processes

Article

The Ascorbic Acid-Modified Fenton System for the Degradation of Bisphenol A: Kinetics, Parameters, and Mechanism

Yanlin Wu [1,*,†], Jiawei Gu [1,†], Zhongyi Fang [2], Yuang Shan [2] and Jie Guan [1,*]

[1] School of Resources and Environmental Engineering, Shanghai Polytechnic University, Shanghai 201209, China
[2] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China
* Correspondence: wuyanlin@fudan.edu.cn (Y.W.); guanjie@sspu.edu.cn (J.G.)
† These authors contributed equally to this work.

Abstract: Bisphenol A (BPA) has been extensively used in the commercial production, especially the production of plastic products. It has endocrine-disrupting effects and poses potential risks to health, which is also related to the development of various diseases. Nevertheless, using conventional biological treatment techniques has proved challenging in fully breaking down this particular hazardous substance. The degradation ability of the target substance was explored by investigating the effect of an ascorbic acid (Vc)-modified Fenton-like system. The results showed that the degradation rate of the modified system reached 74.6% after 20 min, which was much higher than the 9.1% degradation rate without Vc. Under different ratios of Vc and Fe(III), when the ratios were 1:1 and 1/2:1, the reaction efficiency was the best, and the degradation rate exceeded 83%. When pH = 6.5 and the ratio of Vc to Fe(III) was 1:1, the optimal conditions were achieved, and 83.5% of the BPA could be degraded within 60 min. The results of the quenching experiment provided evidence that $^{\bullet}$OH was the main reactive oxidizing species (ROS). Analysis of the BPA degradation pathway and the product toxicity evaluation revealed a reduction in the acute/chronic toxicity of BPA from toxic/very toxic to non-harmful/harmful levels. The presented evidence demonstrates that Vc significantly enhances the performance of the modified Fenton-like system and has definite potential for application.

Keywords: Fenton-like reaction; ascorbic acid; bisphenol A; radicals; toxicity

check for updates

Citation: Wu, Y.; Gu, J.; Fang, Z.; Shan, Y.; Guan, J. The Ascorbic Acid-Modified Fenton System for the Degradation of Bisphenol A: Kinetics, Parameters, and Mechanism. *Processes* **2024**, *12*, 2588. https://doi.org/10.3390/pr12112588

Academic Editor: Guining Lu

Received: 20 October 2024
Revised: 11 November 2024
Accepted: 13 November 2024
Published: 18 November 2024

1. Introduction

Endocrine-disrupting chemicals (EDCs) are exogenous compounds that disrupt the regular operation of the endocrine system upon entering the human body. The endocrine system is very important for daily activities, growth and development, and even the survival capabilities of humans [1]. So, EDCs have garnered considerable interest from society and the academic community. Bisphenol A (BPA) is a typical EDC that can bind to estrogen receptors and cause an abnormal level of sex hormones in the human body, resulting in damage to the nervous and reproductive systems [2]. BPA also has intestinal toxicity due to increasing intestinal permeability, decreasing intestinal sIgA levels, and intestinal lysozyme expression [3]. However, BPA plays a crucial role in industrial production and is present in various consumer products, particularly epoxy resins and polycarbonate plastics [4–6]. The global annual output amount of BPA was around 8 million tons [7]. Owing to its high consumption and yield, BPA was unavoidably discharged into the surrounding environment. Nevertheless, EDCs cannot thoroughly be removed by traditional sewage treatment technologies. Thus, EDCs, including BPA, are frequently discharged into natural water bodies along with the effluent. It was reported that the BPA concentrations in surface water were 8.8–1000 ng/L and 250–12,205 ng/L in municipal wastewater and sewage treatment plant effluents [2,8]. With transmission within the food chain, BPA has been detected in food [9], environmental mediums [10], and living organisms [11,12]. Hence, research on efficient methods for BPA elimination in water is particularly essential.

The common treatment methods of BPA include ozone oxidation [13–15], photocatalytic oxidation [16–19], biodegradation [20,21], and Fenton/Fenton-like processes [22,23]. However, the ozone oxidation processes have high energy consumption, and ozone is sometimes unstable. Furthermore, there are also some disadvantages of photocatalysis technologies, including the limited efficiency of light utilization, the high cost of noble metal, and the difficult recovery of powder catalysts. Meanwhile, biodegradation processes take a very long time compared with chemical methods. In contrast, Fenton/Fenton-like processes are relatively suitable chemical methods for BPA degradation. Fenton processes usually refer to the reaction involving Fe(II) and H_2O_2, while Fenton-like processes usually involve Fe(III) and H_2O_2. Both of these processes will produce large amounts of strong oxidizing radicals to make the pollutant degrade. These kinds of methods are economical, efficient, and straightforward to implement. However, the conventional Fenton/Fenton-like processes are strongly affected by pH because the form and amount of Fe(II) are controlled in neutral and alkaline solution. The dissolved Fe(II) is the key component for H_2O_2 activation. Thus, some reducing agents, such as phenolic compounds [24], quinone species [25], and hydroxylamine [26] have been applied in Fe(III)/H_2O_2 systems to continuously generate Fe(II), and the formation of radicals is significantly increased. However, many of them present certain toxicity. A non-toxic, efficient, and environmentally friendly reducing agent is being searched for.

In this study, L-ascorbic acid was selected as the suitable reducing agent to enhance the Fenton-like system to achieve the efficient removal of BPA. L-ascorbic acid, well known as vitamin c (Vc), is a polyhydroxy compound with a five-membered heterocyclic structure and has very strong reducibility [27]. Vc is also cost-effective and safe. Figure S1 shows the chemical structure of Vc. It was introduced into the Fe(III)/H_2O_2 system to improve the formation of Fe(II), which could active H_2O_2 to facilitate the production of oxidative radicals for BPA degradation. The construction of this system resulted in an improved Fenton-like system that might be efficient, non-toxic, and environmentally friendly and have great potential for application. The effects of the Vc/Fe(III) ratio and pH conditions were investigated. Quenching experiments were performed to detect which free radicals play important roles in BPA degradation. The mechanism of the modified Fenton-like system was investigated. The degradation byproducts of BPA were identified with liquid chromatography-mass spectrometry (LC-MS), and the ecological structure activity relationships (ECOSAR, v2.2, Washington, DC, USA) software was used to evaluate the toxicity of these intermediate products. This research aimed to advocate for the implementation of an environmentally sustainable system that would effectively degrade EDCs and greatly mitigate the toxicity of the targeted pollutants.

2. Materials and Methods

2.1. Materials

Bisphenol A (BPA, 99%), methanol (CH_3OH, 99.95%), acetonitrile (C_2H_3N, 99.99%), formic acid (HCOOH, 99.9%), and chloroform ($CHCl_3$, ≥99.0%) were purchased from J&K Scientific, Beijing, China. Iron(III) perchlorate hydrate ($Fe(ClO_4)_3 \cdot xH_2O$, 10.7% of Fe (*w*/*w*)) was obtained from Sigma-Aldrich. Hydrogen peroxide (H_2O_2, ~30%), isopropanol (C_3H_8O, 99%), sodium hydroxide (NaOH, ≥99.0%), perchloric acid ($HClO_4$, 70.0~72.0%), and ascorbic acid ($C_6H_8O_6$, ≥99.7%) were purchased from Sinopharm Chemical Reagent, Shanghai, China.

2.2. Degradation Experiment

Degradation experiments were all carried out in 40 mL brown glass bottles. A total of 20 mg/L mother solution of BPA and 9.89 mM mother solution of H_2O_2 were prepared before the degradation experiment. The Fe(III) solution was 5.0 mM and kept at 4 °C. The Vc solution was freshly prepared just before the experiment started. The solutions were mixed with the designed concentration to constitute the Vc/Fe(III)/H_2O_2 system for the degradation of BPA. Samples were taken at the reaction times of 2 min, 5 min, 10 min, 20 min, 40 min, and 60 min. A total of 100.0 µL methanol was placed in the vials in advance to terminate the oxidation reaction of samples.

2.3. Quenching Experiment

Isopropanol and chloroform were used as quenchers for $^{\bullet}OH$ and $O_2^{\bullet-}$, respectively, attributing to the very high second-order reaction rate constant of the reaction between isopropanol and $^{\bullet}OH$/chloroform and $O_2^{\bullet-}$ ($k_{\text{isopropanol}, \bullet OH} = 1.9 \times 10^9$ mol·L^{-1}·s^{-1} and $k_{\text{chloroform}, O2\bullet-} = 3.0 \times 10^{10}$ mol·L^{-1}·s^{-1} [28,29]). A total of 5.0 mM of isopropanol and chloroform was added to the reaction, and it was about 500 times higher than the concentration of BPA. The high concentration of quenchers ensured complete cleaning of the radicals.

2.4. Analysis Methods

High-performance liquid chromatography (HPLC) produced by Dionex company (Ultimate 3000, DIONEX, Sunnyvale, CA, USA) was used for the detection of BPA concentration. It was equipped with a diode array detector (DAD) and a C-18 reverse column. Methanol (70%) and water (30%) were used as mobile phases at a flow rate of 0.8 mL/min. The single injection volume was 20 µL, and the column temperature was set at 40 °C (±0.5 °C). The retention time of BPA was 7.1 min with the detector wavelengths at 226 nm and 280 nm [30].

The BPA degradation byproducts were analyzed by an ultra-high-performance liquid chromatography-quadrupole time-of-flight mass spectrometer (UPLC-QTOF-MS, Agilent 1290 UPLC coupled with an Agilent 6550 Q-TOF mass spectrometer, Santa Clara, CA, USA), which was equipped with waters BEH C18 column (2.1 mm × 50 mm, 1.7 µm). The ionization source was electrospray negative ion mode. The solution of methanol and water (70:30, *v*/*v*) was used as the mobile phase with the flow rate of 0.2 mL/min [31]. The mass spectrum parameters were as follows: capillary voltage was 2.8 kV, RF lens voltage was 0 V, source temperature was 150 °C, temperature was 400 °C, gas flow was 1000 L/h, impact chamber pressure was 3.1×10^{-3} mbar, and cone hole voltage was 30 V.

3. Results and Discussion

3.1. Kinetics of BPA Degradation in Different Systems

The degradation of BPA in a traditional Fenton-like system (Fe(III)/H_2O_2) and a modified Fenton-like system (Vc/Fe(III)/H_2O_2) were investigated. The initial BPA concentration was 2 mg/L (8.8 µM). The results in Figure 1 show that 28.1% of the BPA was degraded in the Fe(III)/H_2O_2 system with a 60 min reaction. The degradation curve was fitted as a pseudo first-order reaction kinetics curve ($R^2 = 0.9965$), and the $k_{obs} = (3.58 \pm 0.32) \times 10^{-3}$ min^{-1}. It was not supervised to see if the degradation efficiency of the BPA was low because the reaction between the Fe(III) and H_2O_2 was slow. The reaction is shown as Equation (1), and the second-order rate constant was $k_{\text{Fe(III)}, H2O2} = 0.01$ M^{-1} s^{-1} [32]. Thus, the formation of reactive oxidizing species (ROS) was slow and in small amounts, which led to the low degradation efficiency of the BPA.

When the Vc was added to the solution, the degradation rate of the BPA in the modified Fenton-like reaction increased rapidly, reaching 74.6% after 20 min and 83.5% after a 60 min reaction. The degradation curve was fitted as a pseudo first-order reaction kinetics curve ($R^2 = 0.9939$), and the $k_{obs} = (1.49 \pm 0.12) \times 10^{-1}$ min^{-1}. Meanwhile, control experiments (Vc/Fe(III) and Vc/H_2O_2 systems) were also performed to exclude some accessory reactions. The results of the control experiments show that there was almost no degradation of BPA in either the Vc/Fe(III) or Vc/H_2O_2 system. The key factor for improving the BPA degradation efficiency was the production of Fe(II). Vc is a well-known reductant, and it can reduce Fe(III) to form Fe(II) quickly (Equation (2)) [33]. The high degradation efficiency of the BPA was mainly due to the large amount of $^{\bullet}OH$ produced from the reaction between the Fe(II) and H_2O_2, as shown in Equation (3) [34]. The second-order rate constant of $k_{Fe(II),\,H2O2}$ = 76 M^{-1} s^{-1} [32] was 7600 times higher than in the Fe(III)/H_2O_2 system. A large amount of $^{\bullet}OH$ was formed, and BPA was degraded by the attack of ROS. In general, the Vc-modified Fenton-like system activated the H_2O_2 and promoted the formation of $^{\bullet}OH$, which greatly increased the oxidation ability of the system. The concentration of total organic carbon (TOC) in the BPA/Vc/Fe(III)/H_2O_2 system was also analyzed because TOC is an important indicator for evaluating degradation efficiency [35]. The result is shown in Figure S2. The TOC was measured with 8 h reaction, and there was only 23.6% mineralization at the end of the reaction. It seemed there were still many degradation byproducts remaining in the system.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \tag{1}$$

$$2Fe^{3+} + C_6H_8O_6 \rightarrow 2Fe^{2+} + C_6H_6O_6 + 2H^+ \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \tag{3}$$

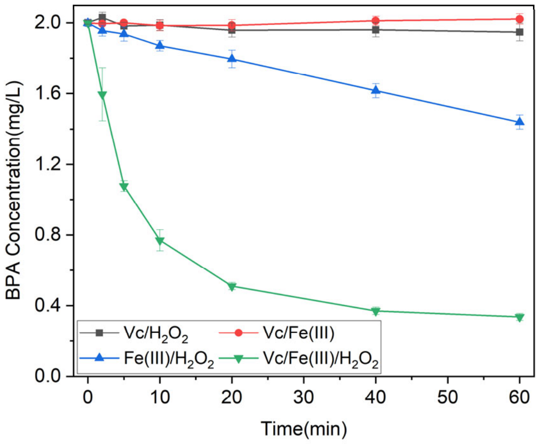
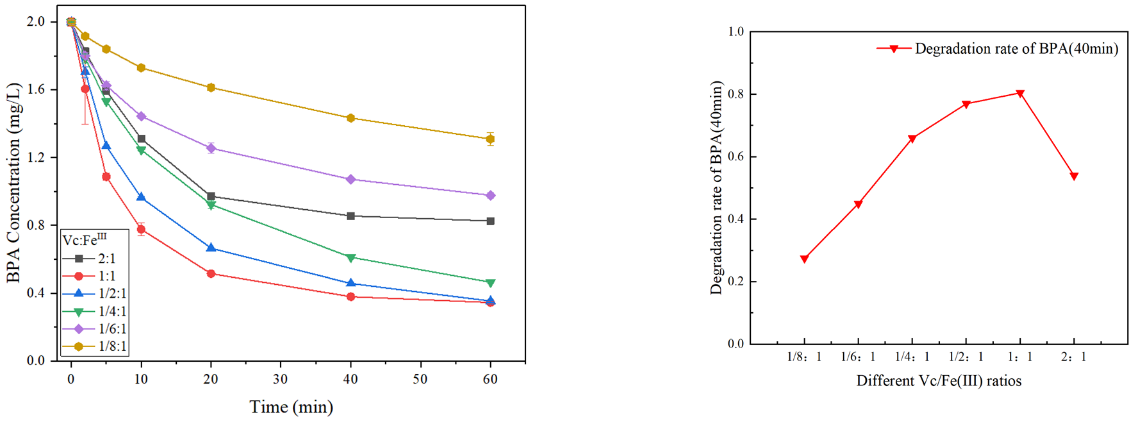


Figure 1. The degradation of BPA in different systems ([Vc] = 50 µM, [Fe(III)] = 50 µM, [H_2O_2] = 50 µM, initial pH = 6.5).

3.2. The Effect of Vc/Fe(III) Ratio on the Degradation of BPA

According to the literature [33], Vc could reduce Fe(III) in a ratio of 1/2:1 (Equation (2)). Hence, the Vc/Fe(III) ratios set in this experiment were 2:1, 1:1, 1/2:1, 1/4:1, 1/6:1, and 1/8:1, resulting in a total of six distinct ratios. Such a ratio setting had the potential to enhance the precision of the following investigations. The experimental findings (as shown in Figure 2) indicate that the degradation rate of BPA within 60 min exhibited an upward trend when the Vc ratio increased, particularly when less than 1:1. With a Vc/Fe(III) ratio of 1:1, the reaction reached optimal performance, resulting in a degradation rate above 84%. A reduction in the Vc ratio to 1/8:1 resulted in a decreasing BPA degradation rate, and 65.5% of the BPA remained. However, when the Vc/Fe(III) ratio reached 2:1, there was also a noticeable drop in the BPA degradation rate in contrast to the 1:1 ratio. The interaction between the concentration of Vc and the oxidation ability of the system exhibited a multidirectional characteristic.

According to relevant research [33], it could be assumed that the mechanism of the role of Vc involved the reduction of Fe(III) to produce Fe(II), therefore converting a Fenton-like reaction into a Fenton reaction. The theoretical dosage ratio of the reduction between Vc and Fe(III) was 1/2:1. Thus, when the Vc amount was not sufficient, the Fe(II) formation was restricted, which led to the incomplete activation of H_2O_2. The small number of generated radicals led to the low degradation efficiency of BPA. Nevertheless, in cases when Vc was present in excess (Vc/Fe(III) = 2:1), a great amount of $^{\bullet}OH$ would attack Vc itself due to its high reducibility [36], hence impeding the degradation of BPA. In theory, the highest BPA degradation rate should be obtained with the ratio Vc/Fe(III) = 1/2:1. However, additional Vc dosage was required for the reduction of the produced Fe(III) from the Fenton reaction (Equation (3)). Thus, it was reasonable to obtain the optimal BPA degradation rate with the ratio Vc/Fe(III) = 1:1.



(**a**) (**b**)

Figure 2. (**a**) Effects of different Vc/Fe(III) ratios on modified Fenton-like systems; (**b**) degradation rates of different Vc/Fe(III) ratios at 40 min ($[Fe^{3+}]$ = 50 µM, $[H_2O_2]$ = 25 µM, initial pH = 6.5).

3.3. The Effect of Initial pH Value on the Degradation of BPA

The degradation of BPA with different pHs is shown in Figure 3. It was observed that when pH ≥ 8.0, the degradation of the BPA almost stopped completely. However, the BPA degradation rate was increased with the pH increasing from 3.0 to 6.5. The optimal pH for BPA degradation was 6.5, and 82.5% of the BPA was removed after 60 min reaction.

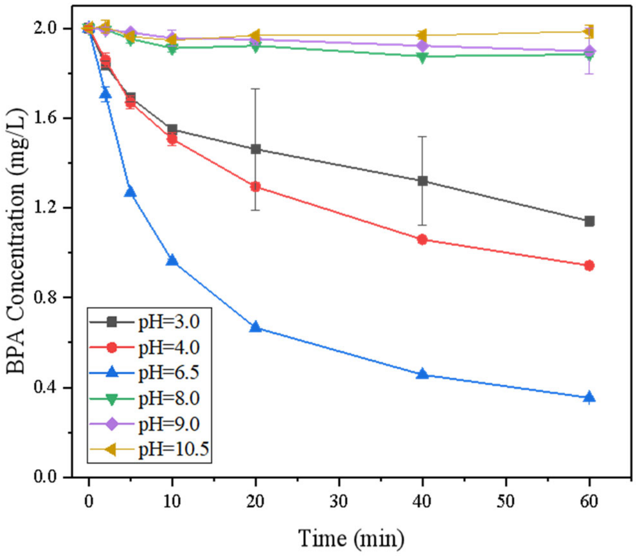


Figure 3. Effect of different pHs on BPA degradation ([Fe(III)] = 50 µM, [Vc] = 50 µM, $[H_2O_2]$ = 50 µM).

The pKa value of the BPA was 9.73 [37]. In the variable pH range in this study (3.0–10.5), BPA was almost kept in the molecular form. When the pH was in alkaline range (≥8.0), an elevated pH level led to the precipitation of Fe^{3+} ions, resulting in the formation of iron precipitation, which would significantly restrict the availability of H_2O_2 activation and Fe(III)/Fe(II) cycling [38]. Meanwhile, H_2O_2 could self-decompose into oxygen and water at higher pH values [39]. Thus, the degradation of the BPA was almost completely inhibited. When the pH was in acid range (≤6.5), iron ions were able to exist in the solution, and the dissolved iron was very important for the H_2O_2 activation. Meanwhile, Vc is a hexosaldehyde acid with strong reducing ability, and the Fe(III) could be reduced to Fe(II) efficiently, especially within acidic conditions. Moreover, Vc can also complex with Fe(II), and in this case the redox potential between Fe(III) and Fe(II) was reduced, which meant Fe(III) was easily reduced to Fe(II) in the presence of Vc [40,41]. The high cycle efficiency of Fe(III)/Fe(II) enhanced H_2O_2 activation and increased BPA degradation ability. However, it was also noted that in a strong acid environment (pH = 3.0), the degradation performance was not very good, which was similar to a previous study [42]. Vc is a diprotic acid, and it can ionize 2 H^+ at different pH values. The $pk_{a1} = 4.25$, and $pk_{a2} = 11.79$ [43]. When the pH is lower than 4.25, Vc has a molecular morphology, which might not be conducive to forming the complex with iron and suppresses the activation of H_2O_2. In general, both strong acidic and alkaline environments were favorable for BPA degradation. The optimal pH was 6.5.

3.4. Identification of ROS

To explore the types of ROS in the improved Fenton-like system, three groups of quenching experiments were performed. The experimental results in Figure 4 show BPA degradation with different scavengers. Isopropanol was used to quench $^{\bullet}OH$ ($k = 1.9 \times 10^9$ M^{-1} s^{-1}) [44]. In the presence of isopropanol with a concentration (5.0 mM) ~600 times higher than that of BPA (8.8 μM), it could be approximated considering that isopropanol competitively consumed all the free radicals. There was only 6% BPA degradation with isopropanol. Thus, BPA degradation was almost completely suppressed after the addition of isopropanol, which meant $^{\bullet}OH$ was the main ROS in the system, about 92.7% of all the ROS.

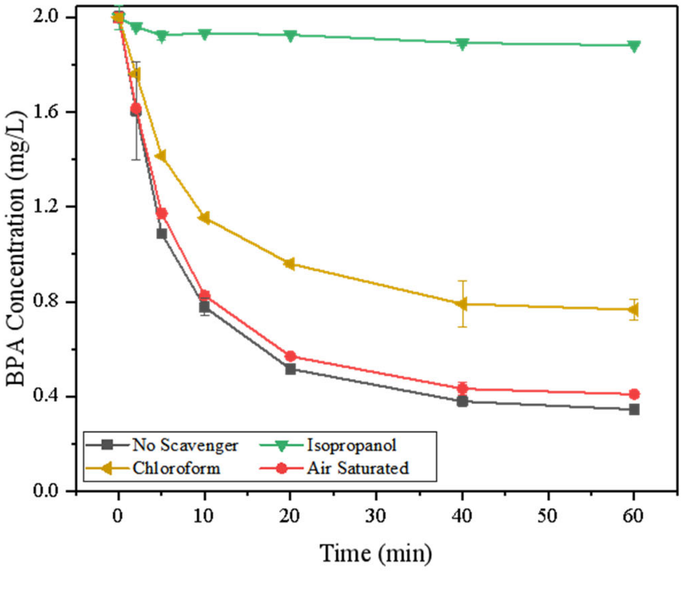


Figure 4. Effect of different ROS on BPA degradation ([Fe(III)] = 50 μM, [Vc] = 25 μM, [H_2O_2] = 50 μM, [isopropanol] = 5 mM, [chloroform] = 5 mM).

Aeration was conducted to achieve an air-saturation state to examine the impact of oxygen on BPA degradation. However, there was almost no effect on BPA degradation with aeration. This means that O_2 and $O_2^{\bullet -}$ had little contribution to BPA degradation, about 7.3% of all the ROS. With the addition of chloroform, BPA degradation was obviously inhibited, nearly 20%. The prevailing hypothesis was that the quenching process of chloroform involved competition for available electrons [45], therefore disrupting the electron transfer pathway. Chloroform is usually considered as the quencher of $O_2^{\bullet -}$ ($k = 1 \times 10^9$ M^{-1} s^{-1}) [46] because it can capture electrons to prevent the formation of $O_2^{\bullet -}$ between O_2 and electrons. However, the decreased 20% BPA degradation in this study was mainly due to the electron trapping from Vc to Fe(III). In the presence of chloroform, the electron transfer of Vc was inhibited, which restricted the generation of Fe(II), thereby leading to the reduced production of $^{\bullet}$OH. Consequently, the introduction of chloroform into the system resulted in the disruption of a portion of the electron transfer pathway, hence diminishing the formation of $^{\bullet}$OH and degradation of BPA.

3.5. Reaction Mechanism

The Vc was used to modify the Fenton-like reaction in this study. Vc reacted with Fe(III) and transformed it into Fe(II). Fe(II) could efficiently react with H_2O_2 in the traditional Fenton reaction to produce $^{\bullet}$OH and Fe(III) (Equation (3)), therefore triggering a chain reaction that generated other radicals, which further degraded the organic pollutant BPA. The added reagent Vc can promote the circulation of iron ions and improve the efficiency of radical generation. Thus, BPA was efficiently degraded in the Vc/Fe(III)/H_2O_2 system by the attack of oxidative radicals, and byproducts were formed. Finally, the BPA byproducts subsequently decomposed into CO_2 and H_2O with a further prolonged oxidation reaction. The reaction mechanism is depicted in Figure 5.

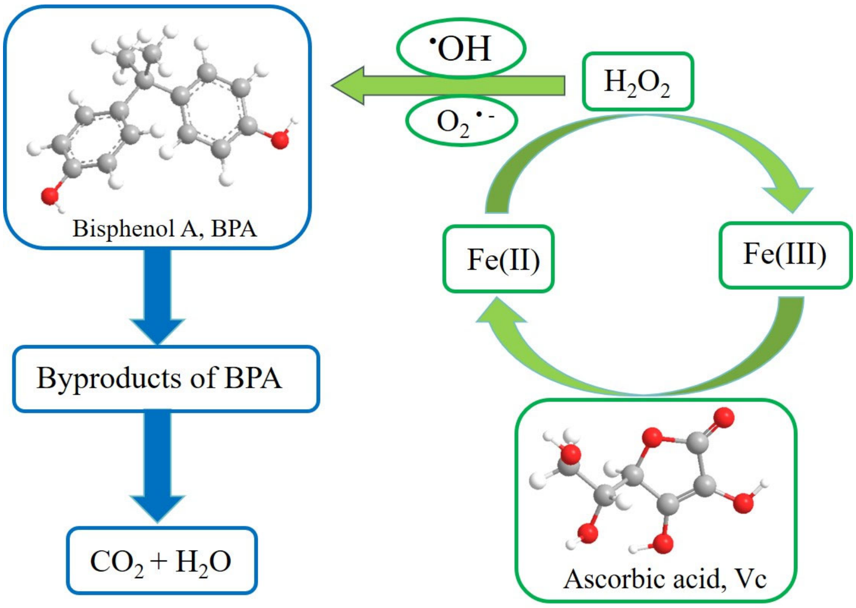


Figure 5. The reaction mechanism of Vc improved the Fenton-like reaction.

3.6. BPA Degradation Pathways and Product Toxicity Assessment

The degradation byproducts of BPA were analyzed by LC-MS, and 11 possible byproducts were identified. The possible structures are listed in Table S1. The BPA was degraded in two main pathways. Firstly, due to the electron absorption of the phenol hydroxyl group and the conjugation of the two benzene rings, $^{\bullet}$OH is more likely to attack the ortho-position and para-position of the phenol hydroxyl group, and in a few cases attack the intermediate position [5]. Upon attacking the ortho-site of the phenol hydroxyl group, the benzene ring underwent oxidation to produce a polyphenolic hydroxyl group (P1), hence initiating the breakdown pathway a. Meanwhile, p-isopropyl phenol (P2) was produced with C-C bond cleavage (pathway b). With the addition of the hydroxyl group (-OH) to the hydrocarbon chain, P3 was formed through pathway b1. P4 was also formed with the further oxidation and breaking of P2 and P1. Subsequently, the double bonds of P4 were oxidized again to produce hydroxyl (-OH) and carbonyl (-C=O) products [47], including P5, P6, P7, and P8. The unsaturated carbon oxygen double bonds (C=O) of P7 and P8 were easily attacked. Hydroquinone (P9) and phenol (P10) were produced, which were then easily further oxidized to benzoquinone (P11) with their strong reducibility. Ultimately, the benzene ring was opened, and it gradually degraded to chain hydrocarbon, finally producing CO_2 and H_2O as demonstrated in Figure 6.

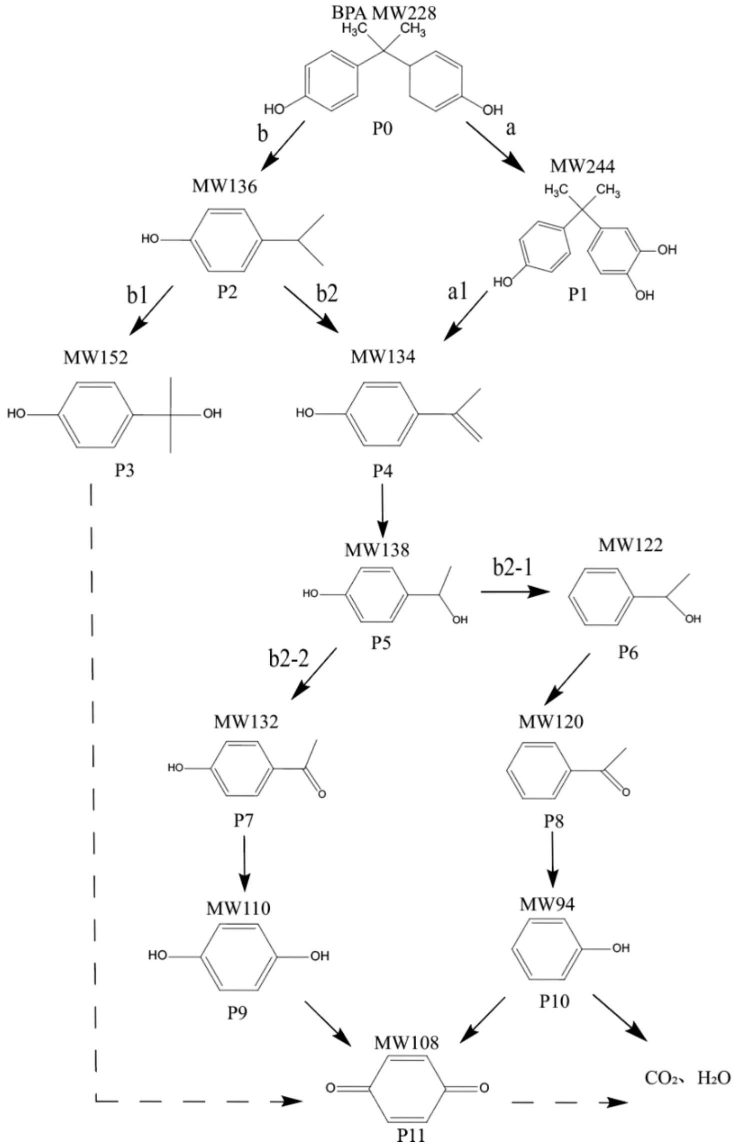


Figure 6. BPA degradation pathway.

The toxicities of the possible byproducts were evaluated by ECOSAR, and the LC50/EC50 (lethal concentrations 50%/effective concentrations 50%) of fish, daphnia, and green algae are shown in Table 1. The low LC50/EC50 means high toxicity. According to the Globally Harmonized System of Classification and Labelling of Chemicals, acute toxicity is divided into four levels: highly toxic (LC50/EC50 $\leq$ 1 mg/L), toxic ($1 <$ LC50/EC50 $\leq$ 10 mg/L), harmful ($10 <$ LC50/EC50 $\leq$ 100 mg/L), and harmless (LC50/EC50 $>$ 100 mg/L) [48–50]. As shown in Table 1, the LC50/EC50 of BPA is 6.27 mg/L for fish, 4.15 mg/L for daphnid, and 5.78 mg/L for green algae, which means BPA is toxic. However, the LC50/EC50 of byproducts clearly show exponential growth to the level of hundreds mg/L with 60 min oxidation. Therefore, it can be concluded that most of the byproducts in the BPA degradation process are in a harmless state. So, the modified Fenton-like system in this study is efficient for the harmless treatment of wastewater.

Table 1. Toxicity of products during the degradation of BPA.

Compounds	Concentration (mg/L)		
	Fish (96h-LC50)	**Daphnid (48h-LC50)**	**Green Algae (96h-EC50)**
BPA (P0)	6.27	4.15	5.78
MW244 (P1)	18.1	11.5	13.3
MW136 (P2)	15.1	10.37	10.1
MW152 (P3)	377	204	124
MW134 (P4)	15.1	9.35	10.1
MW138 (P5)	874	453	232
MW122 (P6)	286	155	105.2
MW132 (P7)	593	313	171
MW120 (P8)	194	107	70.2
MW110 (P9)	669	347	179
MW94 (P10)	212	115	71.1
MW108 (P11)	3330	1610	614

Harmless > 100 mg/L; harmful: 10–100 mg/L; toxic: 1–10 mg/L; very toxic: <1 mg/L.

4. Conclusions

This study presents the verification of BPA degradation by a Vc-modified Fenton-like system via improved reaction conditions, and it analyzed the byproducts. The addition of Vc increased the BPA degradation rate at 60 min from 28.1% in the Fe(III)/H_2O_2 system to 83.5% in the Vc/Fe(III)/H_2O_2 system. The effects of different pH values and Vc and Fe(III) concentrations were investigated. The optimal reaction conditions were the 1:1 Vc/Fe(III) ratio with pH = 6.5. The oxidative species that worked for BPA degradation were identified, and $^\bullet$OH was the main oxidative species that contributed to BPA degradation. Through the analysis of the degradation byproducts of BPA, the degradation pathway and toxicity of byproducts were deduced. The organic pollutant was oxidated to small molecules and finally mineralized. The toxicity assessment results show that toxic BPA was transformed to a harmless state after oxidation in the modified Fenton-like system. They show that Vc has positive impact on the Fenton-like system, and there is great application potential for the modified system in organic pollutant removal.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr12112588/s1, Figure S1: The chemical formula of ascorbic acid and 3D structure diagram; Figure S2: The TOC degradation in Vc/Fe(III)/H_2O_2 system; Table S1: Possible structure of BPA degradation intermediates.

Author Contributions: Methodology, Y.W.; software, J.G. (Jiawei Gu); investigation, Y.W.; data curation, Z.F.; writing—original draft preparation, J.G. (Jiawei Gu) and Y.S.; writing—review and editing, Y.W.; supervision, J.G. (Jie Guan); funding acquisition, Y.W. and J.G. (Jie Guan). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Fundamental Research Funds of Shanghai Polytechnic University (EGD23QD04) and the Open Project Program of Shanghai Innovation Center of Reverse Logistics and Supply Chain.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Céspedes, R.; Petrovic, M.; Raldúa, D.; Saura, Ú.; Piña, B.; Lacorte, S.; Viana, P.; Barceló, D. Integrated procedure for determination of endocrine-disrupting activity in surface waters and sediments by use of the biological technique recombinant yeast assay and chemical analysis by LC-ESI-MS. *Anal. Bioanal. Chem.* **2004**, *378*, 697–708. [PubMed]
2. Mohapatra, D.P.; Brar, S.K.; Tyagi, R.D.; Surampalli, R.Y. Physico-chemical pre-treatment and biotransformation of wastewater and wastewater sludge—Fate of bisphenol A. *Chemosphere* **2010**, *78*, 923–941. [CrossRef] [PubMed]

3. Malaisé, Y.; Ménard, S.; Cartier, C.; Lencina, C.; Sommer, C.; Gaultier, E.; Houdeau, E.; Guzylack-Piriou, L. Consequences of bisphenol a perinatal exposure on immune responses and gut barrier function in mice. *Arch. Toxicol.* **2018**, *92*, 347–358. [CrossRef]
4. Pivonello, C.; Muscogiuri, G.; Nardone, A.; Garifalos, F.; Provvisiero, D.P.; Verde, N.; de Angelis, C.; Conforti, A.; Piscopo, M.; Auriemma, R.S.; et al. Bisphenol A: An emerging threat to female fertility. *Reprod. Biol. Endocrinol.* **2020**, *18*, 22. [CrossRef]
5. Wu, W.; Li, M.; Liu, A.; Wu, C.; Li, D.; Deng, Q.; Zhang, B.; Du, J.; Gao, X.; Hong, Y. Bisphenol A and the Risk of Obesity a Systematic Review with Meta-Analysis of the Epidemiological Evidence. *Dose Response* **2020**, *18*, 1559325820916949. [CrossRef]
6. Luo, D.; Tang, X.; Wang, Y.; Ying, S.; He, Y.; Lin, H.; Khoso, P.A.; Li, S. Selenium deficiency exacerbated Bisphenol A-induced intestinal toxicity in chickens: Apoptosis and cell cycle arrest mediated by ROS/P53. *Sci. Total Environ.* **2024**, *913*, 169730. [CrossRef]
7. Gorini, F.; Bustaffa, E.; Coi, A.; Iervasi, G.; Bianchi, F. Bisphenols as environmental triggers of thyroid dysfunction: Clues and evidence. *Int. J. Environ. Res. Public Health* **2020**, *17*, 2654. [CrossRef] [PubMed]
8. Vethaak, A.D.; Lahr, J.; Schrap, S.M.; Belfroid, A.C.; Rijs, G.B.; Gerritsen, A.; Boer, J.; Bulder, A.S.; Grinwis, G.C.M.; Kuiper, R.V.; et al. An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of the Netherlands. *Chemosphere* **2005**, *59*, 511–524. [CrossRef]
9. Zimmers, S.M.; Browne, E.P.; O'keefe, P.W.; Anderton, D.L.; Kramer, L.; Rechhow, D.A.; Arcaro, K.F. Determination of free Bisphenol A (BPA) concentrations in breast milk of U.S. women using a sensitive LC/MS/MS method. *J. Chemosphere* **2014**, *104*, 237–243. [CrossRef]
10. Wang, X.; Li, M.; Wu, M.; Shi, Y.; Yang, J.; Shan, J.; Liu, L. Simultaneous Determination of Bisphenol A and Bisphenol S Using Multi-Walled Carbon Nanotubes Modified Electrode. *Int. J. Electrochem. Sci.* **2018**, *13*, 11906–11922. [CrossRef]
11. Salgueiro-Gonzalez, N.; Castiglioni, S.; Zuccato, E.; Turnes-Carou, I.; Lopez-Mahia, P.; Muniategui-Lorenzo, S. Recent advances in analytical methods for the determination of 4-alkylphenols and bisphenol A in solid environmental matrices: Acritical review. *Anal. Chim. Acta* **2018**, *1024*, 39–51. [CrossRef] [PubMed]
12. Huang, R.; Liu, Z.; Yin, H.; Dang, Z.; Wu, P.; Zhu, N.; Lin, Z. Bisphenol A concentrations in human urine, human intakes across six continents, and annual trends of average intakes in adult and child populations worldwide: A thorough literature review. *Sci. Total Environ.* **2018**, *626*, 971–981. [CrossRef] [PubMed]
13. Tanatti, N.P.; Balkaya, E.; Sengil, I.A. Kinetic and statistical analysis of Bisphenol A in wastewaters by ozonation and electrooxidation-ozonation processes. *Desalination Water Treat.* **2020**, *204*, 429–437. [CrossRef]
14. Porcar-Santos, O.; Cruz-Alcalde, A.; Sans, C. Aqueous oxidation of bisphenol analogues by ozone: Relevance of substituents on reactivity. *J. Environ. Chem. Eng.* **2023**, *11*, 110849. [CrossRef]
15. Porcar-Santos, O.; Cruz-Alcalde, A.; Bayarri, B.; Sans, C. Reactions of bisphenol F and bisphenol S with ozone and hydroxyl radical: Kinetics and mechanisms. *Sci. Total Environ.* **2022**, *846*, 157173. [CrossRef]
16. Reddy, P.V.L.; Kim, K.H.; Kavitha, B.; Kumar, V.; Raza, N.; Kalagara, S. Photocatalytic degradation of bisphenol A in aqueous media: A review. *J. Environ. Manag.* **2018**, *213*, 189–205. [CrossRef]
17. Guo, J.; Sun, H.; Yuan, X.; Jiang, L.; Wu, Z.; Yu, H.; Tang, N.; Yu, M.; Yan, M.; Liang, J. Photocatalytic degradation of persistent organic pollutants by Co-Cl bond reinforced CoAl-LDH/$Bi_{12}O_{17}C_{l2}$ photocatalyst: Mechanism and application prospect evaluation. *Water Res.* **2022**, *219*, 118558. [CrossRef] [PubMed]
18. Huang, Z.; Yu, H.; Wang, L.; Liu, X.; Ren, S.; Liu, J. Ferrocene-modified Uio-66-NH2 hybrids with g-C_3N_4 as enhanced photocatalysts for degradation of bisphenol A under visible light. *J. Hazard. Mater.* **2022**, *436*, 129052. [CrossRef]
19. Ji, M.; Xia, J.; Di, J.; Liu, Y.; Chen, R.; Chen, Z.; Yin, S.; Li, H. Graphene-like boron nitride induced accelerated charge transfer for boosting the photocatalytic behavior of $Bi_4O_5I_2$ towards bisphenol a removal. *Chem. Eng. J.* **2018**, *331*, 355–363. [CrossRef]
20. Tong, T.; Li, R.; Chen, J.; Ke, Y.; Xie, S. Bisphenol A biodegradation differs between mudflat and mangrove forest sediments. *Chemosphere* **2021**, *270*, 128664. [CrossRef]
21. Frankowski, R.; Zgola-Grzeskowiak, A.; Smulek, W.; Grzeskowiak, T. Removal of Bisphenol A and Its Potential Substitutes by Biodegradation. *Appl. Biochem. Biotechnol.* **2020**, *191*, 1100–1110. [CrossRef] [PubMed]
22. Jiang, J.; Gao, J.; Niu, S.; Wang, X.; Li, T.; Liu, S.; Lin, Y.; Xie, T.; Dong, S. Comparing dark- and photo-Fenton-like degradation of emerging pollutant over photo-switchable Bi_2WO_6/$CuFe_2O_4$: Investigation on dominant reactive oxidation species. *J. Environ. Sci.* **2021**, *106*, 147–160. [CrossRef] [PubMed]
23. Zhu, J.; Zhu, M.; Peng, J. Fenton-like degradation of bisphenol A by Fe_3O_4 rhombic dodecahedrons. *New J. Chem.* **2023**, *47*, 10857–10865. [CrossRef]
24. Aguiar, A.; Ferraz, A.; Contreras, D.; Rodríguez, J. Mechanism and applications of the Fenton reaction assisted by iron-reducing phenolic compounds. *Quim. Nova* **2007**, *30*, 623–628. [CrossRef]
25. Xiao, J.; Wang, C.; Liu, H. Fenton-like degradation of dimethyl phthalate enhanced by quinone species. *J. Hazard. Mater.* **2020**, *382*, 121007. [CrossRef] [PubMed]
26. Chen, L.; Ma, J.; Li, X.; Zang, J.; Fang, J.; Guan, Y.; Xie, P. Strong enhancement on Fenton oxidation by addition of hydroxylamine to accelerate the ferric and ferrous iron cycles. *Environ. Sci. Technol.* **2011**, *45*, 3925–3930. [CrossRef] [PubMed]
27. Borsook, H.; Keighley, G. Oxidation-Reduction Potential of Ascorbic Acid (Vitamin C). *J. Proc. Natl. Acad. Sci. USA* **1933**, *19*, 875–878. [CrossRef] [PubMed]
28. Buxton, G.V.; Greenstock, C.L.; Helman, P.; Ross, A.B. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O− in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886. [CrossRef]

29. Hart, E.J.; Gordon, S.; Thomas, J.K. Rate Constants of Hydrated Electron Reactions with Organic Compounds1. *J. Phys. Chem.* **1964**, *68*, 1271–1274. [CrossRef]
30. Webb, J.D.; Czanderna, A.W. End-Group Effects on the Wavelength Dependence of Laser-Induced Photodegradation in Bisphenol-A Polycarbonate. *J. Macromol.* **1986**, *19*, 2810–2825. [CrossRef]
31. Zhang, Q.; Wang, W.; Li, J.; Chang, Y.; Wang, Y.; Zhang, J.; Zhang, B.; Gao, X. Simultaneous determination of catechin, epicatechin and epicatechin gallate in rat plasma by LC-ESI-MS/MS for pharmacokinetic studies after oral administration of Cynomorium songaricum extract. *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.* **2012**, *880*, 168–171. [CrossRef] [PubMed]
32. Bautista, P.; Mohedane, A.F.; Casas, A.; Zazo, J.A. An overview of the application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biot.* **2008**, *83*, 1323–1338. [CrossRef]
33. Lynch, S.R.; Stoltzfus, R.J. Iron and Ascorbic Acid: Proposed Fortification Levels and Recommended Iron Compounds. *J. Nutr.* **2003**, *133*, 2978S–2984S. [CrossRef] [PubMed]
34. Sun, T.L.; Zhu, G.; He, H.; Huang, B.; Xiong, Z.; Lai, B. Research prospect of single-atom catalysts for Fenton-like water treatment. *J. Appl. Chem.* **2019**, *41*, 217–229.
35. Molla, M.A.I.; Furukawa, M.; Tateishi, I.; Katsumata, H.; Kaneco, S. Mineralization of Diazinon with nanosized-photocatalyst TiO_2 in water under sunlight irradiation: Optimization of degradation conditions and reaction pathway. *Environ. Technol.* **2020**, *41*, 3524–3533. [CrossRef]
36. Schöneshöfer, M. Pulsradiolytische Untersuchung zur Oxidation der Ascorbinsäure durch OH-Radikale und Halogen-Radikal-Komplexe in wäßriger Lösung/Pulse Radiolysis Studies of the Oxidation of Ascorbic Acid by OH-radicals and Halide Radical Anion Complexes in Aqueous Solution. *J. Zeitschrift für Naturforschung B.* **2014**, *27*, 649–659.
37. Choi, Y.J.; Lee, L.S. Partitioning Behavior of Bisphenol Alternatives BPS and BPAF Compared to BPA. *Environ. Sci. Technol.* **2017**, *51*, 3725–3732. [CrossRef]
38. Gu, T.; Dong, H.; Lu, T.; Han, L.; Zhang, Y. Fluoride ion accelerating degradation of organic pollutants by Cu(II)-catalyzed Fenton-like reaction at wide pH range. *J. Hazard. Mater.* **2019**, *377*, 365–370. [CrossRef] [PubMed]
39. Han, X.L.; Wang, N.N.; Zhang, W.; Liu, X.D.; Yu, Q.; Lei, J.Y.; Zhou, L.; Xiu, G.L. Ascorbic acid promoted sulfamethoxazole degradation in MIL-88B(Fe)/H_2O_2 Fenton-like system. *J. Environ. Chem. Eng.* **2023**, *11*, 109144. [CrossRef]
40. Yuan, Y.; Shi, J.X.; Xie, W.S.; Wang, G.W.; Wang, Y.; Tang, J.; Lu, H.J. Enhancing the Fenton-like degradation of organic contaminants with silicate-iron in aquifer media by ascorbic acid. *Colloid. Surface. Asp.* **2024**, *685*, 133307. [CrossRef]
41. Sun, H.W.; Xie, G.H.; He, D.; Zhang, L.Z. Ascorbic acid promoted magnetite Fenton degradation of alachlor: Mechanistic insights and kinetic modeling. *Appl. Catal. B Environ.* **2020**, *267*, 118383. [CrossRef]
42. Wu, T.T.; Wu, C.H.; Xiang, Y.C.; Huang, J.Q.; Luan, L.L.; Chen, S.G.; Hu, Y.Q. Kinetics and mechanism of degradation of chitosan by combining sonolysis with H_2O_2/ascorbic acid. *RSC Adv.* **2016**, *6*, 76280–76287. [CrossRef]
43. Han, C.; Yu, H.; Ma, L. Degradation of atrazine in water by ascorbic acid activated persulfate. *Environ. Sci. Technol.* **2021**, *34*, 33–37.
44. Cheng, Y.; Zhang, G.; Liu, H.; Qu, J. Confining free radicals in close vicinity to contaminants enables ultrafast Fenton-like processes in the interspacing of MoS_2 membranes. *Angew. Chem. Int. Ed.* **2019**, *58*, 8134–8138. [CrossRef]
45. Ivanov, V.L.; Lyashkevich, S.Y. Effect of Electron Scavengers on the Chain Reaction of Sulfo-Group Substitution for Bromine in 1-Bromo-2-hydroxynaphthalene Photosensitized with Tris (2,2′-bipyridyl) ruthenium(II). *J. High Energy Chem.* **2005**, *39*, 304–308. [CrossRef]
46. Fang, Z.; Zhao, J.; Li, Y.; Wang, Y.; Qiu, T.; Wu, Y.; Dong, W.; Mailhot, G. Improving Fenton-like system with Catechin, an environmental-friendly polyphenol: Effects and mechanism. *Chem. Eng. J.* **2021**, *426*, 127946. [CrossRef]
47. Dorn, P.B.; Chou, C.S.; Gentempo, J.J. Degradation of bisphenol A in natural waters. *Chemosphere* **1987**, *16*, 1501–1507. [CrossRef]
48. Lu, Z.; Fan, Y.; Chen, J.; Yang, J.; Wu, C.; Sun, Q. Prediction and toxicity assessment of halogenated flame retardants by ultraviolet/hypochlorous acid system based on Gaussian and ECOSAR models. *J. Environ. Chem.* **2024**, *43*, 82–91.
49. Chen, J.; Fan, Y.; Yang, J.; Cai, K.; Zheng, Y.; Wang, F.; Sun, Q. Degradation Pathway and Toxicity prediction of nitrogen and phosphorus flame retardants based on Guassian, Multiwfn and ECOSAR in UV/PDS system. *J. Environ. Sci.* **2022**, *12*, 39–48.
50. Tarko, L.; Putz, M.V.; Ionascu, C.; Putz, A.M. QSTR studies regarding the ECOSAR toxicity of benzene-carboxylic acid′ esters to fathead minnow fish (*Pimephales promelas*). *Curr. Comput. Aided Drug Des.* **2014**, *10*, 99–106. [CrossRef]