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OXIDATION OF AQUEOUS CHLOROBIPHENYLS WITH PHOTO-FENTON PROCESS

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ABSTRACT

Research of 4-CBP and 4,4'-CBP in aqueous solution using the photo-Fenton process was conducted in two parts. The first part of the study explored the treatment efficiency, revealing that 4-CBP and 4,4'-CBP were easily adsorbed onto glass. As a result, the true treatment efficiencies of the photo-Fenton processes were calculated by subtracting the amount of 4-CBP and 4,4'-CBP adsorbed onto glass from the total amount decreased during the treatment processes. The results further showed that the most optimum pH for the degradation and the mineralization of chlorobiphenyls was pH 3. In the second half of this study, the reaction rate expressions of 4-CBP and 4,4'-CBP were simulated. With respect to the simulated experimental data, the relationship between the reaction rate of 4-CBP with the H_2O_2 concentration was expressed as a first-order reaction, that for 4,4'-CBP was a zero-order reaction, and that between the reaction rate and the Fe(II) concentration was a saturation-type reaction.

Keywords: 4-Chlorobiphenyl; 4,4'-dichlorobiphenyl; photo-Fenton process; reaction rate expression.

INTRODUCTION

One emerging and very promising technology, based on the total oxidation of hazardous organic compounds, is the use of advanced oxidation processes (AOPs). AOPs use a combination of two or three oxidants: ozone and ultraviolet (UV) radiation, hydrogen peroxide and UV radiation, ozone and hydrogen peroxide, etc., to generate very oxidizing reactive free radicals, mainly hydroxyl radicals (OH •), in aqueous solutions. Hydroxyl radicals are the principal agents responsible for the oxidation of numerous aqueous organic contaminants [1,2].

In general, the oxidation rate or the amount of organic compounds oxidized is calculated following the disappearance of the target compound as a function of time. This approach can provide a good picture of the oxidation process but due to the possibility of intermediate species formation, the total degradation of the target compound does not always correspond to the total mineralization of the organics to CO_2 and H_2O [3~5].

For example, the Fe(II)/H_2O_2 and Fe(III)/H_2O_2 reagents are able to destroy organic pollutants in the dark, although neither one is able to mineralize organic pollutants completely in a short time [6~8]. The starting material is partially transformed to some intermediate product, which appears to resist further oxidation. Mineralization with Fe(II)/H_2O_2 or Fe(III)/H_2O_2 is improved considerably by irradiation with near-UV and visible light [6, 8~10], of which the resulting process is called the "photo-Fenton reaction" [12]. Indeed, quick mineralization can be achieved through this process, especially organic pollutants that are hard to degrade, such as polychlorinated biphenyls (PCB).

PCB is one of the most widespread hazardous wastes found in the environment [12, 13]. Vast quantities of PCB are present in public buildings, landfills, and industrial plants. They are quite resistant to ordinary mechanisms of environmental degradation. Even though PCBs express low acute toxicity, they have been demonstrated to be carcinogenic in test animals.

The current practices of indefinite storage and incineration of PCB, although widely used, are unacceptable from an environmental standpoint. The objective of this research is to develop a new photochemical procedure for PCB processing. Direct photolysis of PCB by UV radiation has been studied for some time [14~17]. However, the generation of UV radiation required for the reaction is quite expensive, and the reactions yield a myriad of decomposed and rearranged products. The processes described above occur at rates too slow to be applied industrially.

This paper presents the results of investigations on 4-chlorobiphenyl (4-CBP) and 4,4'-dichlorobiphenyl (4,4'-CBP) treatment by the UV/Fe(II)/H_2O_2 process as a quick degradation process.

MATERIALS AND METHODS

Sample Preparation

4-CBP and 4,4'-CBP (Chem Service Co., S. G. grade 99+%) was chosen as the model compound. Methyl alcohol (Merck, G. R. grade) containing 4-CBP and 4,4'-CBP were used as stock solution (50 mg/L), which was diluted with deionized water (Milli-Q SP) to the required concentration before use. All other agents used were of Merck, G. R. grade.

Analytical Methods

4-CBP and 4,4'-CBP were analyzed by modification of *Standard Method 6431* [18] and *EPA method 608* [19] on GC (Hewlett Packard 5890 series II plus). The extraction method for 4-CBP and 4,4'-CBP is described in detail by Kuo and Lo (1997) [13]. Samples were analyzed for the remaining concentrations for 4-CBP and 4,4'-CBP. The analytical peaks did not overlap. To ensure the accuracy of the results, all detailed analyses strictly followed the QA/QC procedure suggested by *Standard Method 6020* [18].

Experimental Method and Design

The photo-Fenton degradation of 4-CBP and 4,4'-CBP was investigated. All experiments were performed in the photochemical reactor described previously [13], in which the geometric dimensions of the reactor and lamp were provided in detail. The reactor basically consists of an annular glass reactor equipped with a 500-W high-pressure mercury vapor lamp (Oriel 6285) in an axial position at 254 nm. Samples from the reactors were placed into 40-ml extraction bottles containing several drops of 6 N NaOH and 0.02 mL of 1 M sodium sulfite. The addition of NaOH raised the pH higher than 10, and the sodium sulfite reacted with $OH \cdot$, thereby stopping the Fenton reaction.

RESULTS AND DISCUSSION

Quality Assurance and Quality Control (QA/QC)

Experimental runs were conducted in triplicate to validate the precision of the experiments and are displayed with error bars in the Figures. QA/QC of the analytical methods is important for proving the accuracy and usefulness of the experimental data. To ensure precision, double analysis was performed, and the relative difference was controlled at $\pm 20\%$. Accuracy was confirmed by spike analysis and shown by a near-80% recovery. To determine the method detection limit (MDL), 4-CBP (5 μg/L, estimation of 10 times MDL concentration) and 4,4'-CBP (5 μg/L) were analyzed separately on GC seven times. The MDL values for 4-CBP and 4,4'-CBP, the best of which should be the smallest possible value, were 0.5 μg/L and 0.2 μg/L.

Treatment of 4-CBP and 4,4'-CBP

Aqueous 4-CBP and 4,4'-CBP at varying degrees of contamination were treated by UV/Fe(II)/H_2O_2 (light reaction) and Fe(II)/H_2O_2 (dark reaction). The background tests displayed that 4-CBP and 4,4'-CBP were easily adsorbed onto glass [13] and that a portion of the compounds were lost through adsorption during the experimental processes. Therefore, the true treatment efficiencies of the photo-Fenton processes

should be calculated by subtracting the amount of 4-CBP and 4,4'-CBP adsorbed onto glass from the total amount decreased during the treatment processes.The treatment efficiencies of these two processes are presented in Fig. 1. As can be seen, the light reaction is more efficient by a factor of 2 after 30 minutes. Figure 2 provides further details on the extent of the degradation of total organic carbon (TOC) concentration for these two processes. Both Figs. 1 and 2 show that the degradation of aqueous chlorobiphenyls increased with the existence of UV light. In the dark reaction, a large amount of intermediates was formed probably within the first 5 mins, evidenced by the TOC concentrations for 4-CBP and 4,4'-CBP surpassing 100% (Fig. 2), and then slowly degraded. In the light reaction, on the other hand, a small amount of intermediates was produced, and degradation was more rapid than in the dark reaction. Because some of these intermediates could be more toxic than the primary compound [20~23], mineralization to a harmless form in the dark reaction was improved by irradiation with near-UV light.

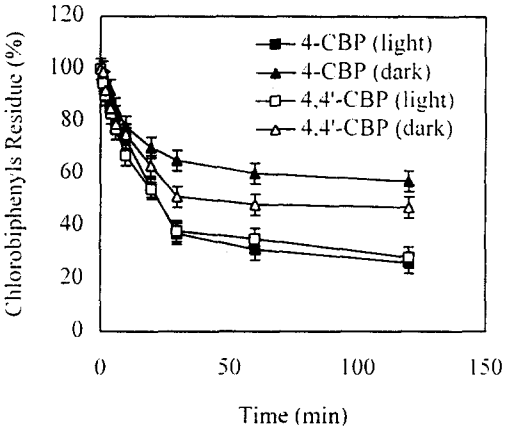

Figure 1. Comparison of the remaining chlorobiphenyl concentrations after photo-Fenton and Fenton treatment (initial 4-CBP and 4,4'-CBP concs. = 500 μg/L, $[Fe^{2+}]$ = 0.1 mM, pH = 3 ± 0.25, 20°C, $[H_2O_2]$ = 0.5 mM, UV light intensity = 5 mW/cm^2).

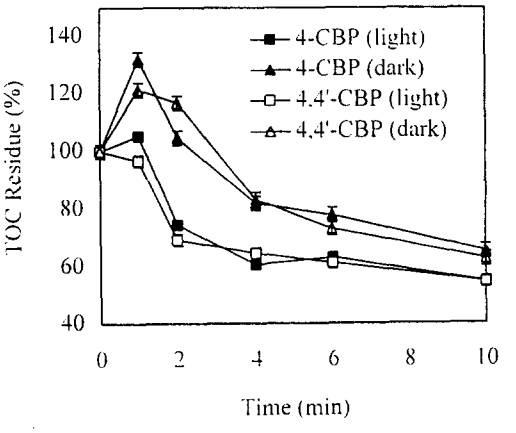

Figure 2. Comparison of the remaining TOC concentrations after photo-Fenton and Fenton treatment.

The effect of pH, represented by the degradation of the primary compound, using the photo-Fenton process was pH 3 > pH 2 > pH 4 (Figs. 3 and 4) and was similar to the effect of pH on TOC. Although much target compounds degradation occurred at pH 2, a large amount of intermediates (TOC) was also rapidly formed early in the reaction and degraded later. At pH 3,where the most efficient degradation of chlorobiphenyls occurred, a smaller amount of intermediates was produced and degraded rapidly. At pH 4, both the target compounds and intermediates were degraded at a slower rate (Figs. 3 and 4). Therefore, these

results reveal that the degradation efficiency and intermediate forms of aqueous 4-CBP and 4,4'-CBP are controlled by pH. The most optimum pH for the degradation and the mineralization of chlorobiphenyls is pH 3.

In addition, Manilal [23] monitored the toxicity of pure aqueous solutions of 2,4,-DCP irradiated in the presence of TiO_2 and observed that toxicity towards activated sludge increased during the oxidation of 2,4,-DCP. Comparing our experiment results with those of Manilal *et al.* [23], it was found that the oxidative ability of UV/TiO_2 is less than that of the UV/Fe(II)/H_2O_2 process (Figs. 3 and 4) although both processes destroy organic pollutants. It is believed that the more powerful process causes not only primary compound but also intermediate production to decrease, especially when the latter is more toxic than the former.

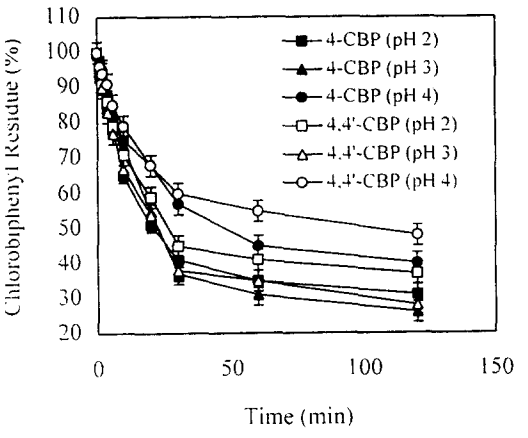

Figure 3. Degradation of chlorobiphenyls at different pH using the photo-Fenton process (initial 4-CBP and 4,4'-CBP concs. = 500 μg/L, $[Fe^{2+}]$ = 0.1 mM, 20°C, $[H_2O_2]$ = 0.5 mM, UV light intensity = 5 mW/cm^2).

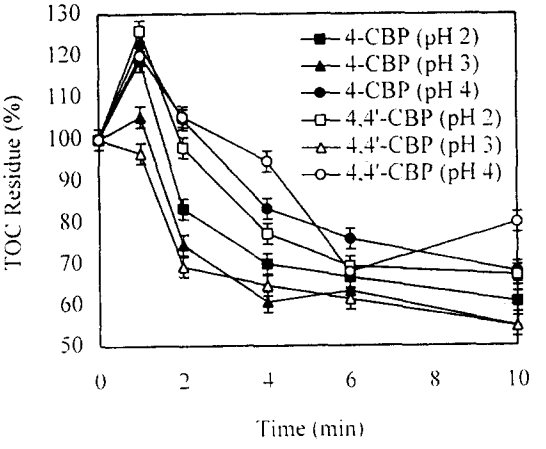

Figure 4. Degradation of TOC at different pH using the photo-Fenton process.

Figs. 5 and 6 show the degradation of several aqueous 4-CBP and 4,4'-CBP concentrations with different H_2O_2 concentrations by UV/Fe(II)/H_2O_2. The most efficient degradation occurred at a H_2O_2 concentration of 1.25 mM. The primary compounds were degraded with the least efficiency at 0.25 mM H_2O_2 . At this concentration, the greatest amount of intermediates was produced within the first 10 mins. and then degraded slowly over a period of two hours, which was the slowest time observed of the experiments.

To explore the treatment efficiency of Fe(II), several aqueous 4-CBP and 4,4'-CBP solutions containing varying concentrations of Fe(II) were treated by the UV/Fe(II)/H_2O_2 process. Figs. 7 and 8 show

that the degradation of primary compounds increase with increasing concentration of Fe(II). At 0.05 mM Fe(II), however, the production of intermediates decreased and degradation was delayed. Fe(II) concentration is an important factor in the photo-Fenton process, as exhibited by its effect on intermediate degradation. Because pH affects the species of Fé in solution, the degradation of chlorobiphenyls is governed by both pH and the Fe(II) concentration in this process.

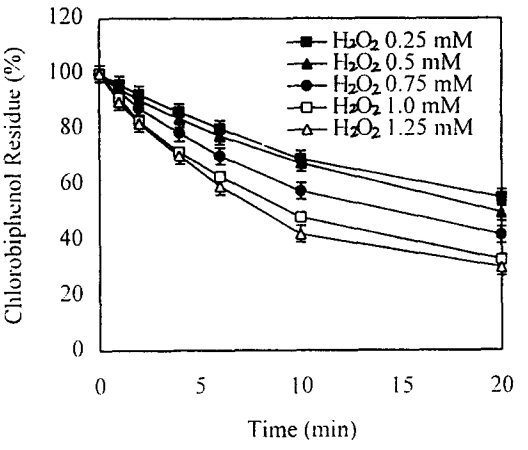

Figure 5. Degradation of 4-CBP at different H_2O_2 concentrations using the photo-Fenton process (Initial 4-CBP conc. = 500 μg/L, $[Fe^{2+}]$ = 0.1 mM, pH = 3 ± 0.25, 20°C, UV light intensity = 5 mW/cm^2).

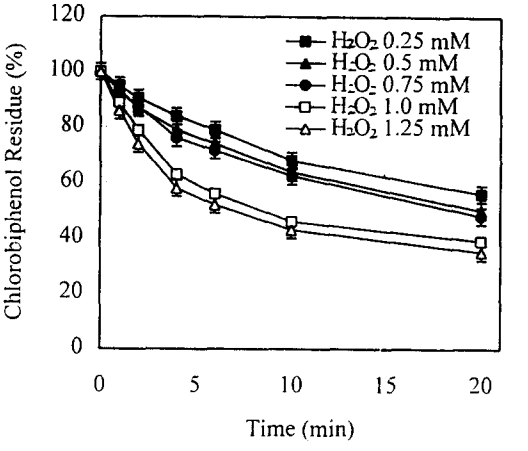

Figure 6. Degradation of 4,4'-CBP at different H_2O_2 concentrations using the photo-Fenton process (initial 4,4'-CBP conc. = 500 μg/L, $[Fe^{2+}]$ = 0.1 mM, pH = 3 ± 0.25, 20°C, UV light intensity = 5 mW/cm^2).

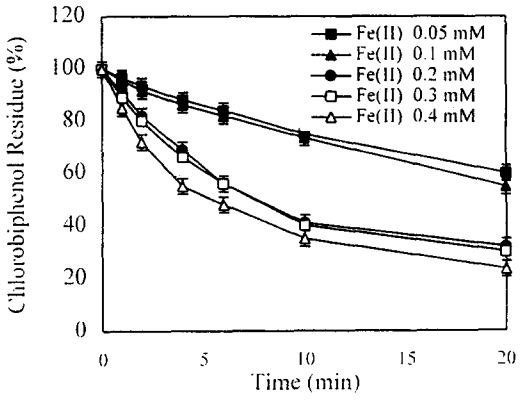

Figure 7. Degradation of 4-CBP at different Fe(II) concentrations using the photo-Fenton process (initial 4-CBP conc. = 500 μg/L, $[H_2O_2]$ = 0.5 mM, pH = 3 ± 0.25, 20°C, UV light intensity = 5 mW/cm^2).

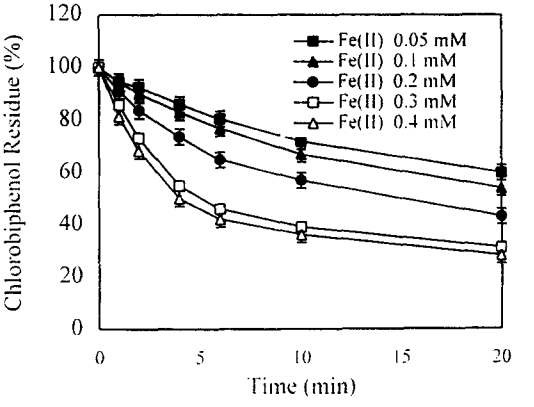

Figure 8. Degradation of 4,4'-CBP at different Fe(II) concentrations using the photo-Fenton process (initial 4,4'-CBP conc. = 500 μg/L, $[H_2O_2]$ = 0.5 mM, pH = 3 ± 0.25, 20°C, UV light intensity = 5 mW/cm^2).

Reaction rate of 4-CBP and 4,4'-CBP

The reaction of Fe(II) with H_2O_2 is known as Fenton's reaction [11,24], which is written as

$$Fe(II) + H2O2 \rightarrow Fe(III) + OH^- + \cdot OH \qquad k = 63\ M^{-1}S^{-1} \tag{1}$$

The hydroxyl radical formed can either react with Fe(II), producing Fe(III),

$$\cdot OH + Fe(II) \rightarrow Fe(III) + OH^- \tag{2a}$$

or react with and initiate the oxidation of organic pollutants present in the solution.

$$\cdot OH + nRH \rightarrow \text{oxidized products} \tag{2b}$$

Assuming that [2b] is the rate-determining step, the reaction rate equation is written as

$$\frac{d[RH]}{dt} = k_{OH}[\cdot OH][RH]^n = k_{exp}[RH]^n \tag{3}$$

where [RH] is the chlorobiphenyl concentration (μg/L), k_{OH} is the reaction rate constant, and $k_{exp} = k[\cdot OH]$ is assumed to be a pseudo n-order reaction rate constant. It is further assumed that the relationship between the reaction rate and H_2O_2 concentration is an m-order reaction. Consequently, the following equation is written as

$$k_{exp} = k[H_2O_2]^m \tag{4}$$

Calculations using the values listed in Table 1 are expressed as the following for 4-CBP:

$$k_{exp} = 9 \times 10^{-4}[H_2O_2]^{0.91} \qquad R^2 = 0.87 \tag{5}$$

With respect to the simulated results, the relationship between the reaction rate and H_2O_2 concentration can be expressed as a first-order reaction, and that for 4,4'-CBP is a zero-order reaction.

Table 1. k_{exp} and R^2 of photo-Fenton-degraded 4-CBP and 4,4'-CBP at different H_2O_2 concentrations

H_2O_2 (mM)	0.25	0.5	0.75	1.0	1.25
4-CBP					
$k \times 10^2$ (L/μg sec)	1.8	2.4	3	16.2	7.8
n order	2.08	2.04	2.07	1.78	1.98
R^2	0.923	0.946	0.977	0.980	0.918
4,4-CBP					
$k \times 10^4$ ($L^2/\mu g^2$/sec)	4.1	3.4	4.6	2.2	2.8
n order	2.94	3.06	3.00	3.35	3.35
R^2	0.922	0.938	0.903	0.922	0.959

It is also assumed that the relationship between the reaction rate and Fe(II) concentration is a saturation-type reaction. Therefore, the following equation is written as

$$k_{exp} = \frac{k[Fe(II)]}{K_S + [Fe(II)]}[H_2O_2] \tag{6}$$

where k is the maximum reaction constant and K_S represents the concentration at half-saturation. Again, using the values in Table 2, the calculations of k and K_S for 4-CBP are

$$k_{exp} = \frac{13.6[Fe(II)]}{1+[Fe(II)]}[H_2O_2] \qquad R^2 = 0.98 \tag{7}$$

and for 4,4'-CBP are

$$k_{exp} = \frac{39.7[Fe(II)]}{7.9+[Fe(II)]} \qquad R^2 = 0.84 \tag{8}$$

The reaction rate expression is thus written as

$$\frac{d[RH]}{dt} = \frac{13.6[Fe(II)]}{1+[Fe(II)]}[H_2O_2][RH]^2 \qquad \text{for 4-CBP} \tag{9}$$

$$\frac{d[RH]}{dt} = \frac{37.9[Fe(II)]}{7.9+[Fe(II)]}[RH]^3 \qquad \text{for 4,4'-CBP} \tag{10}$$

Table 2. k_{exp} and R^2 of photo-Fenton-degraded 4-CBP and 4,4-CBP at different Fe(II) concentrations

Fe(II) (mM)	0.05	0.1	0.2	0.3	0.4
4-CBP					
$k\times10^2$ (L/μg sec)	1.3	2.2	2.7	2.8	3.3
n order	2.09	2.01	2.22	2.23	2.29
R^2	0.886	0.725	0.865	0.930	0.969
4,4-CBP					
$k\times10^4$ ($L^2/\mu g^2$/sec)	4.4	6.4	6.7	15.1	13.7
n order	2.88	2.87	2.99	3.00	3.08
R^2	0.656	0.983	0.967	0.936	0.955

For the above simulated reaction expressions, the relation between H_2O_2 concentration, which ranges from 0.25~2.0 mM. If the H_2O_2 concentration is greater than 2.0 mM, the increased concentration decreases the reaction rate [4], because the H_2O_2 concentration could shade UV-illuminated chlorophenols. Therefore, the maximum contributive value of H_2O_2 may exist under some H_2O_2 concentration. Reaction rate expressions (9) and (10) are suitable at a H_2O_2 concentration of 2.0 mM. An increasing chlorobiphenyl concentration, however, increases the production of colored intermediates, shading UV-illuminated H_2O_2 and Fe(II) and decreasing the degradation rate during the photo-Fenton process.

The maximum contributive value of Fe(II) exists under the experimental conditions and in other literature [4]. Consequently, the saturated-type reaction was used and evidenced by simulation results. Reaction rate expressions (9) and (10) indicate that the maximum reaction rate constant value of 4-CBP and 4,4'-CBP are 13.6 and 39.7 ($\mu g^{-1}Ls^{-1}$), respectively. The results show that the degradation of 4,4'-CBP

occurs more easily than 4-CBP, because the dipole moment of 4,4'-CBP is less than that of 4-CBP, allowing the C-Cl bond to be easily broken by OH • . The Fe(II) concentration is an important factor in the photo-Fenton degradation of 4-CBP and 4,4'-CBP.

CONCLUSIONS

This paper explores the oxidation of 4-CBP and 4,4'-CBP in aqueous solution using the photo-Fenton process to evidence the treatment efficiency of UV-light. When the initial concentration of 4-CBP and 4,4'-CBP was 100 μg/L, degradation was more efficient by a factor of 2 after 30 minutes in the light reaction; a greater amount of intermediates was produced but degradation was slower in the dark reaction. According to simulation with experimental data, the relationship between the reaction rate of 4-CBP with the H_2O_2 concentration was expressed as a first-order reaction, that for 4,4'-CBP was a zero-order reaction. The relationship between the two target compound reaction rates and the Fe(II) concentration is a saturation-type reaction. The degradation of 4-CBP and 4,4'-CBP in aqueous solution using the photo-Fenton process (light reaction) was greater than using Fenton process (dark reaction). Previous works on UV-illuminated TiO_2 of chlorophenols and dichlorobenzenes have shown the formation of traces of chlorohydroxy derivatives of biphenyls [21]. In this study, the oxidative ability of the UV/Fe(II)/H_2O_2 process is greater than that of the UV/TiO_2 process. The formation of chlorohydroxy derivatives of biphenyls should be further studied.

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