**Degradation of bisphenol AF in water by periodate activation with
FeS (mackinawite) and the role of sulfur species in the generation of
sulfate radicals**

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Abstract

The heterogeneous catalyst Mackinawite (FeS) was applied to activate periodate (IO_4^-) to degrade endocrine disruptors bisphenol AF (BPAF). This study investigated the influence of FeS dosage, periodate dosage, BPAF concentration, initial pH value and inorganic ions on BPAF degradation by FeS/ IO_4^- system. The results showed that the BPAF was effectively degraded by FeS/ IO_4^- system. The acidic pH exhibited higher efficiency in BPAF degradation compared with alkaline and neutral conditions. Furthermore, the BPAF degradation was dramatically promoted in the presence of Cl^- and SO_4^{2-} , whereas CO_3^{2-} inhibited BPAF degradation. The radical scavenging tests and EPR indicated that singlet oxygen ($^1\text{O}_2$), superoxide radicals ($\text{O}_2^{\bullet-}$) and $\text{SO}_4^{\bullet-}$ were committed to the degradation of BPAF, among which $\text{O}_2^{\bullet-}$, $^1\text{O}_2$ were predominant radicals. The separate experiments showed that Fe(II) participated in the

activation of periodate. Furthermore, the effects of sulfur species (including the S^{2-} , SO_3^{2-}) on BPAF degradation by FeS/IO_4^- system were studied. The radical quenching tests suggested that S^{2-} and SO_3^{2-} were responsible for producing $SO_4^{\bullet-}$. The findings of this study elucidated an approach for the removal of micro-pollutants in the water environment through heterogeneous activation of periodate by FeS.

Keywords: periodate; Mackinawite (FeS); superoxide radical; singlet oxygen; sulfate radicals; sulfur species

1. Introduction

Bisphenol A (BPA) has been extensively adopted in polycarbonate and epoxy plastics as a type of industrial chemical and more than 4.5 million tons were produced annually [1, 2]. Nevertheless, BPA is considered as an endocrine-disrupting chemical (EDC), adversely affecting the genital system and embryo development of the organism [3-5]. Thus, both the sale and application of BPA have been strictly restricted in a number of countries over the past few decades [6, 7]. In present studies, microbiological biodegradation [8], adsorption [9], photocatalytic [10-12] and chemical oxidation [13, 14] have been reported to have the ability to remove BPA from wastewater, whereas the degradation of BPA analogues has been rarely studied. Bisphenol AF (BPAF) exhibits a similar structure with BPA. It has been extensively adopted as a substitute for BPA in the market. Recent studies suggested that BPAF could also lead to endocrine disruption which exists in a range of environments [15,

16]. BPAF has been widely used in the fields of fluoroelastomers, food processing, optical fiber and electronic equipment [17]. The maximal concentration of BPAF was ascertained with up to 15.3 $\mu\text{g/g}$ in the river, the dry weight was 0.2 $\mu\text{g/g}$ in the sediment, the dry weight concentration of indoor dust reached up to 0.739 $\mu\text{g/g}$, and the well water concentration was 0.3 $\mu\text{g/g}$ [7]. Based on previous studies, traditional biological treatment techniques and photocatalysis cannot effectively degrade BPAF [18]. Therefore, it is meaningful to seek an appropriate treatment method.

Advanced Oxidation Processes (AOPs) can effectively produce highly reactive free radicals to degrade organic matter in solution by chemical oxidation, including the oxidants below: hydrogen peroxide (H_2O_2), ozone (O_3) and peroxymonosulfate (HSO_5^-), peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) and periodate (IO_4^-) [19-22]. Periodate exhibits high oxidation with an oxidation–reduction potential of +1.60 V, whereas its activation is required to produce highly reactive intermediates [23]. The activation of periodate to generate reactive radical intermediates by means of UV (UV/ IO_4^- process) or ultrasonic radiation has been performed to lower the chemical oxygen demand in organic pollutants and industrial wastewater [19, 24-26]. Recently, a study from Bokare et al., alkali–mediated ($\text{pH} > 8$) activation of IO_4^- , singlet oxygen ($^1\text{O}_2$) acted as the dominant radical of $\text{OH}^-/\text{IO}_4^-$ system was produced by spontaneous reaction between periodate and OH^- (Eqs. 1–3) [27]. Meantime, Choi et al. reported that periodate could be activated by being frozen to degrade pollutants [28]. Li et al. used I–GAC as catalyst to activate periodate, thus generating $\text{IO}_3^\bullet$ radicals to degrade AO7 [4, 29]. Additionally, Lee et al. showed that bimetallic $n\text{Fe}^0$ could effectively activate

IO₄[−] to generate IO₃[•] by single electron reduction of nFe⁰–Cu (or Ni), while nFe⁰ without adding Ni or Cu only cause IO₄[−] reduction rather than degradation of pollutants. Thus, periodate must be activated to produce highly active intermediates for removing pollutants [30]. Recently, Mn²⁺–mediated activated periodate to degrade contaminants without external energy, which superoxide radicals were considered as the main reactive species to decompose contaminants [31]. In the above case, periodate has limited ability oxidization by degrading contaminants individually and selectively.

On the whole, transition metals are economically effective activators in the contrast of other substances. Especially, iron–based materials are characterized by relative efficiency, less pollution and lower costs, while the activation of periodate by Fe²⁺ has poor degradation effect on pollutants [31]. Mackinawite (FeS) is formed by biological reduction of sulfate. FeS acts as an innocuous metastable mineral. It is also one of the sulfide minerals with considerable ferrous ions [32, 33]. FeS₂ acts as a source of Fe(II), Fe(II) activated persulfate (S₂O₈^{2−}) to produce SO₄^{•−}, noticeably oxidizing methyl tert–butyl ether (MTBE) [34]. Moreover, [•]OH was produced by H₂O oxidation at the sulfur deficiency site and through two–electron reduction of O₂ on the surface of pyrite in the presence of oxygen [35]. Liu et al. reported that molecular oxygen activation was caused by Fe²⁺ on the surface of syn–FeS₂, accelerating the mutual

conversion between Fe(II) and Fe(III) on the surface to promote more decomposition of H_2O_2 to produce $\cdot\text{OH}$ [36]. As Fan et al. reported, the Fe(II) could be regenerated by the S(-II) species on the surface of FeS, which reduced the decomposition of persulfate (PS) and promoted PCA degradation [37]. The recent studies have found that SO_3^{2-} , S_5^{2-} , S_8^0 and $\text{S}_2\text{O}_3^{2-}$ intermediates were formed by sulfur transformation in the peroxymonosulfate (PMS)–FeS system, in which SO_3^{2-} induced the formation of $\text{SO}_4^{\cdot-}$. The conversion of sulfur should be understood in terms of free radical generation, since the interaction between the sulfur intermediate, activator and oxidant impacts the production of highly reactive radical intermediates and the degradation of pollutants [38]. However, the study on the degradation effect and mechanisms of pollutants in the FeS/ IO_4^- system has not been conducted. Besides, the role of S species has not been investigated comprehensively.

In this work, the process in which FeS activates periodate to degrade BPAF was studied. The major aims of this study include: 1) to evaluate the effects of various operating parameters (including the FeS dosage, periodate dosage, different initial pH values, BPAF concentration and inorganic ions) on BPAF degradation; 2) to determine the major free radicals with the reaction process, the electron paramagnetic resonance (EPR) and free radical quenching experiments were performed; 3) to elucidate the impact of sulfur species (including the S^{2-} and SO_3^{2-}) in periodate activated by FeS, X-ray photoelectron spectroscopy (XPS) and radical quenching experiments were performed.

2. Materials and methods

2.1. Materials

Bisphenol AF ($C_{15}H_{10}F_6O_2$, $\geq 98\%$, BPAF), p-Benzoquinone ($C_6H_4O_2$, $\geq 98\%$, p-BQ), 5,5-Dimethyl-1-pyrrolidine N-oxide ($\geq 97\%$, DPMO), 2,2,6,6-tetramethyl-4-piperidinol ($\geq 97\%$, TEMP) were obtained from Aladdin Industry Co (Shanghai, China). The methanol with the purity of 99.99% and phosphoric acid were purchased from Fisher Chemical (Shanghai, China), adopting for HPLC. Ferrous sulfide ($\geq 70\%$, 100mesh, FeS) and Sodium periodate ($\geq 99.5\%$, $NaIO_4$) were obtained from Sinopharm (Shanghai, China). Other chemical reagents overall purchased from Chengdu Chron Chemicals Co.Ltd were used in the research (including $FeSO_4 \cdot 7H_2O$, $Fe(NO)_3 \cdot 9H_2O$, $Na_2S \cdot 9H_2O$, Na_2SO_3 , NaCl, Na_2SO_4 , $NaNO_3$, Na_2CO_3 , as well as tert-butyl-alcohol (TBA)). The lowest grade for all of the chemicals and solvents in the experiments were analytical level. All aqueous solutions were obtained by a filter system (resistivity ≥ 18.2 M Ω cm, Ulupure, China).

2.2 Experimental procedure

The degradation experiments were conducted at ambient temperature ($24 \pm 4^\circ C$) in 250 mL conical flask. Each 200 mL reaction solution was performed using magnetic agitator for 120 min. BPAF stock solution and periodate stock solution with pre-determined volume were injected into the reaction solution. Subsequently, the predetermined dosage of FeS was added in mixed liquor to initiate the reaction. The baseline condition of the test covered 20 μM of BPAF, 1 mM periodate and 1 g/L FeS. The initial pH of the experiment was 5.5 without being regulated except for

discussing the effect of pH on BPAF degradation. Considering the influence of Cl^- on the system, nitric acid (HNO_3) and sodium hydrate (NaOH) solutions were adopted to regulate the value of pH. During the BPAF degradation reaction, the samples of 4mL were withdrawn from the reactor by 5 mL syringe at designed time intervals and filtered through a 0.22 μm PES. The samples were not degraded within 24 hours. Therefore, no quenching agent was employed for degradation experiment.

NaN_3 and p-Benzoquinone as radical scavenger were applied to verify the primary reactive species in the quenching experiment. To identify the effect of the dissolved oxygen on reaction, air or nitrogen was purged into the deionized water for 30 min before the experiment. Nitrogen was continuously purged to maintain the anoxic condition during the reaction. The tests were overall performed at least twice and error bars represented deviations from the average value.

2.3. Analytical methods

The concentration of BPAF, IO_4^- and IO_3^- within the reaction process were obtained via a high-pressure liquid chromatography (HPLC) system (Waters 2695, USA) which was equipped with a Waters C18 (4.6 mm $\times$ 150 mm, 5mm, USA) column and a UV detector. The absorbance wavelength of BPAF was set at 280 nm and 20 μL reaction liquid was injected. The eluent compositions covered 75% Methyl alcohol and 25% ultrapure water and the speed of mobile phase was set to 1.0 mL/min. Meanwhile, the mobile phase of periodate and iodate were consisted by mixing phosphoric acid with ethanol at a ratio of three to one, and the speed of mobile phase

was set to 0.75 mL/min. The 1,10-phenanthroline method was used to measure the concentration of ferrous ions and total iron ions in the mixed liquor by using UV-vis spectrophotometer (UV4802, Unic instruments Co., Ltd, China) at 510 nm [39]. The degradation rate constant of BPAF was calculated according to the eq. (4):

$$\ln(C_0/C_t)=K_{\text{obs}}t \quad (4)$$

Where C_0 is the BPAF concentration before the reaction, C_t is the BPAF concentration with the change of reaction time in the FeS/periodate system, and k_{obs} represents the pseudo-first-order constant (min^{-1}).

The electron spin resonance (ESR, JEOL JES-FA200) was used to identify radicals by the addition of DMPO or TEMP. The parameters and program settings for the ESR experiment were as follows: microwave frequency at 9.87 GHz, sweep width of 100 G, modulation amplitude at 0.5 G, modulation frequency of 100 kHz, receiver gain of 1×10^4 , sweep time of 40.96 ms, time constant of 20.48 ms and time per single scan of 40 s. In addition, the surface morphology and elemental composition of FeS were observed in Fig. S1. The X-ray photoelectron microscopy (XPS, Thermo Fisher Scientific ESCALAB Xi+) was used to analysis the surface composition of the FeS materials. The instrument has a rotating Al anode that produces 1486.6 eV of AlK alpha x-rays. The scanning electron microscope (SEM, EVO 18) and energy-dispersive X-ray (EDS, SU8010, Hitachi) system was applied to characterize the morphology and elemental composition of the FeS. The crystal texture of FeS was obtained by X-ray diffraction (XRD, PANalytical B.V.). The possible byproducts of BPAF degradation were identified using 3000 UHPLC-Q Exactive with a waters BEH

C18 column (1.7 μ m, 100mm $\times$ 2.1mm). The mineral ization of BPAF was measured by using an elementar vario TOC select analyzer.

3. Results and discussion

3.1 Effect of FeS dosage on BPAF degradation

To evaluate the influence of FeS (0–4 g/L) dose on the degradation of BPAF, parallel experiments were carried out by adding FeS to reaction solution. As shown in Fig. 1, the BPAF degradation was less than 4% over 120 min in the absence of FeS. The result indicated that the BPAF was hardly degrade by periodate without any activator. However, the BPAF was remarkably degraded in FeS/ IO_4^- system. With the FeS dose varied from 0.25 g/L to 1 g/L, the removal efficiency of BPAF was 45.6%, 77.6% and 98.6% after 120 min, respectively. Moreover, when the dosage of FeS increased from 1 g/L to 4 g/L, the reaction time for complete BPAF degradation reduced from 120 min to 20 min. This might ascribe to that as increment of FeS dosage, more active sites on the surface of FeS were used to generate active species to efficiently degrade BPAF. Furthermore, the release of ferrous ions concentration increased with increasing of mackinawithe dosage (Fig. S2), which may accelerate the activation of periodate by ferrous ions and increase the amount of active species [30].

3.2 Effect of periodate concentration on BPAF degradation

The effect of different concentration periodate ranging from 0–4 mM on degradation of BPAF was presented in Fig. 2. The removal rate of BPAF was only 3%

in the absence of periodate, suggesting that FeS could not efficiently adsorb BPAF. Besides, BPAF concentration decreased dramatically upon the addition of 0.5 mM periodate solution. These results indicated that the coexistence of periodate and FeS were essential for the oxidative degradation of BPAF. When the concentration of periodate increased from 0.5 to 1 mM, the decomposition rate of BPAF increased progressively. The effect might be associated with increased amount of active species produced from FeS/ IO_4^- system. It can be observed that BPAF was completely removed within 60 minutes when periodate concentration increased to 4 mM, which might be attributed to that the periodate were not completely occupied the active sites on the FeS surface [4].

3.3 Effect of initial BPAF concentration

To analyze the effect of the initial BPAF concentration (10–40 μM) on the removal efficiency of BPAF in FeS/ IO_4^- system. As shown in Fig. S3, as the increase of BPAF concentration, the degradation efficiency shown decline trend. As can be seen from Table S1, the k_{obs} values of BPAF removal reduced from 0.1117 to 0.0168 min^{-1} as the initial BPAF concentrations increased from 10 μM to 40 μM . The consequence was attributed to a certain amount of reactive oxygen species (ROS) were formed in the FeS/ IO_4^- system, so the BPAF at lower initial concentration tended to be attacked by ROS, leading to the higher decomposition rate [40]. The reaction temperature also has a certain influence on the removal of target pollutants. Fig. S4 showed that increasing temperature was conducive to the degradation of

BPAF.

3.4 Effect of pH on BPAF degradation

The effect of pH on BPAF degradation during periodate activation by FeS was evaluated by regulating the pH level from 3 to 10 without buffering. As shown in Fig. 3(a), under the condition that the initial reaction solution was acidic, the degradation of BPAF reached to 100% within 60 min of the reaction, and the k_{obs} of BPAF was 0.0783 min^{-1} (Table S2). In the meantime, BPAF degradation was slightly reduced and the k_{obs} was decreased to 0.0372 min^{-1} within 60 min of the reaction at pH = 5.5. When the initial solution was neutral and alkaline, BPAF degradation exerted some adverse impact. The decomposition of BPAF reached 91.6% and the k_{obs} decreased to 0.0214 min^{-1} at the initial pH of the neutral solution. Nevertheless, the degradation rate of BPAF was reduced to 60.5% and the k_{obs} was 0.008 min^{-1} at pH = 10. The above experiments clearly showed that the degradation efficiency of BPAF dropped with increment of pH. It is obvious that the degradation rates of BPAF was not less than 60% regardless of the acidic or alkaline solution, indicating that BPAF could be noticeably degraded in a wide range of initial pH and FeS/ IO_4^- system exhibited a good potential for practical application [4]. Considering that the leached Fe^{2+} also played a certain role in the activation of periodate and acidic conditions may facilitate the continuous release of dissolved Fe^{2+} . Therefore, the concentration of dissolved Fe^{2+} in the FeS/ IO_4^- system at different initial pH was measured. The released Fe^{2+} concentration was the highest (1.23 mg/L) at pH 3 within 120 min and then gradually

decreased to 0.3 mg/L when the pH reached to 10 (Fig. S5). At the same time, the pH value of the solution increases, leading to the formation of iron based oxy-hydroxides, FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$, which were adsorbed on the surface of FeS. Therefore, the leached Fe^{2+} and the heterogeneous activation of periodate by surface bound Fe(II) were inhibited. In addition, it could also be seen that the decomposition of IO_4^- increased with decreasing of pH (Fig. 3(b)). IO_4^- is converted to the dimerized species ($\text{H}_2\text{I}_2\text{O}_{10}^{4-}$) at high pH which reactivity is not as good as the former [29]. Therefore, ROS concentration would be decrease at higher pH, resulting in low removal rate of BPAF.

3.5 Mechanism of periodate activation by FeS

The XPS spectra were used to explore the surface chemical composition of FeS before and after reaction. As illustrated in Fig. S6, the full-scan results of XPS spectra showed that FeS contained C, O, S and Fe elements. It was observed that the Fe 2p spectra of FeS peaked at 710.5 eV and 712.6 eV before the reaction, respectively [41]. The S 2p spectrum of FeS was shown in Fig. 4(b) before activation reaction, the peaks at 161.5 eV, 163.10 eV and 168.6 eV represented S (-II), polysulfide (S_n^{2-}) and surface-bound SO_4^{2-} [37, 42, 43]. The S 2p peak of surface-bound SO_4^{2-} before the reaction was probably related to oxidation. After the activation, Fe 2p_{3/2} spectra suggested that the content of Fe(II) decreased from 58.7% to 52.5%, and Fe(III) increased from 41.3% to 47.5%, demonstrating that the Fe(III) species was oxidized by 6.2% Fe(II). Meanwhile, the new peaks for elemental sulfur (S^0) was observed at

164.8 eV, the proportion of surface-bound SO_4^{2-} increased from 42.4% to 57.8% and S(-II) decreased from 14.4% to 11.2%, indicating that remarkable oxidation of S was occurred in FeS/IO_4^- system, and SO_4^{2-} was finally generated.

3.5.1 The role of Fe in BPAF degradation by FeS/IO_4^- system

The certain amount of Fe^{2+} or Fe^{3+} was added to the solution to further analyze the role of Fe^{2+} and Fe^{3+} for periodate activation. The concentration of 6 mg/L Fe^{2+} or Fe^{3+} was added to periodate solution to initiate experiment (Fe^{2+} or Fe^{3+} dose was equivalent to total amount of dissolved Fe based on reaction of 1 mM periodate and 1 g/L FeS in 120 min oxidation (Fig. S7)). As presented in Fig. 5(a), the BPAF was only slightly degraded in the $\text{Fe}^{3+}/\text{IO}_4^-$ system after 120 min. In addition, the BPAF was rapidly oxidized about 22% by adding Fe^{2+} to the solution, suggesting that IO_4^- could be activated by Fe^{2+} to produce active substances. The addition of Fe^{3+} avoided the BPAF from being degraded, indicating that Fe^{3+} cannot activate IO_4^- or promote the self-activation of IO_4^- . Compared with the FeS/IO_4^- system (98.6%), the BPAF displayed a noticeably lower degradation rate in the $\text{Fe}^{2+}/\text{IO}_4^-$, revealing that IO_4^- could be activated by Fe^{2+} to produce active substances and dissolved Fe^{2+} had only a certain contribution to BPAF degradation by FeS/IO_4^- system. Further revealed that the main process of BPAF degradation by FeS/IO_4^- was heterogeneous reaction.

3.5.2 Generation of sulfate radical by Fe and S species

In order to study the mechanism of sulfur in the system, the concentrations of SO_3^{2-}

and SO_4^{2-} were measured in aqueous solution. As shown in Fig. S8, when the oxidation reaction was performed for 5 min, the concentrations of SO_3^{2-} and SO_4^{2-} reached 7.45 mg/L and 16.03 mg/L, respectively. As the reaction carried out to 90 min, the concentration of SO_3^{2-} decreased from 7.45 mg/L to 0 mg/L, the concentration of SO_4^{2-} increased from 16.03 mg/L to 23.78 mg/L and finally reached to 24.98 mg/L. The above research could conclude that the increase of SO_4^{2-} concentration with reaction time resulted from the oxidation reaction of diverse sulfur species. On the one hand, these sulfates derived from the sulfur species oxidation reactions on the surface of FeS, on the other hand, they came from the oxidation of S^{2-} and sulfur oxides in the solution.

It has been reported that the co-existence of SO_3^{2-} with Fe(III) trigger chain reaction to produce $\text{SO}_4^{\bullet-}$ (Eqs. (5)–(7)) [44]. To analyze the source of $\text{SO}_4^{\bullet-}$ in FeS/ IO_4^- system, the degradation rate of BPAF in the Fe(III)/ S^{2-} , Fe(III)/ SO_3^{2-} , Fe(II)/ S^{2-} and Fe(II)/ SO_3^{2-} systems was obtained. The Fig. 5(b) shown that the reaction of Fe(II)/ SO_3^{2-} and Fe(II)/ S^{2-} hardly degraded BPAF, whereas 21% BPAF degradation was obtained in the $\text{Fe}^{3+}/\text{SO}_3^{2-}$. A series of radicals quenching experiments demonstrated that the reaction of Fe^{3+} released into the solution and SO_3^{2-} contributed to the production of sulfate radical in the FeS/ IO_4^- system (Fig. S9).

3.5.3 Periodate activation by S^{2-} for sulfate radical generation

It has been reported that the sulfur atoms could produce various sulfur compounds by complex oxidation under the oxidation of FeS [45]. Similar results were observed in this study, which a series of sulfides was generated (including S^{2-} , Sn^{2-} and SO_4^{2-}) by using XPS to characterize fresh and used FeS. Li et al explored the efficiency of SMX removal by SO_3^{2-} /PMS and found that SO_3^{2-} activate PMS to produce $SO_4^{\bullet-}$ [46]. To study the effect of various sulfur species on BPAF degradation, S^{2-} or SO_3^{2-} (0.5 mmol/L) in the predetermined amount was separately added to the periodate solution under the identical conditions. As shown in Fig. 5(c), BPAF was not obviously decomposed in SO_3^{2-}/IO_4^- system, indicating that SO_3^{2-} could not activate periodate to produce active species.

The BPAF degradation in the presence of S^{2-} was shown in Fig. 9(c). Under ambient conditions, the sole S^{2-} system might not degrade BPAF after 120min, whereas the BPAF degradation rate was 55.8% in the S^{2-}/IO_4^- . It was indicated that S^{2-} was produced in the FeS/IO_4^- system and contribute to the formation of sulfate radical by coexistence of S^{2-} and IO_4^- according to the following reaction (Eq. (8)). To confirm this process, a range of quenching tests were performed in the S^{2-}/IO_4^- system. Fig. S10 illustrated that the addition of excess TBA (5mM) exerted no effect on BPAF degradation, which presented that hydroxyl radical was not the reactive species for the S^{2-}/IO_4^- . Meanwhile, the addition of MeOH (5mM) had complete inhibitory effect on the degradation of BPAF, indicating that the reaction of S^{2-} with periodate effectively form $SO_4^{\bullet-}$ to degrade BPAF. The aforementioned experiments suggested that SO_3^{2-} exerted limited effect on the formation of free radicals, while S^{2-}

was a reactive species reacted with periodate to form $\text{SO}_4^{\bullet-}$.

3.6 Identification of reactive species

The study has shown that $^1\text{O}_2$, $\text{O}_2^{\bullet-}$ and $\text{HO}^\bullet$ played an significant role in the decomposition of contaminants in IO_4^- activation process [27, 31]. In order to reveal the main active species for BPAF degradation in the FeS/IO_4^- system, a range of quenching tests were first performed. It has been demonstrated that MeOH rapidly react with hydroxyl radicals ($^\bullet\text{OH}$) and sulfate radical ($\text{SO}_4^{\bullet-}$) ($k_{\text{SO}_4^{\bullet-}/\text{MeOH}} = 3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $k_{^\bullet\text{OH}/\text{MeOH}} = 9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), while tert-butyl alcohol (TBA) incline to quench $^\bullet\text{OH}$ than $\text{SO}_4^{\bullet-}$ ($k_{^\bullet\text{OH}/\text{TBA}} = 3.8 \times 10^8$ – $7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{TBA}/\text{SO}_4^{\bullet-}} = 4.0$ – $9.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [21, 47]. The research found that sodium azide (NaN_3) could react with $^1\text{O}_2$ ($2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) rapidly as well as quenching $^\bullet\text{OH}$ [48]. p-Benzoquinone (p-BQ) is a typical $\text{O}_2^{\bullet-}$ scavenger, which is used to verify the existence of $\text{O}_2^{\bullet-}$ [49]. As depicted in Fig. 6(a), there was no inhibition effect for BPAF removal in FeS/IO_4^- system by using TBA as a radical quenching agent, indicating that hydroxyl radical was not the ROS in this system. The addition of excess MeOH decreased the k_{obs} of BPAF to 0.0287 min^{-1} ($R^2 = 0.9861$), suggesting that $\text{SO}_4^{\bullet-}$ was involved in BPAF degradation. As shown in Fig. 6(b), the addition of NaN_3 significantly inhibited the degradation rate of BPAF. The FeS/IO_4^- system degraded BPAF from 98.6% to 19.2%, as the concentration of NaN_3 increased from 0 mM to 50 mM. This result is consistent with the research of the $\text{Mn}^{2+}/\text{IO}_4^-$ system [31], which demonstrated that $^1\text{O}_2$ played

an important role for the BPAF removal in the FeS/IO₄⁻ system and other active substances was involved in the reaction. As illustrated in Fig. 6(c), 98.6%, 94.2%, 81.5% and 35.1% of BPAF were degraded after 120 min with the addition of p-BQ (0–3 mM) in the reaction system. It can be found that the addition of p-BQ significantly inhibited the BPAF degradation and a certain amount of O₂^{•-} was produced in the reaction process.

Furthermore, the splitting constant of the aminooxy group is closely bound up with the spin trap and the free radical due to the synthetic spectrum, the EPR spectroscopy was used to identify the reactive oxygen species that may exist in the degradation of BPAF by FeS/IO₄⁻ [50]. The 5,5-dimethyl-1-pyrroline (DMPO) was employed to trap SO₄^{•-}, •OH and O₂^{•-}, which contributing to the production of the DMPO–OH•, DMPO–SO₄^{•-} or DMPO–O₂^{•-}, respectively [51, 52]. In the meantime, 2,2,6,6-tetramethyl-4-piperidinol (TEMP) has adopted to trap ¹O₂ to form spin-adduct TEMP [53]. The characteristic peak signal of DMPO–OH• adduct and the hyperfine splitting constant of α_N = 14.25 G, α_H = 12.45 G in the FeS/IO₄⁻ system were obtained at room temperature in Fig. 6(d). No signal of DMPO–SO₄^{•-} adduct was observed in the reaction. This result may be that the DMPO–SO₄^{•-} adduct could rapidly converted into DMPO–OH• adduct by nucleophilic substitution [54]. The reaction was described in the following Eq. (9) [55]. Combined with the free radical quenching experiment and EPR tests, the SO₄^{•-} was produced in FeS/IO₄⁻ system. The specific explanation would be further analyzed in next section.

In order to detect $\text{O}_2^{\bullet-}$, the methanol was applied to replace water as the reaction medium, prolonging the half-life of superoxide anion radical. The quadruple peak of equal strength with hyperfine splitting constants of $\alpha_{\text{N}} = 14.25 \text{ G}$ and $\alpha_{\text{H}} = 12.45 \text{ G}$ were obtained in the FeS/IO_4^- system, suggesting that the superoxide anion radical existed in the reaction process. The ESR spectra showed a triplet characteristic signal with a strength ratio of 1:1:1, and the hyperfine splitting constants of $\alpha_{\text{N}} = 7.2 \text{ G}$ and $\alpha_{\text{H}} = 4.1 \text{ G}$, confirming that $^1\text{O}_2$ may participate in the reaction of FeS/IO_4^- system. The quenching experiments and ESR spectral showed the sulfate radical ($\text{SO}_4^{\bullet-}$) may be produced during the activation process of IO_4^- by FeS. Furthermore, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ were main reactive species in FeS/IO_4^- system, which played an important role in the reaction process.

The studies revealed that the degradation rate of BPAF by $\text{Mn}^{2+}/\text{IO}_4^-$ system under anoxic condition was significantly lower than the condition of air purging [31]. Therefore, the dissolved oxygen might affect the degradation of BPAF in the FeS/IO_4^- system. The Fig. 7 shown that the removal rate of BPAF was only 65.4% under the condition of nitrogen purging and the corresponding k_{obs} reduced from 0.0372 min^{-1} to 0.0094 min^{-1} (Table S3). Compared to the initial experimental conditions of FeS/IO_4^- system, the degradation of BPAF was completely degrade after 90 min by purging air and the k_{obs} of BPAF reached to 0.0423 min^{-1} from 0.0372 min^{-1} . The studies shown that the redox reaction of FeS_2 was occurred via Eqs. (10–13) [56], and FeS might carry out the similar reaction. When the periodate was added in the reactive solution, FeS would be oxidized to produce Fe^{3+} and further reacted with residual FeS

to form ferrous ions. The ferrous ions were adsorbed on the surface of FeS, thereby facilitated the reaction of ferrous iron with oxygen. $O_2^{\bullet-}$ might be obtained by providing an electron from ferrous substance to oxygen. In addition, it was found that the decomposition of periodate was enhanced under the condition of air purging. (Fig. S11) [56]. Therefore, oxygen acted an significant role in the activation of periodate by FeS. In addition, the inhibition effects at various initial pH (3.0-10.0) were evaluated (Fig. S12), and found that $O_2^{\bullet-}$ and 1O_2 were the main active species.

Based on the radical scavenge and purging gas experiment in our study, a plausible processes of periodate activation by FeS was proposed as follows. Both homogeneous Fe^{2+} and heterogeneous Fe(II) are involved in the activation process of periodate (Eq. 14) . The surface Fe(II) of FeS could activate molecular oxygen to generate $O_2^{\bullet-}$ (Eq. 13), and 1O_2 was generated through reaction of IO_4^- with $O_2^{\bullet-}$ (Eq. 3) [27]. Meanwhile, Sulfur species contribute to the formation of sulfate radical to degrade BPAF (Eqs. 5-8).

3.7 Effect of inorganic anions on FeS–periodate system

Inorganic anions were ubiquitous in natural water bodies. Considering the research reported, common coexisting ions could exert different effects on IO_4^- activation process [4, 5, 29]. Accordingly, it is necessary to research the function of the anions on the BPAF degradation in the FeS/IO_4^- system. The impact of sulfate (SO_4^{2-}), chloride (Cl^-), nitrate (NO_3^-) and carbonate (CO_3^{2-}) with concentration gradients of 0.1 mM, 0.5 mM, 1 mM on the removal of BPAF by FeS/IO_4^- system were evaluated. As shown in Fig. 8, the Cl^- , SO_4^{2-} and CO_3^{2-} significantly impacted reaction process, whereas the degradation of BPAF was negligible by introducing NO_3^- (0.1-1mM) (Fig. 8(d)).

The efficiency of different chloride and sulfate concentrations on BPAF degradation was presented in Fig. 8(a) and Fig. 8(c). The efficiency of BPAF degradation increased with increasing Cl^- or SO_4^{2-} concentration from 0.1 mM to 1 mM. When the Cl^- concentration reached 1mM, BPAF was almost completely degraded within 60 min. The BPAF decomposition followed pseudo-first-order kinetics. The k_{obs} of BPAF risen to 0.069 min^{-1} from 0.0372 min^{-1} with increasing Cl^- concentration from 0 mM to 1 mM (Table S4). The complete decomposition time of BPAF was narrowed from 120 min to 90 min, 60 min by the addition of 0.1, 0.5 and 1 mM SO_4^{2-} , respectively. The BPAF degradation process could be explained by pseudo-first-order kinetics for any specific SO_4^{2-} concentration. When the SO_4^{2-} concentration increased from 0 mM to 1 mM, the k_{obs} of BPAF gradually elevated to 0.069 min^{-1} .

Li et al. reported that $\text{Cl}\cdot$ with 2.4 V higher redox potential could be produced by

the reaction of Cl^- and reactive radical [4, 29]. In addition, it has been found that the introduction of SO_4^{2-} slightly impacted the decomposition of organic pollutants by I-GAC/ IO_4^- system [29]. Existing studies could not elucidate the significant effect of Cl^- and SO_4^{2-} on BPAF removal by FeS/IO_4^- system, the preliminary explanation was as follows.

This could be Cl^- inhibits the corrosion of FeS [57], which give rise to more FeS to activate the periodate and produce more active species [58]. Meanwhile, the improvement of the BPAF degradation efficiency may closely relate to the high redox potential active chlorine species which was generated by the reaction of Cl^- and active free radicals according to Eqs. (15)–(17) ($E^0 (\text{Cl}^\bullet/\text{Cl}^- = 2.4\text{v})$; ($E^0 (\text{Cl}_2^{\bullet-}/2\text{Cl}^- = 2.1\text{v})$) [5, 59]. Meanwhile, chloride ions can probably promote the production of chloride substitutes, which is conducive to attracting nucleophilic active substances, so that aromatic rings is more vulnerable to be attacked [48]. Notably, Fig. S13 showed that degradation of BPAF was not suppressed by the addition of MeOH . According to section 3.6, the $\text{SO}_4^{\bullet-}$ existed in the FeS/IO_4^- system, indicating that the present of SO_4^{2-} could quench $\text{SO}_4^{\bullet-}$. It could be further inferred that other active species participated in the degradation of bisphenol AF.

Besides, it is reported that the addition of SO_4^{2-} or Cl^- could increase the ionic

strength, thereby surface reactions and the degradation of PPCP are enhanced through using zero-valent iron to activate PDS [58].

The studies have shown that the addition of inorganic anions may promote the production of active substances [48, 58]. In order to study the effect of Cl^- and SO_4^{2-} on the reactive oxygen species being formed in the FeS/IO_4^- system, the p-BQ and NaN_3 were applied to carry out the radicals quenching experiments. The removal rate of BPAF decreased with increasing p-BQ concentration in presence of Cl^- or SO_4^{2-} in the solution (Fig. 9(c) and Fig. 9(d)). When the p-BQ concentration was 0.5 mM, 1 mM and 3 mM, the removal rate of BPAF was 97.7%, 69.7% and 24.8% in the presence of SO_4^{2-} solution, respectively. Meanwhile, the 97.2%, 59.8% and 9% BPAF were degraded in the presence of SO_4^{2-} solution, whereas the degradation rate was 94%, 81.5% and 35% without Cl^- and SO_4^{2-} , respectively. This indicated that Cl^- and SO_4^{2-} could promote the production of $\text{O}_2^{\bullet-}$ and thus improve the degradation of BPAF by the FeS/IO_4^- system. Meanwhile, it could further conclude that sulfate had more significant effect than chloride ions to promote the production of $\text{O}_2^{\bullet-}$. This is consistent with the study of Wang et al, in which $\text{O}_2^{\bullet-}$ played a more important role in oxidation of PHBA with the present of NaCl [48]. When adding NaN_3 to a solution containing chloride or sulfate ions, the complete degradation time of BPAF increased from 60 min to 120 min. (Fig. 9(a) and Fig. 9(b)). However, with the addition of NaN_3 to the reaction solution, it could obtained that the presence of Cl^- could more remarkably inhibit BPAF degradation than the addition of SO_4^{2-} , suggesting that Cl^- could more effectively promote the role of $^1\text{O}_2$ for the BPAF degradation in the

FeS/IO₄⁻ system.

As observed from Fig. 8(b), the presence of carbonate has a negative influence on the removal of BPAF. Compared with reactions without CO₃²⁻, the degradation efficiency of BPAF gradually decreased from 98.6% to 63.7%. The k_{obs} of BPAF had a decline trend from 0.0372 min⁻¹ to 0.0089 min⁻¹ with increasing the dosage of CO₃²⁻ from 0 mM to 1 mM. The degradation process of the pH variations was observed in Fig. S14, and the solution pH increased with the increasing of CO₃²⁻ concentration in the system. The surface properties of FeS and existing forms of periodate were affected at higher pH, thereby decreasing the removal efficiency of BPAF and explaining it in the pH section. The addition of carbonate to the solution cause a hydrolysis reaction of CO₃²⁻ with H₂O. Moreover, the H₂CO₃ with weak acidity was ionize to achieve the balance of H₂CO₃–HCO₃⁻–CO₃²⁻ system (Eqs. (18)–(20)) [60]. SO₄^{•-} with excess CO₃²⁻ ions to produce low reactivity CO₃^{•-} radicals [59] (Eqs. 21). At the same time, carbonate acts as a scavenger for superoxide (Eqs. (22)–(23)) [27].

3.8 intermediates and mineralization of BPAF

The intermediate products of BPAF degradation in FeS/IO_4^- system were analyzed by LC-MS. Based on the identified intermediate products (Table. S5), the degradation pathway of BPAF in FeS/IO_4^- system was presented in Fig. S15. In addition, the variation value of TOC with reaction time was also evaluated (Fig. S16). The TOC removal was 54.22% after 240min, suggesting that BPAF could be mineralized in FeS/IO_4^- system. It can be seen from Fig. S17 that IO_4^- was mostly reduced to IO_3^- , indicating that potential for further formation of toxic iodized by-products such as HOI was low during the process of BPAF degradation by FeS/IO_4^- system.

3.9 Mechanism of periodate activation by FeS

Based on the analysis of the above experiments, the possible mechanism of BPAF degradation in the FeS/IO_4^- system was proposed, as illustrated in Fig. 10. After the FeS was added to an aqueous solution containing periodate, surface Fe(II) (unstable ionic species attached to the catalyst surface) or Fe^{2+} reacted with periodate to produce $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$. At the same time, S(-II) on the surface of FeS was oxidized by IO_4^- to form polysulfide (S_n^{2-}), elemental sulfur (S^0) and $\text{SO}_4^{\bullet-}$. The SO_3^{2-} was produced by electron transfer and oxidation of S^{2-} in solution. Fe(III) oxidated SO_3^{2-} to produce $\text{SO}_4^{\bullet-}$. In summary, the reaction of $\text{Fe(II)}/\text{IO}_4^-$ contributed to the generation of $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ in FeS/IO_4^- system. Meanwhile, $\text{S}^{2-}/\text{IO}_4^-$ and $\text{Fe(III)}/\text{SO}_3^{2-}$ system could generate $\text{SO}_4^{\bullet-}$.

4. Conclusion

In this study, an efficient approach was proposed to degrade BPAF by FeS/IO_4^- system. Compared with the addition of single FeS or periodate addition, the removal efficiency of BPAF in FeS/periodate system reached 97.7%. Meanwhile, the degradation efficiency increased with increasing the dosages of FeS or periodate. The pH of the solution exerted certain effect on BPAF degradation and the acidic pH was more effective than neutral or alkaline. The influence of various inorganic anions on the removal efficiency of BPAF was also investigated. The presence of Cl^- and SO_4^{2-} had a positive influence on the removal of BPAF. The effect of NO_3^- was very weak and CO_3^{2-} showed a marked inhibition effect.

Through ESR tests and radicals quenching experiments demonstrated that $\text{O}_2^{\bullet-}$, $^1\text{O}_2$ and $\text{SO}_4^{\bullet-}$ were produced in the FeS/periodate system, while $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ acted as the dominant active species. Fe(II) or $\equiv\text{Fe}(\text{II})$ could activate IO_4^- effectively. The XPS spectrum indicated that the content of different sulfur species varied during the oxidation reaction of FeS/ IO_4^- . Moreover, the quenching experiments showed that the oxidation reaction of S^{2-} and periodate played an significant role in the generation of $\text{SO}_4^{\bullet-}$. In addition, Fe(III) can effectively activate SO_3^{2-} to trigger the radical chain reaction to produce $\text{SO}_4^{\bullet-}$.

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