

Degradation of bisphenol A in water by the photo-Fenton reaction

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Abstract

The photodegradation of bisphenol A (BPA), a representative endocrine disrupting chemical, was carried out in the presence of the Fenton reagent. The degradation rate was strongly influenced by the pH, and initial concentrations of H₂O₂ and Fe(II). An initial BPA concentration of 10 mg l⁻¹ was completely degraded after 9 min under the optimum conditions. This reaction was found to follow the first order kinetics law. The formation of CO₂ as a result of mineralization of BPA was observed during the photo-Fenton process. The degree of BPA conversion to CO₂ was more than 90% under UV irradiation for 36 h. The decomposition of BPA during the photo-Fenton treatment gave six kinds of intermediate products, such as phenol, *p*-hydroquinone, etc. The degradation mechanism of BPA was proposed on the base of the evidence of the identified intermediates. Based on these results, the photo-Fenton reaction could be useful technology for the treatment of wastewater containing BPA.

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1. Introduction

Recently, endocrine disrupting chemicals have been spread over the environment and have deteriorated the generative function of some species of living things on the earth [1]. Although, it is still being discussed whether such chemicals have an influence upon human beings or not, it is necessary to develop technology for their elimination and decomposition as soon as possible. The photodegradation of such chemicals diluted by water seems to be one of the most promising methods for elimination.

Bisphenol A (BPA) is manufactured in high quantities, 90% or more being used as a monomer for the production of polycarbonate and epoxy resins, unsaturated polyester-styrene resins and flame retardants. The final products are used as coating on cans, as powder paints, as additives in thermal paper, in dental fillings and as antioxidants in plastics [2]. It is well known that BPA has an estrogenic activity, that is, it serves as an environmental endocrine disrupter [3]. Nearly 30% of world production is within EU, with 210,000 t being reported to have been produced in Germany in 1995 [4]. The release into the natural environment as well as in surface water is possible during

manufacturing process and by leaching from final products. In fact, leaching of BPA from polycarbonate baby bottle [5] and reusable container [6] has been reported. In addition, BPA was detected in plastic waste [7], in plasma stored in polycarbonate tube [8], in aquatic environment and air [9], and on land [9]. Moreover, high concentration of BPA can be contained in wastewater from its production factories because it is partially removed during wastewater treatment. The wastewater containing BPA can be source of contamination in aquatic environment [9,10]. Although BPA is readily degraded by microorganisms [9], biological methods commonly require long times for the wastewater containing BPA at high concentration. Therefore, the rapid and simple wastewater treatment of BPA is now required urgently.

A variety of treatment techniques for wastewater which contains phenolic compounds have been examined by using chemical [11], biological [12], photochemical [13], and electrochemical [14] procedures. However, only a few reports have appeared on the treatment of wastewater which contains BPA [15–17]. They examined the degradation of BPA in the presence of TiO₂ as a photocatalyst. Recent reports indicate that a combination of H₂O₂ and UV irradiation with Fe(II), so-called the photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds. Until now, the photo-Fenton process has been applied to the degradation of pesticides [18,19], nitrobenzene and other organics [20], chlorophenols [21–23],

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nitrophenols [24], dibutyl-phthalate [25] and PCBs [26]. The acceleration for decomposition of organic compounds is believed to be in order to photolysis of iron aquacomplex, $\text{Fe}(\text{OH})^{2+}$, to provide a new importance source of OH^\bullet radicals [27,28]. Further, the photolysis of $\text{Fe}(\text{OH})^{2+}$ regenerates $\text{Fe}(\text{II})$, which means that the photo-Fenton reaction would need low $\text{Fe}(\text{II})$ concentration compared with the Fenton process. Furthermore, the $\text{Fe}(\text{OH})^{2+}$ can absorb light at wavelengths up to ca. 410 nm, while TiO_2 photocatalysis can use photon with wavelength close to 380 nm [29]. Therefore, the photo-Fenton process can be expected to an efficient and inexpensive method for wastewater treatment and promotes the rate of degradation of various organic pollutants.

In the present study, we have investigated the degradation of BPA to CO_2 in water as a result of the photo-Fenton process. The many factors, such as pH value, and initial concentrations of $\text{Fe}(\text{II})$ and H_2O_2 , affected on the degradation were evaluated. Furthermore, the intermediate products of BPA during the photo-Fenton process have been identified by gas chromatography-mass spectrometry (GC–MS). The degradation pathway was proposed on the base of the evidence of the intermediate formation.

2. Experimental

2.1. Reagents

BPA was obtained from Nacalai Tesque, Inc. as highly pure reagent grade (GC grade >99%). Analytical grade hydrogen peroxide solution (30% w/w) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Wako Pure Chemical Industries, Ltd. and Nacalai Tesque, Inc., respectively, and were used as received. All other chemicals used were of analytical grade and were used without further purification. All solutions were prepared with demineralized water.

2.2. Photodegradation procedure

Photodegradation was conducted in a Pyrex glass cell of 30 ml capacity. The reaction mixture inside the cell, consisting of 20 ml of BPA solution and the precise amount of Fenton reagent, was continuously stirred with a magnetic bar. The pH of the sample solution was adjusted with HCl and/or NH_3 solution. The initial concentration of BPA in all experiments was 10 mg l^{-1} ($4.4 \times 10^{-5} \text{ mol l}^{-1}$). In the majority of the experiments, temperature was kept at $25 \pm 1^\circ\text{C}$ with a water bath. The sample solution was illuminated with a Xe lamp (990 W, Ushio Electronics Co.). In this case, the short UV radiation ($\lambda < 300 \text{ nm}$) was filtered out by the vessel wall. The intensity of the light was measured by a UV radio meter (UVR-400, Iuchi Co.). The light intensity with wavelength 320–410 nm was 0.5 mW cm^{-2} . The degradation reaction was quenched by adding 1 ml of methanol for HPLC and of H_3PO_4 for total organic carbon (TOC) analyses.

2.3. Analyses

After illumination, the sample solution was filtered through a membrane filter ($0.45 \mu\text{m}$) in order to remove a precipitation. The decrease of UV absorption was monitored with an UVDEC-610 double-beam spectrometer (JASCO Co.). The progress in the degradation of BPA was followed with a HPLC (Model L-4000, Hitachi Co.) equipped with a UV detector (217 nm). A separation column used was a RS pak DE-413L ($250 \text{ mm} \times 4.6 \text{ mm i.d.}$, Showa Denko Co.). The mobile phase was 70% acetonitrile and the flow rate was 0.7 ml min^{-1} .

TOC of the sample solution was measured with a Shimadzu TOC- V_E instrument. The detection limit of the instrument was 0.5 mg l^{-1} and the relative standard deviation for 5 determinations was 2.6%. The evolution of CO_2 as an end product of BPA was assayed by a GL Science GC-353B GC equipped with methanizer + FID detector and a Porapak Q column in nitrogen carrier gas.

The intermediate products during photodegradation of BPA were extracted by the solid phase extraction (C18 disk, 3 M Empore). A mixture of dichloromethane and ethyl acetate (1:1 (v/v)) was used to elute the intermediate products. This solution was concentrated under nitrogen flow for the analysis of the by-products. A GC–MS (Shimadzu GC–MS QP-5000) was used for separation and detection of the intermediate products. The GC was equipped with an HP-5 capillary column ($30 \text{ m} \times 0.25 \text{ mm i.d.}$) in helium carrier gas.

3. Results and discussion

3.1. Effect of variables on the degradation of BPA

The UV absorption spectra of BPA solution are presented in Fig. 1. The disappearance of 223 and 276 nm absorption bands was observed with increasing degradation time. However, absorbance at 240–260 nm of the solution after the reaction increased comparing with that before the reaction. All reagents such as $\text{Fe}(\text{II})$, H_2O_2 , HCl , and methanol did not exist the absorption band around the wavelength. Furthermore, BPA solution before the reaction included $\text{Fe}(\text{II})$, HCl , and methanol (Fig. 1a). Therefore, the increase of absorbance might be due to the presence of intermediate products derived from BPA. This consideration would be supported by the absorption spectrum of BPA after the reaction of 90 min (Fig. 1e), in which the absorbance at 240–260 nm decreased compared with that before the reaction. From the observed absorbance at $\lambda_{\text{max}} = 276 \text{ nm}$, ϵ was estimated to be $3.31 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Consequently, it was confirmed that Fenton reagent was effective photocatalyst for the decomposition of BPA under UV illumination.

Effect of pH on the degradation of BPA by use of the photo-Fenton process was investigated over the pH range of 2.0–4.5 because much precipitation of $\text{Fe}(\text{OH})_3$ occurred

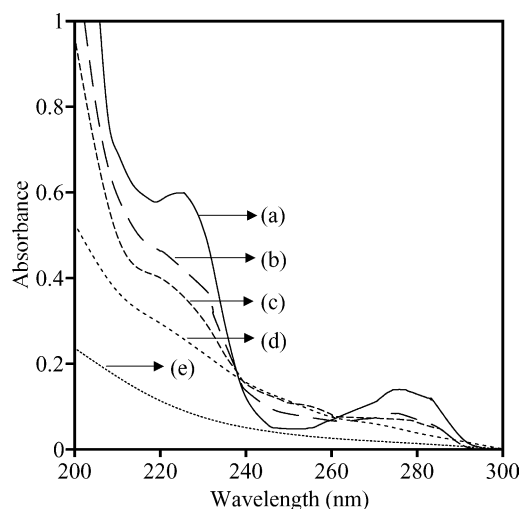


Fig. 1. UV absorption spectra of BPA before and after the photo-Fenton treatment: (a) before reaction; (b) after 10 min; (c) after 20 min; (d) after 45 min; (e) after 90 min ($[\text{H}_2\text{O}_2]_0 = 1 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{Fe(II)}]_0 = 1 \times 10^{-5} \text{ mol l}^{-1}$; pH 2.8).

during the process above pH 4.5. These results are shown in Fig. 2. The degradation percentage of BPA rapidly increased with increasing pH value up to 4.0, decreasing at pH above 4.0. Therefore, the photo-Fenton reaction is strongly affected by the solution of pH. Generally, the optimal pH of the photo-Fenton reaction is around 3 [30] because the main species at pH 2–3, $\text{Fe(OH)}^{2+}(\text{H}_2\text{O})_5$, is the one with the largest light absorption coefficient and quantum yield for OH^\bullet radical production, along with Fe(II) regeneration, in the range 280–370 nm [31]. However, the optimal pH in this process was obtained as 4.0. Previously, Fukushima et al.

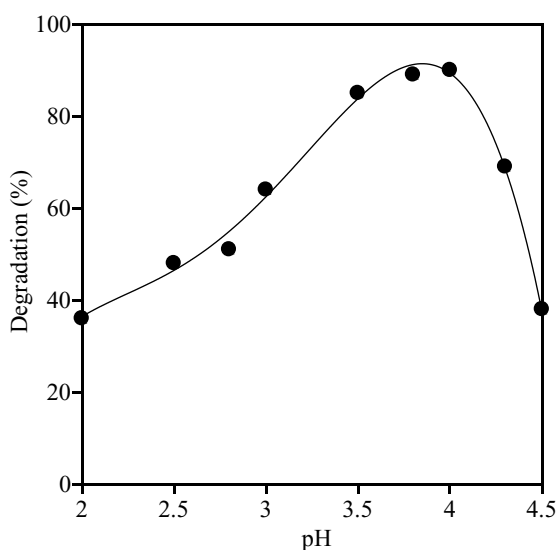


Fig. 2. Effect of pH on the degradation of BPA by use of the photo-Fenton process ($[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-4} \text{ mol l}^{-1}$; $[\text{Fe(II)}]_0 = 4 \times 10^{-5} \text{ mol l}^{-1}$; irradiation time = 5 min).

[23,32] reported that the degradation of pentachlorophenol (PCP) and aniline was enhanced at pH 5 by the presence of humic acid (HA) in the photo-Fenton system because the complexation of Fe(III) with HA contributed to the stabilization of iron species. In the present study, BPA or its intermediate products might react with iron species followed by the formation of iron complexes and these could assist the catalytic cycles of iron in the photo-Fenton system. Therefore, the degradation efficiency of BPA may be the highest at pH 4.

Effect of reaction temperature on the degradation of BPA was examined in the range of 5–55 °C. The degradation percentage of BPA linearly increased with increasing temperature (data not shown). The optimum temperature was selected as 25 °C, considering practical application and degradation cost.

To obtain the optimal initial Fe(II) concentration, the investigation was carried out in the range of $(0 \text{ to } 4) \times 10^{-5} \text{ mol l}^{-1}$ at pH 4 ($[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-4} \text{ mol l}^{-1}$). These results are shown in Fig. 3. As it can be seen from Fig. 3, the degradation rate of BPA increased with increasing initial Fe(II) concentration. Complete degradation of BPA under these conditions was reached at Fe(II) concentration of above $1 \times 10^{-5} \text{ mol l}^{-1}$ within 30 min, while low concentration of Fe(II) did not allow achieving complete degradation in photo-Fenton process. Especially, when Fe(II) concentration was selected as $4 \times 10^{-5} \text{ mol l}^{-1}$, BPA was completely degraded after 9 min.

Fig. 4 shows the effect of initial H_2O_2 concentration on the degradation of BPA with the use of photo-Fenton process. As expected, the degradation rate of BPA increased with increasing the concentration of H_2O_2 added. This can be explained by the effect of the additionally

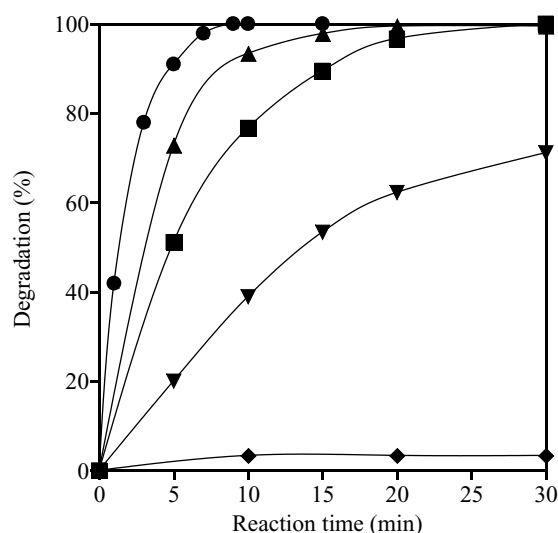


Fig. 3. Effect of initial concentration of Fe(II) on the degradation of BPA by use of the photo-Fenton process: (\blacklozenge) 0; (\blacktriangledown) 4×10^{-6} ; (\blacksquare) 1×10^{-5} ; (\blacktriangle) 2×10^{-5} ; (\bullet) $4 \times 10^{-5} \text{ mol l}^{-1}$ ($[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-4} \text{ mol l}^{-1}$; pH 4.0).

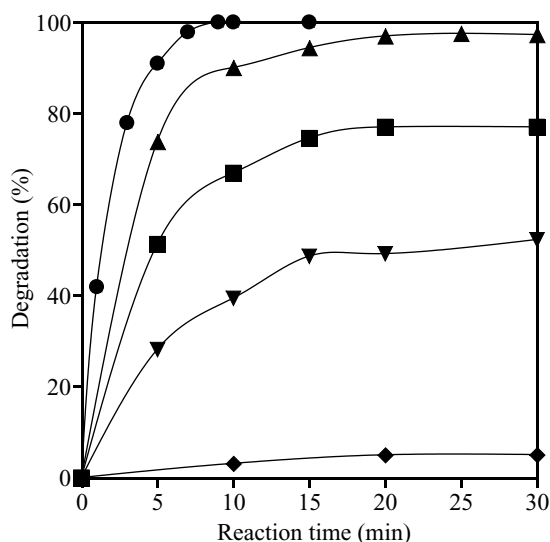


Fig. 4. Effect of initial concentration of H₂O₂ on the degradation of BPA by use of the photo-Fenton process: (♦) 0; (▼) 4×10^{-5} ; (■) 1×10^{-4} ; (▲) 2×10^{-4} ; (●) 4×10^{-4} mol l⁻¹ ([Fe(II)]₀ = 4×10^{-5} mol l⁻¹; pH 4.0).

produced OH• radicals. When concentration of H₂O₂ was below 2×10^{-4} mol l⁻¹, BPA did not achieve the complete degradation within 30 min. Therefore, it can be considered that a certain amount of H₂O₂ is required in the photo-Fenton process due to archive the complete degradation of BPA.

Fig. 5 shows a comparison of the degradation of BPA in both the dark and light. In the presence of Fe(II) or H₂O₂ only, the degradation of BPA was slightly observed after 30 min of irradiation (<5%) as seen in Figs. 3 and 4. Similarly, only 4.6% of BPA was degraded in the absence of Fe(II) and H₂O₂ for the case of light condition. On the other hand, in the presence of Fe(II) or H₂O₂ only, no decrease of BPA was observed in the dark after 30 min. Furthermore, the Fe(II)/H₂O₂ system in the dark (Fenton reaction) was evaluated for the degradation of BPA. For this case, although more than 90% of BPA was degraded after 9 min at pH 4.0, it could not achieve complete degradation within 30 min (ca. 95% degradation). These results indicate that the photo-Fenton reaction is useful for the treatment of wastewater containing BPA.

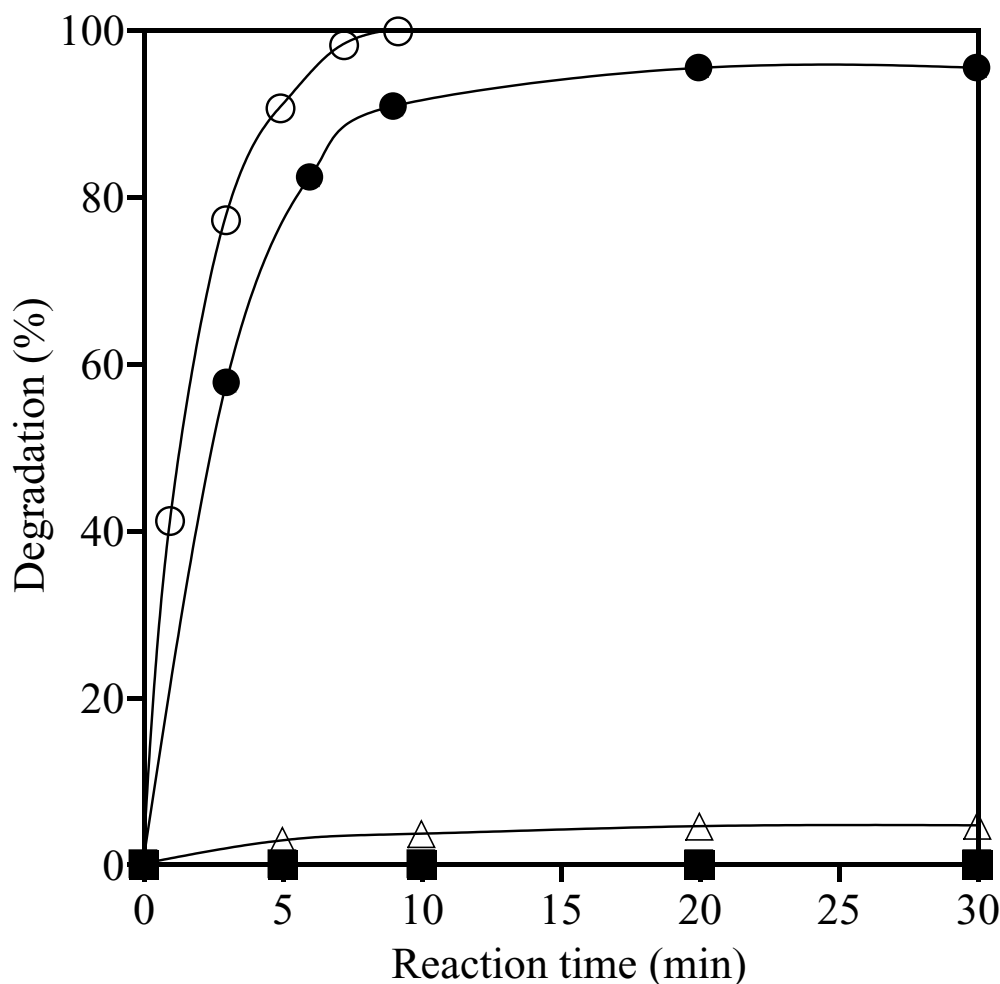


Fig. 5. Degradation characteristics of BPA under dark and light conditions: (○) light, Fe(II)/H₂O₂; (○) light; (●) dark, Fe(II)/H₂O₂; (▲) dark, Fe(II); (■) dark, H₂O₂. ([Fe(II)]₀ = 4×10^{-5} mol l⁻¹; [H₂O₂]₀ = 4×10^{-4} mol l⁻¹; pH 4.0).

Table 1

First-order rate constant (k), correlation coefficient (R^2), half-lives ($t_{1/2}$), and 90% degradation ($t_{90\%}$) times for treatment of BPA with the photo-Fenton reaction

$[\text{Fe}^{2+}]_0$ (mol l^{-1})	$[\text{H}_2\text{O}_2]_0$ (mol l^{-1})	k (s^{-1})	R^2	$t_{1/2}$ (s)	$t_{90\%}$ (s)
1.0×10^{-5}	4.0×10^{-4}	2.67×10^{-3}	0.989	260	861
2.0×10^{-5}	4.0×10^{-4}	4.32×10^{-3}	0.998	160	532
4.0×10^{-5}	4.0×10^{-4}	8.70×10^{-3}	0.992	80	264

The photo-Fenton reaction of BPA under the optimum conditions ($[\text{Fe}^{2+}]_0 = (1 \text{ to } 4.0) \times 10^{-5} \text{ mol l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-4} \text{ mol l}^{-1}$) described above was estimated to follow a pseudo first-order kinetic law, according to the equation,

$$\frac{dC_{\text{subs}}}{dt} = -k_{\text{obs}} C_{\text{subs}}$$

where C_{subs} is BPA concentration and k_{obs} is the observed first-order rate constant. In order to confirm the speculation, $\ln(C/C_0)$ was plotted as a function of the reaction time. The calculated results indicated that the first-order model gives a better fit (data not shown). Therefore, the primary photodegradation dynamics of BPA would be a pseudo first-order kinetics. The substrate half-lives, 90% conversion times, and first-order rate constant for the degradation of BPA calculated from the equation are summarized in Table 1.

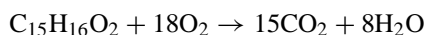
Although the Fenton reaction has been widely studied, there is no agreement on the ratio $[\text{H}_2\text{O}_2]_0/[\text{Fe(II)}]_0$ that gives the optimal results. Many authors have reported the use of different ratios of the two reactants. For example, Eisenhauer [33] used 3:1:1 ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}/\text{phenol}$ for an efficient oxidation of the substrate. Sedlak and Andren [34] used 1:4:20 ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}/\text{chlorobiphenyls}$ in their degradation process. Molar ratio of H_2O_2 as high as 100:1:16 ($\text{H}_2\text{O}_2/\text{Fe(II)}/\text{chlorophenols}$) were reported by Bardeni et al. [35]. Tang and Huang [36] reported 11:1 ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}$ for 2,4-dichlorophenol decomposition. Bauer and Fallmann [37] used 400:1 ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}$ for treating real wastewater. Chamorro et al. [38] used ($\text{H}_2\text{O}_2/\text{Fe(II)}$) ratios from 5000:1 to 50:1 mg l^{-1} , and the results showed so far in this paper were obtained with 100:1:50 mg l^{-1} ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}/\text{wastewater}$. Usually, $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratios from 10:1 to 40:1 are recommended as optimal for the Fenton process [39,40]. However, the reports for the optimal $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio restrict for the photo-Fenton treatment. The optimal ratios of chemicals in photo-Fenton treatment recommended from the results of the present study could be from 9:0.25:1 to 9:0.9:1 ($\text{H}_2\text{O}_2/\text{Fe(II)}/\text{BPA}$). These results coincide with the results reported by Goi and Trapido [24]. They reported that the optimal ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}/\text{di-nitrophenol}$ in photo-Fenton process was 10:0.25:1.

The results of this study were compared with the results obtained by using TiO_2 . Ohko et al. [16] reported that an initial BPA concentration of 40 mg l^{-1} (4 times

that of the present study) in water was degraded by TiO_2 -photocatalyzed reaction under UV irradiation of 10 mW cm^{-1} (20 times that of the present study) for 15 h. One gram per liter of TiO_2 was used in their experiments. The amount of catalysis was ca. 90 times greater than that of Fe(II) using as a catalyst of the photo-Fenton reaction. Watanabe et al. [17] performed the degradation of BPA in the presence of TiO_2 under the experimental conditions in which an initial BPA concentration, amount of TiO_2 and light intensity were 20 mg l^{-1} , 2 g l^{-1} , and 2.5 mW cm^{-1} , respectively. It took 2 h for BPA complete degradation under the conditions. Therefore, it can be considered that the photo-Fenton treatment is the available method for the degradation of BPA from the viewpoints of degradation time and cost.

3.2. Mineralization of BPA

The CO_2 mineralization yield for BPA is illustrated in Fig. 6. When the total mineralization of BPA proceeds stoichiometrically using oxygen as oxidizing agent, the mineralization reaction can be estimated as follows:



As seen in Fig. 6, the generation of CO_2 had scarcely occurred after 9 min, although BPA archived complete degradation after the irradiation time. This difference indicates that intermediate products were produced during the photo-Fenton process. The CO_2 mineralization for BPA was reached 54% after 24 h of irradiation under the conditions shown in Fig. 6a. This yield value indicates that the two benzene rings of BPA were cleaved during the degradation reaction. Since the intermediate products could

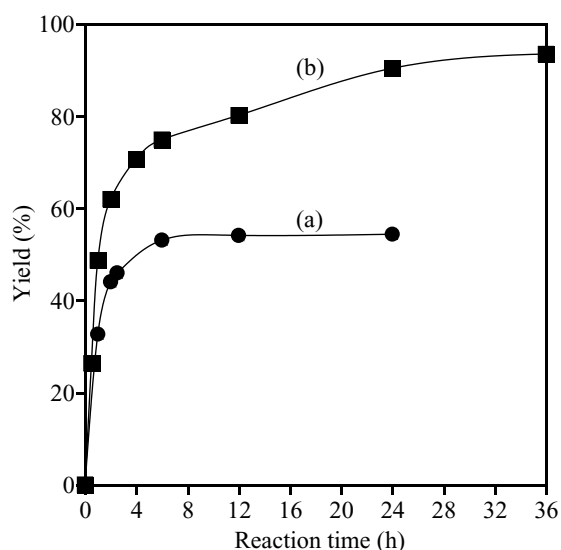


Fig. 6. Yield of CO_2 from BPA degradation by use of the photo-Fenton process: (a) $[\text{Fe(II)}]_0 = 4 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-4} \text{ mol l}^{-1}$; (b) $[\text{Fe(II)}]_0 = 4 \times 10^{-4} \text{ mol l}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-3} \text{ mol l}^{-1}$.

Table 2

Percentages of CO₂ yield and TOC remaining in the sample solution

[Fe ²⁺] ₀ (mol l ⁻¹)	[H ₂ O ₂] ₀ (mol l ⁻¹)	Reaction time (h)	CO ₂ (%)	TOC (%)	CO ₂ + TOC (%)
4.0 × 10 ⁻⁵	4.0 × 10 ⁻⁴	24	54	37	91
4.0 × 10 ⁻⁴	4.0 × 10 ⁻³	36	93	13	106

not be completely decomposed to CO₂, we performed the mineralization experiments in which both concentrations of catalysis and H₂O₂ were 10 times higher than those for the condition shown in Fig. 6a. These results are shown in Fig. 6b. Under the conditions, the CO₂ generation reached 93% after 36 h of irradiation time. Therefore, it is considered that H₂O₂ concentration (mg l⁻¹) needed ca. 17 times higher than carbon concentration of BPA (mg C l⁻¹) in order to completely decompose to CO₂.

The percentage of CO₂ mineralization yield and that of TOC remaining in the sample solution are summarized in Table 2. As shown in Table 2, it was found that there was the correlation between CO₂ generation from BPA and TOC remaining in the solution during the photo-Fenton treatment.

3.3. Identification of intermediate products and photodegradation mechanism of BPA

Table 3 summarizes the main fragments (*m/z*) and relative abundances (%) obtained for the intermediate products after 5 min of irradiation time by GC–MS. Six compounds were found in the GC–MS chromatogram (Fig. 7) and identified by comparisons of mass spectra with the library data of NIST. 4-Hydroxyacetophenone, peak no. 6, was also reported as one of the by-products for the photodegradation of BPA by Ohko et al. [16]. Another compound, for example 3-(4-hydroxyphenyl)-3-methyl-2-oxobutanoic acid and 4-isopropylphenol, have been identified by LC–MS [16,17]. The percentage of the sum of the six intermediate products and remaining BPA concentrations to the initial BPA

Table 3

Mass fragment ions (*m/z*) and relative abundance (%) of intermediates and BPA obtained from GC–MS spectra

Peak no.	Retention time (min)	Detected ions, <i>m/z</i> (% abundance)	Molecular weight (<i>m/z</i>)	Molecular structure
1	5.4	108 (76), 82 (40), 54 (100)	108	
2	7.3	94 (100), 66 (39)	94	
3	16.9	134 (100), 119 (87), 91 (40)	134	
4	17.1	110 (100)	110	
5	19.0	134 (100), 119 (53)	134	
6	20.6	136 (29), 93 (40), 121 (100), 65 (40)	136	
7	37.3	228 (22), 119 (31), 213 (100)	228	

Peak numbers correspond to those in Fig. 7.

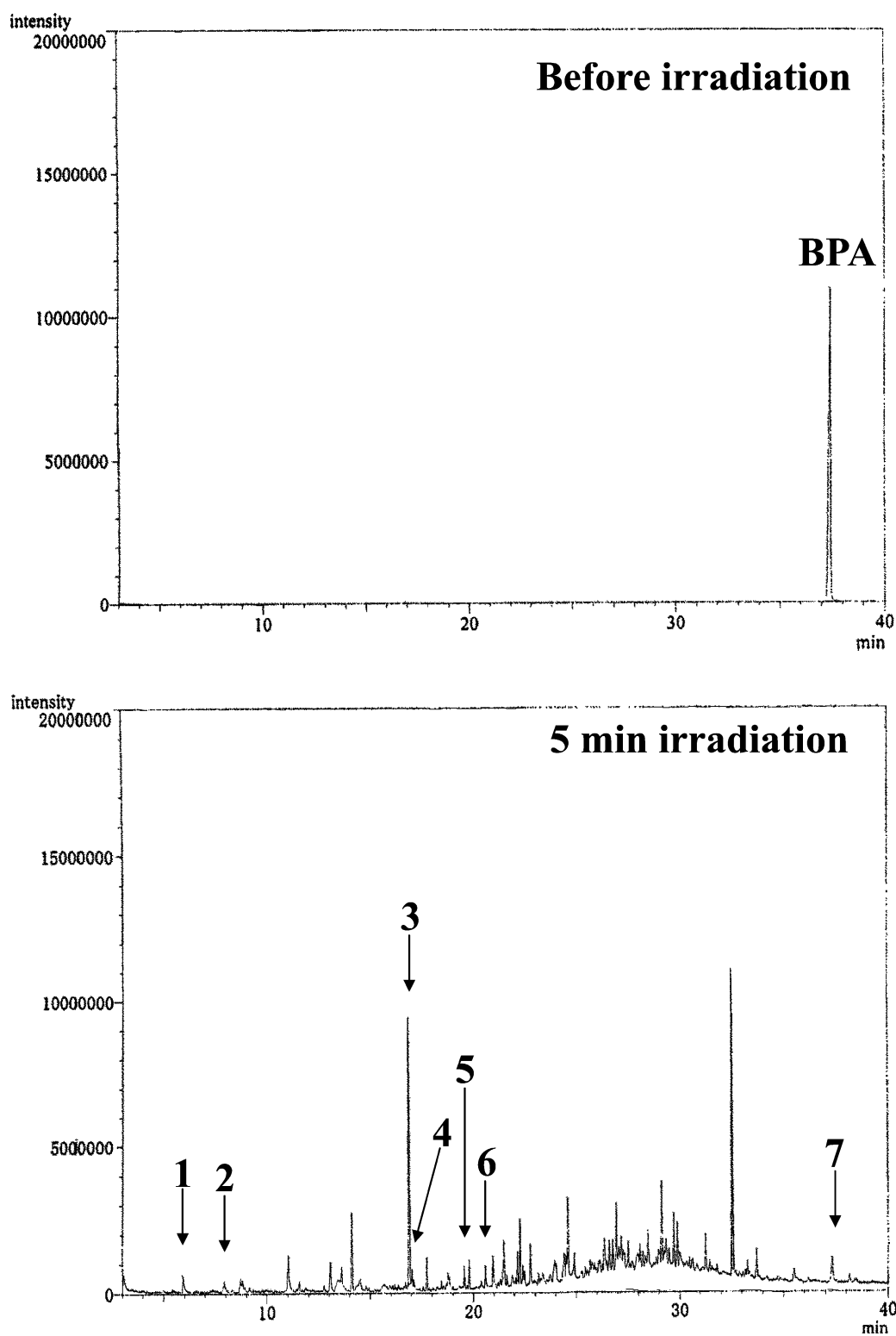
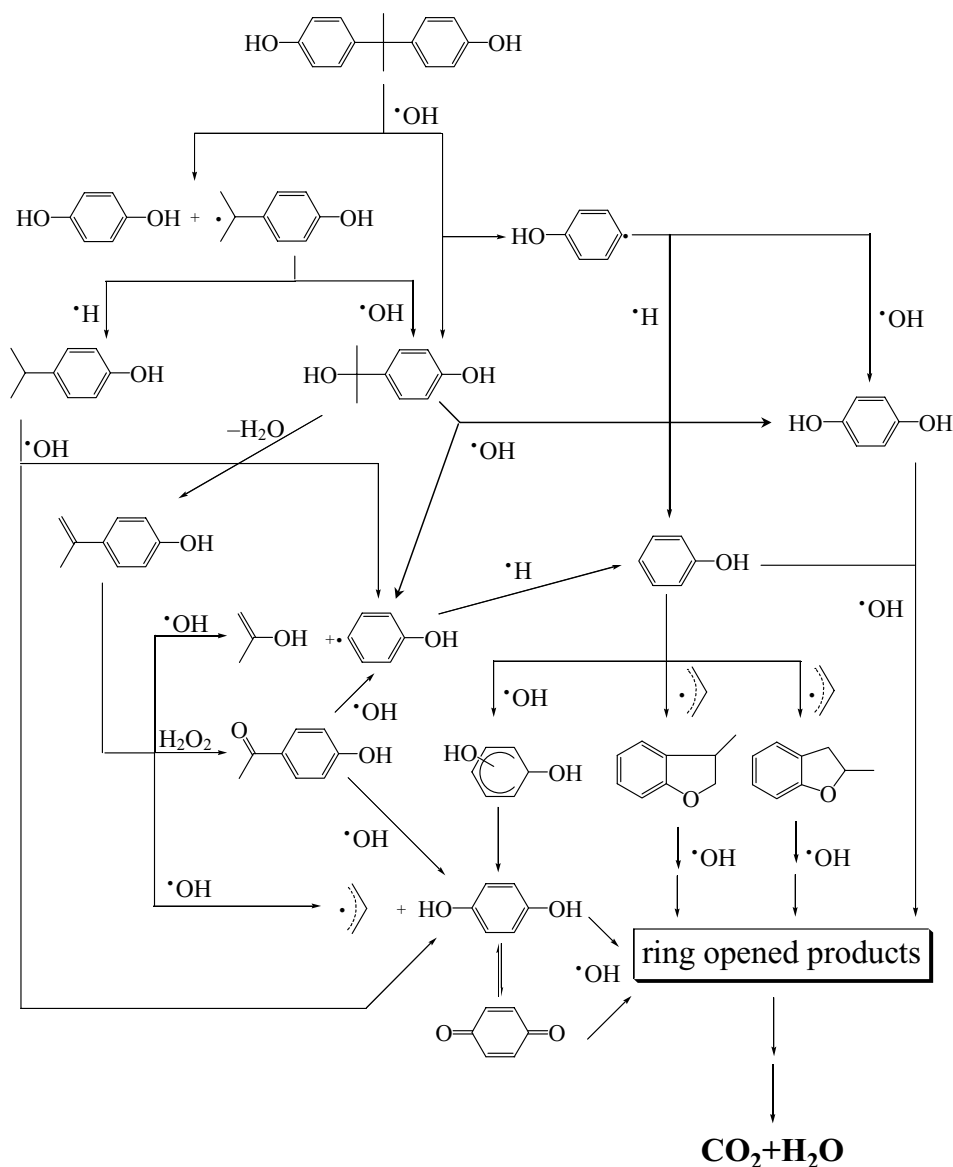


Fig. 7. GC–MS chromatograms of sample solution before and after irradiation. Peak numbers correspond to those listed in Table 3. Other peaks are unidentified compounds and contaminants.



Scheme 1. Proposed degradation mechanism of BPA by use of the photo-Fenton process.

one was 93% for the photo-Fenton process after 5 min. The remaining percentage may be attributed to the presence of unidentified intermediates, analytical error, and/or loss of the intermediates during the analytical process. It was reported that the dimerization of the reaction intermediates from PCP occurred during the photo-Fenton process [23]. However, there were no peaks in the GC–MS chromatogram corresponding to a dimer, indicating that dimer was not formed in the reaction after 5 min of irradiation.

Based on the intermediate products listed in Table 3 and the results obtained by other researchers [16,17], the possible degradation pathway for BPA is proposed in Scheme 1. In the initial oxidation reaction, 4-isopropylphenol (IPP), *p*-hydroquinone (*p*-HQ), 4-(1-hydroxy-1-methyl-ethyl)phenol (HMEP), and phenol are formed in the photocleavage of phenyl groups in BPA by attack of OH^\bullet radicals. 4-Isopropenylphenol (IpeP) is generated by

dehydration of HMEP, followed by the formation of 4-hydroxyacetophenone (HAP) by an oxidizing agent such as H_2O_2 . Furthermore, IPP, HMEP, IpeP, and HAP are converted to *p*-HQ and phenol by OH^\bullet radicals. Methylbenzofurans would be produced from phenol by attack of propenyl radicals originating from IpeP. *p*-HQ is further oxidized to *p*-quinone. An oxidative ring-opening reaction at the level of C–C bonds between adjacent hydroxyl or ketone groups leads to the formation of aliphatic compounds [41–44], such as HCOOH , CH_3COOH , and CH_3CHO [17], followed by evolution of CO_2 gas.

4. Conclusions

The photodegradation of BPA in aqueous solution was investigated by the photo-Fenton treatment. The degradation

rate was strongly affected by many factors, such as the pH value and the initial concentrations of H_2O_2 and Fe(II) . For BPA complete degradation was achieved after 9 min under the optimum conditions. It was found that the primary photocatalytic decomposition reaction follows a pseudo first-order kinetic law, and the rate constant, k , was $8.70 \times 10^{-3} \text{ s}^{-1}$. The optimal ratios of chemicals in photo-Fenton treatment recommended from the results of the present study could be from 9:0.25:1 to 9:0.9:1 ($\text{H}_2\text{O}_2/\text{Fe(II)}/\text{BPA}$).

The CO_2 generation from BPA reached 93% after 36 h of irradiation in the presence of $4 \times 10^{-3} \text{ mol l}^{-1} \text{ H}_2\text{O}_2$ and $4 \times 10^{-4} \text{ mol l}^{-1} \text{ Fe(II)}$. From the results, it was found that H_2O_2 concentration (mg l^{-1}) needs ca. 17 times higher than carbon concentration (mg C l^{-1}) of BPA in order to completely decompose to CO_2 . Furthermore, we identified six kinds of intermediate products of BPA during the photo-Fenton process. The degradation pathway of BPA was proposed based on the identified by-products.

The advantages of the photo-Fenton process as an oxidative treatment are low cost, rapid degradation, and simple handling. Therefore, the photo-Fenton reaction would be applied to wastewater treatment works as a new developing methodology for reducing levels of other endocrine disrupting chemicals.

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References

- [1] E. Harries, T. Runnalls, E. Hill, C.A. Harris, S. Maddix, J.P. Sumpter, C.R. Tyler, *Environ. Sci. Technol.* 34 (2000) 3003.
- [2] C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O'Block, L.R. Harris, *Chemosphere* 36 (2002) 2149.
- [3] A.V. Krishnan, P. Stathis, S.F. Permuth, L. Yokes, D. Feldman, N. Sonoyama, *Endocrinology* 132 (1993) 2279.
- [4] A. Leisewitz, Stoffstrome wichtiger hormonell wirkender Substanzen (Behavior of important hormonal active substances). Project No. 10601076, German Federal Environmental Agency, Berlin, 1997.
- [5] Y. Takao, H.C. Lee, Y. Ishibashi, S. Kohra, N. Tominaga, K. Arizono, *J. Health Sci.* 45 (1999) 39.
- [6] J.E. Biles, T.P. McNeal, T.H. Begley, H.C. Hollifield, *J. Agric. Food. Chem.* 45 (1997) 3541.
- [7] T. Yamamoto, A. Yasuhara, *Chemosphere* 38 (1999) 2569.
- [8] J. Sajiki, K. Takahashi, J. Yonekubo, *J. Chromatogr. B* 736 (1999) 255.
- [9] C.A. Staples, P.B. Dorn, G.M. Klecka, S.T. O'Block, D.R. Branson, L.R. Harris, *Chemosphere* 36 (1998) 2149.
- [10] M. Fürhacker, S. Schaf, H. Weber, *Chemosphere* 41 (2000) 751.
- [11] Y.S. Li, *Waste Manage.* 19 (1999) 495.
- [12] P.M. Armenante, D. Kafkewitz, G.A. Lewandowski, C.J. Jou, *Water Res.* 33 (1999) 681.
- [13] D.W. Chem, A.K. Ray, *Water Res.* 32 (1998) 3223.
- [14] A.M. Polcaro, S. Palmas, *Ind. Eng. Chem. Res.* 56 (1997) 1791.
- [15] S. Tanaka, Y. Nakata, H. Kuramitz, M. Kawasaki, *Chem. Lett.* (1999) 943.
- [16] Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, A. Fujishima, *Environ. Sci. Technol.* 35 (2001) 2365.
- [17] N. Watanabe, S. Horikoshi, H. Kawabe, S. Sugie, J. Zhao, H. Hidaka, *Chemosphere* 52 (2003) 851.
- [18] J.J. Pignatello, Y. Sun, *Water Res.* 29 (1995) 1837.
- [19] P.L. Huston, J.J. Pignatello, *Water Res.* 33 (1999) 1238.
- [20] R.G. Zepp, B.C. Faust, J. Hoigne, *Environ. Sci. Technol.* 26 (1992) 313.
- [21] M. Trapido, Y. Veressina, R. Munter, *J. Environ. Eng.* 124 (1998) 690.
- [22] M.Y. Ghaly, G. Härtel, R. Mayer, R. Haseneder, *Waste Manage.* 21 (2001) 41.
- [23] M. Fukushima, K. Tatsumi, *Environ. Sci. Technol.* 35 (2001) 1771.
- [24] A. Goi, M. Trapido, *Chemosphere* 46 (2002) 913.
- [25] M. Halmann, *J. Photochem. Photobiol. A: Chem.* 66 (1992) 215.
- [26] J.J. Pignatello, G. Chapa, *Environ. Toxicol. Chem.* 13 (1994) 423.
- [27] J.J. Pignatello, *Environ. Sci. Technol.* 26 (1992) 944.
- [28] S.F. Kang, H.M. Chang, *Water Sci. Technol.* 36 (1997) 215.
- [29] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [30] J.J. Pignatello, D. Liu, P. Huston, *Environ. Sci. Technol.* 33 (1999) 1832.
- [31] H.J. Benkelberg, P. Warneck, *J. Phys. Chem.* 99 (1995) 5214.
- [32] M. Fukushima, K. Tatsumi, K. Morimoto, *Environ. Sci. Technol.* 34 (2000) 2008.
- [33] H.R. Eisenhauer, *J. Water Pollut. Control Fed.* 36 (1964) 1116.
- [34] D.L. Sedlak, A.W. Andren, *Environ. Sci. Technol.* 25 (1991) 777.
- [35] M. Barbeni, C. Minero, E. Pelizzetti, E. Borgarello, N. Serpone, *Chemosphere* 16 (1987) 2225.
- [36] W.Z. Tang, C.P. Huang, *Environ. Technol.* 17 (1996) 1371.
- [37] R. Bauer, H. Fallmann, *Res. Chem. Intermed.* 23 (1997) 341.
- [38] E. Chamarro, A. Marco, S. Esplugas, *Water Res.* 35 (2001) 1995.
- [39] G. Ruppert, R. Bauer, G. Heisler, *Chemosphere* 28 (1994) 1447.
- [40] W.Z. Tang, C.P. Huang, *Environ. Technol.* 18 (1997) 13.
- [41] N.V. Raghavan, S. Steenken, *J. Am. Chem. Soc.* 102 (1980) 3495.
- [42] M.A. Oturan, N. Oturan, C. Lahitte, S. Trevin, *J. Electroanal. Chem.* 507 (2001) 96.
- [43] C. Wu, X. Liu, D. Wei, J. Fan, L. Wang, *Water Res.* 35 (2001) 3927.
- [44] A. Hong, Y. Zeng, *Water Res.* 36 (2002) 4243.