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Oxidative degradation of bisphenol A by Bio-Fenton reaction equipped with glucose oxidase and ferric citrate: Degradation kinetics and pathway

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ABSTRACT

The Bio-Fenton reaction was applied to degrade bisphenol A (BPA, 0.1 mM), a commonly used plastic additive, via in-situ produced hydrogen peroxide (H_2O_2) from glucose oxidase (GOx, 10 U), glucose (32 mM), and Fe(III)-citrate (0.5 mM) at pH 5.3. The reaction produced 0.15–1.1 × 10^{-16} M of •OH at a steady-state ($[•OH]_{ss}$), which contributed significantly to BPA degradation. The second-order rate constant (k) for BPA degradation was 1.39–2.38 × 10^9 M^{-1} s^{-1}, with 80% degradation of 0.1 mM BPA in 10 days of incubation and the production of hydroxylated intermediates, 4-hydroxyacetophenone, and hydroquinone, which were further filtered into small carboxylic acids via •OH-mediated reactions: hydroxylation, oxidation, scission of the C-C bond between the two BPA aromatic rings, and ring cleavage. Based on the successful application of the Bio-Fenton reaction to the radical scavenger and plastic additive BPA, microorganisms capable of producing H_2O_2 through diverse oxidase enzymatic systems can be applied to degrade diverse pollutants in environments where ubiquitous Fe(III) with organic iron chelators is present.

1. Introduction

Bisphenol A (2,2-Bis(4-hydroxyphenyl)propane, BPA) has been broadly used as a chemical building block in the manufacture of polycarbonate and epoxy resins, flame retardants, and various plastics, such as polyester-styrene and polysulfone [1,2]. Their resins are commonly used in daily products, including protective coatings, optical lenses, thermal paper, food storage containers, linings, and dental fillings [2–4]. In addition, BPA exhibits antioxidant activity by scavenging radicals produced during weathering from ultraviolet (UV) light exposure, which can delay the overall oxidative degradation of plastics [5]. Thus, BPA is a commonly used additive in plastic production to enhance the properties and functionalities of polymers and prolong their lives.

Approximately 6.3 billion metric tons (Mt) of plastic waste was generated from 1950 to 2015, and this is expected to increase continuously to 26 billion Mt by 2050 [6]. Seriously, 60% of waste plastic is discarded into landfills or accumulated in the natural environment [6]. With tremendous demands for plastics worldwide, the global consumption of BPA increased to approximately 7.7 million Mt in 2015, and it is estimated to reach to 10.6 million Mt in 2022 [7]. Waste plastic buried in soil could be another source of BPA release into the environment, along with the effluent discharge of BPA manufacturing plants. BPA has been detected in various environmental samples, such as soil, sediments, water, and wastewater treatment plants in different countries; there have been many reports on the concentration of residue BPA in different environments: 1.9–11.1 μg/L in industrial wastewater [8], 0.3–2.0 ng/L in drinking water [9], 4–140 μg/kg in soil [10], 273–3584 μg/kg in river and marine sediment [11], and 0.05–0.18 μg/L and 0.1–34.0 μg/kg, respectively, in the water and sediment of agricultural reservoirs [12]. More seriously, 269 μg/L of BPA was detected in landfill leachates of waste plastic, which indicates that a hydrolytic or leaching process might induce BPA release from waste plastic to the leachate [13]. Accordingly, removing residual BPA from the soil is a critical in preventing its release into the environment and protecting against its exposure to living organisms.

Various strategies have been employed to degrade BPA, including

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conventional treatments (adsorption, flocculation, and filtration), physicochemical treatments (ozone, UV/hydrogen peroxide [H_2O_2], and UV photo-catalysts), and electrochemical treatments (including the Fenton reaction) [14–18]. Among them, advanced oxidation processes using Fenton reagents, such as H_2O_2 and iron, have frequently been adopted to remove BPA due to their high performance, simplicity, and low toxicity [19–25]. Specifically, the Fenton reaction produces highly reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and hydroperoxyl radicals (•OOH). •OH has strong oxidation potential (E_0= 2.8 V/SHE [standard hydrogen electrode]) and rapid reactivity (10^8-10^{10} M^{-1} s^{-1}) with organic compounds at non-specific moieties, which results in structural fragmentation or mineralization [26–29]. Despite the advantages of the Fenton reaction, the reaction should be carried out under acidic conditions (pH ≤3.0) to maintain Fe(III) in a soluble form for reaction efficiency [30]. Indeed, Fe(III) is likely to precipitate as iron oxides ($Fe(OH)_2$) at neutral pHs, which interrupts iron cycling and eventually affects the decomposition of H_2O_2 [31]. To overcome this drawback, organic chelating agents such as citrate, oxalate, and ethylenediamine-*N,N*-disuccinic acid (EDDS) can be used to form a soluble Fe(III)-complex, which enables the Fenton reaction to operate within a broad pH range, from acidic to neutral conditions [31–33].

Bio-Fenton reaction could be a sustainable and environmentally-friendly strategy to remove organic pollutants from the view of application to the environment. In other words, the Bio-Fenton reaction could be supported by continuous H_2O_2 production by diverse microorganisms and their enzymes, abundant amounts of iron(III) and organic acids such as citrate that could act as iron(III) chelator in the environment. Moreover, products from the pollutants by the Bio-Fenton reaction would be degraded and metabolized by the diverse microbial metabolic systems. Recently, microorganisms or their enzymes that support Bio-Fenton reaction have drawn attention as promising substances for the elimination of organic pollutants and polymers, owing to the continuous *in-situ* H_2O_2 production [34–38]. For example, various enzymes can generate H_2O_2, including lactate oxidase (LOx), pyruvate oxidase (POx), and glucose oxidase (GOx). GOx converts glucose to gluconic acid by producing H_2O_2 and lowering the pH, which facilitates the Fenton reaction [39]. Several studies have reported that GOx supports the Bio-Fenton reaction when applied to dye decolorization and degradation of organic pollutants and polymers [34,35,40,41].

Meanwhile, evaluating the efficiency of Fenton system is important in terms of application to the environment. There have been numerous kinetic studies on abiotic Fenton reactions to evaluate their efficiency in removing pollutants; however, few investigations into principle-based kinetic parameters of Bio-Fenton reactions have been performed.

In the present study, a Bio-Fenton reaction using GOx from *Aspergillus niger* and Fe(III)-citrate was employed for the oxidative degradation of BPA, during which the amount of H_2O_2 generated by GOx and •OH was measured and the steady-state •OH ($[•OH]_{ss}$) generation and BPA degradation with •OH exposure were assessed. In addition, the intermediate products from the Bio-Fenton degradation of BPA were identified, and a possible degradation pathway was proposed.

Taken together, our results suggest a promising application of in-situ Bio-Fenton reactions via H_2O_2 generated by diverse microorganisms. In addition, essential Fenton reagents, such as Fe(III) and organic iron chelators, can be supplied from the environment to non-specifically degrade other plastic additives that could be leached from buried waste plastic into the soil. Moreover, the kinetic study of BPA degradation in the present study could shed light on the application potential of the biological system by comparing it with abiotic systems.

2. Materials and methods

2.1. Chemicals

BPA (≥99%), lyophilized GOx from *Aspergillus niger* (167 U/mg), D-(+)- glucose, Fe(III)-citrate, ferric chloride, potassium hexacyanoferrate (III), *tert*-butanol (*t*-BuOH, >99%) and *para*-chlorobenzoic acid (*p*-CBA, >98%) were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). H_2O_2 (30%) was purchased from Duksan Pure Chemicals Co. Ltd. (Ansan, Republic of Korea). High-purity grade ethyl acetate, acetonitrile, and methanol were purchased from Thermo Fisher Scientific (Waltham, MA, U.S.A.). The Amplex® Red Hydrogen Peroxide/Peroxidase Assay Kit was purchased from Invitrogen (Carlsbad, CA, U.S.A.). A 100 mM BPA stock solution was freshly prepared in methanol prior to the experiments.

2.2. Bio-Fenton degradation of BPA

Bio-Fenton degradation of BPA was carried out in 150 mL serum bottles sealed with Teflon-lined rubber septa and aluminum caps, containing 30 mL of citrate phosphate buffer (50 mM, pH 5.3), GOx (10 U), glucose (32 mM), Fe(III)-citrate (0.5 mM), and BPA (0.1 mM). The control samples were prepared simultaneously as follows: (1) Fe(III)-citrate and BPA, (2) GOx and BPA, and (3) GOx and Fe(III)-citrate. All control samples contained the same amount of glucose as the Bio-Fenton reaction samples. The reaction mixture was reacted at 30 °C and 120 rpm until the Bio-Fenton reaction completely consumed the H_2O_2. During the incubation, the Teflon-lined rubber septa of the serum bottles were not in contact with the reaction solution. The 1.5 mL of the reaction mixture was periodically sampled to measure the pH and quantify the residual H_2O_2 and BPA during the Bio-Fenton reactions. After every sampling, 0.1 mL from the taken sample was stored at − 20 °C to quantify H_2O_2. The rest of the sample was heated at 70 °C for 15 min to inactivate GOx and then stored at 4 °C for the analysis of residual BPA and its degradation products. All experiments were performed in triplicate.

2.2.1. Measurement of H_2O_2 during Bio-Fenton reaction

For every sample, residual H_2O_2 in the reaction mixture was immediately qualified by dropping 5 μL of the sample on a Prussian blue (PB) agar plate [42]. Residual H_2O_2 during the Bio-Fenton reaction was quantified using an Amplex® red hydrogen peroxide/peroxidase assay kit according to the manufacturer's instructions. The amount of H_2O_2 in the reaction mixture was calculated based on a standard curve of H_2O_2 ranging from 1 to 5 μM ($R^2 = 0.99$).

2.2.2. Quantification of the residual BPA during Bio-Fenton reaction

The residual BPA during the Bio-Fenton reaction was analyzed using high-performance liquid chromatography (HPLC). The supernatant of the reaction mixture was sampled at a volume of 400 μL, extracted vigorously with an equal volume of acetonitrile, and filtered using a polyvinylidene fluoride (PVDF) syringe filter for HPLC analysis. HPLC was equipped with a photodiode array detector (PDA) and a reverse-phase ODS-2 column (Inertsil™, 4.6 ×250 mm, 5 μm in particle size) (GL Sciences, Tokyo, Japan). The mobile phase was composed of deionized water containing 0.1% formic acid (solvent A) and acetonitrile (solvent B). Isocratic elution was performed at a 1:1 ratio of solvent A and solvent B at a flow rate of 1 mL/min. The column temperature was maintained at 40 °C, and BPA was monitored at 205 nm. The residual BPA was quantified based on a standard curve ranging from 0.05 to 0.25 mM ($R^2 = 0.99$).

2.3. Determination of •OH generation and degradation kinetics with •OH exposure during Bio-Fenton reaction of BPA

The concentration of •OH during the Bio-Fenton reaction was indirectly measured by degradation of *p*-CBA as a probe compound, as it has high reactivity with •OH. The Bio-Fenton reaction conditions for indirectly measuring the concentration of •OH were composed of a buffer solution containing *p*-CBA (5 μM), GOx (10 U), glucose (32 mM), and Fe (III)-citrate (0.5 mM). In addition, the change in •OH concentration

during the degradation of BPA (final concentration of 0.1 mM) was also measured over time in the same Bio-Fenton reaction system containing *p*-CBA (5 μM). Simultaneously, control samples that did not undergo the Bio-Fenton reaction were prepared as follows: (1) Fe(III)-citrate, BPA, *p*-CBA, and no GOx and, (2) GOx, BPA, *p*-CBA, and no Fe(III)-citrate. All control samples contained the same amount of glucose as the Bio-Fenton reaction samples. Periodically, the reaction samples (500 μL) were quenched with *tert*-BuOH (10 mM). Aliquots were filtered using a PVDF syringe filter (Whatman-GE Healthcare, Pittsburgh, PA, U.S.A.) for HPLC analysis. HPLC was equipped with a PDA (JP/Nexera X2, Shimadzu, Kyoto, Japan) and a C18 reversed-phase column (Eclipse XDB, 4.6 ×150 mm, 5 μm in particle size) (Agilent). The mobile phase was composed of deionized water containing 0.1% phosphoric acid (solvent A) and acetonitrile (solvent B). Isocratic elution was performed at a 1:1 ratio of solvent A and solvent B at a flow rate of 1 mL/min. *p*-CBA was monitored at 193 nm and quantified using a standard curve drawn with different concentrations of *p*-CBA ranging from 0.1 to 10 μM ($R^2 = 1$). The concentration of •OH at steady-state ($[\bullet OH]_{ss}$) was calculated using the following Eq. (1) [43]:

$$\int [\bullet OH]dt = -\frac{\mathrm{Ln}\left(\frac{[p-CBA]}{[p-CBA]0}\right)}{k_{\bullet OH,p\_CBA}} \quad (1)$$

The observed degradation kinetics of *p*-CBA was obtained from the slope of the logarithmic degradation of *p*-CBA, and $[\bullet OH]_{ss}$ was calculated using the second-order rate constant of the reaction of *p*-CBA with •OH (5×10^9 M^{-1} s^{-1}) [44].

Statistical analysis of BPA degradation kinetics with •OH exposure during the Bio-Fenton reaction was conducted using SigmaPlot 12.0 and Excel (Microsoft). The second-order rate constants of BPA with •OH exposure were obtained by linear regression analysis and compared using Analysis of Covariance (ANCOVA). The null hypothesis of the second-order rate constants was identical, within a p value of 0.05 as the threshold level.

2.4. Identification of products from Bio-Fenton degradation of BPA

The possible products of the Bio-Fenton degradation of BPA were identified using gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). After 10 days of Bio-Fenton reaction, the reaction mixture was centrifuged at 10,000 xg for 10 min to remove debris, such as proteins. Ten milliliters of the supernatant were vigorously extracted with 10 volumes of ethyl acetate, and the organic phase was evaporated using a rotary evaporator (EYELA, NY, U.S.A.). The residue was dissolved in 1 mL of methanol, filtered through a PVDF syringe filter, and immediately analyzed using LC-MS and GC-MS.

LC/MS analysis was performed using a Xevo G2-XS-quadrupole-time-of-flight (Q-TOF)-mass spectrometry (Waters, Milford, MA, U.S.A.) equipped with an electrospray ionization (ESI) source. Chromatographic separation was carried out using a C18 reversed-phase column (ACQUITY UPLC CSH™, 2.1 ×100 mm, 1.7 μm in particle size) (Waters) at a column temperature of 35 °C. The mobile phase was composed of deionized water containing 0.1% formic acid (solvent A) and acetonitrile containing 0.1% formic acid (solvent B). The linear gradient for solvent B was as follows: 15–100% for 0–20 min, and 100% for 20–25 min, with subsequent equilibrium achieved in the initial condition for 25–30 min at a rate of 0.4 mL/min. The mass spectrometer was operated in negative ionization mode with the following conditions: nitrogen as a desolvation gas at a flow rate of 800 L/h; desolvation temperature, 400 °C; source temperature, 120 °C; and capillary voltage, 3.0 kV. The resulting deprotonated ions were acquired in the mass range of *m/z* 50–1200.

GC/MS analysis was performed using a 7890 A gas chromatography coupled with a 5975 mass selective detector and 7693 A injector (Agilent). Chromatographic separation was carried out with a DB-624 Ultra Inert capillary column (30 m × 0.25 mm i.d., 1.40 μm film thickness) (Agilent). Helium was used as a carrier gas at a flow rate of 1.0 mL/min, and the oven temperature was set at 60 °C for 2 min, elevated to 250 °C at a rate of 10 °C/min, and held for 9 min. The mass spectrometer was operated with the following parameters: temperature of injector, transfer line, source, 250 °C; MS quadrupole temperature, 150 °C; split injection mode with a split ratio of 2:1; and ionization voltage, 70 eV; mass scan range from *m/z* 10–300.

The products from Bio-Fenton degradation of BPA were predicted based on the overall consideration of the following information: **(i)** their *m/z* values, **(ii)** NIST spectra library, **(iii)** mass spectra interpretation compared with available authentic standards.

3. Results and discussion

3.1. H_2O_2 kinetics-supported Bio-Fenton degradation of BPA

The Bio-Fenton degradation experiment using the radical scavenger BPA, which is present in most commercial plastic products, was performed using H_2O_2 produced *in-situ* by GOx in the presence of glucose with Fe(III)-citrate as an iron source. We tracked the amount of H_2O_2 in the control sample, which consisted of GOx, glucose, BPA, and no Fe (III)-citrate, and in the Bio-Fenton reaction samples with and without BPA. The control experiment with no Fe(III)-citrate produced 8–9 mM of H_2O_2, which remained at the end of the reaction (Fig. 1a). The Bio-Fenton reaction sample without BPA showed produced 6 mM H_2O_2 in day 1, which disappeared after 3 days of the reaction. Interestingly, H_2O_2 slowly diminished in the Bio-Fenton reaction sample containing BPA, followed by gradual consumption until the end at day 10. Periodic sampling was carried out until residual H_2O_2 was not detected on the PB agar plate (no blue colored-precipitate), indicating the complete

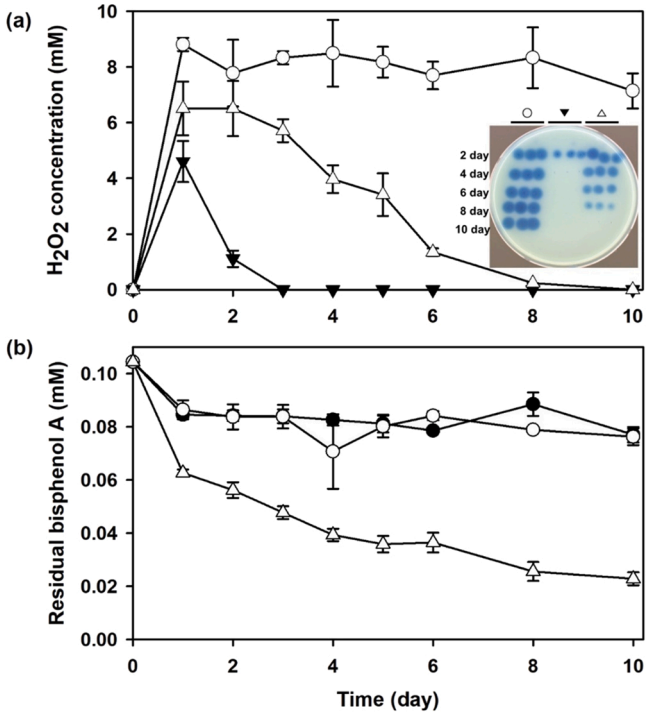

Fig. 1. Measurement of hydrogen peroxide (H_2O_2) (a) and residual bisphenol A (BPA) (b) during the Bio-Fenton reaction. The inserted image in (a) is the result of qualitative analysis of H_2O_2 using Prussian blue (PB) agar plate. A blue precipitate on the PB agar plate indicates the presence of H_2O_2 from the combination of hexacyanoferrate(III) and Fe(III) ion. GOx + BPA (-○-), Fe(III)-citrate + BPA (-●-), GOx + Fe(III)-citrate (-▼-), and GOx +Fe(III)-citrate + BPA (-△-). All samples were supplied 32 mM of glucose. Values are the mean of triplicate determinations ± standard deviation.

consumption of H_2O_2 by the Bio-Fenton reaction (Fig. 1a, insert). Our previous experiments also showed a similar phenomenon in which the time to reach the complete consumption of H_2O_2 during the Bio-Fenton degradation of five different chloroacetanilide herbicides varied [35]. Thus, the factors governing the consumption of H_2O_2 by the Bio-Fenton reaction in the presence of substrates should be addressed to improve the degradation efficiency of the reaction. The Bio-Fenton reaction was initially set at pH 5.3 because the high enzyme activity of GOx was previously observed at pH 5.0–6.0 [45]. The pH of all treatments containing GOx and glucose rapidly dropped from 5.3 to 4.3 on 1 day of the reaction, followed by a gradual decrease to 4.0 due to the production of gluconic acid from glucose by the GOx enzyme activity. The pH drop made the reaction conditions more acidic, which might contribute to the efficiency of Fenton reaction. In addition, the pH decrease during the Bio-Fenton reaction would probably provide favorable reaction conditions for the stable iron-chelator complex under the attack of •OH [46]. In addition, citrate seemed a stable Fe(III) chelator without no effect on GOx itself, considering the optimal enzyme activity of GOx in the citrate-phosphate buffer. Moreover, using citrate as the iron chelator has advantage in the application of Bio-Fenton reaction to the environment due to its abundant supply by soil microorganisms and plant. Thus, Fe (III)-organic chelators, such as citrate, would allow Fenton reaction to be feasible in the environment with ubiquitous presence of Fe(III), even though a reaction rate would be slower than that of Fe(II).

Compared with the control experiments without either GOx or Fe (III)-citrate, the Bio-Fenton reaction degraded BPA substantially to 40% after 1 day and gradually degraded it up to 80% by 10 days of reaction (Fig. 1b).

3.2. Quantification of •OH and degradation kinetics with •OH exposure during Bio-Fenton degradation of BPA

Generation of steady-state •OH concentration ($[•OH]_{ss}$) was assessed using *p*-CBA because of its rapid reaction kinetics with •OH (second-order rate constant, $k_{•OH,\ p\text{-CBA}} = 5 \times 10^9\ M^{-1}\ s^{-1}$) [47]. Significantly, the logarithmic-scale degradation of *p*-CBA concentration followed biphasic linear regressions during the Bio-Fenton reaction without BPA (Fig. 2a). Interestingly, *p*-CBA concentration steadily decreased by 4 days of the reaction and gradually decreased by day 10, with slopes of $0.55 \times 10^{-6}\ s^{-1}$ ($R^2 = 0.99$) and $0.75 \times 10^{-7}\ s^{-1}$ ($R^2 = 0.83$), respectively. Based on Eq. (1) in the Methods, the $[•OH]_{ss}$ values of 1st phase and 2nd phase were calculated as 1.1×10^{-16} M and 0.15×10^{-16} M, respectively. In contrast, the concentration of *p*-CBA was maintained in the Bio-Fenton sample with BPA. Interestingly, the Bio-Fenton sample with BPA indicated that BPA might scavenge •OH produced more strongly than *p*-CBA. The concentration of *p*-CBA did not decrease in the control samples without either GOx or Fe(III)-citrate, indicating that there was no production of •OH.

Huang et al. [29] reported that $[•OH]_{ss}$ was 10^{-9}-10^{-10} M in an abiotic Fenton reaction using 0.5 mM of Fe(III)-EDDS and 5 mM of H_2O_2 at pH 3–9, which is 10^6 folds more •OH than the current Bio-Fenton reaction at pH 5.3. The difference in $[•OH]_{ss}$ between the two reactions might be due to the different reaction conditions, such as sources of H_2O_2, iron, and pH. In other words, H_2O_2 was supplied to the abiotic Fenton reaction by one-time spiking, which could cause immediate activation. In contrast, the Bio-Fenton reaction steadily supplied H_2O_2 by the enzyme activity of GOx in the presence of glucose, resulting in the highest production at day 1 of the reaction, followed by slow H_2O_2 consumption and •OH production. In addition, the presence of •OH scavengers, such as proteins and organic acids, in the Bio-Fenton reaction mixture could affect *p*-CBA degradation during the reaction. •OH might attack these organic compounds non-specifically, as well as *p*-CBA. Consequently, the organoradicals produced could interrupt the redox mechanisms of the Fenton reagents. Indeed, the efficiency of *p*-CBA degradation in real wastewater treatment decreased due to high concentrations of organic contaminants in the sample, which could be

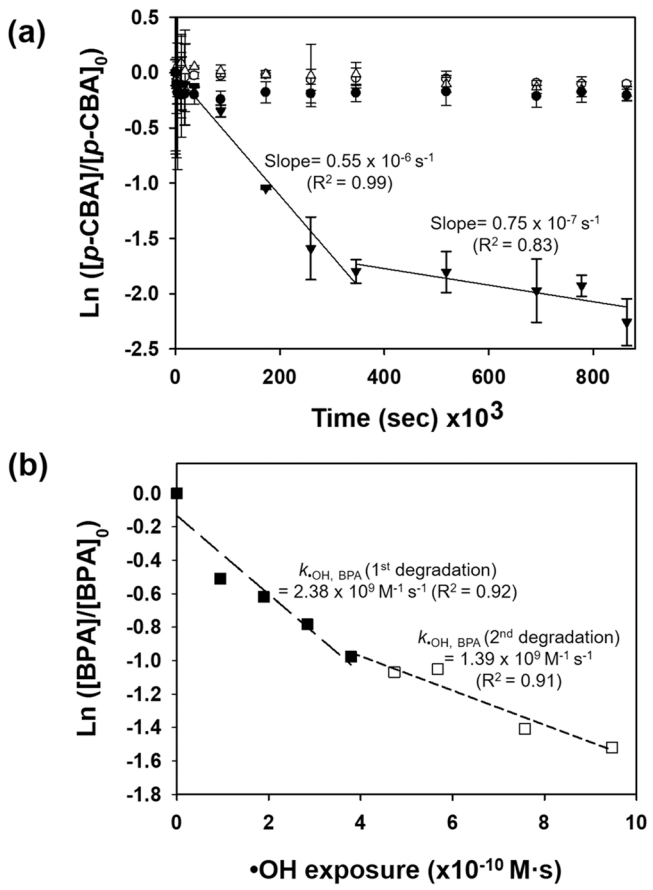

Fig. 2. Logarithmic-scale degradation of *p*-CBA (a) and bisphenol A (BPA) (b) as a function of •OH exposure during the Bio-Fenton reaction. GOx + BPA + *p*-CBA (-○-), Fe(III)-citrate + BPA + *p*-CBA (-●-), GOx + Fe(III)-citrate + *p*-CBA (-▼-), and GOx + Fe(III)-citrate + BPA + *p*-CBA (-△-). All samples were supplied 32 mM of glucose. Long (— —) and short (-–) dash lines represent the linear regressions of the experimental data, following on biphasic degradation kinetics for the 1st degradation (■) and the 2nd degradation (□). Values are the mean of triplicate determinations ± standard deviation.

•OH scavengers and further organoradicals that significantly affect the •OH concentrations in the system [48]. Based on our results, *in-situ* H_2O_2 production by enzyme activity could significantly influence the efficiency of the Bio-Fenton reaction; further investigation is needed to enhance Bio-Fenton performance. The influence of •OH exposure on the BPA degradation was investigated based on the $[•OH]_{ss}$ in the Bio-Fenton reaction. The logarithmic-scale degradation of BPA exhibited a linear correlation with •OH exposure during the Bio-Fenton reaction (Fig. 2b); the results indicated that •OH was the principal reactive species responsible for BPA degradation. The resulting second-order rate constants (k) derived from the slope of the linear regression were $2.38 \times 10^9\ M^{-1}\ s^{-1}$ ($R^2 = 0.92$) (1st degradation) and $1.39 \times 10^9\ M^{-1}\ s^{-1}$ ($R^2 = 0.91$) (2nd degradation). Compared with the theoretical data of k for BPA with •OH (Collins-Kimall approach; $k_{•OH,\ BPA} = 1.03 \times 10^{10}\ M^{-1}\ s^{-1}$) [49], overall, the 1st and 2nd degradation of BPA by the Bio-Fenton reaction was likely to be very fast reaction ranging between 0.25 and 0.14. These findings may contribute to the comparison between the degradation kinetics of the abiotic- and Bio-Fenton reactions, and further development of Bio-Fenton use.

3.3. Identification of products and proposed pathway for Bio-Fenton degradation of BPA

The products of the Bio-Fenton degradation of BPA were analyzed using LC/MS and GC/MS. From the base peak chromatograms (BPCs) of

LC-MS and GC/MS analysis, eight peaks **(a-h)** distinctly appeared in the Bio-Fenton reaction of BPA (Fig. 3 red line) compared with the control samples. These peaks were examined through MS analysis with careful consideration of their *m/z* values, NIST spectra library, and mass spectra, which were compared to authentic standards when available. The products of the Bio-Fenton degradation of BPA were identified as follows: **(a)** 4-hydroxyacetophenone ($[M-H]^-$ *m/z* 135.0432), **(b)** dihydroxylated BPA ($[M-H]^-$ *m/z* 259.0958), **(c)** monohydroxylated BPA ($[M-H]^-$ *m/z* 243.1074), **(d)** hydroxyacetone (*m/z* 74.07), **(e)** propionic acid (*m/z* 74.07), **(f)** isobutyric acid (*m/z* 88.10), **(g)** 4-acetylbutyric acid (*m/z* 130.14), and **(h)** hydroquinone (*m/z* 110.11) (Fig. 4). Information on the identified products from BPA is summarized in Table S1, including molecular formula, *m/z* value, retention time, and analytical method. There was an exact match of *m/z* values and the typical fragmental patterns between the products from the Bio-Fenton reaction **(a, d-h)** and the authentic standards (Figs. 4 and S1). Authentic standards for dihydroxylated BPA **(b)** and monohydroxylated BPA **(c)** were unavailable; therefore, it was assumed based only on the MS spectra.

Based on these interpretations, a possible pathway for the Bio-Fenton degradation of BPA is proposed in Fig. 5. The •OH produced by the Bio-Fenton reaction may behave as an electrophile and nucleophile. Therefore, •OH might initially produce non-specific hydroxylation of the aromatic rings of BPA and the C-C bond between them, resulting in the conversation of BPA to monohydroxylated BPA **(c)**, which was further converted to dihydroxylated BPA **(b)** via sequential hydroxylation. From the LC/MS results, the BPC area of monohydroxylated BPA **(c)** was higher than other peaks, which might indicate the formation of **(c)** as a main initial intermediate in the Bio-Fenton degradation of BPA. Indeed, the formation of hydroxylated products mediated by •OH was predicted by concerted studies on the degradation of contaminants, such as BPA and diuron, through the calculation of frontier electron densities in the molecules [50–52]. According to the Frontier Orbital Theory, electrons located at the positions with higher frontier electron densities in the highest occupied molecular orbital (Fed^2_{HOMO}) tend to be extracted [51,53]. In other words, the electrons at these positions are most readily attacked by •OH; therefore, the reaction sites for hydroxylation could be predicted [52]. Zhu et al., found that the *ortho*- and *para* positions of the aromatic rings and C-C bond of the aliphatic chain between two aromatic rings of BPA exhibited a higher Fed^2_{HOMO} [52]. Following these references, the initial products of the Bio-Fenton degradation of BPA are formed from the hydroxylation and scission of C-C between the two aromatic rings.

Meanwhile, •OH might attack the electron-rich alkyl groups of C-C between the two aromatic rings, and may produce intermediates, *p*-isopropylphenol and 4-isopropanol-phenol, and further oxidized them to 4-hydroxyacetophenone **(a)** and hydroquinone **(h)** via a sequential hydroxylation reaction. Consequently, the catechol form of **(h)** could be subject to the ring cleavage and further hydroxylation and oxidation reactions, resulting in the production of small carboxylic acids, **(d)**, **(e)**, **(f)**, **(g)**. In addition, the hydroxylated BPA intermediates **(b** and **c)** would be eventually filtered into aliphatic carboxylic acids via the catechol form of intermediates and further serial reactions of ring cleavage, hydroxylation, and oxidation mediated by •OH attack. These

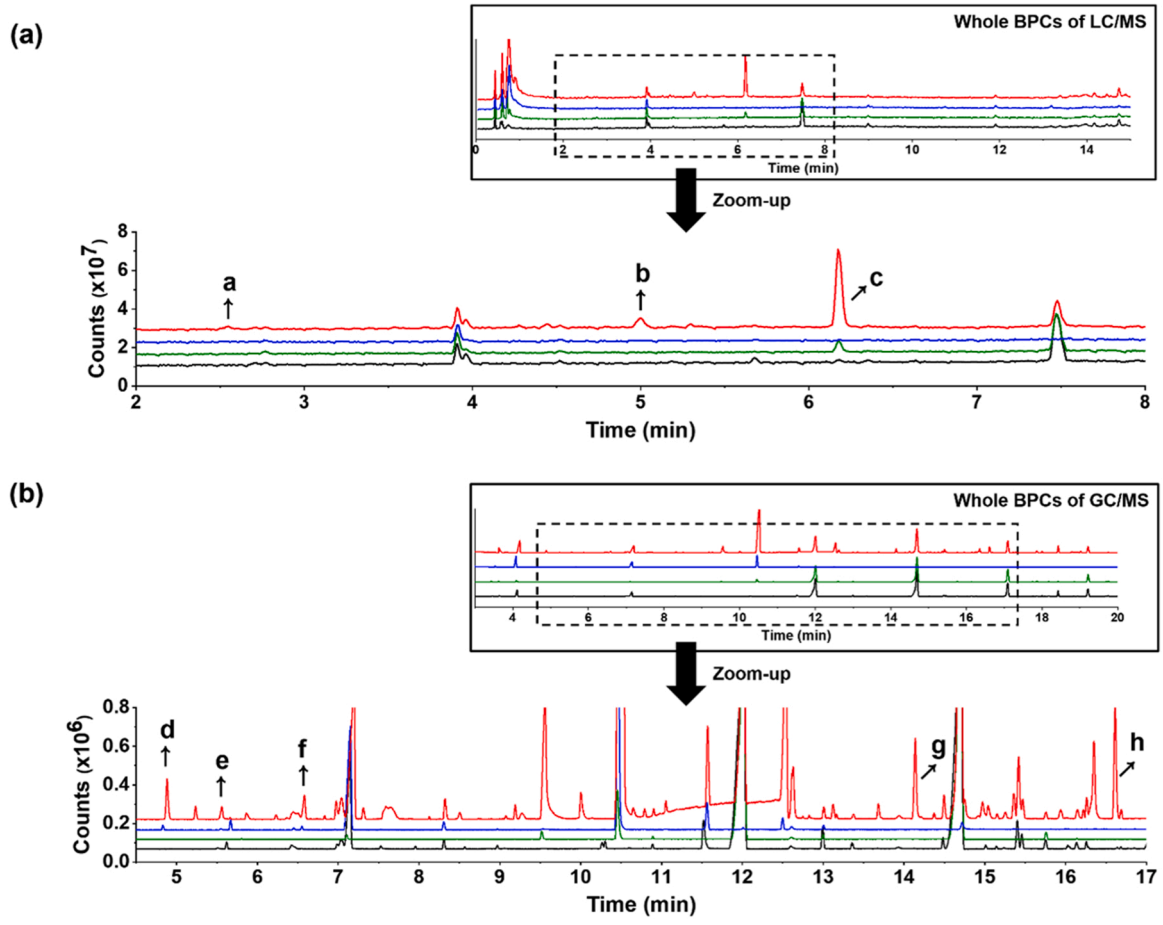

Fig. 3. Enlarged base peak chromatograms (BPC) of (a) LC-MS and (b) GC-MS analysis of products from the Bio-Fenton degradation of bisphenol A (BPA). Black line, Fe(III)-citrate + BPA; Green, GOx + BPA; Blue, GOx + Fe(III)-citrate; Red, GOx + Fe(III)-citrate + BPA. All samples were supplied 32 mM of glucose. The chromatograms at the upper right side are whole BPCs of the analysis. Letters a to h and pointing arrows indicate peaks markedly detected in the Bio-Fenton degradation of BPA.

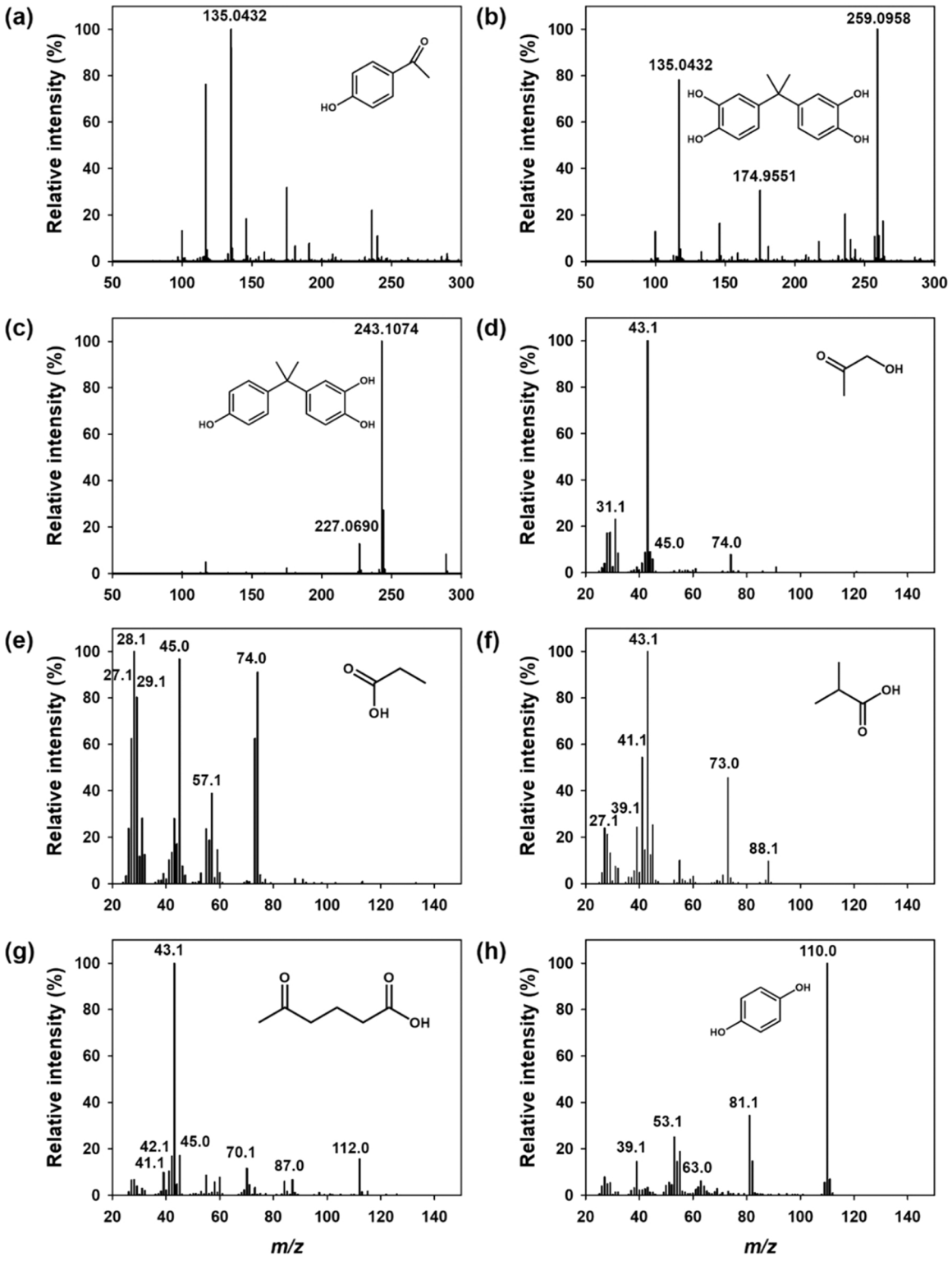

Fig. 4. MS spectra of products from (a-c) LC-MS and (d-h) GC-MS. (a) 4-hydroxyacetophenone (*m/z* 135.04), (b) dihyroxylated BPA (*m/z* 259.09), (c) monohydroxylated BPA (*m/z* 243.10), (d) hydroxyacetone (*m/z* 74.07) (e) propionic acid (*m/z* 74.07), (f) isobutyric acid (*m/z* 88.10), (g) 4-acetylbutyric acid (*m/z* 130.14), and (h) hydroquinone (*m/z* 110.11).

small carboxylic acids would be mineralized by the continuous attack of •OH.

The products from the current Bio-Fenton reaction toward BPA could be partially found in previous research on biodegradation of BPA using well-known microbes, such as *Pseudomonas putida*, *Sphingobium* sp., *Desmodesmus* sp., including oxidized forms of BPA and small acids [54–56]. Notably, monohydroxylated BPA is common intermediates, which could be produced from BPA by oxidation enzymes, such as cytochrome P450, as well as the current Bio-Fenton reaction that induces oxidation reaction through •OH. However, the advantage of the current Bio-Fenton reaction is no need of electron supplying cofactor, such as NADH, required from microbial enzyme mediated reactions.

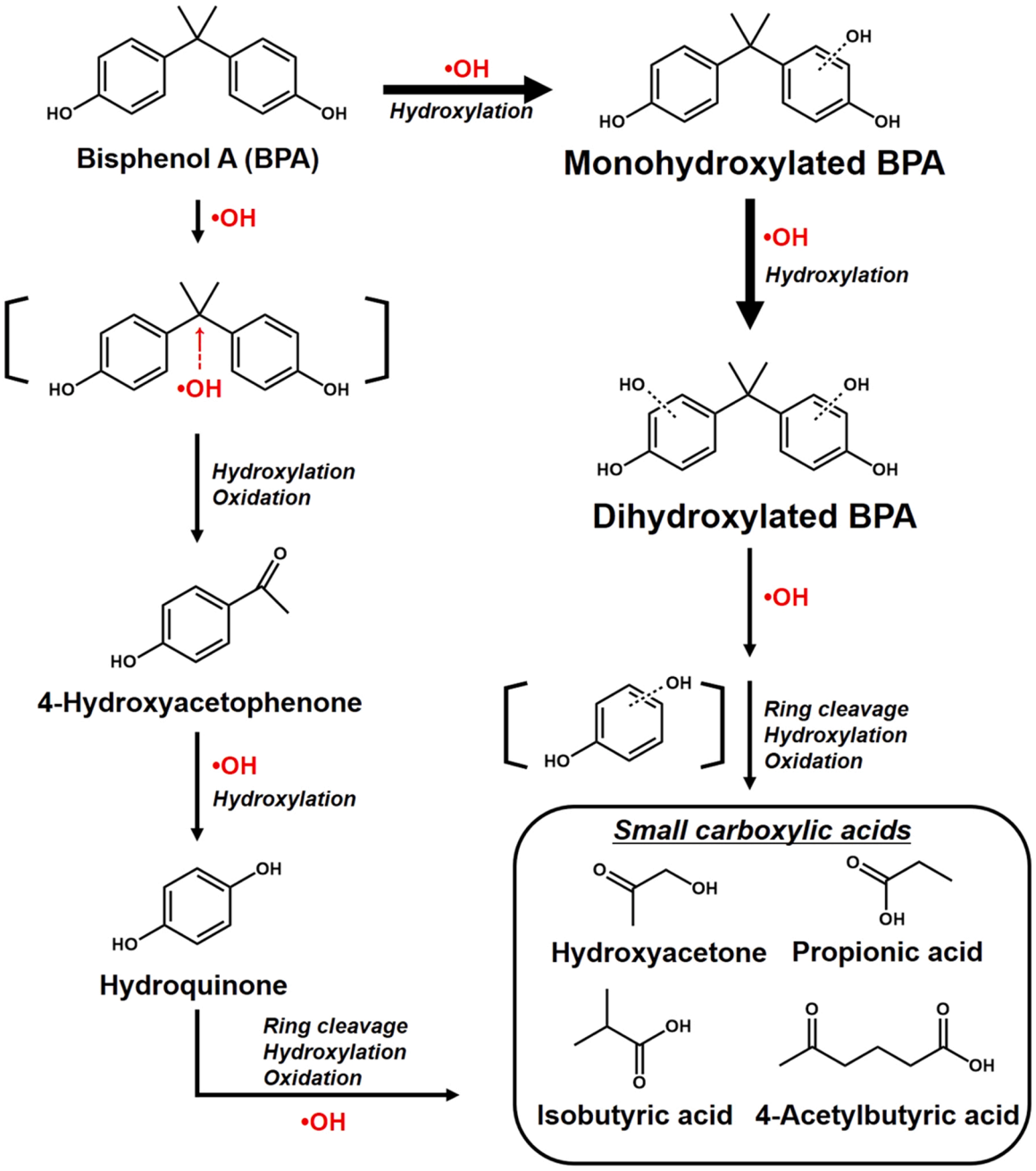

Fig. 5. Proposed degradation pathway of bisphenol A by the Bio-Fenton reaction.

Even though several intermediates from the Bio-Fenton degradation of BPA were detected in the condition controlled-lab scale experiments, it would be difficult to examine a toxicity of each intermediate to microorganisms in real environment. However, these intermediates would be easily decomposed or metabolized through diverse microbial metabolism when the current Bio-Fenton system is applied in the soil environment. Simultaneously, the intermediates would be subjected to degrade by continuous supplying of H_2O_2 from H_2O_2 producing microorganisms and ubiquitous Fe(III) chelating organic acids in environment.

4. Conclusion

In the present study, the Bio-Fenton reaction, supported by in-situ H_2O_2 production (8–9 mM) by GOx (10 U) and Fe(III)-citrate (0.5 mM), was applied to degrade BPA (0.1 mM), a commonly used plastic additive. •OH was steadily produced from H_2O_2 generated in-situ by GOx and Fe(III)-citrate, significantly contributing to BPA degradation. A plausible pathway for the Bio-Fenton degradation of BPA was proposed based on the identified products, including the scission of the C-C bond between two aromatic rings of BPA, ring cleavage, and a series of hydroxylation and oxidation reactions. This study may promote the application of the Bio-Fenton reaction to degrade other plastic additives such as plasticizers and antioxidants that could be released from plastic waste, which could be applied eventually to degrade plastic waste. Furthermore, the results of principle-based kinetic parameters, including the determination of $[\bullet OH]_{ss}$ ($0.15–1.1 \times 10^{-16}$) and second-order rate constants of BPA ($1.39–2.38 \times 10^{9}$ M^{-1} s^{-1}), could contribute to the comparison of kinetics with previous reports on abiotic Fenton reactions and further the development of the Bio-Fenton reaction. The Bio-Fenton reaction also alleviates the drawbacks of traditional Fenton systems used in electrochemistry and photocatalysis, such as the

self-quenching of •OH by a high concentration of H_2O_2 [57]. Thus, the current mechanism could provide biological systems applicable to the degradation of plastics with additives once microbial systems can operate the Bio-Fenton reaction, as suggested; however, further research is required to increase the H_2O_2 supply and optimize the iron sources to enhance the reaction's efficiency.

CRediT authorship contribution statement

Sihyun An carried out the overall experiments, including data analysis and interpretation. **Younggun Yoon** performed to determine degradation kinetics. **Sihyun An**, **Younggun Yoon**, and **Youri Yang** drafted the manuscript. **Jae-Hyung Ahn**, **Hang-Yeon Weon**, **Dayeon Kim**, **Ye-eun Kim**, and **Hor-Gil Hur** revised the manuscript. **Youri Yang** directed all procedures of experiments and critically reviewed the manuscript to improve the quality of the draft. All authors read and approved the final manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.109349.

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