

Chemical Degradation of Polychlorinated Biphenyls by the UV-Fe²⁺/Fe³⁺-H₂O₂ System and its Application for Polychlorinated Biphenyl-polluted Electric Insulating Oil

Takashi Azuma and Yoshiki Mino*

Laboratory of Environmental Analysis, Osaka University of Pharmaceutical Sciences, 4–20–1 Nasahara, Takatsuki, Osaka 569–1094, Japan

(Received July 28, 2011; Accepted August 3, 2011; Published online August 19, 2011)

The application of an optimized Fenton reaction and UV irradiation to the degradation of highly chlorinated biphenyls (PCBs) was performed. Recommended conditions were: Fe²⁺/Fe³⁺ concentration (16 mM), H₂O₂ concentration (12%), temperature (70°C), pH (2.0), reaction time under stirring (≥ 2 hr), re-addition of iron solution (1 hr intervals) and H₂O₂ (30 min intervals) and UV irradiation (254 nm, intensity 0.4 mW cm⁻²). When the system was applied to mixtures of PCBs at 5 ppm [PCBs congeners Kanechlor (KC)-400/600], low chlorine substituted biphenyls (Cl: 2–5) were completely decomposed after 2 hr, and even > 90% of high chlorine substituted biphenyls (Cl: 6–8) could be degraded. When the present system was first applied to PCBs present in polluted electric insulating oil (25 ppm), > 80% of PCBs were successfully degraded after 8 hr. These results suggest that the present UV-Fe²⁺/Fe³⁺-H₂O₂ system could be employed as a new technique for combating persistent organic pollutants such as PCBs.

Key words— chemical degradation, polychlorinated biphenyl, UV-Fe²⁺/Fe³⁺-H₂O₂ system, Fenton and Fenton-like reactions, polychlorinated biphenyl-polluted electric insulating oil

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of toxic biphenyl compounds that are substituted by chlorines (≤ 10) and exist as a mixture of 209 congeners.¹⁾ PCBs were widely used in industry as heat media and as electric insulating oil. However, the considerable chemical stability and biological toxicity these compounds possess means that they currently pose a severe threat to the natural environment.^{2,3)} Because of their bio-accumulation characteristics and resistance to biodegradation, strict regulations have been implemented against the use of PCBs, and many countries have prohibited their use entirely.³⁾ The signatories of the Stockholm Treaty committed themselves to stopping production of products containing PCBs by 2025 and completing the disposal of stored PCBs by 2028.³⁾ Given the considerable amount of PCBs remaining in the environment and in storage, numerous studies on the degradation of PCBs have been undertaken, including biodegradation using microorganisms,^{4–6)} chemical and physicochemical degradations using TiO₂,⁷⁾ combination of O₃ and UV,⁸⁾ ultrasonication,⁹⁾ UV radiation,¹⁰⁾ hydrodechlorination by palladium on activated carbon (Pd-C),¹¹⁾ and microwave irradiation.¹²⁾ Although these degradation methods are useful for decomposition of PCBs, some are lengthy and/or expensive.¹³⁾

Successful decomposition of PCBs in electric insulating oil has been achieved using γ -ray radiation,¹⁴⁾ sodium dispersion,³⁾ and incineration.¹⁵⁾ However, despite their efficacy, these methods are costly and require the application of specialized techniques in order to perform them safely.

On the other hand, degradation by interaction with radical \cdot OH generated by Fenton-type reactions is a relatively powerful, safe and economical method for removing decay-resistant organic materials. In fact, for several decades, Fenton/Fenton-like reactions combined with UV or solar radiation have been widely employed to degrade pollutants such as trichloroethylene,¹⁶⁾ phenol,¹⁷⁾ trinitrotoluene,¹⁸⁾ pharmaceuticals in water,¹⁹⁾ pesticides,²⁰⁾ dioxin or dioxin-like pollutants,^{21,22)} as well as to decolorize aqueous pigments,²³⁾ and PCBs.^{13,24)} In most of these studies however, degradation was limited to low chlorine substituted biphenyls (degree of chlorination ≤ 4).

In this study, we employed a combination of the

*To whom correspondence should be addressed: Laboratory of Environmental Analysis, Osaka University of Pharmaceutical Sciences, 4–20–1 Nasahara, Takatsuki, Osaka 569–1094, Japan. Tel.: +81-72-690-1071; Fax: +81-72-690-1005; E-mail: mino@gly.oups.ac.jp

Fenton reaction and UV irradiation (UV-Fe²⁺/Fe³⁺-H₂O₂ system), and applied it to the degradation of PCBs present in electric insulating oil.

MATERIALS AND METHODS

Reagents — Mixtures of PCBs, Kanechlor (KC)-400 and 600, were purchased from GL Science Inc. (Tokyo, Japan) and diluted with *N-N'*-dimethylformamide to make a 0.1% (W/V) solution as a stock solution. Paraffin electric insulating oil was obtained from Cosmo Oil Lubricants Co., Ltd. (Tokyo, Japan). The stock solution of PCBs was diluted with pure insulating oil to make a standard 25 ppm solution of PCBs in insulating oil. The standard solution was used immediately after preparation. Standard 0.4 M iron solutions were made by solubilization of solid FeCl₂, FeCl₃, Fe(ClO₄)₂, or Fe(ClO₄)₃ separately in distilled water and were used immediately after preparation. All other chemicals were reagent grade.

Procedures for PCBs Analysis — The reaction mixture was prepared by mixing the stock solution of PCBs, iron solution, and H₂O₂ solution in a 50-ml Erlenmeyer flask. The final volume of the reaction mixture was adjusted to 5 ml with water. The reaction mixture was incubated for 1–4 hr at 30–70°C and concentrations of iron and H₂O₂ were varied from 1 to 16 mM and 1–12%, respectively. The reaction was initiated by addition of the iron solution, then each reaction flask was capped with a silicon rubber stopper with a glass tube (5 × 350 mm) inserted in the stopper as a simple cooling device. The temperature was regulated by a water bath, and the pH of the reaction mixture was adjusted by addition of 1 M NaOH solution.

At the end of the reaction, the deep-red colored precipitates which formed were dissolved by the addition of 2 ml of 1 M HCl before 10 ml of *n*-hexane was added to the flask. After stirring for 5 min, the solution was poured into a funnel flask and the organic layer was separated. The water layer was extracted twice with *n*-hexane (10 ml). The combined organic layer was washed with aqueous saturated NaCl solution (25 ml), dried over anhydrous sodium sulfate, and evaporated to low volume by rotary evaporation at room temperature. The final volume of the solution was adjusted to 2 ml by flash evaporation under nitrogen gas before being used for GC-MS analysis.

Photolysis — Degradation of PCBs was conducted in a 50-ml beaker covered with a polychlorovinylidene wrap and irradiated using a hand-held UV lamp (254 nm, 0.4 mW cm⁻²; 6 W 100 V, Funakoshi UVGL-58, Funakoshi Co. Ltd., Tokyo, Japan) 4–5 cm from the surface of the beaker. The energy of the UV light was measured with a high-resolution quantum radiometer (Model UVC-254, Sato Shouji Inc., Kawasaki, Japan). The wrap was replaced at hourly intervals. Except for UV irradiation, the reaction mixture was treated as described in "Procedure for PCBs analysis."

Degradation of PCBs in Insulating Oil — The reaction mixture (10 ml) containing PCBs (25 ppm), insulating oil (1 ml), 16 mM FeCl₃ or Fe(ClO₄)₃, and 6% H₂O₂ (as final concentration) in a 50-ml beaker with a wrap was irradiated using UV irradiation as described above. After treatment, *n*-hexane (20 ml) was added to the solution, and the mixture was stirred with a magnetic stirrer for 10 min. The solution was transferred to a funnel flask and the organic layer was separated and manipulated as described elsewhere (Ministry of Health, Labor and Welfare, Japan, July 3rd 1992). Briefly, to this solution, dimethyl sulfoxide (DMSO) saturated with *n*-hexane (25 ml) was added and the solution was shaken for 10 min. After extraction with DMSO (25 ml, three times), the combined DMSO fraction (100 ml) was washed with *n*-hexane (40 ml). The DMSO solution was then back-extracted with a mixture of *n*-hexane (75 ml) and *n*-hexane-washed water (100 ml) by shaking for 5 min, followed by removal of the *n*-hexane layer. The remaining DMSO layer was then extracted twice with *n*-hexane (75 ml). The combined *n*-hexane layers were washed with 2 M KOH (20 ml) and water (20 ml × 2), dried over anhydrous sodium sulfate, and evaporated to 1.0 ml under reduced pressure. This solution was diluted with *n*-hexane (100 ml) and transferred to a funnel flask where the *n*-hexane layer was treated at least three times with 30–40 ml of *c*-H₂SO₄ until the elimination of color in the sulfuric acid layer. After this treatment, the *n*-hexane layer was washed with *n*-hexane-washed water, adjusted to pH 4–5, dried over anhydrous sodium sulfate, and concentrated to 2 ml. This solution was subjected to silica gel chromatography (10 × 300 mm, Wakogel C-200, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and PCB fractions were eluted with *n*-hexane (25 ml). The *n*-hexane recovered was concentrated to 2.0 ml and PCBs in the solution were analyzed by GC-MS.

Table 1. Effect of Fe³⁺ and H₂O₂ Concentration on PCB Degradation

Reagent	Concentration		PCBs Degradation (%)			
	Fe ³⁺ (mM)	H ₂ O ₂ (%)	5Cl-PCB	6Cl-PCB	7Cl-PCB	8Cl-PCB
FeCl ₃	4	1	25	15	0	0
	4	4	29	12	0	0
	4	8	30	13	3	0
	4	12	43	26	15	19
FeCl ₃	8	1	41	18	0	0
	8	4	55	30	5	5
	8	8	45	50	23	20
	8	12	70	55	16	19
FeCl ₃	16	1	39	17	10	8
	16	4	50	36	27	19
	16	8	55	55	30	21
	16	12	80	70	54	60
Fe(ClO ₄) ₃	16	1	47	39	29	18
	16	4	64	50	45	33
	16	8	69	58	46	38
	16	12	84	75	54	55

Conditions; PCBs: 5 ppm, [Fe³⁺]: 4–16 mM, H₂O₂: 1–12%, pH ≈ 2, 70°C, 1 hr.

PCB Analysis by GC-MS— Analysis of PCBs was carried out on a Hitachi 3DQS mass spectrometer M-9000 (Hitachi, Ltd., Tokyo, Japan) coupled to a Hitachi gas chromatograph G-7000. Helium was used as a carrier gas at a flow rate of 1.5 ml/min with a split ratio of 1/50. The injector and transfer line temperatures were set to 280°C. An SGE capillary column forte HT8-PCB 50 m × 0.22 mm, 0.25 μm (SGE Analytical Science, Pty. Ltd., Ringwood, VIC, Australia) was used with a temperature profile of 80°C (2 min hold) to 170°C at a rate of 30°C/min to 299°C (5 min hold) at a rate of 3°C/min.

Identification of PCB peaks was performed according to the method of Matsumura *et al.*²⁵⁾ and quantitative analysis was carried out by measurement of peak areas in the selective ion monitoring (SIM).²⁴⁾ Duplicate measurements were performed and an average value was calculated. For estimating the degradation rates of di- to octa-chlorinated PCBs, peak areas of corresponding components in KC-400/600 solutions [2Cl: 4, 5, 8 (IUPAC No.); 3Cl: 18, 28, 31; 4Cl: 52, 69, 70; 5Cl: 101, 110, 120; 6Cl: 132, 139, 149; 7Cl: 174, 180, 182; 8Cl: 196, 199, 203] were also calibrated in duplicate.

RESULTS AND DISCUSSION

Degradation of PCBs by the Fe³⁺-H₂O₂ System

The effects of reagent concentration on PCB degradation by the present Fenton reactions for 1 hr

at pH 2 and 70°C are shown in Table 1. Since lower ratios of Fenton reagents (iron ion/hydrogen peroxide) have been reported to be important for degradation,^{26,27)} concentration ratios of 1/1–1/3 for Fe³⁺ (4–16 mM)/H₂O₂ (1–12%) were examined. However, the results did not reveal a clear relationship of the Fenton ratio, but rather indicated the reagent concentration dependence. However, at concentrations higher than 16 mM, the reaction proceeded too rapidly to control and loss of PCBs might occur due to generation of gas by H₂O₂. Consequently, the concentration of ferric ion and H₂O₂ for degradation of PCBs was fixed at 16 mM and 12%, respectively. Also, the results showed that Fe(ClO₄)₃ was slightly superior to FeCl₃ as a ferric ion source for the degradation of PCBs.

Next, we analyzed the effect of temperature (30–70°C) on degradation of PCBs. As shown in Fig. 1, the effect of temperature on PCB degradation revealed a negative relationship between the degree of chlorination and decomposition rate as reported by Pignatello and Chapa.²⁴⁾ At 30°C, PCBs having up to 3 degrees of chlorination were successfully decomposed (up to 80%). As the reaction temperature increased, decomposition of PCBs having higher degrees of chlorination also progressed. Taken together, these findings suggest that temperature is an important factor affecting decomposition by the Fe³⁺ (or Fe²⁺)-H₂O₂ system, which is in accordance with previous studies on dioxin²¹⁾ and pesticides.^{28,29)}

The pH of the reaction solution is one of the

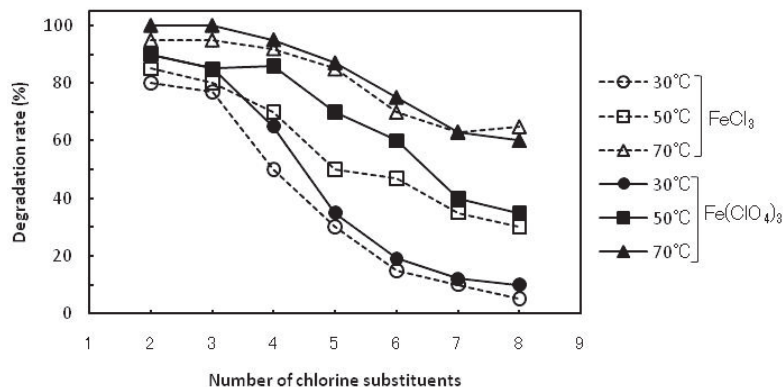


Fig. 1. Effect of Temperature on PCB Degradation

Conditions; PCBs: 5 ppm, $[\text{Fe}^{3+}]$: 16 mM, H_2O_2 : 12%, $\text{pH} \approx 2$, 30–70°C, 1 hr FeCl_3 or $\text{Fe}(\text{ClO}_4)_3$ was used as an iron compound.

most important factors for degradation activity in this reaction system.²¹⁾ The relationship between pH and degradation activity was also investigated. When iron compounds were dissolved in water, the pH of the solution decreased to approximately pH 2, with a slight decrease in pH being observed by the addition of H_2O_2 . For this solution (pH 2.0), strongest activity (degradation rates of > 90% per 1 hr and 70°C for PCBs having 3 degrees of chlorination) was observed, and a clear decrease in activity was seen for pH near 6 or 10 (up to 10%). In fact, a preference for acidic conditions (pH 2.0–2.8) was reported previously.^{23, 30)} The reaction in the present Fe^{3+} - H_2O_2 system could therefore be conducted under acidic conditions without any pH adjustment. The reaction at a low pH of 2.0 appeared to be optimal for the degradation of PCBs and we therefore selected pH 2.0 for subsequent experiments.

Degradation of PCBs by the UV- $\text{Fe}^{2+}/\text{Fe}^{3+}$ - H_2O_2 System

The effect of UV irradiation on the degradation of PCBs was analyzed by comparing degradation rates with and without UV irradiation. Irradiation with UV light at 254 nm and 0.4 mW cm^{-2} significantly improved the degradation of PCBs after reaction for 2 hr (Fig. 2). Under this condition, biphenyls having a high number of chlorines (7–8), which are difficult to degrade without UV irradiation, were decomposed at rates exceeding 90% when $\text{Fe}(\text{ClO}_4)_3$ was used as an iron compound. The combined use of UV with the Fenton/Fenton-like system has previously been reported to accelerate the generation of $\cdot\text{OH}$.^{31, 32)} The main reason for the improved degradation rate with UV irradiation is attributed to this induction of radical formation and dechlorination by UV.¹⁰⁾

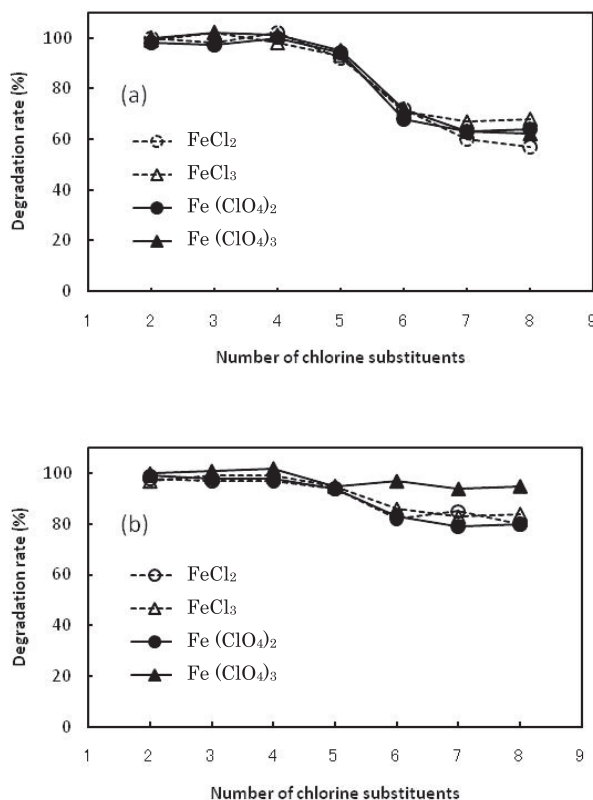


Fig. 2. PCB Degradation under Combined UV Illumination Regimes

(a): Without UV, (b): with UV.

Both iron chloride and iron perchlorate were usable as iron compounds, although the perchlorates were slightly superior to the chlorides for PCBs degradation. No noticeable difference was observed between Fe^{2+} and Fe^{3+} , which suggests the occurrence of not only the classic Fenton reaction catalyzed by Fe^{2+} , but also the reaction in which Fe^{3+} was reduced to Fe^{2+} by perhydroxyl radical ($\text{HO}_2\cdot$) generated from hydrogen peroxide by the Haber-Weiss reaction.³³⁾

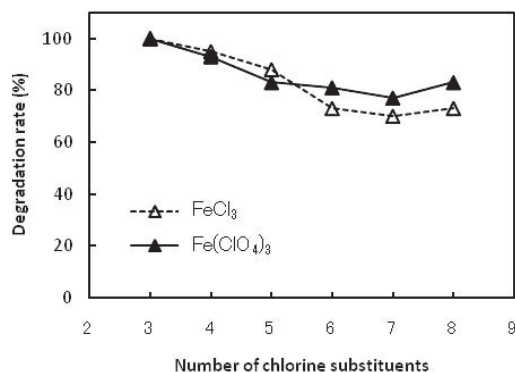


Fig. 3. Degradation of PCBs in Insulating Oil

Conditions; PCBs: 25 ppm, $[\text{Fe}^{2+}/\text{Fe}^{3+}]$: 16 mM, H_2O_2 : 6%, UV intensity $\cong 0.4 \text{ mW cm}^{-2}$, pH $\cong 2$, 50°C , 8 hr, 0.4 ml of 0.4 M iron solution $\times 7$, 2 ml of 30% $\text{H}_2\text{O}_2 \times 15$.

Degradation of Small Amounts of PCBs Contained in Electric Insulating Oil by the UV- $\text{Fe}^{2+}/\text{Fe}^{3+}$ - H_2O_2 System

Figure 3 shows degradation rates of PCBs when the developed UV- $\text{Fe}^{2+}/\text{Fe}^{3+}$ - H_2O_2 system was applied to PCB-polluted paraffin electric insulating oil. The result clearly indicates the efficacy of this chemical method for degrading PCBs in the oil. The rate of PCB degradation in the electric insulating oil was lower than that observed for pure PCBs, particularly in biphenyls having 6–8 chlorine substituents. However, 3–5 chlorine substituted biphenyls were efficiently decomposed to levels exceeding 85% after 8 hr.

Further study might be needed to conduct complete decomposition of PCBs having higher numbers of chlorine substitutions. To elucidate the degradation mechanism of PCBs in this system, GC-MS detection of the intermediates from PCBs in the degradation reaction would be indispensable.

In conclusion, this report demonstrated the application of an improved Fenton reaction for degrading PCBs by combining the $\text{Fe}^{2+}/\text{Fe}^{3+}$ - H_2O_2 system with UV irradiation. Under optimal conditions [16 mM $\text{Fe}^{2+}/\text{Fe}^{3+}$, 12% H_2O_2 , 70°C , 2 hr stirring/reaction, iron ion addition every 1 hr and H_2O_2 every 30 min, and UV irradiation (254 nm , 0.4 mW cm^{-2}), PCBs having low (Cl: 2–5) and high (Cl: 6–8) numbers of chlorine substituents were either decomposed completely or to levels exceeding 90%, respectively. When this system was applied to PCBs in insulating oil, about 80% of PCBs were successfully degraded, even for PCBs having high chlorine substitutions. The main features of our highly effective degradation method are that the reagents are inexpensive and that secondary

environmental pollution is negligible, since H_2O_2 will spontaneously decay into oxygen and water. In addition, the time required for treatments is short. This chemical degradation method using the UV- $\text{Fe}^{2+}/\text{Fe}^{3+}$ - H_2O_2 system has the potential to be applied as a new tool for removing persistent organic pollutants, such as PCBs in electric insulating oil.

Acknowledgement This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

- 1) Arensdorf, J. J. and Focht, D. D. (1994) Formation of chlorocatechol meta cleavage products by a pseudomonad during metabolism of monochlorobiphenyls. *Appl. Environ. Microbiol.*, **60**, 2884–2889.
- 2) Seto, M., Kimbara, K., Shimura, M., Hatta, T., Fukuda, M. and Yano, K. (1995) A novel transformation of polychlorinated biphenyls by *Rhodococcus* sp. strain RHA1. *Appl. Environ. Microbiol.*, **61**, 3353–3358.
- 3) Noma, Y., Mitsuhara, Y., Matsuyama, K. and Sakai, S. (2007) Pathways and products of the degradation of PCBs by the sodium dispersion method. *Chemosphere*, **68**, 871–879.
- 4) Rodrigues, J. L., Maltseva, O. V., Tsoi, T. V., Helton, R. R., Quensen, J. F., Fukuda, M. and Tiedje, J. M. (2001) Development of a *Rhodococcus* recombinant strain for degradation of products from anaerobic dechlorination of PCBs. *Environ. Sci. Technol.*, **35**, 663–668.
- 5) Fuse, H., Takimura, O., Murakami, K., Inoue, H. and Yamaoka, Y. (2003) Degradation of chlorinated biphenyl, dibenzofuran, and dibenzo-*p*-dioxin by marine bacteria that degrade biphenyl, carbazole, or dibenzofuran. *Biosci. Biotechnol. Biochem.*, **67**, 1121–1125.
- 6) Sietmann, R., Gesell, M., Hammer, E. and Schauer, F. (2006) Oxidative ring cleavage of low chlorinated biphenyl derivatives by fungi leads to the formation of chlorinated lactone derivatives. *Chemosphere*, **64**, 672–685.
- 7) Huang, I. W., Hong, C. S. and Bush, B. (1996) Photocatalytic degradation of PCBs in TiO_2 aqueous suspensions. *Chemosphere*, **32**, 1869–1881.
- 8) Vollmuth, S. and Niessner, R. (1995) Degradation of PCDD, PCDF, PAH, PCB and chlorinated phenols during the destruction-treatment of landfill seepage

- water in laboratory model reactor (UV, ozone, and UV/ozone). *Chemosphere*, **30**, 2317–2331.
- 9) Zhang, G. and Hua, I. (2000) Cavitation chemistry of polychlorinated biphenyls: Decomposition mechanisms and rates. *Environ. Sci. Technol.*, **34**, 1529–1534.
 - 10) Chang, F. C., Chiu, T. C., Yen, J. H. and Wang, Y. S. (2003) Dechlorination pathways of *ortho*-substituted PCBs by UV irradiation in *n*-hexane and their correlation to the charge distribution on carbon atom. *Chemosphere*, **51**, 775–784.
 - 11) Kume, A., Monguchi, Y., Hattori, K., Nagase, H. and Sajiki, H. (2008) Pd/C-catalyzed practical degradation of PCBs at room temperature. *Appl. Catal.*, **B 81**, 274–282.
 - 12) Liu, X. and Yu, G. (2006) Combined effect of microwave and activated carbon on the remediation of polychlorinated biphenyl-contaminated soil. *Chemosphere*, **63**, 228–235.
 - 13) Dercova, K., Vrana, B., Tandlich, R. and Subova, L. U. (1999) Fenton's type reaction and chemical pretreatment of PCBs. *Chemosphere*, **39**, 2621–2628.
 - 14) Jones, C. G., Silverman, J., Al-Sheikhly, M., Neta, P. and Poster, D. L. (2003) Dechlorination of polychlorinated biphenyls in industrial transformer oil by radiolytic and photolytic methods. *Environ. Sci. Technol.*, **37**, 5773–5777.
 - 15) Wu, W., Xu, J., Zhao, H., Zhang, Q. and Liao, S. (2005) A practical approach to the degradation of polychlorinated biphenyls in transformer oil. *Chemosphere*, **60**, 944–950.
 - 16) Li, K., Stefan, M. I. and Crittenden, J. C. (2004) UV photolysis of trichloroethylene: product study and kinetic modeling. *Environ. Sci. Technol.*, **38**, 6685–6693.
 - 17) Kavitha, V. and Palanivelu, K. (2004) The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere*, **55**, 1235–1243.
 - 18) Liou, M. J., Lu, M. C. and Chen, J. N. (2004) Oxidation of TNT by photo-Fenton process. *Chemosphere*, **57**, 1107–1114.
 - 19) Perez-Estrada, L. A., Malato, S., Gernjak, W., Aguera, A., Thurman, E. M., Ferrer, I. and Fernandez-Alba, A. R. (2005) Photo-Fenton degradation of diclofenac: identification of main intermediates and degradation pathway. *Environ. Sci. Technol.*, **39**, 8300–8306.
 - 20) Pignatello, J. J. (1992) Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.*, **26**, 944–951.
 - 21) Mino, Y., Moriyama, Y. and Nakatake, Y. (2004) Degradation of 2,7-dichlorodibenzo-*p*-dioxin by Fe³⁺-H₂O₂ mixed reagent. *Chemosphere*, **57**, 365–372.
 - 22) Katsumata, H., Kaneco, S., Suzuki, T., Ohta, K. and Yobiko, Y. (2006) Degradation of polychlorinated dibenzo-*p*-dioxins in aqueous solution by Fe(II)/H₂O₂/UV system. *Chemosphere*, **63**, 592–599.
 - 23) Hsueh, C. L., Huang, Y. H., Wang, C. C. and Chen, C. Y. (2005) Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. *Chemosphere*, **58**, 1409–1414.
 - 24) Pignatello, J. J. and Chapa, G. (1994) Degradation in PCBs by ferric ion, hydrogen peroxide and UV light. *Environ. Toxicol. Chem.*, **13**, 423–427.
 - 25) Matsumura, C., Tsurukawa, M., Nakano, T., Ezaki, T. and Ohashi, M. (2002) Elution orders of all 209 PCBs congeners on capillary column "HT8-PCB." *Kankyo Kagaku*, **12**, 855–865.
 - 26) Chan, K. H. and Chu, W. (2003) Modeling the reaction kinetics of Fenton's process on the removal of atrazine. *Chemosphere*, **51**, 305–311.
 - 27) Chu, W., Chan, K. H., Kwan, C. Y. and Lee, C. K. (2004) The system design of UV-assisted catalytic oxidation process—degradation of 2,4-D. *Chemosphere*, **57**, 171–178.
 - 28) Liou, R. M., Chen, S. H., Hung, M. Y. and Hsu, C. S. (2004) Catalytic oxidation of pentachlorophenol in contaminated soil suspensions by Fe³⁺-resin/H₂O₂. *Chemosphere*, **55**, 1271–1280.
 - 29) Lopez, A., Mascolo, G., Detomaso, A., Lovecchio, G. and Villani, G. (2005) Temperature activated degradation (mineralization) of 4-chloro-3-methyl phenol by Fenton's reagent. *Chemosphere*, **59**, 397–403.
 - 30) Chu, W., Kwan, C. Y., Chan, K. H. and Chong, C. (2004) An unconventional approach to studying the reaction kinetics of the Fenton's oxidation of 2,4-dichlorophenoxyacetic acid. *Chemosphere*, **57**, 1165–1171.
 - 31) Lee, C. and Yoon, J. (2004) Temperature dependence of hydroxyl radical formation in the hv/Fe³⁺/H₂O₂ and Fe³⁺/H₂O₂ systems. *Chemosphere*, **56**, 923–934.
 - 32) Kusic, H., Koprivanac, N., Bozic, A. L. and Selanec, I. (2006) Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study. *J. Hazard. Mater.*, **136**, 632–644.
 - 33) Motohashi, N. and Mori, I. (1983) Superoxide-dependent formation of hydroxyl radical catalyzed by transferrin. *FEBS Lett.*, **157**, 197–199.