Advanced Oxidation Degradation of Dichlorobenzene in Water by the UV/H2O2 Process

Tao Xu [a]; Xian-Ming Xiao [a]; Hong-Ying Liu [a]
[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, P.R. China

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Advanced Oxidation Degradation of Dichlorobenzene in Water by the UV/H$_2$O$_2$ Process

Tao Xu, Xian-Ming Xiao, and Hong-Ying Liu

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, P.R. China

Through UV/H$_2$O$_2$ photocatalytic advanced oxidation technique the performance, kinetics, pathway, and mechanism of ortho-dichlorobenzene (O-DCB) in water and the effect parameters of degradating reaction were studied systematically. The results showed that the reaction of photocatalytic degradation of O-DCB was fast and accorded well with the pseudo-first-order kinetics. The roles of some parameters, such as the pH, the initial concentrations of O-DCB, H$_2$O$_2$, and some anions in reaction solution, were examined in detail. It was found that weak acidic or neutral environment was favorable to the degradation reaction and some anions slowed down the photocatalytic degradation rate. Input amount of H$_2$O$_2$ possessed the best value under specified condition. The intermediates of O-DCB degradation were also tentatively identified 2,3-dichlorophenol, 3,4-dichlorophenol, formic acid, acetic acid, and oxalic acid mainly adopting GC/MS and ion chromatogram (IC) techniques. According to this, the pathway and mechanism of UV/H$_2$O$_2$ photocatalytic degradation of O-DCB were deduced and led.

Key Words: UV/H$_2$O$_2$ process; AOPs; Ortho-dichlorobenzene; Kinetics; Degradation pathway and mechanism.

INTRODUCTION

Organic pollution, especially organic micropollution, is nowadays known as a distinct characteristic problem of water. A variety of toxic and harmful organic micropollutants have been found not only in source water but also in drinking water. However, conventional water treatment methods (e.g., chlorination) may readily yield disinfection by-products (DBPs), such as trihalomethanes

(THMs), haloacetic acids (HAAs), and halobenzene.[1] Therefore, the development of techniques to remove the organic micropollutants in drinking water treatment is important.

During the past two decades, advanced oxidation processes (AOPs) have been considered as effective methods to destroy organic pollutants in water.[2–5] The hydroxyl radical, the primary oxidant in AOPs, is a strong, nonselective oxidant with rate constants often in the order of 10^9 $dm^3mol^{-1}s^{-1}$ and a standard electrode potential (relative to the hydrogen electrode) of 2.8 V.[6] The UV/H_2O_2 process, an AOP, has been applied successfully to mineralize some toxic and hazardous organic micropollutants to inorganic materials or convert them to readily biodegradable intermediates.[7–11] Furthermore, the UV/H_2O_2 process also has been used in advanced drinking water treatment.[12]

Ortho-dichlorobenzene (O-DCB), one of the 114 priority organic pollutants listed by the U.S. Environmental Protection Agency (EPA),[13] is a toxic and biorefractory compound, which can accumulate in organisms and restrain and anesthetize the central nervous system of humans and animals. On the other hand, as organic solvents, insecticides, disinfector, and an intermediate of some organic compound's (e.g., dye and pesticide), O-DCB is extensively used in the chemical industry. Therefore, O-DCB is often observed in the effluents of industrial wastewater treatment plants, and sometimes detected in source water or chlorination tap water. However, as a foreign pollutant of environment, O-DCB cannot be retrogressed by the natural microbe that is usually short of essential enzyme.[14] Now several kinds of bacteria, which have been found via domestication and separation by some researchers, can decompose the O-DCB partially or completely but only slowly.[15–17] Hence, along with the development of society, pollution has become a perplexing problem for the people, and we demand more and more safe drinking water. Recently, several kinds of deep process were used for production of safe drinking water. However, to our knowledge, there have been no previous studies of the O-DCB degradation performance, kinetics, pathway, and reaction mechanism by the UV/H_2O_2 process.

In this study, O-DCB was studied as the typical toxic halo-organic compound and disinfection by-products of drinking water. During the O-DCB degradation reaction, the roles of some parameters, such as the pH, the initial concentrations of O-DCB, H_2O_2, and some ions in reaction solution, were examined in detail in order to provide a full description. Furthermore, an attempt was made to elucidate the degradation pathway and reaction mechanism of O-DCB.

MATERIALS AND METHODS

Materials

O-DCB was commercially purchased from Fluka, N; O-bis (trimethylsilyl)-trifluoro-acetamide (BSTFA) was obtained from Pierce. Petroleum ether

(boiling point: $30°$–$60°$C) was purified by distillation. NaOH and H_2SO_4 were guaranteed reagent grade, H_2O_2 and other chemicals used in the experiments were analytical reagent grade. The water used for preparing reaction solution was purified by a Film Tec RO TW30-4040 system, with conductivity lower than 5.37 μs cm^{-1} except for the water used in the experiments on studying the matrix effects of tap water and source water. The reaction solutions were prepared by diluting O-DCB stock solution to the desired concentration. The pH of reaction solutions was adjusted with H_2SO_4 and NaOH solutions before the experiments.

Apparatus and Procedure

The photocatalytic reactions were carried out in an annular glass photoreactor with a virtual volume of 1.4 dm^3 (32 cm high, 7.8 cm diameter). A low pressure UV lamp (S2-Q-PA12, Canada R-Can Environmental, Inc.), with a monochromatic radiation at 254 nm and a nominal power of 14 W, was separated from the water by a double-walled quartz sleeve inside the glass reactor. The external wall of the reactor was covered with silver paper to improve the efficiency of photocatalytic reaction and avoid direct irradiation of UV to experimenter. A magnetic stirrer was placed at the bottom of reactor to provide agitation during the reaction. The photon flux (at 254 nm) entering the reactor from the UV lamp was 3.14×10^{-6} Einstein s^{-1} as determined by potassium ferrioxalate actinometry.[18]

The desired initial concentrations of O-DCB and hydrogen peroxide were fed in the reactor. After 3 min premixing, the sample was immediately taken as the initial sample. Then, the UV lamp and the magnetic stirrer were tuned on, and the samples were taken at desired intervals for further analysis. The pH of the reaction solutions was the natural pH of dissolved O-DCB (about 5.86).

Analytical Methods

O-DCB was extracted with petroleum ether from reaction solution and quantified with gas chromatograph (GC) with a flame ionization detector (FID). A Finnegan Trance GC with FID detector was used for quantitatively determining the concentrations of O-DCB. In this study, the GC column was a DB-5.625 capillary column (30 m $\times$ 0.25 mm ID $\times$ 0.25 μm film). The initial oven temperature was held at $50°$C for 5 min, then programmed at a rate of $5°$C min^{-1} up to $250°$C and held at $250°$C for 15 min. The total organic carbon was determined with the TOC analyzer (Shimadzu Corporation, Japan). The concentrations of hydrogen peroxide were obtained iodometrically.[19] The pH value of solution was analyzed using a pHS-25 acidity detector (Shanghai Chemical Apparatus, Inc., China).

   To qualitatively identify the intermediates produced during the O-DCB degradation, the reaction mixture was extracted with 5 cm³ petroleum ether at desired intervals. The extract was blown to dryness under a gentle N_2 stream, and then was dissolved into 0.2 cm³ petroleum ether for GC/MS analysis. One portion of the extract was also silylated by addition of BSTFA in a small sealed vial overnight. Under these conditions the hydroxyl groups were derivatized as trimethylsilyl ethers. A Hewlett-Packard (HP) 5890 GC with a 5972 mass selective detector (MSD) operated on the scan mode was used for qualitatively identifying the intermediates. The GC column was a HP-5 fused-sillca capillary column (50 m × 0.32 mm ID × 0.17 μm film) and the initial oven temperature was held at 50°C for 5 min, then programmed at a rate of 5°C min⁻¹ up to 250°C and held at 250°C for 15 min. At the same time, a 761 compact IC (Metrohm Ion Analysis, Switzerland) was used for quantitatively identifying the intermediates in the residual solution after extracting. The IC column was a Metrosep A Supp 5 (6.1006.510) column (4.0 mm × 100 mm, Part size: 7.0 μm), the sample volume of inlet was 10.0 μl, temperature was 25.0°C, and the eluent were Na_2CO_3(3.2 mmol L⁻¹)/NaHCO_3(0.8 mmol L⁻¹)/ methanol(3%).

RESULTS AND DISCUSSION

Degradation of O-DCB by the UV/H₂O₂ Process

   When the UV irradiation or hydrogen peroxide was used alone, control experimental results showed that the concentration of O-DCB decreased slightly, which indicated that O-DCB was relatively stable during the treatment by hydrogen peroxide or UV irradiation alone. However, a significant reduction of O-DCB concentration can be observed in the treatment by the combination of the UV irradiation and hydrogen peroxide. The variety of O-DCB concentration is shown in Figure 1. It can be seen that the UV radiation combined with
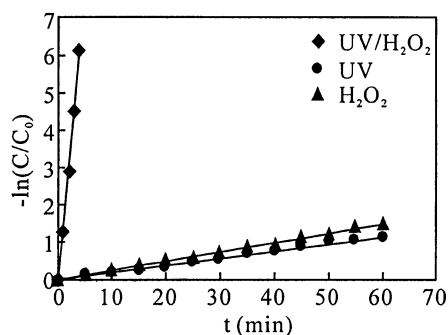
Figure 1: Profiles for the concentrations of O-DCB vs. time during the degradation in three methods.

hydrogen peroxide was an effective method for O-DCB degradation. The removal of O-DCB may be attributed to the hydroxylation of hydroxyl radicals through which an OH group was added to the O-DCB molecule. The hydroxyl radicals came from the system of UV catalysis H_2O_2.

Kinetics Study

As described above, the removal of O-DCB was attributed to the hydroxylation of hydroxyl radicals. Generally, direct reactions between H_2O_2 and organic molecules are described as a bimolecular reaction. The apparent reaction rate is expressed as first order with respect to dissolved H_2O_2 concentration $[H_2O_2]$ and first order with respect to the organic compound C.[20] On the other hand, indirect reaction between H_2O_2 and organic compound occurs via hydroxyl radical generated from H_2O_2 catalysis decomposition. The indirect reaction is described as first order with respect to the radical concentration $[\cdot OH]$ and first order with respect to the organic compound concentration. A mass balance in a reactor operating in a batch mode respect to the liquid phase yields:[21]

$$-dC/dt = k_{H_2O_2}C[H_2O_2] + k_{OH\cdot}C[\cdot OH]$$

where k_{H2O2} and $k_{OH\cdot}$ are the second-order rate constants corresponding to the direct and indirect reactions, respectively. The above equation could be rewritten as follows:

$$-dC/dt = k_1 C$$

where $k_1 = k_{H_2O_2}[H_2O_2] + k_{OH\cdot}[\cdot OH]$

Where k_1 is the apparent rate constant considering a simple first-order kinetic model to describe the substrate oxidation, then define it as a pseudo-first-order rate constant.[22,23] A common form of the pseudo-first-order rate kinetic equation can be obtained by integrating the equation above:

$$-\ln(C_t/C_0) = k_1 t$$

where k_1 (in s^{-1}) is the pseudo-first-order rate constant, and C_t and C_0 are the concentrations at irradiation time t and the initial concentration, respectively.

The experimental data indicated that more than 99% of O-DCB was decomposed within 5 min. It can be concluded that O-DCB photocatalytic degradation accords well with the pseudo-first-order kinetics and the apparent rate constant is 2.50×10^{-2} ($R^2 = 0.9976$) (see Fig. 2). The reason why O-DCB disappeared so rapidly is that the hydroxyl radical has a high rate constant with O-DCB. The profiles also showed that the TOC was reduced dramatically with the degradation of O-DCB, while the TOC removal was much slower than the degradation rate of O-DCB (see Fig. 2), which indicated that O-DCB was not mineralized to CO_2, H_2O, and inorganic substances directly but via a series of intermediates.
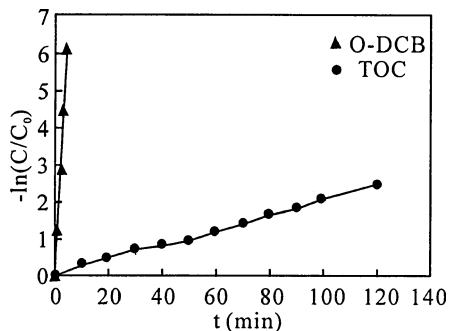
Figure 2: Profiles for the concentrations of O-DCB and TOC vs. time during the degradation.

In this study, more than 99.9% of O-DCB can be mineralized completely within 8 min. The reaction mechanism of O-DCB degradation by UV/H_2O_2 process will be discussed below in detail.

The variation of pH value also indicated that inorganic acids and organic acids, which caused the pH of solution to drop, were formed in degradation process (see Fig. 3). In this study, IC was used for detecting the ions of formic acid, acetic acid, oxalic acid, and Cl^- that were produced during photocatalytic degradation process. The changes of their concentrations are shown in Figure 4.

The Effects on Photocatalytic Degradation Kinetics

Effect of Initial Concentration of O-DCB

In order to learn clearly about the effect of the initial concentration of O-DCB on photocatalytic degradation kinetics, experiments on the relationship between the initial concentration and the O-DCB degradation were carried out, and the profiles are shown in Figure 5. It can be observed that the disappearance rate of O-DCB significantly increases with decreasing O-DCB initial concentrations. For example, the apparent rate constant increases from
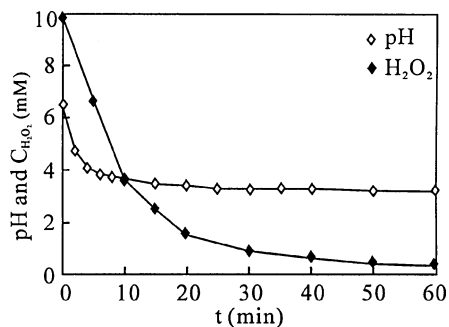
Figure 3: Change of solution pH and residual concentration of H_2O_2 during the degradation of O-DCB.
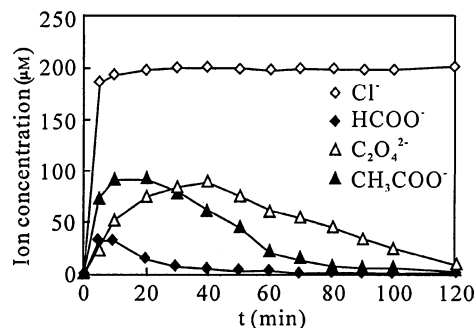
Figure 4: Change of Cl$^-$ and organic acid ions concentrations during the degradation of O-DCB.

6.36×10^{-3} s^{-1} (R^2 = 0.9952), 2.51×10^{-2} s^{-1} (R^2 = 0.9962) to 3.49×10^{-2} s^{-1} (R^2 = 0.9948) when the O-DCB initial concentration is varied from 0.2 mM, 0.1 mM to 0.05 mM. The results also confirmed that the concentration of O-DCB was important in the photocatalytic degradation process; that is, the initial concentration of O-DCB would determine the rate constant because the generated amount of ·OH would be a constant at special time when the other experimental conditions were controlled.

Effect of pH Value

The effect of pH on the O-DCB degradation by the UV/H$_2$O$_2$ process is shown in Figure 6. It is obvious that the degradation rate decreases rapidly with increasing the pH values except for pH = 2.50. For example, the apparent rate constant is reduced from 2.93×10^{-2} s^{-1} (R^2 = 0.9977) at pH = 3.62 to 1.43×10^{-2} s^{-1} (R^2 = 0.9988) at pH = 10.05 except for 1.14×10^{-2} s^{-1} (R^2 = 0.9963) at pH = 2.50. This is due to the fact that under strong alkaline conditions the CO$_2$ produced during the O-DCB degradation will be converted to CO$_3^{2-}$ and HCO$_3^-$, both of which have high rate constants with hydroxyl radicals (3.9×10^8 M^{-1} s^{-1}, 8.5×10^6 M^{-1} s^{-1}, respectively), therefore, O-DCB
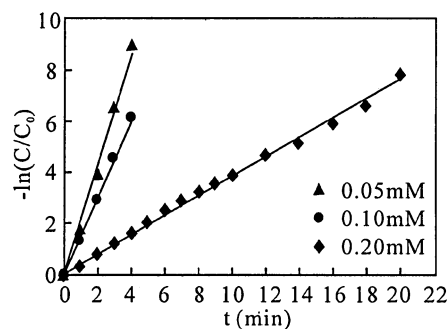
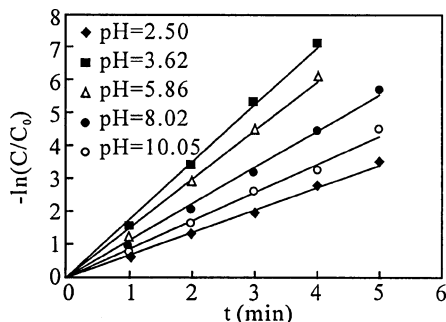**Figure 5:** Effect of initial concentration of O-DCB.

Figure 6: Effect of pH value.

degradation will be retarded with the increase of them in the reaction solution. Furthermore, alkaline conditions are favored for the dissociation of hydrogen peroxide to form HO_2^-. The HO_2^- has a higher reactivity than hydrogen peroxide with hydroxyl radicals, which leads to a decrease in the number of hydroxyl radicals.[24] This might also lead to the reduction of the O-DCB degradation rate. On the other hand, strong acidic environment (i.e., pH = 2.50), under which chlorine atoms may be difficult to remove from O-DCB molecule in the degradation reaction, at the same time, helps HO· react with H^+. As a consequence, strong acidic environment is also not favorable for the O-DCB photocatalytic degradation process. From the above discussion, it can be concluded that the O-DCB photocatalytic degradation by the UV/H_2O_2 process is more favorable in weak acidic than in alkaline environment.

Effect of H_2O_2 Concentration

In order to clarify the effect of the initial concentration of hydrogen peroxide, experiments on the relationship between the initial hydrogen peroxide concentration and the O-DCB degradation were conducted and the profiles are shown in Figure 7. As can be seen, the disappearance rate of O-DCB significantly
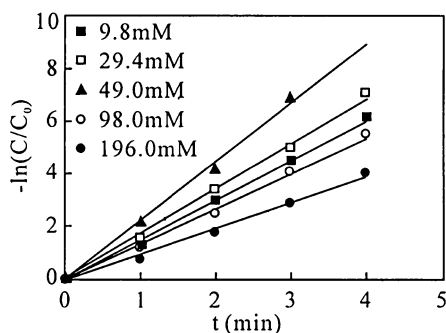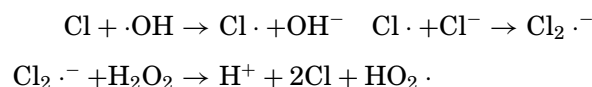

Figure 7: Effect of initial concentration of H_2O_2.

increases with increasing hydrogen peroxide concentrations. However, when the hydrogen peroxide concentration is higher than 49.0 mM, the oxidation rate drops dramatically. Corresponding to this, the apparent rate constant increases from $2.49 \times 10^{-2} \, s^{-1}$ ($R^2 = 0.9956$) at $C_{H2O2} = 9.8$ mM to $2.726 \times 10^{-2} \, s^{-1}$ ($R^2 = 0.9979$) at $C_{H2O2} = 49.0$ mM; however, the apparent rate constant decreases from $2.248 \times 10^{-2} \, s^{-1}$ ($R^2 = 0.9949$) at $C_{H2O2} = 98.0$ mM to $1.617 \times 10^{-2} \, s^{-1}$ ($R^2 = 0.9951$) at $C_{H2O2} = 196.0$ mM. The result could be interpreted by the dual actions of hydrogen peroxide on the ·OH concentration. If the hydrogen peroxide increases to a certain concentration, more ·OH will be generated to accelerate the O-DCB degradation. However, when the hydrogen peroxide concentration is higher than 49.0 mM, the scavenging effect of hydrogen peroxide on ·OH becomes an important factor and the O-DCB degradation rate decreases significantly. Liao and Mirat also observed this phenomenon in the degradation of n-chlorobutane.[25]

The residual concentrations of H_2O_2 at various reaction intervals were also illustrated in Figure 3. It was found that the disappearance rate of hydrogen peroxide was quick along with the degradation process, and finally its concentration approached zero. A possible reason may be that the Cl^- anions (see Fig. 4) react with hydroxyl radicals to form $Cl_2^- \cdot$ or $Cl \cdot + OH^-$ by the following reactions,[26,27] which leads to the reducing of the H_2O_2 concentration.

$$Cl + \cdot OH \rightarrow Cl \cdot + OH^- \quad Cl \cdot + Cl^- \rightarrow Cl_2 \cdot^-$$

$$Cl_2 \cdot^- + H_2O_2 \rightarrow H^+ + 2Cl + HO_2 \cdot$$

Effect of the Matrix of Solution

In general, there are many kinds of familiar anions and natural organic matters in aquatic environment, such as Cl^-, NO_3^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, and other organic micropollutants. Though some of them can generate the hydroxyl radical under certain condition,[28] most anions act as scavengers of free radicals and have remarkable influence on the photocatalytic degradation kinetics. However, until now the effects of them on the O-DCB degradation kinetics by the UV/H_2O_2 process have not been reported.

The effects of above anions and the matrix of tap water and source water on the O-DCB degradation kinetics are listed in Table 1. It is clear that the O-DCB degradation rates decrease significantly in the presence of those anions in comparison to that without anions. For example, when the concentration of HCO_3^- and CO_3^{2-} were 10 mM, the reaction rate constants decreased by the factors of 0.34 and 0.92, respectively, while for Cl^-, NO_3^-, and SO_4^{2-} with the same concentration, the rate constants reduced by the factors of 0.06, 0.05, and 0.03, respectively.

The detrimental effects of carbonate and bicarbonate and their mechanism of scavenging hydroxyl radicals have been reported by several researchers.[29,30]

Table 1: Effects of the familiar anions and the matrix of tap water and source water.

Ions and matrix	$k_1(s^{-1})$	R^2
Cl^-, NO_3^-, HCO_3^-, CO_3^{2-}, $SO_4^{2-} = 0$	2.50×10^{-2}	0.9976
$Cl^- = 5$ mM	2.38×10^{-2}	0.9932
$Cl^- = 10$ mM	2.34×10^{-2}	0.9962
$NO_3^- = 5$ mM	2.40×10^{-2}	0.9991
$NO_3^- = 10$ mM	2.38×10^{-2}	0.9912
$SO_4^{2-} = 5$ mM	2.40×10^{-2}	0.9905
$SO_4^{2-} = 10$ mM	2.43×10^{-2}	0.9919
$HCO_3^- = 1$ mM	2.38×10^{-2}	0.9974
$HCO_3^- = 5$ mM	2.23×10^{-2}	0.9961
$HCO_3^- = 10$ mM	1.65×10^{-2}	0.9942
$CO_3^{2-} = 0.5$ mM	1.36×10^{-2}	0.9982
$CO_3^{2-} = 1$ mM	7.67×10^{-3}	0.9935
$CO_3^{2-} = 10$ mM	1.90×10^{-3}	0.9924
Tap water*	2.04×10^{-2}	0.9978
Source water**	2.76×10^{-2}	0.9956

*Taken from laboratory tap.
**Taken from Pearl River of Guangzhou, which contained 0.06 mM O-DCB.

Carbonate and bicarbonate anions can react quickly with hydroxyl radicals to consume hydrogen peroxide. Thus, it can be expected that the photocatalytic degradation of O-DCB will be reduced evidently in the presence of carbonate and bicarbonate anions.

The presence of Cl^-, NO_3^-, and SO_4^{2-} anions leads to the reduction of the O-DCB degradation rate, but their influences on the degradation rate are smaller than that of the other two anions, HCO_3^- and CO_3^{2-}. It can be explained that the nitrate anions can serve as an inner filter substance to reduce the photons, sheltering the photolysis of hydrogen peroxide[30] and the Cl^- anions can react with hydroxyl radicals as mentioned above; therefore, both of them can reduce the degradation rate to a certain extent. Although the effect mechanism of SO_4^{2-} is not known presently, Yawalkar et al.[31] also found in their research that the sulfate anions could prevent the similar degradation reaction.

In order to learn about the matrix effect and find out the practical value of the O-DCB degradation by the UV/H_2O_2 process in water deep process, we dissolved O-DCB (0.1 mM) into the tap water that was taken from laboratory tap. At the same time, we took 10 L source water samples from the Pearl River of Guangzhou, which contained 0.06 mM O-DCB. They were treated under the same experimental conditions as above. The results are also listed in Table 1. From parallel experimental (one reaction solution was real source water, the other was the same to the previous reaction solutions, and both of them contained the same O-DCB concentration) results, it is known that the apparent

rate constant is reduced from $3.23 \times 10^{-2}\,\mathrm{s}^{-1}$ ($R^2 = 0.9969$) to $2.76 \times 10^{-2}\,\mathrm{s}^{-1}$ ($R^2 = 0.9956$) for source water. Though the degradation reaction rate constants are high enough, it is clear that the matrix effects of tap water and source water have remarkable influence on the O-DCB degradation by the UV/H_2O_2 process. It is possible that all kinds of ions and micropollutants in aquatic environment reduce the degradation reaction rate.

Degradation Pathway and Reaction Mechanism of O-DCB

Some researchers reported the reaction mechanism of aryl chlorides by photocatalytic oxidation degradation. For example, phenol and Cl^- were identified as major intermediates in the photocatalytic degradation of monochlorobenzene.[32,33] In this study, the intermediates produced during the O-DCB photocatalytic degradation by the UV/H_2O_2 process were qualitatively identified by comparison of mass spectrometry with corresponding authentic standards and quantitatively identified by IC. It is found that 2,3-dichlorophenol, 3,4-dichlorophenol, formic acid, acetic acid, and oxalic acid are the predominant intermediates. The mass spectrum of 2,3-dichlorophenol (trimethylsilyl derivative) and 3,4-dichlorophenol (trimethylsilyl derivative) are shown in Figures 8 and 9, respectively.

The above discussion suggests that the removal rate of O-DCB is very important during the reaction process in this study. At the same time, the 2,3-dichlorophenol, 3,4-dichlorophenol, formic acid, acetic acid, and oxalic acid are the predominant intermediates in the preliminary oxidation degradation of O-DCB.
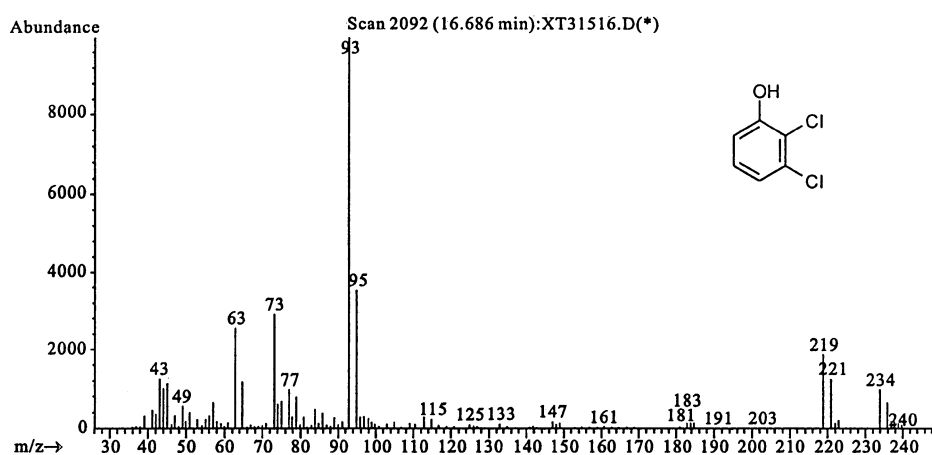

Figure 8: The mass spectrum of 2,3-dichlorophenol identified during the degradation of O-DCB.
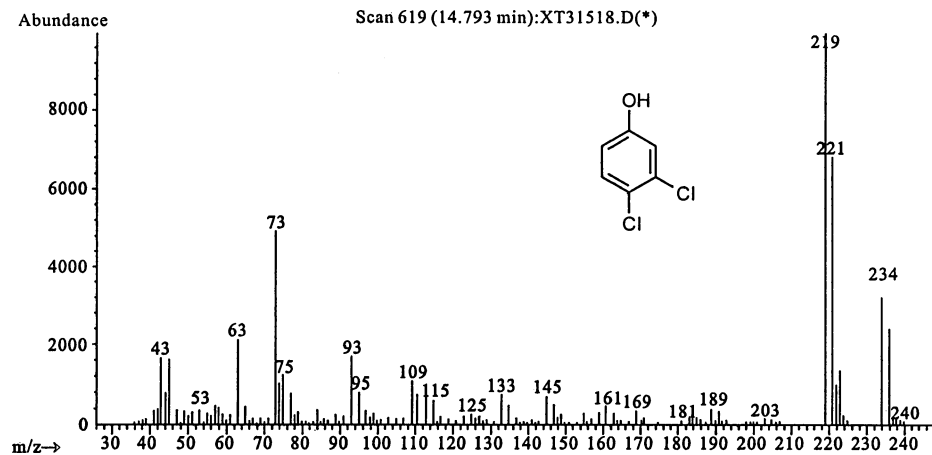
Figure 9: The mass spectrum of 3,4-dichlorophenol identified during the degradation of O-DCB.

Based on the identification of intermediates, a possible degradation pathway of O-DCB by the UV/H$_2$O$_2$ process is proposed (see Fig. 10). First, ·OH replaces the hydrogen atom in ortho- or para-position of ortho-dichlorobenzene molecule, which leads to the formation of 2,3-dichlorophenol and 3,4-dichlorophenol. After electron-donor group –OH is added to the benzene ring, the electrophilic reagent ·OH can replace the Cl atom of ortho-dichlorobenzene molecule to form 1,2,3-trihydroxybenzene and 1,2,4-trihydroxybenzene in solution. It is well-known that organic molecule with two hydroxyl groups connecting to two conjoint carbon atoms is readily oxidized and easily changes its structure to form adjacent carbonyl compound. Bond cleavage then arises between conjoint carbon atoms to produce the small molecule organic acids, such as formic acid, acetic acid, and oxalic acid, and entire mineralization is finally achieved.
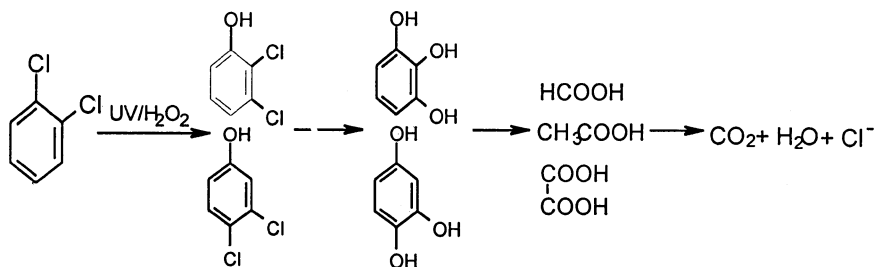
Figure 10: Pathway of the degradation of O-DCB by the UV/H$_2$O$_2$ process.

CONCLUSIONS

Photocatalytic degradation of O-DCB by the UV/H_2O_2 process accords well with pseudo-first-order kinetics; more than 99.9% of O-DCB can be removed within 8 min and the TOC removal is up to 93% within 120 min. The O-DCB concentration is an important parameter in photocatalytic degradation process; the lower C_{O-DCB} is, the higher degradation rate observed. Proper control of hydrogen peroxide concentration is very important to gain the most advantage of O-DCB degradation rate; that is to say, input amount of H_2O_2 possesses the best value under specified condition. The photocatalytic degradation process is more readily available in weak acidic environment than in alkaline environment. The O-DCB photocatalytic degradation rate is remarkably reduced in the presence of some hydroxyl radical scavengers, such as CO_3^-, HCO_3^-, and Cl^-. The O-DCB degradation mechanism by the UV/H_2O_2 process could be summarized as: ortho- or para-position of the O-DCB molecule is substituted by the electrophilic reagent $\cdot OH$ to form 2,3-dichlorophenol, 3,4-dichlorophenol, and polyhydroxy-benzenes, then ring cleavage arises from the polyhydroxy-aromatic compounds to produce some small molecule intermediates. Complete mineralization of O-DCB would ultimately take place.

ACKNOWLEDGMENT

REFERENCES

1. Lv, X.W.; Yan, X.S. Photochemistry oxidation organic priority pollutants in drinking water. China Environ. Sci. **1992**, *12* (1), 71–75.

2. Hoffmann, M.R.; Martin, S.T.; Won, Y.C. Environmental application of semiconductor photocatalysis. Chem. Rev. **1995**, *95* (1), 69–96.

3. Zhang, W.B.; An, T.C.; Xiao, X.M.; Fu, J.M.; Sheng, G.Y.; Cui, M.C. Photochemical degradation performance of quinoline aqueous solution in the presence of hydrogen peroxide. J. Environ. Sci. Heal. A **2003**, *38* (11), 2599–2611.

4. Legrini, O.N.; Oliveres, E.; Braun, A.M. Photochemical processes for water treatment. Chem. Rev. **1993**, *93* (2), 671–698.

5. Zhang, W.B.; Xiao, X.M.; An, T.C.; Song, Z.G.; Fu, J.M.; Sheng, G.Y.; Cui, M.C. Kinetics, degradation pathway and reaction mechanism of advanced oxidation of 4-nitrophenol in water by a UV/H_2O_2 process. J. Chem. Technol. Biotechnol. **2003**, *78* (7), 788–794.

6. Pontius, F.W. Complying with the new drinking water quality regulations. J. Am. Water Works Assoc. **1990**, *82* (2), 2–52.

7. Adams, C.D.; Kazhikannil, J.J. Effects of UV/H_2O_2 preoxidation on the aerobic biodegradability of quaternary amine surfactants. Water Res. **2000**, *34* (2), 668–672.

8.   De-laat, J.; Dore, M. Degradation of chloroethanes in dilute aqueous solution by H_2O_2/UV. Water Res. **1994**, *28* (12), 2507–2519.

9.   Guittonneau, S.; De-Laat, J.; Duguet, J.P.; Bonnel, C.; Dore, M. Oxidation of para-chloronitrobenzene in dilute aqueous solutions by O_3 + UV and H_2O_2 + UV: A comparative study. Ozone-Sci. Eng. **1990**, *73* (1), 12–18.

10.   Lyseffe, P.; Martin, J. Hydrogen peroxide: A potent force to destroy organics in wastewater. Chem. Eng. **1994**, *101*, 16–20.

11.   Sundstrom, D.W.; Weir, B.A.; Barber, T.A.; Klei, H.E. Destruction of pollutants and microorganisms in water by UV light and hydrogen peroxide. Water Pollut. Res. J. Canada **1992**, *27* (1), 57–68.

12.   Hirvonen, A.; Tuhkanen, T.; Kalliokoski, P. Treatment of TCE- and PCE-contaminated groundwater using UV/H_2O_2 and O_3/H_2O_2 oxidation process. Water Sci. Technol. **1996**, *33* (6), 67–73.

13.   Zhang, Z.L. Study on the environmental elements of priority monitoring for priority pollutants. Shanghai Environ. Sci. **1994**, *13* (2), 28–30.

14.   Gan, P.; Zhu, T.T.; Fan, Y.B.; Wang, M.J. Biodegradation of chlorobenzenes—A review. Tech. Equip. Environ. Pollut. Contr. **2000**, *1* (4), 1–12.

15.   Haigler, B.E. Degradation of 1,2-dichlorobenzene by a pseudomonas sp. Appl. Environ. Microbiol. **1988**, *54* (2), 294–301.

16.   Feidieker, D. Microbiological and chemical evaluation of a site contaminated with chlorinated aromatic compounds and hexachlorocyclohexanes. FEMS Microbiol. Ecol. **1994**, *15* (3–4), 265–278.

17.   Spiess, E.; Sommer, C. Degradation of 1,4-dichlorobenzene by xanthobacter flavus14pl. Appl. Environ. Microbio. **1995**, *61* (11), 3884–3888.

18.   Kuhn, H.J.; Braslavsky, S.E.; Schmidt, R. Chemical actinometry. Pure Appl. Chem. **1989**, *61*, 187–210.

19.   Snell, F.D.; Ettre, L.S. *Encyclopedia of Industrial Chemical Analysis*, Vol. 14. Wiley: New York, 1987; 427–439.

20.   Hoigne, J. *The Handbook of Environmental Chemistry*. II: *Chemistry of Aqueous Ozone and Transformation of Pollutants by Ozonation and Advanced Oxidation Processes*, Vol. 5, Part C. Springer-Verlag: Berlin, Heidelberg, 1998; 83–141.

21.   Calderara, V.; Jekel, M.; Zaror, C. Kinetics of ozone reactions with 1-naphthalene, 1,5-naphthalene and 3-nitrobenzene sulphonic acids in aqueous solutions. Water Sci. Technol. **2001**, *44* (5), 7–13.

22.   Beltran, F.J.; Gonzalez, M.; Gonzalez, J.F. Industrial wastewater advance oxidation. Part I: UV radiation in the presence and absence of hydrogen peroxide. Water Res. **1997**, *31* (10), 2405–2414.

23.   Liao, C.H.; Kang, S.F.; Wu, F.A. Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H_2O_2/UV process. Chemosphere **2001**, *44* (5), 1193–1200.

24.   Liao, C.H.; Mirat, D.G. Chemical oxidation by photolytic decomposition of hydrogen peroxide. Environ. Sci. Technol. **1995**, *29* (12), 3007–3014.

25.   Stefan, M.I.; Hoy, A.R.; Bolton, J.R. Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide. Environ. Sci. Technol. **1996**, *30* (7), 2382–2390.

26.   Nadtochenko, V.; Kiwi, J. Primary photochemical reactions in the photo-Fenton system with ferric chloride. 1. A case study of xylidine oxidation as a model compound. Environ. Sci. Technol. **1998**, *32* (21), 3273–3281.

27.   Nadtochenko, V.; Kiwi, J. Photochemical reactions in the photo-Fenton system with ferric chloride. 2. Implications of the precursors formed in the dark. Environ. Sci. Technol. **1998**, *32* (21), 3282–3285.

28.   Meyer, C.; Hirel, B.; Morot-Gaudry, J.F.; Caboche, M. Lütisation de Iäzote par les plantes. Recherche **1995**, *24*, 956–962.

29.   Peyton, G.R.; Glaze; W.H. Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aquaeous ozone. Environ. Sci. Technol. **1988**, *22* (7), 761–767.

30.   Martin, S.; Fritz, H.F. Photochemical degradation of hydrophilic xenobiotics in the UV/H_2O_2 process: Influence of nitrate on the degradation rate of EDTA, 2-amino-1-naphthalenesulfonate, diphenyl-4-sulfonate and 4,4′-diaminostilbene-2,2′-disulfonate. Water Res. **1997**, *31* (11), 2885–2891.

31.   Yawalkar, A.A.; Bhatkhande, D.S.; Pangarkar, V.G.; Beenackers, A.A. Solar-assisted photochemical and photocatalytic degradation of phenol. J. Chem. Technol. Biotechnol. **2001**, *76* (4), 363–370.

32.   Bunce, N.J.; Bergsma, J.P.; Bergsma, M.D. Structure and mechanism in the photoreduction of aryl chlorides in alkane solvents. J. Org. Chem. **1980**, *45* (18), 3708–3713.

33.   Tissot, A.; Boule, P.; Lemaire, J. Photochimie et environnement. V. Photohydrolyse du monochlorobenzene en solution aqueuse diluee. Chemosphere **1983**, *12* (6), 859–872.