Transformation of the Fungicide Chlorothalonil by Fenton Reagent

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A modified Fenton reagent (Fe^{3+}/H_2O_2) transformed the fungicide chlorothalonil within 60 min in aqueous solution at unadjusted pH. Transformation varied with ferric salt. Transformation was greatest with ferric nitrate and least when ferric sulfate was used. UV irradiation enhanced the transformation of chlorothalonil. The transformation of chlorothalonil was enhanced, which increased with ferric ion or hydrogen peroxide concentration. Maximum transformation was achieved at 2 mM ferric ion and 100 mM hydrogen peroxide. Additionally, chlorothalonil was more dechlorinated in the UV irradiation condition. The proposed reaction pathway includes reduction of chlorothalonil to trichloroisophthalo-nitrile, dichloroisophthalonitrile, and monochloroisophthalonitrile; oxidation of trichloroisophthalonitrile to trichloro-3-cyanobenzoic acid and 3-carbamyltrichlorobenzoic acid; and oxidation of hydroxychloro-thalonil to trichloro-3-cyanohydroxybenzoic acid and trichlorocyanophenol.

KEYWORDS: Chlorothalonil, Fenton reagent, transformation, UV irradiation

INTRODUCTION

Chlorothalonil is a nonsystemic foliar fungicide, which disrupts glycolysis in the respiratory system (*1*). With 5 million kg used annually, chlorothalonil is one of the most commonly applied fungicides in the United States (*2*). Chlorothalonil use has gradually increased in Korea, and over 1.5 thousand MT was produced in 2001 (*3*).

Although chlorothalonil is not highly toxic to mammals, it is extremely toxic to fish (*4*) and is classified in the B2 group, which is considered as a "probable human carcinogen", by the U.S. EPA due to the carcinogen hexachlorobenzene that is produced as a byproduct during synthesis of the active ingredient (*2*). In soils, chlorothalonil is mainly transformed to 4-hydroxy-chlorothalonil and is oxidized to 3-cyano-2,4,5,6-tetrachloro-benzamide and 3-cabamyl-2,4,5-trichlorobenzoic acid (*5, 6*). The intermediate 4-hydroxychlorothalonil is more persistent and mobile in soil than chlorothalonil (*2*). Chlorothalonil has also been found in groundwater in the U.S. (*2*).

Chlorothalonil rapidly photodegrades in groundwater, because the rate of chlorothalonil photodegradation can be affected by organic and inorganic matter included in groundwater (*7*). Additionally, the photodegradation rate of chlorothalonil is enhanced in the presence of dissolved organic matter (DOM) (*8*).

To remove toxic organic compounds, such as pesticides, both biological and chemical treatments have been suggested. Biological treatment, using microorganisms or enzymes pro-duced from microorganisms or plants, is often considered as an environmentally favorable method (*9−14*). However, this approach is limited, because it is difficult to remove organic compounds which are either toxic to the microorganisms or are nonbiodegradable (*15, 16*). Therefore, despite high operation costs, chemical treatments known as advanced oxidation processes (AOPs) have been suggested as an alternative because of their efficiency (*17, 18*). AOPs are oxidation processes involving hydroxyl radicals. Generation of the hydroxyl radical has been accomplished with the following technologies: ultra-violet (UV) irradiation (*19*), ozonation (*20−22*), ozonation in combination with UV or hydrogen peroxide (*23−25*), Fenton reagent oxidation (*26−37*), and photocatalysis with titanium dioxide in combination with UV and oxygen (*38*).

Among these technologies, Fenton reagent oxidation has been widely applied to detoxify various toxic organic compounds in water and soil (*26−37*), since the reaction was first suggested by H. J. H. Fenton in 1894. The Fenton reagent is composed of iron salt and hydrogen peroxide. Although Sawyer et al. (*39*) suggested that Fenton reagent does not produce hydroxyl radicals, it is generally believed that ferrous ions react with hydrogen peroxide to produce the highly reactive hydroxyl radical (*40*). The hydroxyl radical participates in nonspecific oxidation of many toxic organic compounds. Additionally, Fenton oxidation of organic compound is stimulated under UV irradiation (*26−33*). Sun and Pignatello (*32*) have reported that 2,4-dichlorophenoxyacetic acid (2,4-D) was completely mineral-ized by the Fe^{3+}/H_2O_2 system. Li et al. (*28*) have also reported the mineralization of 2,4,6-trinitrotoluene (TNT) by Fenton reagent. In the presence of a sufficient concentration of Fenton reagent, it has been suggested that the reaction could continue to complete degradation of organic compounds to carbon dioxide and low molecular weight organic acids such as oxalate.

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The objective of the current study was to determine the potential use of the Fenton reagent for the transformation of the fungicide chlorothalonil. Dechlorination of chlorothalonil was studied under various reaction conditions, and reaction products were identified.

MATERIALS AND METHODS

Chemicals. The fungicide chlorothalonil used in this study was obtained from Kyung-nong Co. (Seoul, Korea). Chlorothalonil was dissolved in acetone to prepare a 1000 mg/L stock solution, which was diluted to obtain the desired concentrations.

Ferric sulfate, ferric chloride, and ferric nitrate used as sources of ferric ion were purchased from Sigma Chemical Co. (St. Louis, MO). Ferric salts were dissolved with deionized water to prepare stock solutions. Hydrogen peroxide was obtained from Junsei Chemical Co. (Tokyo, Japan). All other chemicals used in this study were reagent grade. For high performance liquid chromatography (HPLC) analysis, HPLC grade methanol was purchased from Merck KgaA (Darmstadt, Germany).

Experimental Procedures. Chlorothalonil (2 mg/L) was dissolved in distilled water with 5% acetone, and a 5 mL sample was treated with Fenton reagent under various reaction conditions. The reaction without ferric ions or hydrogen peroxide served as a control for calculating amount of chlorothalonil. Ferric nitrate, ferric chloride, and ferric sulfate were used to compare the effect of ferric salt type on the transformation. Each ferric salt (1 mM) was applied to 2 mg/L of chlorothalonil solution with 0.1 M hydrogen peroxide, and the mixtures were incubated for 5 h in the dark. Time-course experiments using ferric nitrate (1 and 2 mM) combined with 0.1 M hydrogen peroxide were conducted to estimate reaction rate and the effect of UV irradiation on transformation. Reaction mixtures were subjected to UV irradiation or maintained in the dark at room temperature, and the reaction was quenched after 30, 60, 120, 180, and 300 min. The dependence of chlorothalonil transformation on ferric ion concentration was investigated in the presence of 0, 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, and 3.0 mM ferric nitrate. The affect of hydrogen peroxide concentration on the transformation of chlorothalonil was also investigated with 2 mM ferric nitrate in the presence of 0, 10, 20, 50, 100, 300, and 500 mM hydrogen peroxide under dark and UV irradiation conditions. With the exception of the time-course experiment, reaction mixtures were incubated for 5 h and 100 μL of methanol was added to stop the reaction. After incubation, the reaction mixtures were filtered through a 0.45 μm membrane filter, and the concentration of chlorothalonil remaining in the filtrate was determined by HPLC. Each experiment was conducted in triplicate.

Dechlorination of Chlorothalonil. To investigate the dechlorination of chlorothalonil by Fenton reagent, 2 mg/L of chlorothalonil solution was reacted with 1 and 2 mM ferric nitrate and 0.1 M hydrogen peroxide for 5 h under dark and UV irradiation conditions. After incubation, an aliquot of the reaction mixture was filtered through a 0.45 μm membrane filter and the chloride ion concentration was determined by ion chromatography.

Identification of Reaction Products. To identify the products of chlorothalonil treated with Fenton reagent, 100 mL of chlorothalonil solution (2 mg/L) was reacted with 2 mM ferric nitrate and 0.1 M hydrogen peroxide for 5 h in the dark. The reaction mixture was partitioned with *n*-hexane, ethyl acetate, and methylene chloride using a separatory funnel. Each organic solvent layer was combined and then removed with a rotary evaporator at 40 °C in a water bath. After redissolving with acetone, the sample was analyzed with GC-MS to identify the reaction products.

Analytical Methods. Chlorothalonil concentrations were determined using a Shimazu-10A high performance liquid chromatograph system (Shimazu Co., Kyoto, Japan) equipped with an S 5200 sample injector (Sykam Gmbh, Eresing, Germany) and a UV absorbance detector operated at 280 nm using a 150 mm × 4.6 mm Intersil Phenyl-3 analytical column of 5 μm particle size (MetaChem Technologies Inc., Torrance, CA) with a 2 cm guard column (Waters Co., Milford, MA). The mobile phase for analysis of chlorothalonil was composed of methanol and water (80/20, methanol/water, v/v) at a flow rate of 0.9 mL/min.
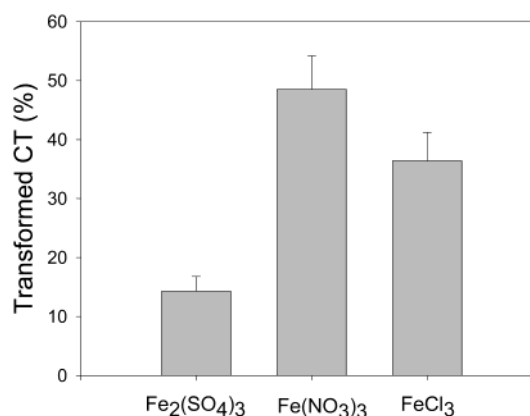
Figure 1. Effects of ferric salts on the transformation of chlorothalonil after treatment with Fenton reagent (Fe^{3+}/H_2O_2 system). Reaction conditions: $[Fe^{3+}] = 1.0$ mM, $[H_2O_2] = 100$ mM, pH = unadjusted, reaction time = 5 h.

The ion chromatography system used for chloride ion analysis consisted of a Waters 600e gradient pump (Waters Co., Milford, MA), a Waters 431 conductivity detector, a model 717 plus autosampler, and an Alltech ERIS 1000HP autosuppressor (Deerfield, IL). A Dionex Ionpac AG14, AS14 (250 mm × 4.0 mm) column (Sunnyvale, CA) was used for the separation with a mobile phase of 3.5 mM sodium carbonate and 1.0 mM sodium bicarbonate at 1.2 mL/min.

Reaction products were identified using a Varian 3800 gas chromatograph system (Walnut Creek, CA) equipped with a Varian Saturn 2000 ion-trap mass detector, a CP-8400 autosampler, and a 60 m (L) × 0.25 mm (i.d.) DB-5MS capillary column (5% phenyl methyl siloxane with 0.25 μm thickness). Analytical conditions were as follows: injection port temperature, 250 °C; column temperature, programmed from 100 °C for 2 min, 12 °C/min until 180 °C, 4 °C/min until 280 °C, held for 20 min; ion trap temperature, 220 °C, mainfold temperature, 50 °C; transfer line temperature, 230 °C; ion source, electron impact (70 eV); acquisition, EI mode with a range of mass scanned between 40 and 400 m/z, scan time of 3 μscan; carrier gas, He at 1.0 mL/min; and injection volume, 1 μL using a splitless mode.

RESULTS AND DISCUSSION

Transformation of Chlorothalonil under Various Reaction Conditions. Since the Fe^{2+}/H_2O_2 system, regarded as the classical Fenton reagent, may consume hydroxyl radicals by reaction with Fe^{2+} ions, the concentration of the hydroxyl radical produced by the Fe^{2+}/H_2O_2 system may be small relative to that for the Fe^{3+}/H_2O_2 system under the same reaction conditions (*29, 32*). This observation was made in preliminary experiments. As chlorothalonil transformation was 71.7% in the Fe^{3+}/H_2O_2 system and 36.1% in the Fe^{2+}/H_2O_2 system, chlorothalonil transformation was greater in the Fe^{3+}/H_2O_2 system than in the Fe^{2+}/H_2O_2 system. Therefore, the Fe^{3+}/H_2O_2 system was selected for subsequent experiments.

The rate of chlorothalonil transformation by Fenton reagent varied with the type of ferric salt used (**Figure 1**). The transformation rate was 48.5%, 36.4%, and 14.3% for ferric nitrate, ferric chloride, and ferric sulfate, respectively. The ferric salts used in this study dissociate in aqueous solution to release anions such as nitrate (NO_3^-), chloride (Cl^-), and sulfate (SO_4^{2-}). Sun and Pignatello (*37*) reported that the Fenton reaction was adversely affected by the presence of chloride ions, which can act as scavengers of hydroxyl radicals, and sulfate, which can complex Fe^{3+}. However, nitrate sensitizes the photodegradation of organic contaminants in an aqueous solution (*41*). Because nitrate absorbs light, it was photolyzed to produce free radicals. The results in this study showed that anions
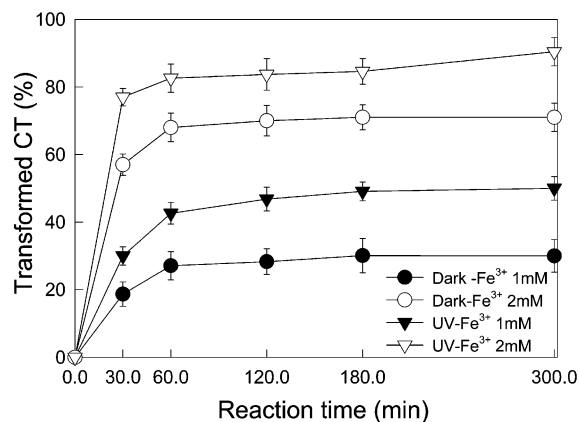
Figure 2. Time course for chlorothalonil transformation after treatment with Fenton reagent (Fe^{3+}/H_2O_2 system). Reaction conditions: $[Fe^{3+}]$ = 1.0 and 2.0 mM, $[H_2O_2]$ = 100 mM, pH = unadjusted, reaction time = 5 h.

Table 1. Reaction Rate Constant (k) and Half-Life ($t_{1/2}$) of Chlorothalonil after Treatment with Fenton Reagent (Fe^{3+}/H_2O_2 System)

| reaction	conditions	reaction rate constant	RSD[a] (%)	half-life (min)
Fe^{3+}/H_2O_2	1.0 mM Fe^{3+} 0.1 M H_2O_2	0.009	1.2	77.0
	2.0 mM Fe^{3+} 0.1 M H_2O_2	0.019	2.6	31.7
Fe^{3+}/H_2O_2/UV	1.0 mM Fe^{3+} 0.1 M H_2O_2	0.014	3.1	49.5
	2.0 mM Fe^{3+} 0.1 M H_2O_2	0.029	3.5	16.9

[a] Relative standard deviation.

released from ferric salt can affect adversely the transformation of chlorothalonil by Fenton reagent. Because the rate of chlorothalonil transformation varied with the ferric salt used as source of ferric ion, ferric nitrate, which was most effective, was used in subsequent experiments.

The time-course experiment indicated that maximum transformation was achieved within 60 min under all experimental conditions (**Figure 2**). The transformation was enhanced with increasing ferric ion concentration under both dark and UV irradiation reaction conditions. For the initial reaction stage (0–60 min), the reaction rate constant (k) ranged from 0.009/min to 0.029/min with corresponding half-lives ($t_{1/2}$) of 77.0–16.9 min (**Table 1**).
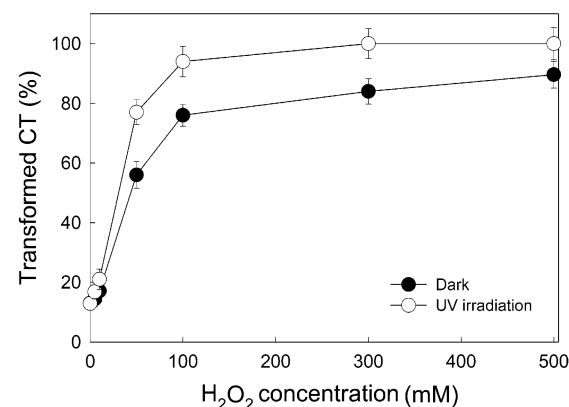
The transformation of chlorothalonil was enhanced under the UV irradiation condition. A number of researchers (*26–33*) have reported that the transformation of an organic compound was enhanced by photoassisted Fenton reaction in a weak acidic condition. Pignatello (*29*) suggested that the enhancement in the transformation of a toxic compound by UV irradiation was due to sensitized reaction with Fe^{3+}. The aquated ferric ion ($Fe(III)_{aq}$) such as Fe^{3+}, $FeOH^{2+}$, and $Fe_2(OH)_2^{4+}$ is photoactive and produces hydroxyl radicals ($OH^\bullet$) with photoreduction to Fe^{2+} under UV irradiation via eq 1.

$$Fe(III)_{aq} \xrightarrow{h\nu} Fe^{2+} + OH^\bullet \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (2)$$
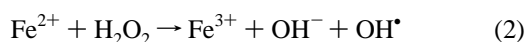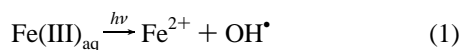
Moreover, ferrous ion produced from ferric ions by UV irradiation may participate in generation of additional hydroxyl
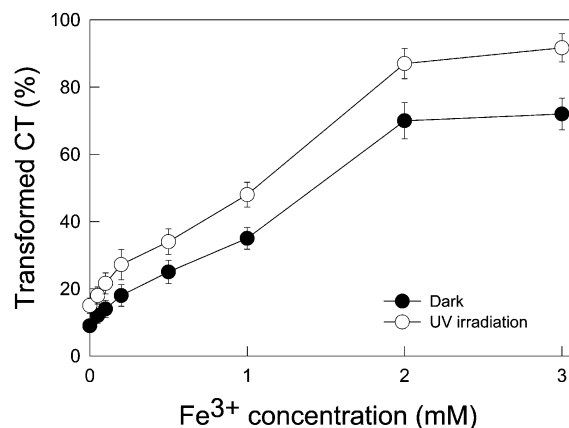
Figure 3. Effect of ferric ion concentration on the transformation of chlorothalonil after treatment with Fenton reagent (Fe^{3+}/H_2O_2 system). Reaction conditions: $[H_2O_2]$ = 100 mM, pH = unadjusted, reaction time = 5 h.

Figure 4. Effect of hydrogen peroxide concentration on the transformation of chlorothalonil after treatment with Fenton reagent (Fe^{3+}/H_2O_2 system). Reaction conditions: $[Fe^{3+}]$ = 2.0 mM, pH = unadjusted, reaction time = 5 h.

radicals via eq 2 in the presence of hydrogen peroxide. Clear evidence for this was presented by Lason et al. (*42*), who reported that the herbicide *s*-triazine was transformed in the presence of ferric ion without peroxide under UV irradiation. Pignatello et al. (*27*) also described production of an additional oxidant, a high-valent oxoiron complex (ferryl complex), produced from $Fe(O_2H)^{2+}$ in the photoassisted Fenton reaction. Thus, the enhanced chlorothalonil transformation by Fenton reagent under UV irradiation condition may be a result of the production of both additional hydroxyl radicals via eq 1 and a ferryl complex.

In the Fe^{3+}/H_2O_2 system, the ferric ion concentration directly influenced the chlorothalonil transformation (**Figure 3**). In the presence of 100 mM hydrogen peroxide, the transformation increased with increasing ferric ion concentration up to 2 mM Fe^{3+} in the reaction mixture. However, no further significant increases in transformation were observed at Fe^{3+} concentrations above 2 mM.
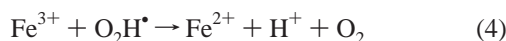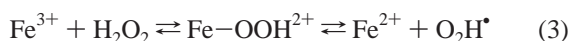
The transformation of chlorothalonil by the Fe^{3+}/H_2O_2 system was also enhanced when the concentration of hydrogen peroxide was increased up to 100 mM (**Figure 4**). In the presence of more than 100 mM hydrogen peroxide, the transformation was not considerably changed. In previous studies (*26, 28–30*), researchers have reported that an increase in hydrogen peroxide concentration enhanced the transformation of organic compounds. In the Fe^{3+}/H_2O_2 system, the production of active

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Table 2. Dechlorination (Cl) and Transformation (Tr) of Chlorothalonil after Treatment with Fenton Reagent (Fe^{3+}/H_2O_2 System)

| reaction	conditions	Tr (μg)	Cl (μg)	DN value[a]
Fe^{3+}/H_2O_2	1.0 mM Fe^{3+} 0.1 M H_2O_2	2.2 ± 0.1	3.8 ± 0.3	1.7
	2.0 mM Fe^{3+} 0.1 M H_2O_2	5.3 ± 0.3	10.4 ± 0.7	2.0
$Fe^{3+}/H_2O_2/UV$	1.0 mM Fe^{3+} 0.1 M H_2O_2	3.6 ± 0.2	9.0 ± 0.6	2.5
	2.0 mM Fe^{3+} 0.1 M H_2O_2	6.8 ± 0.4	18.4 ± 0.9	2.7

[a] DN value means number of chloride ions able to be theoretically released per one molecule of transformed chlorothalonil.

oxidants occurred via eqs 1 and 2 and the following steps (*29*, *32*):

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe-OOH^{2+} \rightleftarrows Fe^{2+} + O_2H^\bullet \qquad (3)$$

$$Fe^{3+} + O_2H^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \qquad (4)$$

A ferric ion is reduced to ferrous via eqs 3 and 4. The hydroxyl radical is then produced by oxidation of ferrous ion through combination with hydrogen peroxide to a ferric ion via eq 2. Under UV irradiation, the aquated ferric ion can produce an additional hydroxyl radical via eq 1 aside from the production via eqs 2−4. In a system in which hydrogen peroxide is continuously supplied, cycling may occur as shown in eq 5 (*32*).

$$(5)$$
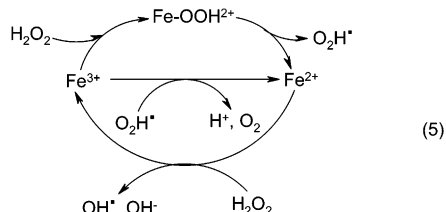
However, under limited hydrogen peroxide concentration, reduction of a ferric ion to a ferrous ion and oxidation of a ferrous ion to a ferric ion for the production of hydroxyl radicals may not repeat continuously in the Fe^{3+}/H_2O_2 system because the hydrogen peroxide is exhausted. Increasing the hydrogen peroxide concentration up to 100 mM enhanced the transformation of chlorothalonil by the Fe^{3+}/H_2O_2 system, because the production of hydroxyl radicals was increased.

Moon et al. (*43*) suggested that the reaction rate may be decreased in the presence of excess of hydrogen peroxide. It was also suggested that excess hydrogen peroxide could scavenge the hydroxyl radical via eq 6 (*29*).

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \qquad (6)$$
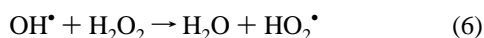
However, in this study, no decreases in chlorothalonil transformation were observed in the range from 100 to 500 mM hydrogen peroxide.

Dechlorination of Chlorothalonil. Chlorothalonil dechlorination was observed in the Fe^{3+}/H_2O_2 system (**Table 2**). In the dark, $3.8-10.4$ μM chloride ion was released when as much as $2.2-5.3$ μM chlorothalonil was transformed. In the UV irradiation condition, $3.6-6.8$ μM chlorothalonil was transformed, and $9.0-18.4$ μM chloride ions was released. Approximately $1.7-2.0$ mol of chloride ions was released per mole of chlorothalonil in the dark, while, under UV irradiation, $2.5-2.7$ mol of chloride
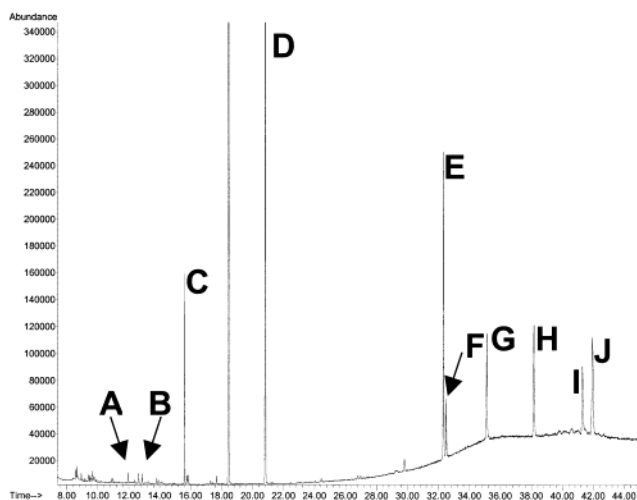
Figure 5. GC-MS chromatogram of chlorothalonil reaction mixture after treatment with Fenton reagent (Fe^{3+}/H_2O_2 system). Reaction conditions: $[Fe^{3+}]$ = 2.0 mM, $[H_2O_2]$ = 100 mM, pH = unadjusted, reaction time = 5 h, dark condition.

Table 3. Mass Spectral Data of Reaction Products

| compd[a]	RT (min)	principal *m/z* (suggested pathway)
A	12.0	163 (MH^+); 135 ($MH^+ - CN$)
B	12.9	196 (M^+); 161 ($M^+ - Cl - H^+$); 125 ($M^+ - 2Cl - 2H^+$)
C	15.6	231 (M^+); 195 ($M^+ - Cl - H^+$); 159 ($M^+ - 2Cl - 2H^+$)
D	20.8	223 (MH^+); 205 ($MH^+ - OH$); 177 ($MH^+ - OH - CH=NH$)
E	32.3	267 (MH^+); 253 ($MH^+ - NH_2$); 207 ($MH^+ - NH_2 - COOH$)
F	34.5	167 ($MH^+ - NH_2 - COOH - C=C=O$)
G	35.1	252 (MH^+); 207 ($MH^+ - COOH$)
H	38.2	
I	41.3	267 (MH^+); 251 ($MH^+ - OH$); 207 ($MH^+ - OH - COOH$)
J	41.9	

[a] Chemical names of the compounds are as follows: **A**, monochloroisophthalonitrile; **B**, dichloroisophthalonitrile; **C**, trichloroisophthalonitrile; **D**, trichlorocyanophenol; **E** and **F**, 3-carbamyltrichlorobenzoic acid; **G** and **H**, trichloro-3-cyanobenzoic acid; **I** and **J**, trichloro-3-cyanohydroxybenzoic acid.

ions was released. When the dark and the UV irradiation conditions are compared, about 1.5 times higher chloride ion release was observed in the UV irradiation condition than in the dark condition.

Identification of Transformation Product of Chlorothalonil. The GC-MS chromatogram showed that chlorothalonil in the Fe^{3+}/H_2O_2 system produced various transient organic intermediates (**Figure 5**). Their GC-MS spectral data are shown in **Table 3**.

Although several trace peaks appeared in the GC-MS chromatogram, some trace reaction products were not identified. Products were identified by comparing the electron impact MS fragmentation patterns with those of expected reaction products, which were based on both the reaction pathway of organic compounds mediated with Fenton reagent (*44*) and the metabolic reaction pathway of chlorothalonil in the environment suggested by Roberts and Hudson (*6*). Compound **C** was identified as trichloroisophthalonitrile, while the trace products (compounds **A** and **B**) corresponded to monochloroisophthalonitrile and dichloroisophthalonitrile produced from the reduction of chlorothalonil. Compound **D** was assumed to be trichlorocyanophenol because the MS spectrum indicated successive loss of hydroxy (*m/z*, 205) and cyano (*m/z*, 177) groups from MH^+ of compound **D**.

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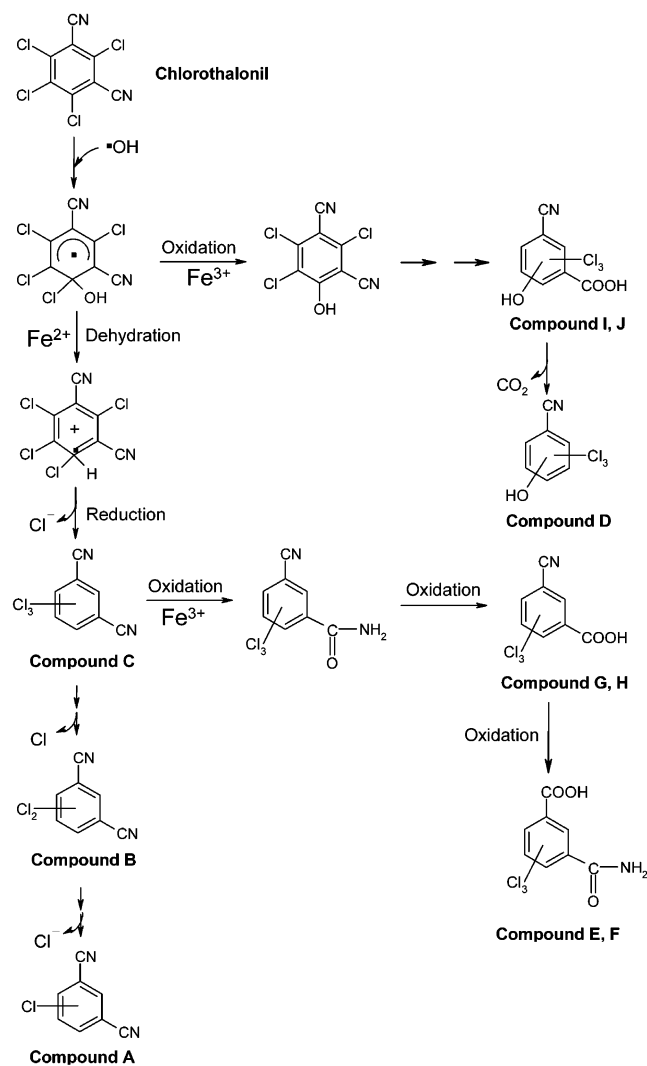
Figure 6. Proposed reaction pathway of chlorothalonil treated with Fenton reagent (Fe^{3+}/H_2O_2 system).

The GC-MS spectra of compounds **E** and **F**, **G** and **H**, and **I** and **J** contained the same fragmentation patterns, respectively, indicating structural isomers. Compounds **E** and **F** contained ions at m/z 253, 253, 207, and 167, which represented a successive loss of $-NH_2$, $-COOH$, and $-C\equiv C=O$ from MH^+. They were assumed to be 3-carbamyltrichlorobenzoic acid. Compounds **G** and **H** were assumed to be trichloro-3-cyanobenzoic acid, because they represented a fragment of $-COOH$ (ion at m/z 207). Compounds **I** and **J** contained ions at m/z 251 and 207, representing sequential loss of $-OH$ and $-COOH$. Thus, they may be assumed to trichloro-3-cyanohydroxybenzoic acid.

Although identification of the reaction products in this study was tentative, it appears reasonable. On the basis of the results obtained in this study, a reaction pathway for chlorothalonil transformation in the Fenton system is proposed (**Figure 6**). Walling (*44*) suggested that substrate can be transformed to an intermediate radical, which can be oxidized, reduced, or dimerized to produce various reaction products in the presence of metal ions, as a result of attack by hydroxyl radicals in the Fenton system. It has also been suggested that the major reaction products could be altered by the oxidation state of the metal ion present in the Fenton system. Therefore, in the initial step of the reaction, chlorothalonil may be transformed to a tetra-chlorodicyanohydroxy cyclohexadienyl radical by the attack of hydroxyl radicals produced in the Fe^{3+}/H_2O_2 system. The

intermediate, tetrachlorodicyanohydroxycyclohexadienyl radical, may then be oxidized to trichlorodicyanophenol by ferric ion (Fe^{3+}) or undergo a reduction to trichloroisophthalonitrile (compound **C**) after dehydration to a radical cation by a ferrous ion (Fe^{2+}). Robert and Hudson (*6*) have suggested that benzamide and benzoic acid derivatives can be produced through oxidation of a cyano group on the chlorothalonil in soil, so it is expected that some reaction products were produced by oxidation of the cyano group on the chlorothalonil in the Fenton system (compounds **D–J**).

In previous studies (*28, 32*), it was reported that chlorophenoxyl herbicides and TNT could be mineralized by Fenton oxidation via oxalic acid found in the reaction mixture. However, oxalic acid was not detected in the Fe^{3+}/H_2O_2 system-catalyzed chlorothalonil degradation when the reaction mixture was analyzed with ion chromatography (data not shown). This result suggests that chlorothalonil may be not mineralized in Fe^{3+}/H_2O_2 system.

CONCLUSIONS

In a previous study (*35*), it was suggested that the Fenton reaction cannot efficiently degrade toxic compounds in a circumneutral pH condition. However, the Fe^{3+}/H_2O_2 Fenton system transformed chlorothalonil effectively in an unadjusted pH condition. Maximum transformation was achieved at 2 mM ferric ions and 100 mM hydrogen peroxide. Chlorothalonil transformation was enhanced by increasing the concentration of ferric ions or hydrogen peroxide. Chlorothalonil was dechlorinated in the Fe^{3+}/H_2O_2 system, and the dechlorination rate was higher in the UV irradiation condition than in the dark condition.

Our results suggest that reaction products were formed by reduction of chlorothalonil to trichloroisophthalonitrile, dichloroisophthalonitrile, and monochloroisophthalonitrile; oxidation of trichloroisophthalonitrile to trichloro-3-cyanobenzoic acid and 3-carbamyltrichlorobenzoic acid; and oxidation of hydroxychlorothalonil to trichloro-3-cyanohydroxybenzoic acid and trichlorocyanophenol.

The results obtained in this study indicate that the Fenton reagent can be an alternative technology for the remediation of aqueous environments contaminated with chlorothalonil.

LITERATURE CITED

(1) *The Pesticide Manual,* 11th ed.; Tomlin, C. D. S., Ed.; British Crop Protection Council: Farnham, U.K., 1997; pp 227−229.
(2) Cox, C. Chlorothalonil. *J. Pest. Reform.* **1997**, *17*, 14−20.
(3) *Agrochemical year book*; Agricultural Chemical Industrial Association: Seoul, Korea, 2002; pp 212−213.
(4) Davies, P. E.; White, R. W. G. The toxicology and metabolism of chlorothalonil in fish, I. Lethal levels for *Salmo gairdueri, Gclaxias maculatus, G. truttaceous* and *G. auratus* and fate of ^{14}C-TCIN in *S. gairdneri. Aquat. Toxicol.* **1985**, *7*, 93−105.
(5) Regitano, J. B.; Tornisielo, A.; Pacovsky, R. S. Transformation pathways of ^{14}C-chlorothalonil in tropical soils. *Arch. Environ. Contam. Toxicol.* **2001**, *40*, 295−302.
(6) Robert, T.; Hudson, D. *Metabolic pathways of agrochemicals. Part 2: Insecticides and fungicides*; The Royal Society of Chemistry: Cambridge, U.K., 1999; pp 1380−1384.
(7) Penuela, G. A.; Barcelo, D. Photodderadation and stability of chlorothalonil in water studied by solid-phase disk extraction, followed by gas chromatographic techniques. *J. Chromatogr., A* **1998**, *823*, 81−90.
(8) Sakkas, V. A.; Lambropoulou, D. A.; Albanis, T. A. Study of chlorothalonil photodegradation in natural waters and in the presence of humic substances. *Chemosphere* **2002**, *48*, 939−945.

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(9) Kim, J.-E.; Fernandes, E.; Bollag, J.-M. Enzymatic coupling of the herbicide bentazon with humus monomer and characterization of reaction products. *Environ. Sci. Technol.* **1997**, *31*, 2392–2398.

(10) Lee, J.-E.; Park, J.-W.; Kim, J.-E. Use of plant materials for decontamination of wastewater polluted with 2,4-dichlorophenol. *Korean J. Environ. Agric.* **1999**, *18*, 292–297.

(11) Lee, J.-E.; Park, J.-W.; Kim, J.-E. Decontamination of wastewater polluted with phenolic and anilinic compounds using plant materials. *Korean J. Environ. Agric.* **2000**, *19*, 228–233.

(12) Behki, R.; Topp, E.; Dick, W.; Germon, P. Metabolism of the herbicide atrazine by *Rhodococcus* strains. *Appl. Environ. Microbiol.* **1993**, *59*, 1955–1959.

(13) Kilbane, J. J.; Chatterjee, D. K.; Karns, J. S.; Kellogg, S. T.; Chakrabarty, A. M. Biodegradation of 2,4,5-trichlorophenoxy-acetic acid by a pure culture of *Pseudomonas cepacia*. *Appl. Environ. Microbiol.* **1982**, *44*, 72–78.

(14) Levanon, D. Roles of fungi and bacteria in the mineralization of the pesticides atrazine, alachlor, malathion and carbofuran in soil. *Soil Biol. Biochem.* **1993**, *25*, 1097–1105.

(15) Alexander, M. Research needs in bioremediation. *Environ. Sci. Technol.* **1991**, *25*, 1972–1973.

(16) Steinberg, S. M.; Pignatello, J. J.; Sawhney, B. L. Persistence of 1,2-dibromoethane in soils; Entrapment in intraparticle micropores. *Environ. Sci. Technol.* **1987**, *21*, 1201–1208.

(17) Ollis, D. F. Comparative aspects of advanced oxidation processes. In *Emerging technologies in hazardous waste management III*; Tedder, D. W., Pohland, F. G., Eds.; ACS Symposium Series 518; American Chemical Society: Washington, DC, 1993; pp 18–34.

(18) Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol.* **1992**, *26*, 1005–1013.

(19) Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water treatment. *Chem. Rev.* **1983**, *93*, 671–698.

(20) Hapeman-Somich, C. J.; Zong, G.-M.; Lusby, W. R.; Muldoon, M. T.; Waters, R. Aqueous ozonation of atrazine. Product identification and description of the degradation pathway. *J. Agric. Food Chem.* **1992**, *40*, 2294–2298.

(21) Hapeman, C. J.; Anderson, B. G.; Torrents, A.; Acher, A. Mechanistic investigations concerning the aqueous ozonolysis of bromacil. *J. Agric. Food Chem.* **1997**, *45*, 1006–1011.

(22) Hoigne, J.; Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water. 2. Dissociating organic compounds. *Water Res.* **1983**, *17*, 185–194.

(23) Staehelin, S.; Hoigne, J. Decomposition of ozone in water. Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.* **1982**, *16*, 676–681.

(24) Adams, C. D.; Scanlan, P. A.; Secrist, N. S. Oxidation and biodegradability enhancement of 1,4-dioxane using hydrogen peroxide and ozone. *Environ. Sci. Technol.* **1994**, *28*, 1812–1818.

(25) Mokrini, A.; Oussi, D.; Esplugas, S. Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water Sci. Technol. 35*, 95–102.

(26) Pignatello, J. J.; Sun, Y. Complete oxidation of metolachlor and methyl parathion in water by the photoassisted fenton reaction. *Water Res.* **1995**, *29*, 1837–1844.

(27) Pignatello, J. J.; Jiu, D.; Huston, P. Evidence for an additional oxidant in the photoassisted fenton reaction. *Environ. Sci. Technol.* **1999**, *33*, 1832–1839.

(28) Li, Z. M.; Comfort, S. D.; Shea, P. J. Destruction of 2,4,6-tri-nitrotoluene by fenton oxidation. *J. Environ. Qual. 26*, 480–487.

(29) Pignatello, J. J. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* **1992**, *26*, 944–951.

(30) Huston, P. L.; Pignatello, J. J. Degradation of selected pesticide active ingredients and commercial formulations in water by the photoassisted fenton reaction. *Water Res. 33*, 1238–1246.

(31) Engwall, M. A.; Pignatello, J. J.; Grasso, D. Degradation and detoxification of the wood preservatives creosote and penta-chlorophenol in water by the photofenton reaction. *Water Res.* **1999**, *33*, 1151–1158.

(32) Sun, Y.; Pignatello, J. J. Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$. *Environ. Sci. Technol.* **1993**, *27*, 304–310.

(33) Fallmann, H.; Krutzler, T.; Bauer, R.; Malato, S.; Blanco, J. Applicability of the photofenton method for treating water containing pesticides. *Catal. Today* **1999**, *54*, 309–319.

(34) Howsawkeng, J.; Watts, G. J.; Washington, D. L.; Teel, A. L.; Hess, T. F.; Crawford, R. L. Evidence for simultaneous abiotic-biotic oxidations in a microbial-Fenton's system. *Environ. Sci. Technol.* **2001**, *35*, 2961–2966.

(35) Pratap, K.; Lemley, A. T. Fenton electrochemical treatment of aqueous atrazine and metolachlor. *J. Agric. Food Chem.* **1998**, *46*, 3285–3291.

(36) Pignatello, J. J.; Baehr, K. Ferric complexes as catalysts for "Fenton" degradation of 2,4-D and metolachlor in soil. *J. Environ. Qual.* **1994**, *23*, 365–370.

(37) Sun, Y.; Pignatello, J. J. Organic intermediates in the degradation of 2,4-dichlorophenoxyacetic acid by Fe^{3+}/H_2O_2 and $Fe^{3+}/H_2O_2/UV$. *J. Agric. Food Chem.* **1993**, *41*, 1139–1142.

(38) Gimenez, J.; Curco, D.; Marco, P. Reactor modeling in the photocatalytic oxidation of wastewater. *Water Sci. Technol.* **1997**, *35*, 207–213.

(39) Sawyer, D. T.; Sobkowiak, A.; Matsushita, T. Metal [ML_x; M=Fe, Cu, Co, Mn]/hydroperoxide-induced activation of di-oxygen for the oxygenation of hydrocarbons; Oxygenated fenton chemistry. *Acc. Chem. Res.* **1996**, *29*, 409–416.

(40) Walling, C. Fenton's reagent revisited. *Acc. Chem. Res.* **1975**, *8*, 125–131.

(41) Vaughan, P. P.; Blough, N. V. Photochemical formation of hydroxyl radical by constituents of natural waters. *Environ. Sci. Technol.* **1998**, *32*, 2947–2953.

(42) Larson, R. A.; Schlauch, M. B.; Marley, K. A. Ferric ion promoted photodecomposition of triazines. *J. Agric. Food Chem.* **1991**, *39*, 2057–2062.

(43) Moon, D.-K.; Maruyama, T.; Osakada, K.; Yamamoto, T. Chemical oxidation of polyaniline by radical generating reagent. *Chem. Lett.* **1991**, 1633–1636.

(44) Walling, C. Intermediates in the reactions of fenton type reagents. *Acc. Chem. Res.* **1998**, *31*, 155–157.