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

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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 ·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
Fenton reaction and UV irradiation (UV-Fe$^{2+}$/Fe$^{3+}$-H$_2$O$_2$ 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 as a stock solution. Paraffin electric insulating oil was obtained from Cosmo Oil Lubricants Co., Ltd. (Tokyo, 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), iron solution (1 ml), 16 mM FeCl$_3$ or Fe(ClO$_4$)$_3$, and 6% H$_2$O$_2$ (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 x 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-H$_2$SO$_4$ 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 x 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 Fe$^{3+}$ and H$_2$O$_2$ Concentration on PCB Degradation

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration</th>
<th>PCBs Degradation (%)</th>
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<tr>
<td></td>
<td>Fe$^{3+}$ (mM)</td>
<td>H$_2$O$_2$ (%)</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>4</td>
<td>1</td>
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<td>8</td>
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<td></td>
<td>4</td>
<td>12</td>
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<tr>
<td>FeCl$_3$</td>
<td>8</td>
<td>1</td>
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<td>8</td>
<td>12</td>
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<tr>
<td>FeCl$_3$</td>
<td>16</td>
<td>1</td>
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<td>16</td>
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<td>8</td>
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<td></td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>Fe(ClO$_4$)$_3$</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>4</td>
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Conditions; PCBs: 5 ppm, [Fe$^{3+}$]: 4–16 mM, H$_2$O$_2$: 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. and quantitative analysis was carried out by measurement of peak areas in the selective ion monitoring (SIM). 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 Fe$^{3+}$-H$_2$O$_2$ 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 Fe$^{3+}$ (4–16 mM)/H$_2$O$_2$ (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 H$_2$O$_2$. Consequently, the concentration of ferric ion and H$_2$O$_2$ for degradation of PCBs was fixed at 16 mM and 12%, respectively. Also, the results showed that Fe(ClO$_4$)$_3$ was slightly superior to FeCl$_3$ 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 Fe$^{3+}$ (or Fe$^{2+}$)-H$_2$O$_2$ system, which is in accordance with previous studies on dioxins21) 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, [Fe$^{3+}$]: 16 mM, H$_2$O$_2$: 12%, pH $\approx$ 2, 30–70°C, 1 hr FeCl$_3$ or Fe(ClO$_4$)$_3$ was used as an iron compound.

Fig. 2. PCB Degradation under Combined UV Illumination Regimes
(a): Without UV, (b): with UV.

Degradation of PCBs by the UV-Fe$^{2+}$/Fe$^{3+}$-H$_2$O$_2$ 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 Fe(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 ·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.$^{10}$

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 (HO$_2^-$) generated from hydrogen peroxide by the Haber-Weiss reaction.$^{33}$
Degradation of Small Amounts of PCBs Contained in Electric Insulating Oil by the UV-Fe$^{2+}$/Fe$^{3+}$-H$_2$O$_2$ System

Figure 3 shows degradation rates of PCBs when the developed UV-Fe$^{2+}$/Fe$^{3+}$-H$_2$O$_2$ 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 Fe$^{2+}$/Fe$^{3+}$-H$_2$O$_2$ system with UV irradiation. Under optimal conditions [16 mM Fe$^{2+}$/Fe$^{3+}$, 12% H$_2$O$_2$, 70°C, 2 hr stirring/reaction, iron ion addition every 1 hr and H$_2$O$_2$ 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$_2$O$_2$ will spontaneously decay into oxygen and water. In addition, the time required for treatments is short. This chemical degradation method using the UV-Fe$^{2+}$/Fe$^{3+}$-H$_2$O$_2$ system has the potential to be applied as a new tool for removing persistent organic pollutants, such as PCBs in electric insulating oil.

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REFERENCES


![Fig. 3. Degradation of PCBs in Insulating Oil](image-url)


