosan degradation in this study can be compared with the result of Sumaeth et al. [29]. Sumaeth et al. reported that, with the similar concentrations of 2-propanol and TiO<sub>2</sub> used in this study, the photolytic and photo-

catalytic degradation efficiencies of 2-propanol was approximately 40% for 2 h, which was less than that of triclosan (~80%) in our study, but can be comparable. This result indicates that 2-propanol can compete with triclosan for the reaction with OH radical; therefore 2-propanol addition resulted in the reduction of triclosan degradation as shown in Fig. 5.

Interestingly, the presence of 2-propanol also significantly suppressed the photolytic degradation of triclosan. Since OH radical is not effectively produced in photolytic condition at UV-A condition (365 nm) compared to UV-C (254 nm) condition [19,20], the inhibition of radical by 2-propanol should be minimal in photolysis at UV-A condition. It is also known that 2-propanol has a maximum absorbance of 204 nm, indicating that 2-propanol can hardly absorb photon at UV-A region [30]. Since much higher



**Fig. 6.** GC/mass spectra of triclosan and its intermediates.

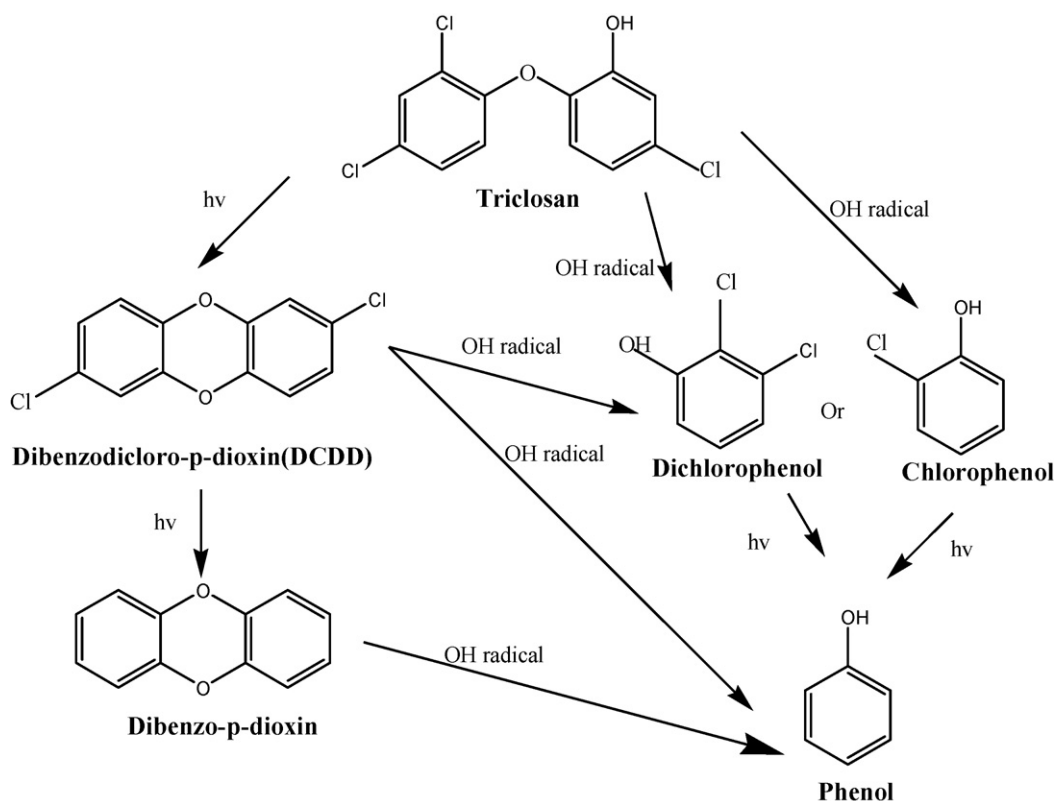


Fig. 7. The proposed mechanism of photolysis and photocatalysis of triclosan.

concentration of 2-propanol (1.3 mM) was used compared to triclosan ( $3 \times 10^{-3}$  mM), the possible inhibition of triclosan degradation in the photolysis by 2-propanol maybe from the molecular interaction between triclosan and 2-propanol, but more detailed study on this phenomenon is required.

While 2-propanol was not degraded during overall reaction time in photolytic condition, the degradation of 2-propanol occurred with the removal of triclosan in photocatalytic process. It indicates that no photolysis of 2-propanol by photon may be achieved and the participation of OH radical in the photolytic reaction with UV-A was almost not identified. However, photocatalytic degradation of triclosan was primary achieved by OH radical.

### 3.5. Intermediates during reaction

During triclosan degradation, dibenzo-dichloro-*p*-dioxin (DCDD), dibenzo-*p*-dioxin, dichlorophenol, phenol and benzoic acid, as the intermediates were identified from GC/MS analysis (Fig. 6). DCDD and dibenzo-*p*-dioxin were found as the intermediates within 20 min in the photolysis of triclosan; however these intermediates were not detected in TiO<sub>2</sub> photocatalysis (Table 2). Interestingly, DCDD and dibenzo-*p*-dioxin were detected in photocatalysis in the presence of 2-propanol, the radical scavenger.

Fig. 7 presents the proposed mechanism showing the formation of dioxin- and phenol-type intermediates of triclosan photolysis and photocatalysis based on the result represented in Table 2. The oxidation of organic compound by OH radical was mostly derived by hydrogen abstraction and the electron transfer. That is, the substitution halogen atom with OH radical is difficult reaction because of their similar electronegativity [18,31]. In addition, Yu et al. [32] reported that attack of OH radical was facilitated in para-position of phenol part in triclosan. The asymmetry of electron density of phenol part in triclosan. The asymmetry of electron density of phenol by OH radical attack may break triclosan into two phenol group. On the other hand, C–Cl bond may also be broken down by photon due to its lower bonding energy compared with O–H and

C–H bondings [33]. This mechanism can explain the formation of DCDD and dibenzo-*p*-dioxin in the photolysis of triclosan.

The disappearance of the dioxin-type intermediates during photocatalysis can be closely related to the production of OH radical by photocatalysis. If there is much production of OH radical, then OH radical can attack the intermediates such as DCDD and dibenzo-*p*-dioxin, break down dioxin bonding, resulting in the production of dichlorophenol, chlorophenol, and phenol. In fact, dichlorophenol, chlorophenol, and phenol as intermediates were detected in the early stage (20 min) in both photolysis and photocatalysis reactions. The detection of DCDD, dibenzo-*p*-dioxin and chlorinated phenols in the photolysis of triclosan is the consistent result with earlier studies [11,12,34]. Considering degradation efficiency of triclosan and the toxicity of dioxins intermediates, therefore, photocatalysis is more effective in triclosan treatment than photolysis.

## 4. Conclusions

Triclosan as an emerging pollutant is detected to trace amount in environment, and can be transformed to dioxin intermediates due to its high sensitivity to photolysis. Therefore, effective treatment should be needed not only to remove triclosan but also to minimize the production of dioxin-type intermediates. The result of this study showed that the oxidation of triclosan by OH radical can greatly reduce the production of dioxin-group intermediates as well as make the effective mineralization of triclosan. This result implicates that photocatalysis of triclosan may be an effective abatement process for triclosan in water.

## Acknowledgements

This work was supported by Korea Research Foundation Grant funded by Korea Government (MOEHRD, Basic Research Promotion Fund)(KRF-2005-00-D00073).

## References

- [1] L.M. McMurry, M. Oethinger, S.B. Levy, Triclosan targets lipid synthesis, *Nature* 394 (1998) 531–532.
- [2] S. Sivaraman, J. Zwahlen, A.F. Bell, L. Hedstrom, P.J.A. Tonge, Structure–activity studies of the inhibition of FabI, the enoyl reductase from *Escherichia coli*, by triclosan: kinetic analysis of mutant FabIs, *Biochemistry* 42 (2003) 4406–4413.
- [3] A. Lindstrom, I.J. Buerge, T. Poiger, P.A. Bergqvist, M.D. Muller, H.R. Buser, Occurrence and environmental behavior of the bactericidal triclosan and its methyl derivative in surface waters and in wastewater, *Environ. Sci. Technol.* 36 (2002) 2322–2329.
- [4] D. Morrall, D. McAvoy, B. Schatowitz, J. Inauen, M. Jacob, A. Hauk, W. Eckhoff, A field study of triclosan loss in river (Cibolo Creek, TX), *Chemosphere* 54 (2004) 653–660.
- [5] R.M. Pemberton, J.P. Hart, Electrochemical behaviour of triclosan at a screen-printed carbon electrode and its voltammetric determination in toothpaste and mouthrinse products, *Anal. Chim. Acta* 390 (1999) 107–115.
- [6] T. Okumura, Y. Nishikawa, Gas chromatography–mass spectrometry determination of triclosans in water, sediment and fish samples via methylation with diazomethane, *Anal. Chim. Acta* 325 (1996) 175–184.
- [7] H. Singer, S. Muller, C. Tixier, L. Pillonel, Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments, *Environ. Sci. Technol.* 36 (2002) 4998–5004.
- [8] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance, *Environ. Sci. Technol.* 36 (2002) 1202–1211.
- [9] C. Tixier, H.P. Singer, S. Canonica, S.R. Muller, Phototransformation of triclosan in surface waters: a relevant elimination process for this widely used biocide—laboratory studies, field measurements, and modeling, *Environ. Sci. Technol.* 36 (2002) 3482–3489.
- [10] M. Mezcua, M.J. Gomez, I. Ferrer, A. Aguera, M.D. Hernando, A.R. Fernandez-Alba, Evidence of 2,7/2,8-dibenzodichloro-*p*-dioxin as a photodegradation in water and wastewater samples, *Anal. Chim. Acta* 525 (2004) 241–247.
- [11] H.S. Son, S.B. Choi, K.D. Zoh, E. Khan, Effects of ultraviolet intensity and wavelength on the photolysis of triclosan, *Water Sci. Technol.* 55 (1–2) (2007) 209–216.
- [12] A. Mills, S.L. Hunte, An overview of semiconductor photocatalysis, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 1–37.
- [13] C.D. Jaeger, A.J. Bard, Spin trapping and electron spin resonance detection of radical intermediates in the photodecomposition of water at TiO<sub>2</sub> particulate systems, *J. Phys. Chem.* 83 (24) (1979) 3146–3152.
- [14] M.R. Hoffmann, S.C. Martin, W.Y. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [15] E.R. Carraway, A.J. Hoffman, M.R. Hoffman, Photocatalytic oxidation of organic acids on quantum-sized semiconductor colloids, *Environ. Sci. Technol.* 28 (1994) 786–793.
- [16] J.N. Demas, W.D. Bowman, E.F. Zalewski, R.A. Velapoldi, Determination of the quantum yield of the ferrioxalate actinometer with electrically calibrated radiometers, *J. Phys. Chem.* 85 (1981) 2766–2771.
- [17] S. Ahmed, Photo electrochemical study of ferrioxalate actinometry at a glassy carbon electrode, *J. Photochem. Photobiol. A: Chem.* 161 (2004) 151–154.
- [18] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processor water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [19] D. Vione, V. Maurino, C. Minero, E. Pelizzetti, Phenol photolysis upon UV irradiation of nitrite in aqueous solution I: effects of oxygen and 2-propanol, *Chemosphere* 45 (2001) 893–902.
- [20] M. Bertelli, E. Selli, Reaction paths and efficiency of photocatalysis on TiO<sub>2</sub> and of H<sub>2</sub>O<sub>2</sub> photolysis in the degradation of 2-chlorophenol, *J. Hazard. Mater. B* 138 (2006) 6–52.
- [21] H.S. Son, S.J. Lee, I.H. Cho, K.D. Zoh, Kinetics and mechanism of TNT degradation in TiO<sub>2</sub> photocatalysis, *Chemosphere* 57 (2004) 309–317.
- [22] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, 3rd ed., John Wiley & Sons Inc., USA, 1996.
- [23] R.W. Matthews, Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide, *J. Catal.* 111 (1988) 264–270.
- [24] G. Mills, M.R. Hoffmann, Photocatalytic degradation of pentachlorophenol on TiO<sub>2</sub> particles: identification of intermediates and mechanism of reaction, *Environ. Sci. Technol.* 27 (1993) 1681–1689.
- [25] D.F. Ollis, Kinetics of liquid phase photocatalyzed reactions: an illuminating approach, *J. Phys. Chem. B* 109 (2005) 2439–2444.
- [26] M. Yujing, A. Mellouki, Temperature dependence for the rate constants of the reaction of OH radicals with selected alcohols, *Chem. Phys. Lett.* 333 (2001) 63–68.
- [27] G.R. Dey, K. Kishore, Silver clusters in 2-propanol: a radiation chemical study, *Radiat. Phys. Chem.* 72 (2005) 565–573.
- [28] M.S. Alam, B.S.M. Rao, E. Janata, \*OH reactions with aliphatic alcohols: evaluation of kinetics by direct optical absorption measurement. A pulse radiolysis study, *Radiat. Phys. Chem.* 67 (2003) 723–728.
- [29] C. Sumaeth, P. Pattamawadee, G. Erdogan, R. Pramoch, S. Thammanoon, Photocatalytic degradation of 2-propanol by using Pt/TiO<sub>2</sub> prepared by microemulsion technique, *Chem. Eng. J.* 137 (2008) 489–495.
- [30] Wikipedia website, [http://en.wikipedia.org/wiki/Isopropyl\\_alcohol](http://en.wikipedia.org/wiki/Isopropyl_alcohol).
- [31] J.P. Da Silva, L.F. Vieira Ferreira, I.F. Machado, A.M. Da Silva, Photolysis of 4-chloroanisole in the presence of oxygen formation of the 4-methoxyphenylperoxyl radical, *J. Photochem. Photobiol. A: Chem.* 182 (2006) 88–92.
- [32] J.M. Yu, T.Y. Kwong, Q. Luo, Z. Cai, Photocatalytic oxidation of triclosan, *Chemosphere* 65 (2006) 390–399.
- [33] P.R. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, John Wiley & Sons Inc., New York, USA, 1993.
- [34] D.E. Latch, J.L. Packer, W.A. Arnold, K. McNeill, Photochemical conversion of triclosan to 2,8-dichlorodibenzo-*p*-dioxin in aqueous solution, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 63–66.