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The Coupling Use of Weak Magnetic Field and $\text{Fe}^0/\text{H}_2\text{O}_2$ Process for Bisphenol a Abatement: Influence of Reaction Conditions and Mechanisms

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Abstract: The coupling use of the heterogeneous Fenton-like process (zero-valent iron (Fe^0)/ H_2O_2) and weak magnetic field (WMF) for bisphenol A (BPA) abatement was systematically investigated in this study. Though both the $\text{Fe}^0/\text{H}_2\text{O}_2$ and WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ processes are sensitive to pH, WMF remarkably enhanced BPA removal under the pH range of 3.0–6.0 by 0.5–9.5 times. The characterization of Fe^0 confirmed the role of WMF in promoting the corrosion of Fe^0 . Radicals, rather than Fe intermediates, were responsible for BPA degradation. Due to the presence of Cl^- as the background ions and its reactivity towards $\text{HO}^\bullet$, reactive chlorine species (RCS, i.e., $\text{Cl}^\bullet$ and $\text{Cl}_2^{\bullet-}$) were produced and considerably contributed to BPA degradation. In addition, ~37% and 54% of degraded BPA was ascribed to RCS in the presence of 2 and 100 mM of Cl^- , respectively. However, 1.9 mg/L of ClO_3^- was detected in the presence of 2 mM of Cl^- in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process. HCO_3^- could diminish ClO_3^- generation significantly through transforming RCS. The concentration of ClO_3^- decreased by 74% and 82% with dosing 1 and 10 mM HCO_3^- , respectively. The results of this study suggest that the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process is a promising approach for BPA removal.

Keywords: bisphenol A; zero-valent iron; hydrogen peroxide; weak magnetic field; chloride

1. Introduction

Bisphenol A (BPA) is one of the most commonly used chemicals, especially in the industry of polycarbonate plastics and epoxy resins, with annual global consumption of ~4.6 million tons [1–3]. Consequently, human exposure to BPA becomes inevitable. As an endocrine disruptor, BPA can mimic the body's hormones and disrupt normal cell function [4–7]. More than 100 studies have demonstrated the negative effects of BPA on structural and neurochemical changes throughout the brain associated with behavioral changes. Worse, these effects may exist throughout the fetal period. Due to incomplete removal at the outlet of sewage treatment plants, BPA was widely detected in surface water, posing a huge challenge to drinking water treatment [8]. Drinking water has become one of the major routes of human exposure to BPA [8]. Liu et al. [3] demonstrated that the distribution of BPA in surface water is related to the development characteristics of industrial areas. The reported maximum concentration of BPA reached up to 12 $\mu\text{g}/\text{L}$ in stream water [9], which seriously threatened human health. In drinking water in Italy

and Malaysia, BPA levels were reportedly between 17 to 56 ng/L and 3.5 to 59.8 ng/L, respectively [10]. Considering the possible adverse health effects of low-dose BPA exposure, many countries/places have set up relevant standards. The European Food Safety Authority has set a tolerable daily intake of BPA at 0.05 mg/kg body weight [10]. BPA removal is becoming essential in waste water and drinking water treatment.

Various chemical oxidation processes can be applied to control BPA in water treatment. Ozonation is effective for BPA removal with second-order rate constants of $1.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for BPA and $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for dissociated BPA [11]. However, the byproducts of BPA oxidation by ozone may play the role of endocrine disruptors [12]. In addition, ozonation suffers the potential formation of bromate when bromide is co-present in water. Permanganate as an environmentally friendly oxidant has been shown to remove BPA, however it is less effective when compared with ozone. The second-order rate constants of permanganate oxidation are 45 and $6.09 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for BPA and BPA^- , respectively [13]. Ferrate is a known powerful oxidant and its redox potentials are 2.20 and 0.72 V in acidic and basic media, respectively [14]. The second-order rate constants between HFeO_4^- and BPA/ BPA^- were reported to be $8.2 \times 10^2/0.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. However, ferrate is unstable and tends to decompose which limits its field treatment application and storage. Owing to the low cost, chlorine is widely used in water treatment, mostly as disinfectant. Chlorine can react with organics containing electron-rich moieties, such as BPA [15]. Unfortunately, various chlorinated byproducts were detected during chlorination of BPA, resulting in a significant increase in the toxicity of the treated sample.

Compared to the above technologies, one process commonly practiced and proven both effective and economical for BPA abatement is the Fenton reaction [8,16]. In the traditional Fenton process, aqueous ferrous ions (Fe^{2+}) are oxidized by H_2O_2 to Fe^{3+} oxides under acidic conditions along with the generation of $\text{HO}^\bullet$, the highly reactive species with $E^0 = 1.9 - 2.7 \text{ V}$ (versus the normal hydrogen electrode) (Equation (1)) [17,18]. However, the formed insoluble Fe^{3+} oxides are unreactive to H_2O_2 , resulting in the accumulation of iron sludge and restrained cyclic utilization of iron [19]. This dilemma commonly exists in the advanced oxidation processes (AOPs) involving Fe^{2+} [20]. Thus, many efforts were made to keep the existence of Fe^{2+} persistently through sustainable Fe^{2+} release and efficient iron circulation from Fe^{3+} to Fe^{2+} .

As an alternative of Fe^{2+} , zero-valent iron (Fe^0) received a lot of attention for use in heterogeneous Fenton processes recently [21]. In the $\text{Fe}^0/\text{H}_2\text{O}_2$ process, Fe^0 is firstly oxidized to Fe^{2+} through oxygen absorption corrosion and hydrogen evolutional corrosion (Equations (2) and (3)). Similar to the traditional Fenton process, the generated Fe^{2+} is converted to Fe^{3+} by H_2O_2 with the generation of $\text{HO}^\bullet$. In the meantime, the Fe^{3+} reacts with Fe^0 and is transformed to Fe^{2+} . Thus, the use of Fe^0 , instead of Fe^{2+} salts, in the Fenton process achieved a continuous supply of dissolved Fe^{2+} . Moreover, the increase of salinity induced by the adding Fe^{2+} salts can be avoided with Fe^0 as the source of Fe^{2+} [22].

However, the commercial iron particles are generally covered by a passive layer of iron oxides which forms during the manufacturing process under high temperature (700–1200 °C), resulting in the low reactivity of Fe^0 towards H_2O_2 [23,24]. In addition, the oxidation of Fe^{2+} is faster than the reduction of Fe^{3+} in the $\text{Fe}^0/\text{H}_2\text{O}_2$ system [19]. As the reaction progressed, a thicker layer of iron oxides formed on the surface of iron particles which impedes further erosion of Fe^0 [23]. Consequently, the performance of the $\text{Fe}^0/\text{H}_2\text{O}_2$ process for pollutant abatement drops over time. In 2014, Guan et al. [23] serendipitously found the depassivation effect of weak magnetic field (WMF) during Fe^0 corrosion. This could be ascribed to the magnetic forces which give rise to convection in the solution and alleviate the accumulation of iron oxides on the Fe^0 surface. Consequently, the corrosion of

Fe^0 was enhanced and the release of Fe^{2+} was promoted. On this account, the efficiency of $\text{Fe}^0/\text{H}_2\text{O}_2$ process in removing pollutants from wastewater is anticipated to be improved by a superimposed WMF.

In this study, the effects of WMF on BPA removal by the $\text{Fe}^0/\text{H}_2\text{O}_2$ process under different reaction conditions were systematically investigated. The optimum reaction condition was pointed out with the 3D-response surface methodology and the degradation mechanism of BPA in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process was illustrated. Previous studies have shown that the reactivity of Fe^0 highly depends on the solution chemistry, especially the coexisting anions [25]. In addition, some widespread anions, such as Cl^- and HCO_3^- , are reactive to radicals (e.g., $\text{HO}^\bullet$) and shift the distribution of reactive species in the AOPs. Thus, multiple roles of anions exist in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process [26] and might be responsible for the performance of the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process for pollutant abatement in real water. Another aim of this study was to disclose the influence of common anions on BPA degradation by the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process and the mechanism behind it.

2. Materials and Methods

2.1. Materials

Hydrogen peroxide (~30%) was offered by Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China), and Fe^0 particles were purchased from Shanghai Haotian Nano Technology Co., Ltd. (Shanghai, China). BPA was offered by Nanjing Dulai Biotechnology Co., Ltd. (Nanjing, China). Methanol was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Phenanthroline was from Chinasun Specialty Products Co., Ltd. (Suzhou, China). Phenol and benzoic acid were from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA). Methyl phenyl sulfoxide (PMSO), methyl phenyl sulfone (PMSO₂), sodium chloride (NaCl), and sodium bicarbonate (NaHCO_3) were obtained from Aladdin Biological Technology Co., Ltd. (Shanghai, China). All chemicals were as received, and all stock solutions were prepared with double distilled water.

2.2. Experimental Procedure

A schematic diagram of the experimental setup is shown in Figure S1. Two pieces of neodymium-iron-boron permanent magnets under the reactor offered the magnetic field. A Teslameter (TD8620, Shanghai Hengtong Magnetic & Electric Technology Co., Ltd. (Shanghai, China)) was employed to detect the magnetic field intensity in the reactor and the maximum was determined to be 20 mT at the bottom.

A glass bottle filled with the 0.5 L solution containing BPA, buffer, background ions, and the constituent(s) of interest was placed in the thermostatic water bath. The temperature was stabilized at 25 °C unless otherwise noted. Fe^0 particles were uniformly dispersed in a solution by continuous mechanical stirring at 400 rpm. Sodium acetate, acetic acid, and 2-(N-morpholino) ethanesulfonic acid (MES) were used to maintain the pH constant at 3.0–4.0, pH = 5.0, and pH = 6.0, respectively. Then, predetermined amounts of H_2O_2 and Fe^0 samples were added simultaneously while the solution was stirred. Samples were periodically withdrawn and filtered with a 0.45 μm membrane, and 10 mM of sodium thiosulfate were employed to quench the reaction. Most of the experiments were performed in duplicates and the data were averaged.

2.3. Chemical Analysis

Concentration of BPA was determined by high performance liquid chromatograph (HPLC, LC-20A, Shimadzu, Kyoto City, Japan). The mobile phase of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture (70/30 *v/v*) was used with a flow rate of 1.0 mL/min. Fe^0 samples were collected by membrane filtration of 0.45 μm after the reaction, then washed with distilled water and freeze-dried. The morphology of the corrosion products of Fe^0 was analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). Oxidation products analysis was performed with gas chromatograph-mass spectrometer (GC-MS, Agilent) technique. The column used was a HP-17 ms quartz capillary column (30 m $\times$ 0.25 mm, 0.25 mm). The

operational conditions of the GC-MS for product detection can be found in the literature [27]. The concentration of chlorate was measured by an ion chromatography system (Dionex Aquion Rfic, Thermo Scientific) equipped with a conductivity detector. The separation was achieved by a high-capacity hydroxide-selective analytical column and 30 mM KOH eluent at a flow rate of 1.2 mL min⁻¹.

3. Results and Discussion

3.1. Influence of WMF on the Removal of BPA by the Fe⁰/H₂O₂ Process at Different pH

Figure S2 shows the time course of BPA oxidation by the Fe⁰/H₂O₂ or WMF-Fe⁰/H₂O₂ process under the pH range of 3.0–6.0. As can be seen, the degradation rate of BPA highly depends on pH. The decrease of the concentration of BPA as the function of time was fitted with pseudo-first-order kinetics. At pH 5.0, the degradation of BPA terminated within the reaction time of this study and we only fitted the data in the period of degradation. The obtained rate constants were shown in Figure 1A. Increase of pH from 3.0 to 6.0 leads to the monotonic decrease of the degradation rate of BPA from 0.33 to 0.0012 min⁻¹ in the Fe⁰/H₂O₂ process and from 0.83 to 0.0021 min⁻¹ in the WMF-Fe⁰/H₂O₂ process, respectively. This can be mainly ascribed to two reasons: On the one hand, low pH increases the solubility of Fe³⁺ and promotes the transformation of Fe³⁺ to Fe²⁺ [19]. On the other hand, decreasing pH accelerates the corrosion of Fe⁰ [23].

Figure 1. (A) Influence of WMF on the pseudo-first-order rate constants of BPA degradation by Fe⁰/H₂O₂ process at different pH. (B) Contribution of different radicals for BPA removal at pH 5.0. Reaction conditions: [BPA]₀ = 0.2 mM, [Fe⁰]₀ = 7 mM, [H₂O₂]₀ = 6 mM, [Cl⁻] = 2 mM.

Under the pH range applied in this study, WMF enhanced BPA removal by the Fe⁰/H₂O₂ process (Figure 1A). As reported by Guan et al. [23], WMF introduces the magnetic field gradient force which leads the transmission of the newly generated Fe²⁺ to the poles of magnetized Fe⁰. In addition, Lorentz force is involved during the movement of the charged species in the presence of magnetic field. These two forces result in the uneven distribution of Fe²⁺ and its oxidation products. Consequently, more reactivity sites on Fe⁰ surface were exposed and the corrosion of Fe⁰ was accelerated. Thus, BPA removal was enhanced. In addition to the degradation rate, WMF also improved the removal capacity of BPA at pH = 5.0 (Figure S2). The incomplete removal of BPA at pH 5.0 suggests the termination of Fe⁰ corrosion and/or H₂O₂ exhaustion.

Negligible BPA could be removed by H₂O₂ alone and Fe⁰ alone (not shown). Thus, the candidates of reactive species responsible for BPA removal can be attributed to radicals and reactive Fe intermediates (e.g., Fe(IV), Fe(V), and Fe(VI)). Methyl phenyl sulfoxide (PMSO) could be transformed to methyl phenyl sulfone (PMSO₂) by Fe intermediates

and is commonly used to determine the involvement of Fe intermediates in the oxidation processes [28]. Comparatively, the oxidation products of PMSO by radicals are hydroxylated and/or polymeric compounds but not PMSO₂. Therefore, PMSO was adopted to differentiate the reactive species in the WMF-Fe⁰/H₂O₂ process. As shown in Figure S3, the concentration of PMSO dropped intermediately without formation of PMSO₂, suggesting that radicals rather than reactive Fe intermediates are responsible for BPA abatement in the WMF-Fe⁰/H₂O₂ process.

It is well known that HO• is produced in the Fenton or Fenton-like system. Due to the addition of Cl[−] as the background ions in the reaction solution, reactive chlorine species (RCS, e.g., Cl• and Cl₂•[−]) might be involved in the WMF-Fe⁰/H₂O₂ process (Table S1). Phenol, benzoic acid, and BPA were used as the probe compounds to quantify HO•, Cl•, and Cl₂•[−], due to their relatively high reactivity towards these radicals (Table S2). Substituting the apparent rate constants and the corresponding second-order-rate constants into Equations (4)–(6), the concentrations of the three radicals could be determined and the results are presented in Table S3.

$$k_{\text{obs,phenol}} = k_{\text{HO}\bullet\text{-phenol}}[\text{HO}\bullet] + k_{\text{Cl}\bullet\text{-phenol}}[\text{Cl}\bullet] + k_{\text{Cl}_2\bullet\text{-phenol}}[\text{Cl}_2\bullet\text{-}] \quad (4)$$

$$k_{\text{obs,benzoic acid}} = k_{\text{HO}\bullet\text{-benzoic acid}}[\text{HO}\bullet] + k_{\text{Cl}\bullet\text{-benzoic acid}}[\text{Cl}\bullet] + k_{\text{Cl}_2\bullet\text{-benzoic acid}}[\text{Cl}_2\bullet\text{-}] \quad (5)$$

$$k_{\text{obs,BPA}} = k_{\text{HO}\bullet\text{-BPA}}[\text{HO}\bullet] + k_{\text{Cl}\bullet\text{-BPA}}[\text{Cl}\bullet] + k_{\text{Cl}_2\bullet\text{-BPA}}[\text{Cl}_2\bullet\text{-}] \quad (6)$$

where $k_{\text{obs,phenol}}$, $k_{\text{obs,benzoic acid}}$, and $k_{\text{obs,BPA}}$ are the apparent rate constants of pollutant oxidation, and $k_{\text{radical-pollutant}}$ is the second-order-rate constant of pollutant oxidation by corresponding radical.

The percentage contributions of HO•, Cl•, and Cl₂•[−] for BPA removal were calculated and are shown in Figure 1B. In total, 3% and 34% of the removed BPA are attributed to the oxidation of Cl• and Cl₂•[−], suggesting the role of RCS cannot be neglected in the AOPs in the presence of Cl[−]. However, previous studies mainly focus on the influence of anions on Fe⁰ corrosion in Fe⁰-based AOPs and the role of RCS in the presence of Cl[−] has often been neglected. To fill the research gap of this issue, the last part of this study was constructed to clarify the impacts of Cl[−] in the WMF-Fe⁰/H₂O₂ process.

3.2. Influence of the Dosages of Fe⁰ and H₂O₂ on BPA Removal in the WMF-Fe⁰/H₂O₂ Process

The influence of reaction conditions (Fe⁰ dosage and H₂O₂ concentration) on the performance of WMF-Fe⁰/H₂O₂ system for BPA removal was analyzed with response surface methodology. A complete 3 × 3 experimental design [29] was performed using Fe⁰ dosage ranging from 3.5 mM to 10.5 mM, and H₂O₂ concentrations from 4 mM to 8 mM. The codes corresponding to the real values of the variables in the factorial design of experiments were displayed in Table S4. The initial pH was adjusted to 5.0 and the initial concentration of BPA was 0.2 mM. The effects of Fe⁰ dosage and H₂O₂ concentrations were ascertained by calculating degradation efficiency of BPA at 5, 10, 20, 30, 40, and 60 min.

Based on the factorial design of experiments, second-order polynomial equations (Equations (7)–(12)) were used to predict the degradation efficiency (1 − C/C₀) of BPA in this study.

$$C_{\text{BPA}(5 \text{ min})} = 0.248 - 0.103X^2 - 0.019Y^2 + 0.013X^2Y + 0.053XY^2 \quad R^2 = 0.94 \quad (7)$$

$$C_{\text{BPA}(10 \text{ min})} = 0.406 - 0.012X - 0.093Y - 0.16X^2 - 0.057Y^2 + 0.111X^2Y + 0.054XY^2 \quad R^2 = 0.99 \quad (8)$$

$$C_{\text{BPA}(20 \text{ min})} = 0.604 + 0.063X - 0.136Y - 0.177X^2 - 0.151Y^2 + 0.111X^2Y \quad R^2 = 0.98 \quad (9)$$

$$C_{\text{BPA}(30 \text{ min})} = 0.726 + 0.13X - 0.13Y + 0.025XY - 0.142X^2 - 0.219Y^2 + 0.1X^2Y \quad R^2 = 0.967 \quad (10)$$

$$C_{\text{BPA}(40 \text{ min})} = 0.698 + 0.108X - 0.119Y + 0.033XY - 0.069X^2 - 0.154Y^2 + 0.01XY^2 \quad R^2 = 0.919 \quad (11)$$

$$C_{BPA(60\text{ min})} = 0.706 + 0.08X - 0.082Y + 0.058XY - 0.05X^2 - 0.136Y^2 + 0.072XY^2 \quad R^2 = 0.915 \quad (12)$$

where C_{BPA} , the removal efficiency of BPA, equals $(C_0 - C)/C_0$.

The experimental results and the calculated data, as well as the standard deviation, are presented in Table S5. As shown in Figure S4, there is an excellent relationship between the experimental data and the predicted values calculated by Equations (7)–(12). The influence of the combination and independent variables is related to the coefficients of the polynomial expressions. The coefficient of Fe^0 dosage term (X) was negative at an initial reaction time (10 min) and conversely became positive along with the reaction. This is because the release of Fe^{2+} from the fresh Fe^0 is fast and a high concentration of Fe^0 and Fe^{2+} decreased the concentration of radicals (Equation (S8) in Table S1). However, with the reaction proceeding, the release rate of Fe^{2+} decreased as part of surface of Fe^0 was covered by Fe oxides. For the H_2O_2 dosage term (Y), the coefficient was negative after 5 min, indicating that the increase of H_2O_2 dosage under the concentration range of this study has an adverse effect on BPA degradation. In addition to the precursor of $HO^\bullet$, H_2O_2 also consumes radicals and depresses the degradation of BPA (Equation (S9) in Table S1). The value of the coefficient decreased firstly followed by an increase. The increased suppression of H_2O_2 at the initial stage was due to the decreased release rate of Fe^{2+} . By the end of the reaction, the adverse effect of H_2O_2 was alleviated due to the decrease of the concentration of H_2O_2 . This suggests that keeping the concentration of H_2O_2 under an appropriate range during the reaction might be an effective method for optimizing the removal of pollutants in the WMF- Fe^0 / H_2O_2 system. The positive coefficients of combined variables (XY, X^2Y , and XY^2) indicate the important role of the synergistic effect of Fe^0 and H_2O_2 . The response curves of degradation efficiency issuing from Equations (7)–(12) are presented in Figure 2. The convex curved surfaces suggest that the optimum dosages of Fe^0 and H_2O_2 for BPA degradation were within the range of the values studied.

Figure 2. 3D response surfaces from Equations (7)–(12).

3.3. Characterization of the Corrosion Production of Fe^0

To explore the corrosion mechanisms of Fe^0 during BPA degradation by the Fenton-like system, the corrosion products of Fe^0 in the absence or presence of WMF were characterized with XRD and SEM. XRD spectra was shown in Figure 3A. The Fe^0 sample before corrosion has diffraction peaks at $2\theta = 45^\circ$, 66° , and 83° , while the corrosion product had new characteristic peaks at $2\theta = 13^\circ$, 28° , and 37° , corresponding to the lepidocrocite. The intensity of the characteristic peaks of lepidocrocite in the WMF- Fe^0 / H_2O_2 process is higher than that in the Fe^0 / H_2O_2 process. In addition, the XRD patterns of magnetite

were also detected in the corrosion product at WMF-Fe⁰/H₂O₂ systems. The significant difference in the crystalline structures of iron oxides should be ascribed to the interference of magnetic field gradient force and Lorentz force [30].

Figure 3. XRD patterns (A) and SEM images (B1–B3) of Fe⁰ particles at different conditions. Reaction conditions: pH = 5.0, [BPA]₀ = 0.2 mM, [Fe⁰]₀ = 7 mM, [H₂O₂]₀ = 6 mM, [Cl[−]] = 2 mM.

The morphologies evolution of Fe⁰ particles was analyzed by monitoring the SEM images, as illustrated in Figure 3(B1–B3). The shape of Fe⁰ particles coarsened slightly in Fe⁰/H₂O₂ systems. However, the surface morphology of Fe⁰ samples collected under WMF irradiation became rough and irregular, and some of the surface of Fe⁰ particles cracked. This might be attributed to the formed iron hydroxide/oxide and the proton (H⁺) dissolution of the Fe_xO_y layer [23]. The different morphologies of the corroded Fe confirmed the promotion of WMF on Fe⁰ corrosion.

3.4. Identification of Intermediate Products and Speculation of Degradation Path

GC-MS was employed to analyze the oxidation intermediates of BPA in the WMF-Fe⁰/H₂O₂ systems at pH 5.0. Five compounds were discriminated with the GC-MS analysis (Figures S5–S9), and the results are shown in Table S6.

The transformation of organics by HO• is primarily via hydrogen atom abstraction from a C–H bond and HO• addition to a C=C double bond [31]. Single electron transfer predominated in the reactions of Cl• and Cl₂•[−] with phenolic compounds. Based on the intermediates listed in Table S6 and the results reported by other researchers [32,33], as well as the oxidation mechanisms of organic pollutants by HO• and RCS, the possible degradation pathway of BPA in WMF-Fe⁰/H₂O₂ systems was speculated, as shown in Figure 4. On the one hand, the radicals attack the C–C bond between the benzene ring and the isopropyl to form some primary oxidation products, such as 3,4-di-tert-butylphenol (DTB) and 4-isopropenylphenol (IPP) [34]. Then, DTB and IPP were converted by radicals into phenol and hydroquinone. The oxhydryl of the opposite position in phenol is reactive to oxidants and easily oxidized to p-benzoquinone. Further, 2-butoxypent-1-ene (BPE) formed through the oxidative ring-opening reaction. On the other hand, the radicals attack the C–O bond between the benzene ring and the hydroxyl radical to form 1,1-diphenyl propylene (DPE). Styrene was generated by degradation of DPE, followed by the formation of maleic acid. The small molecular compounds were eventually mineralized into CO₂ and H₂O.

Figure 4. Possible degradation pathways of BPA in Fenton-like systems. Reaction conditions: $\text{pH} = 5.0$, $[\text{BPA}]_0 = 0.2 \text{ mM}$, $[\text{Fe}^0]_0 = 7 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 6 \text{ mM}$, $[\text{Cl}^-] = 2 \text{ mM}$. Radicals in the figure represent $\text{HO}^\bullet$, $\text{Cl}^\bullet$, and $\text{Cl}_2^{\bullet-}$.

The chlorinated products were not detected during the reaction, suggesting that the addition of Cl^- is not the main reaction mechanisms of BPA degradation. As the chlorinated compounds are thought to be highly toxic, the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ is expected to decrease the toxicity of the BPA solution.

3.5. Influence of Cl^- on BPA Removal and Chlorate Formation in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ Process

Figure 5 shows the influence of Cl^- on BPA degradation in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process. Concentrations of Cl^- of 0.002 and 0.1 M were selected as they are common in fresh water and industrial wastewater [26]. As can be seen, the degradation rate of BPA increased with increasing Cl^- concentration. Phenol and benzoic acid were also added into the reaction solution to analyze the distribution of radicals, and the corresponding degradation kinetics are presented in Figure S10. The concentrations of $\text{HO}^\bullet$, $\text{Cl}^\bullet$, and $\text{Cl}_2^{\bullet-}$ were calculated with competition kinetic methods. As shown in Table S3, the concentration of $\text{HO}^\bullet$ increased with increasing Cl^- dosage despite the transformation of $\text{HO}^\bullet$ by Cl^- into RCS. In addition, the percentage of RCS compared to the total radicals increased with improving Cl^- concentration.

Figure 5. Influence of Cl^- on BPA removal by the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process. Reaction conditions: $[\text{BPA}]_0 = 0.2 \text{ mM}$, $[\text{Fe}^0]_0 = 7 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 6 \text{ mM}$.

Previous studies have demonstrated that the copresence of WMF and Cl^- accelerated the Fe^0 corrosion and Fe^{2+} release [22,25]. As mentioned above, the transmission of Fe^{2+} was driven by the magnetic field gradient force and the Lorentz force. Based on the principle of local electro neutrality, the positive charges must be balanced with negative charges to keep local charge neutrality [25]. Therefore, Cl^- is expected to move together with Fe^{2+} toward the magnetic poles. Therefore reactive sites of Fe^0 centers were exposed in the solution. However, in the system without Cl^- , the accumulation of Fe^{2+} in the magnetic poles inhibited the subsequent transmission of Fe^{2+} due to the electrostatic exclusion. The concentration of Fe^{2+} as the function of time in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process in the presence of different concentrations of Cl^- is shown in Figure S11. Compared with Figure 5, the concentration of Fe^{2+} was quite low during the degradation of BPA and rose after that. Considering the rapid reaction of H_2O_2 with Fe^{2+} (Equation (1)), the rise of Fe^{2+} concentration should be ascribed to the exhaustion of H_2O_2 . In the absence of Cl^- , the concentration of Fe^{2+} was kept low under the reaction time of this study, suggesting that the corrosion rate of Fe^0 was low and H_2O_2 was not completely consumed within the reaction time (Figure S11). Therefore, the increase of the concentration of radicals with increasing Cl^- was mainly due to the enhanced corrosion of Fe^0 .

ClO_3^- is a harmful chemical which potentially forms in the AOPs in the presence of Cl^- [35]. The health reference level of ClO_3^- is $210 \mu\text{g/L}$ according to the U.S. Environmental Protection Agency and the drinking water standards are 200 and $700 \mu\text{g/L}$ in Switzerland and China, respectively. As shown in Figure 6, $\sim 1.9 \text{ mg/L}$ of ClO_3^- was detected during BPA degradation in the WMF- $\text{Fe}^0/\text{H}_2\text{O}_2$ process in the presence of 2 mM Cl^- after a 60 min reaction. According to the study of Hou et al. [35], $\text{Cl}^\bullet$ is the intermediate during the conversion of Cl^- to ClO_3^- . It is supposed that the substance which influences the conversion of $\text{Cl}^\bullet$ may alter the generation of ClO_3^- . HCO_3^- , a common ion present in real water, reacts rapidly with $\text{Cl}^\bullet$ (Equation (S13) in Table S1). In addition, HCO_3^- can also diminish $\text{Cl}^\bullet$ concentrations by consuming $\text{Cl}_2^{\bullet-}$ as there is an equilibrium among $\text{Cl}^\bullet$ and $\text{Cl}_2^{\bullet-}$ (Equations (S16), (S17), and (S19) in Table S1). Thus, HCO_3^- is anticipated to influence the formation of ClO_3^- . Tests were carried out at two HCO_3^- concentrations (1 and 10 mM). As shown in Figure 6, the detected concentration of ClO_3^- decreased to 0.50 and 0.34 mg/L with HCO_3^- dosing of 1 and 10 mM, respectively.

Figure 6. Influence of HCO_3^- on ClO_3^- generation in the WMF/ Fe^0 / H_2O_2 system in the presence of Cl^- . Experimental conditions: $[\text{BPA}]_0 = 0.2 \text{ mM}$, $[\text{Cl}^-] = 2 \text{ mM}$, $[\text{Fe}^0]_0 = 7 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 6 \text{ mM}$.

In addition to RCS, HCO_3^- also reacts with $\text{HO}^\bullet$ and produces $\text{CO}_3^{\bullet-}$ (Equation (S20) in Table S1). Therefore, HCO_3^- changed the distribution of radicals in the WMF- Fe^0 / H_2O_2 process and may influence the degradation of BPA. As shown in Figure S12, the addition of HCO_3^- slightly accelerated the degradation of BPA in the presence of 2 mM Cl^- . The positive effect of HCO_3^- could be explained by two reasons: One reason is that the reactivity of $\text{CO}_3^{\bullet-}$ towards BPA is very high ($k = 2.23 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [36]. The second reason is that the steady state concentrations of $\text{CO}_3^{\bullet-}$ ($\sim 10^{-12} \text{ M}$ level) are generally much higher than $\text{HO}^\bullet$ and $\text{Cl}^\bullet$ [36]. Consequently, the contribution of $\text{CO}_3^{\bullet-}$ for BPA oxidation offset the loss of $\text{HO}^\bullet$ and RCS. The reaction ended after 30 min regardless of whether in the presence or absence of HCO_3^- and the removal efficiencies are similar, suggesting HCO_3^- negligibly influenced the corrosion of Fe^0 .

It should be noted that $\text{CO}_3^{\bullet-}$ is a selective oxidant and tends to oxidation compounds containing electron-donating groups, such as NH_2 - and HO -containing aromatic compounds [37]. The second-order-rate constants of $\text{CO}_3^{\bullet-}$ with organic compounds were reported to range widely from 10^2 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [37]. Thus, the synergy effects of Cl^- and HCO_3^- on AOPs, especially for the degradation kinetics of pollutants, are expected to depend on the structures of compounds which need further study.

4. Conclusions

This study demonstrated the substantial enhancement of WMF on BPA degradation by the Fe^0 / H_2O_2 process. The corrosion rate of Fe^0 decreased significantly with increasing pH which limits the application of the Fe^0 / H_2O_2 process. WMF extended the available pH range of the Fe^0 / H_2O_2 process, saving the dosage of acid for pH adjustment which is the main cost of the Fenton process. Due to the derivational move of Fe^{2+} to the pole of Fe^0 particles under magnetic forces, the Fe^0 will not be covered by the iron oxides, keeping the reactivity of Fe^0 during the reaction. Radicals, rather than reactive Fe intermediate, are responsible for BPA degradation. Cl^- shifts the distribution of radicals from $\text{HO}^\bullet$ towards $\text{Cl}^\bullet$ and $\text{Cl}_2^{\bullet-}$ which are highly reactive towards BPA. However, the undesired ClO_3^- was generated in the presence of Cl^- . HCO_3^- could diminish the formation of ClO_3^- by transforming the radicals into $\text{CO}_3^{\bullet-}$. Due to the high reactivity of $\text{CO}_3^{\bullet-}$ towards BPA, the addition of HCO_3^- also promoted BPA degradation by the WMF- Fe^0 / H_2O_2 / Cl^- system. Thus, the widespread ions, Cl^- and HCO_3^- , in water are beneficial for BPA removal in the Fe^0 / H_2O_2 -WMF process. The WMF used in this study was produced by permanent magnets and did not require energy input. Under WMF, commercial Fe^0 materials could be directly acceptable, without expensive and inconvenient pretreatment methods for removing surface iron oxides. Therefore, applying WMF to enhance the performance of Fe^0 / H_2O_2 process for BPA removal in real water treatment was a promising and environmentally friendly approach.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13131724/s1>, Figure S1: Diagram of experimental device for degradation of BPA; Figure S2: Effect of WMF on the removal of BPA by the $\text{Fe}^0/\text{H}_2\text{O}_2$ process at different pH; Figure S3: Degradation of PMSO and generation of PMSO_2 in the $\text{WMF-Fe}^0/\text{H}_2\text{O}_2$ process; Figure S4: Accuracy of predicted data with respect to the experimental results of BPA removal; Figure S5: GC-MS spectrum of maleic acid; Figure S6: GC-MS spectrum of 4-isopropenylphenol; Figure S7: GC-MS spectrum of 2-butoxypent-1-ene; Figure S8: GC-MS spectrum of 3,4-di-tert-butylphenol; Figure S9: GC-MS spectrum of bisphenol A; Figure S10: Influence of Cl^- on the degradation kinetics of phenol and benzoic acid by the $\text{WMF-Fe}^0/\text{H}_2\text{O}_2$ process; Figure S11: Effect of Cl^- on the concentration of Fe^{2+} in the reaction solution during BPA degradation by the $\text{WMF-Fe}^0/\text{H}_2\text{O}_2$ process; Figure S12: Influence of HCO_3^- on BPA degradation in the $\text{WMF-Fe}^0/\text{H}_2\text{O}_2$ process; Table S1: Principal reactions in the Fenton system in the presence of Cl^- and HCO_3^- ; Table S2: Second-order-rate constants of radicals towards probe compounds; Table S3: Influence of Cl^- on the distribution of radicals in the $\text{WMF-Fe}^0/\text{H}_2\text{O}_2$ process; Table S4: Factorial design of experiments; Table S5: Descriptive statistics of 3D response surface analysis; Table S6: Mass spectra data of intermediate products.

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