

Article

Synergistic Removal of Typical Heavy Metal and Organic Contaminants via $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ from Electronic Industry Wastewater: Insights for Selective Degradation and Promotion

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Abstract

The simultaneous and sustainable removal of a typical heavy metal (Cr(VI)) and benzoic acid (HBA) via an $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ /visible light system without consumption of extra reductive or oxidizing agents was performed to study the influence of HBA degradation on Cr(VI) reduction. The results showed that the influence order of different HBA options in accelerating Cr(VI) reduction was as follows: o-HBA > p-HBA > p-CBA > blank > m-HBA. With the addition of o-HBA, the Cr(VI) removal rate constant was increased by 1.5 times (0.047 to 0.119 min^{-1}). Almost 100% of Cr(VI) and 70% of o-HBA were removed within 60 min under the initial Cr(VI) and o-HBA concentrations of 10 and 5 mg/L. Quenching experiments indicated that photogenerated e^- and $\bullet\text{O}_2^-$ played an important role in Cr(VI) reduction, while photogenerated h^+ and its derived $\bullet\text{OH}$ contributed to HBA degradation. Due to $\bullet\text{O}_2^-$ and $\bullet\text{OH}$, separately ascribed to photogenerated e^- and h^+ , the timely consumption of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ accelerated the separation and generation of photogenerated carriers, further improving light utilization efficiency and resulting in synergetic improved removal performance for both Cr(VI) and o-HBA. Theoretical calculations indicated the electron-donating ability of hydroxy groups in o-HBA was better than that in other HBA, making the activation energy for addition reaction with $\bullet\text{OH}$ lower. Hence, $\bullet\text{OH}$ would be consumed more quickly, leading to a higher promotion effect from o-HBA on Cr(VI) reduction. The real wastewater treatment experiment indicated the high applicability of synthesized $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ for synergetic and sustainable removal of Cr(VI) and coexisting organic pollutants in electronic industry wastewater.

Keywords: electronic industry wastewater; photocatalysis; synergistic removal; Cr(VI); benzoic acids



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1. Introduction

As one of the most widely used metals, chromium (Cr) is playing a significant role in industrial production, such as metallurgy, chemical industry, and electroplating. In the electroplating industry, the Cr clad layer on the metal layer of circuit boards can prevent oxidation and corrosion and further improve the electrical conductivity to ensure reliability and electronic transmission stability in electronic components [1]. However, with the rapid development of industrialization, the utilization and discharge of Cr have caused global contamination. Due to its strong toxicity, high solubility, and mobility, Cr pollution is posing a remarkable threat to human health and surrounding ecological systems [2].

According to the variation in oxygen content in the environment, Cr mainly exists in the forms of trivalent (Cr(III)) and hexavalent (Cr(VI) or chromate) species [3]. Due to the oxic environment in most electroplating and electronic device manufacturing industries, Cr(VI) is often the main form of Cr in electronic industrial wastewater. However, both the solubility and toxicity of Cr(VI) are apparently higher than Cr(III), making Cr(VI) more difficult to remove [3]. Consequently, it is urgent to find novel and efficient methods for Cr(VI) treatment.

Many traditional and modified technologies have been applied for Cr(VI) removal, such as electro-reduction, coagulation, and adsorption [4,5]. In these various technologies, reducing highly hazardous Cr(VI) into kinetically inert and less toxic Cr(III) and then immobilizing it is considered one of the most promising and eco-friendly methods for Cr decontamination, especially in oxic electroplating industry wastewater [6]. Due to their abundant reserves and strong reducibility, pyrite (FeS_2)-based composites have been applied to spontaneously reduce Cr(VI) to Cr(III) due to the reducibility of Fe^{2+} and S_2^{2-} species [7]. However, FeS_2 particles suffer from severe agglomeration and low electronic transmission capability, weakening their surface reaction activity and the contact with Cr(VI), thus limiting the practical application of FeS_2 -based composites [8]. Additionally, FeS_2 is also a semiconductor photocatalyst, and photocatalysis is considered a more efficient and sustainable strategy to further enhance the reducibility of FeS_2 . Based on this modification method, pyrite (FeS_2), goethite ($\alpha\text{-FeOOH}$), and activated carbon (C) were synthesized together to construct $\text{FeS}_2/\alpha\text{-FeOOH/C}$ composites with a C-mediated Z-scheme heterojunction for photo-assisted Cr(VI) reduction, which demonstrated efficient Cr(VI) removal performance in our previous study [9]. However, many other substances such as heavy metals (e.g., Cu, Zn, Ni) and organic pollutants (surfactants, organic acids, and organic solvents) also exist in electroplating wastewater and influence Cr(VI) removal [10]. Especially for the diverse and bio-refractory organic pollutants, they can consume oxidizing and reducing agents or compete functional sites on adsorbents, apparently influencing Cr(VI) reduction and immobilization [11,12]. Hence, with the participation of the photocatalysis process during Cr(VI) reduction, the oxidative ability of photocatalysts can be utilized to simultaneously degrade organic pollutants without extra consumption of oxidizing agents, further improving light utilization, reducing energy consumption and enhancing environmental friendliness. Using the photocatalysis process for simultaneous removal of Cr(VI) and organic pollutants and detecting the influence of organic pollutants on Cr(VI) removal have been investigated in some studies. However, there is a significant difference in these conclusions. Some studies indicate that the degradation of organic pollutants can accelerate Cr(VI) reduction, while other results are opposite [13,14]. Our inference is that different chemical properties of organic pollutants result in different effects. Hence, it is necessary to clarify the specific mechanisms for the influence of typical organic pollutants on Cr(VI) reduction during the photocatalysis process and find the common mechanism.

As typical and frequently used organic acids in the electroplating technology, benzoic acids (HBA) with different substituent groups are selected as the target organic pollutants to investigate their influence on Cr(VI) reduction via an $\text{FeS}_2/\alpha\text{-FeOOH/C}$ /visible light system. Characterization tests, control experiments and theoretical calculation were combined together to study the effect of different HBAs on Cr(VI) reduction. The specific mechanism and the connection between the structure, position and electronegativity of substituent groups in benzoic acids and Cr(VI) reduction were investigated in detail. In the end, the practical ability of the $\text{FeS}_2/\alpha\text{-FeOOH/C}$ /visible light system was comprehensively studied through real electronic industry wastewater treatment. This study supplies a novel photo-assisted technology and deep insight for synergistic and sustainable removal of typical heavy metals and organic contaminants in electronic industry wastewater.

2. Materials and Methods

2.1. Fabrication of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ Composite and Reagents

The $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite with an optimal mass ratio of FeS_2 , $\alpha\text{-FeOOH}$ and C of 50:5:1 was fabricated according to our previous research [9]. The detailed preparation method is shown in Text S1. As for the used chemical reagents, all of them were of analytical reagent grade unless stated otherwise. The related used reagents like p-hydroxybenzoic acid (p-HBA), o-hydroxybenzoic acid (o-HBA), m-hydroxybenzoic acid (m-HBA), and parachlorobenzoic-acid (p-CBA) were purchased from Shanghai Maclean Biochemical Co., Ltd., Shanghai, China. Deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used for all experiments unless stated otherwise.

2.2. Batch Experiments

In order to evaluate the influence of HBA with different substituent groups on simultaneous Cr(VI) reduction via the synthesized $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite, the experiments were performed in a photoreactor with a 300 W xenon lamp (light cut-off filter, $\lambda > 420 \text{ nm}$, light intensity of $2100 \text{ mW}/\text{cm}^2$) as visible light source [9]. As for the typical Cr(VI) reduction experiment, $0.1 \text{ g}/\text{L}$ of photocatalyst was added into a beaker containing 100 mL of aqueous solution with initial Cr(VI) concentration of $10 \text{ mg}/\text{L}$, $5 \text{ mg}/\text{L}$ of benzoic acids, and an initial pH of 3. The photoreactor was switched on and the dispersions were irradiated for 60 min with magnetic stirring. Then, 1 mL of the suspension was taken out at regular intervals and filtered through a $0.22 \mu\text{m}$ polyamide membrane for further testing. Additionally, real electronic industry wastewater from the Yangtze River Delta area of China was treated by the synthesized $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite to comprehensively evaluate its practical applicability.

2.3. Testing Method and Theoretical Calculation

Characterization tests, such as X-ray diffraction (XRD, D8 ADVANCE, Tokyo, Japan), scanning electron microscopy (SEM, Zeiss Gemini 300, Oberkochen, Germany) and transmission electron microscopy (TEM, JEOL JEM 2100F, Tokyo, Japan), were used to analyze the crystal component and morphology of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$. Cr(VI) concentration was analyzed on a UV-vis spectrophotometer at 540 nm through a 1,5-diphenylcarbazide method [15]. Total organic carbon (TOC) was tested on a TOC analyzer (TOC-V CPH, Shimadzu, Kyoto, Japan). As for the test of different benzoic acids, high-performance liquid chromatography (E2695, Waters) with a C18 chromatographic column was selected. The specific analysis methods, like mobile phase, flow velocity and wave length, are shown in Text S2. In order to investigate the degradation mechanism of different benzoic acids and the connection with Cr(VI) reduction, reactive species were identified by quenching experiments and electron paramagnetic resonance (EPR) capture tests. Specifically, benzoquinone (BQ) and potassium bromate (KBrO_3) were used as free radical scavengers of $\bullet\text{O}_2^-$ and e^- . Tertiary butanol (TBA) and Ethylene Diamine Tetraacetic Acid (EDTA-2Na) acted as the quenchers for $\bullet\text{OH}$ and $\text{h}\nu$. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as the spin trapping agent of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ and an EMXplus-10/12 spectrometer was used to identify their electron paramagnetic resonance (EPR) signals. Additionally, the high-performance liquid chromatography–tandem mass spectrometry analysis method (HPLC-MS) was applied to analyze the intermediate products during benzoic acid degradation to study their potential degradation pathway.

More importantly, based on the inferred potential degradation pathway, the activation energy for addition reaction between benzoic acids with different substituent groups and the main reactive species (e.g., $\bullet\text{OH}$) was calculated through Density Functional Theory to further reveal the influence of the substituent group's location and electronegativity on

Cr(VI) removal. The specific steps for theoretical calculation performed using the Gaussian 16 software package based on the B3LYP function are shown in Text S3.

3. Results and Discussion

3.1. Influence of Benzoic Acids with Different Substituent Groups on Cr(VI) Reduction

Firstly, the synthesized $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite with an optimal FeS_2 , $\alpha\text{-FeOOH}$ and C mass ratio of 50:5:1 and a Z-scheme heterojunction was fabricated according to our previous research [9]. The XRD pattern in Figure 1 shows the peaks representing typical crystal planes of carbon, FeS_2 , and $\alpha\text{-FeOOH}$, which is in accordance with the XRD patterns in our previous study [9]. The SEM and TEM figures indicated spheroidal or needle-like particles with relatively small diameter dispersed on the layered matrix, showing that FeS_2 and $\alpha\text{-FeOOH}$ were successfully supported and combined with activated carbon. Particles in $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ showed a rough and uneven surface, beneficial for the absorption of visible light and contact with molecular oxygen, Cr(VI) and organic contaminants. Additionally, the TEM image indicated that many bright spots existed in the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ particles, showing a porous structure with various pores, further beneficial for the exposure of functional groups related to photocatalysis or contact with contaminants (Fe-S-Fe, Fe-OH, -CO, -C-OH, -COOH, etc.) [9,16]. More importantly, high-resolution TEM (HRTEM) of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ showed an apparent lattice spacing of 0.240 and 0.440 nm, which was attributed to the (210) plane of FeS_2 and (200) plane of $\alpha\text{-FeOOH}$, respectively [17,18]. All these phenomena proved that the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite was successfully prepared [9]. Furthermore, the Cr(VI) removal efficiency without the addition of benzoic acids was similar to that in our previous study, indicating that the photo-assisted Cr(VI) reduction capacity of the newly prepared $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ was similar to our previous composite [9].

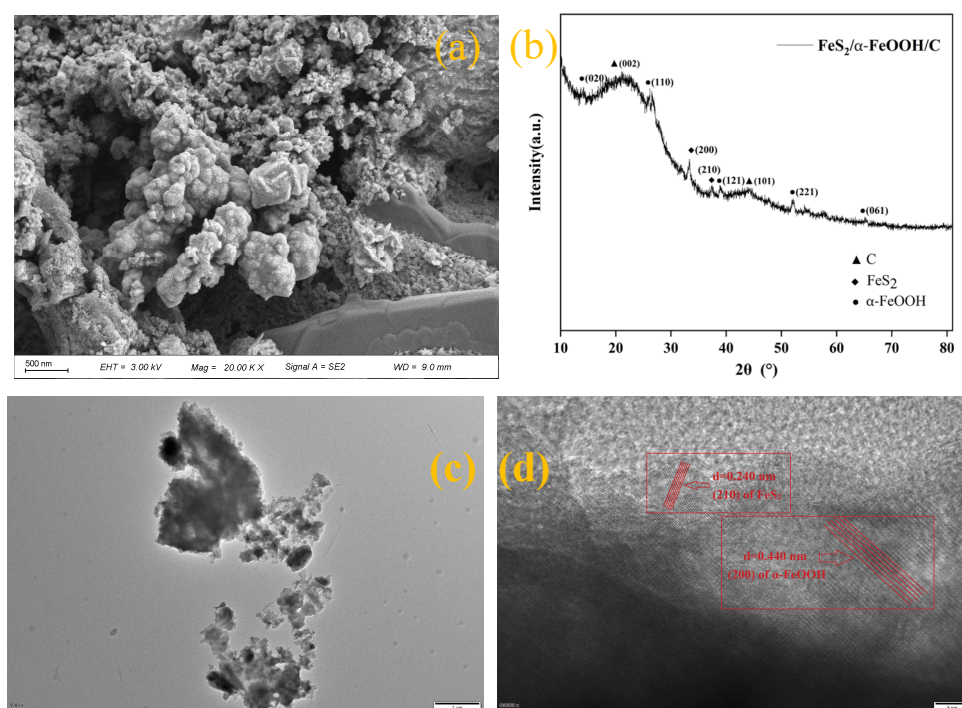


Figure 1. (a) SEM, (b) XRD, (c) TEM and (d) HRTEM of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite.

To investigate the effect of different typical coexisting benzoic acids (usually used as electroplating additives or surfactants) on Cr(VI) reduction via the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composite, simultaneous removal experiments were performed. Figure 2 showed that all

the Cr(VI) could be removed within 60 min, indicating the high Cr(VI) reduction ability of the photo-assisted $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ system. The Cr(VI) removal kinetic constants (k_{obs}) were apparently increased after the addition of p-CBA, p-HBA, and o-HBA. Especially for o-HBA, the k_{obs} of Cr(VI) was increased by 1.5 times (0.047 to 0.119 min^{-1}) after o-HBA addition. However, the k_{obs} of Cr(VI) in the system with Cr(VI) and m-HBA was lower than the system with only Cr(VI). Overall, the benzoic acids exhibited the following order of effectiveness in accelerating Cr(VI) reduction: o-HBA > p-HBA > p-CBA > blank > m-HBA. According to our previous study, the photogenerated e^- and its derived $\bullet\text{O}_2^-$ during the photocatalysis of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ played an important role in Cr(VI) reduction. Certainly, the photogenerated h^+ and its derived oxidative reactive species (e.g., $\bullet\text{OH}$, H_2O_2 , $^1\text{O}_2$, etc.) would retard the process of Cr(VI) reduction [18]. If these oxidative reactive species can be consumed in time, the Cr(VI) reduction process may be further promoted [14]. According to this theory, the degradation of benzoic acids would utilize oxidative reactive species and promote Cr(VI) removal. Hence, the degradation performance for benzoic acids with different substituent groups is shown in Figure 2c,d. According to the results, the order of removal efficiencies and the first-order degradation rate constants (o-HBA > p-HBA > p-CBA > m-HBA) was consistent with the aforementioned trend of their influence on Cr(VI) reduction. This phenomenon verified the inferred strategy that consuming the photogenerated h^+ and its derived oxidative reactive species could accelerate Cr(VI) reduction. Additionally, because the structure, position, and electronegativity of substituent groups (-OH or -Cl, shown in Figure S1) on the benzene ring of the benzoic acids were different, the degradation performance of various benzoic acids via different oxidative reactive species would exhibit significant variations, which might be the key point for the different influence on Cr(VI) reduction [19].

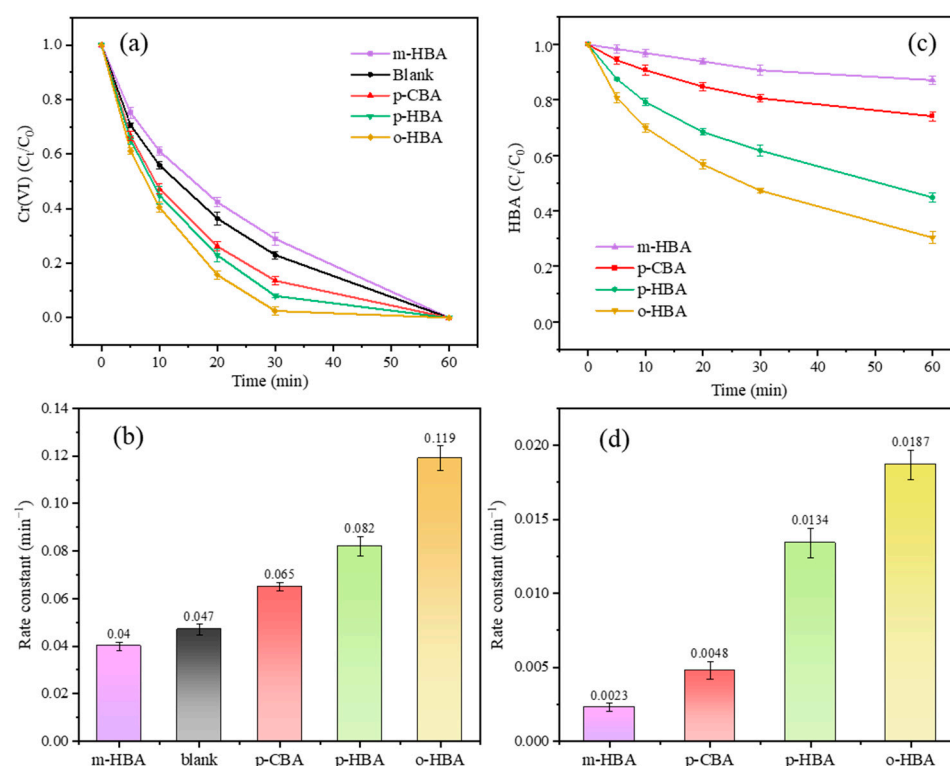


Figure 2. Effect of different benzoic acids on Cr(VI) removal by $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ composites: (a) Cr(VI) removal efficiency and (b) the corresponding Cr(VI) removal rate constants of the first-order kinetic model; (c) removal efficiencies of four benzoic acids and (d) the corresponding degradation rate constant of the first-order kinetic model ($C_{\text{Cr(VI)0}} = 10.0 \text{ mg/L}$, $C_{\text{HBA0}} = 5.0 \text{ mg/L}$, $M_{\text{cat}} = 0.1 \text{ g/L}$, $\text{pH} = 3.0$).

3.2. Identification of Main Reductive and Oxidative Reactive Species

Photocatalytic process can utilize photons to generate free electrons (e^-) and protons (h^+) with reduction and oxidation capability, thereby deriving various reactive species (ROS), such as $\bullet O_2^-$, $\bullet OH$, H_2O_2 , $^1O_2$, etc., to further facilitate oxidation–reduction reactions [20]. Consequently, to investigate the specific contribution of different ROS in the $FeS_2/\alpha\text{-FeOOH}/C/\text{visible light}$ system to $Cr(VI)$ reduction and benzoic acid degradation, a radical scavenging experiment was conducted in the system with $Cr(VI)$ and *o*-HBA due to the superior performance of *o*-HBA in accelerating $Cr(VI)$ reduction. The results in Figure 3 indicate that the $Cr(VI)$ removal efficiencies and k_{obs} were apparently inhibited after the addition of $KBrO_3$ and BQ, which were considered as the scavengers for e^- and $\bullet O_2^-$. These phenomena indicated that both e^- and $\bullet O_2^-$ participated in $Cr(VI)$ reduction, consistent with our previous study [9]. Additionally, the inhibiting effect of $KBrO_3$ was higher than that of BQ, showing that the contribution of e^- was apparently higher, as most of the $\bullet O_2^-$ was derived from photogenerated e^- according to our previous study (Equations (1) and (2)) [9]. Certainly, e^- may also be ascribed to Fe or S with low chemical valence. The results in our previous study confirmed that the ratio of e^- from photocatalysis was higher than that from Fe or S with low chemical valence under visible light (Equations (3)–(5)) [9,17].

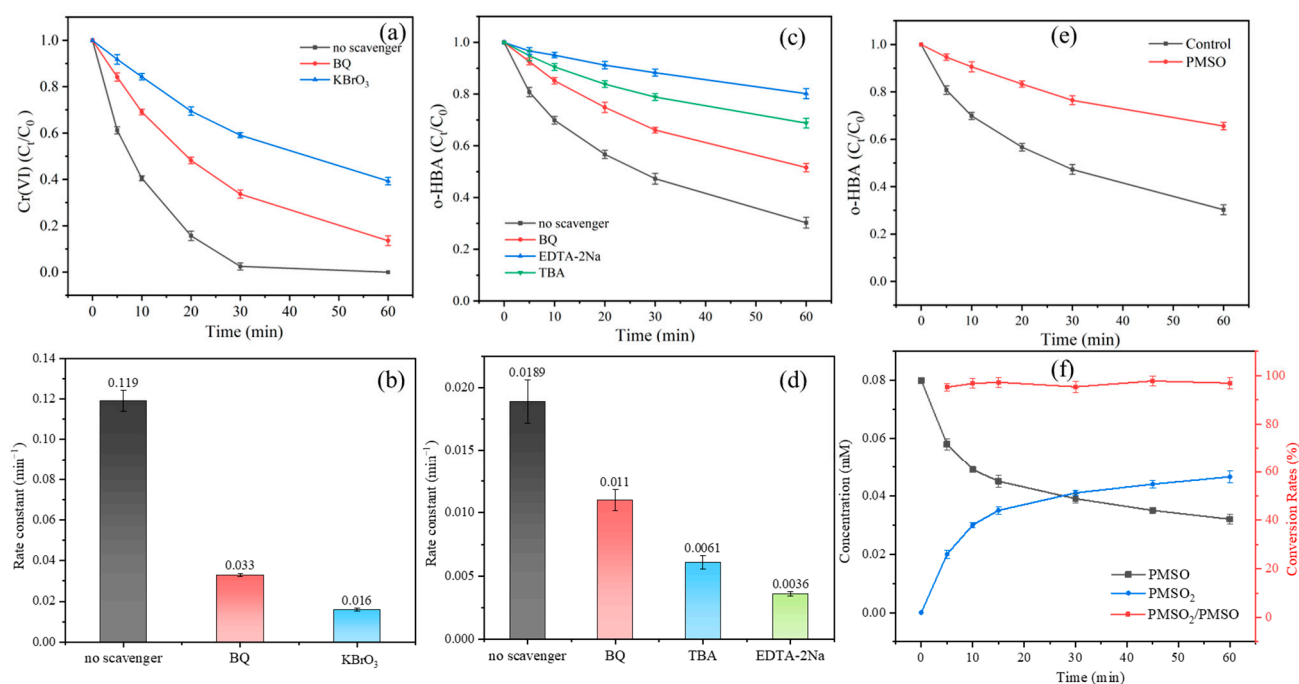
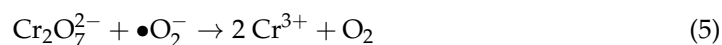
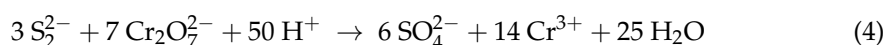
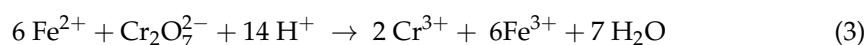
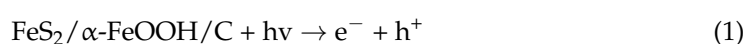


Figure 3. Effect of different quenchers on $Cr(VI)$ and *o*-HBA removal in $FeS_2/\alpha\text{-FeOOH}/C$ system: (a) $Cr(VI)$ removal rate and (b) degradation rate constant; (c) *o*-HBA removal rate and (d) degradation rate constant; (e) effect of $Fe^{IV}=O$ on *o*-HBA degradation; (f) the conversion of PMSO/PMSO₂ ($C_{Cr(VI)0} = 10.0 \text{ mg/L}$, $C_{HBA0} = 5.0 \text{ mg/L}$, $M_{cat.} = 0.1 \text{ g/L}$, $pH = 3.0$).

As for the degradation of o-HBA, TBA, EDTA-2Na and BQ were added and used as quenchers for $\bullet\text{OH}$, h^+ and $\bullet\text{O}_2^-$, respectively [21]. According to the results in Figure 3c,d, o-HBA degradation efficiencies were decreased from 69.7% to 31.2%, 19.8% and 48.4% after the addition of these quenchers, indicating that $\bullet\text{OH}$ and h^+ had greater contributions to o-HBA degradation. Importantly, the inhibitory effect of h^+ for o-HBA degradation was the highest, as most oxidative reactive species were derived from photogenerated h^+ , especially for $\bullet\text{OH}$ (Equations (6)–(12)) [22,23]. Additionally, during the Fe-based advanced oxidation system, high-valent iron–oxo species were considered important ROS for degradation of organic contaminants [24,25]. PMSO is usually used as the probe and scavenger for high-valent iron–oxo species because PMSO can be oxidized by high-valent iron–oxo species to generate PMSO_2 ($k = 1.23 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) [26]. After the addition of PMSO, the o-HBA removal efficiency was decreased from 69.7% to 34.4%, confirming the role of high-valent iron–oxo species in o-HBA degradation. To further prove the generation of high-valent iron–oxo species, a change in the PMSO/PMSO₂ concentration in the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible}$ light system was detected. As time went on, the PMSO concentration shown in Figure 3f gradually decreased and transformed into PMSO₂, whose conversion rate was close to 100%, clearly confirming the generation of high-valent iron–oxo species [27]. It has been confirmed that high-valent iron–oxo species could be generated through direct oxidation via the photocatalysis reaction or a series of indirect conversion reactions from other oxidative species (e.g., H_2O_2 , etc.) [24,28–30]. To accurately compare the contribution of different reactive species to Cr(VI) reduction and benzoic acid degradation, the specific contribution rate was calculated according to the equations in Text S4 based on the change in k_{obs} after the addition of corresponding quenchers [31]. As for the derived reactive oxygen species from photocatalysis, the results in Table 1 indicate that $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ played the primary role in Cr(VI) reduction and o-HBA degradation. Because $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ were separately ascribed to the transformation of photogenerated e^- and h^+ , the timely consumption of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ could accelerate the separation and generation of photogenerated carriers, further improving light utilization, reducing energy consumption and enhancing the environmental friendliness of the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible}$ light system. In this way, synergetic improved removal performance for both Cr(VI) and o-HBA would occur [18].

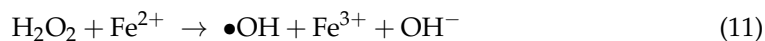
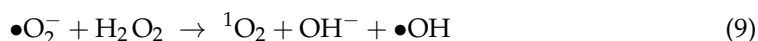
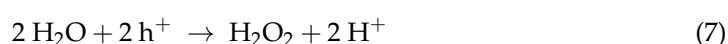


Table 1. Contribution rates of different reactive species to Cr(VI) reduction and o-HBA degradation.

	Quencher	ROS	$\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{Cr(VI)} + \text{o-HBA/Light}$	
			k_{obs} (min ^{−1})	Contribution Rate (%)
Cr(VI)	control	--	0.1191	--
	KBrO ₃	e^-	0.0165	86
	BQ	$\bullet\text{O}_2^-$	0.0332	65

Table 1. Cont.

	Quencher	ROS	FeS ₂ /α-FeOOH/C/Cr(VI) + o-HBA/Light	
			k _{obs} (min ^{−1})	Contribution Rate (%)
o-HBA	control	--	0.0189	--
	TBA	•OH	0.0061	67
	BQ	•O ₂ [−]	0.0112	40
	EDTA-2Na	hν	0.0036	80
	PMSO	Fe ^{IV} =O	0.0069	61

3.3. Proposed Mechanism and Connection Between Degradation of Benzoic Acids and Their Effect on Cr(VI) Reduction

3.3.1. Proposed Degradation Paths for Different Benzoic Acids

As discussed above, the consumption of photogenerated h⁺-derived oxidative reactive species by o-HBA apparently promoted photocatalysis and Cr(VI) reduction. However, the effect of different benzoic acids on Cr(VI) reduction was different, which might be attributed to the varying reactivity of reactive species towards different benzoic acids [32,33]. In reality, the consistent trend between TOC removal efficiencies (Figure 4e) and degradation efficiencies of different benzoic acids further corroborated the proposed inference. To solve this problem, the proposed degradation path for different benzoic acids was firstly studied. After comprehensive analysis of HPLC-MS results and the generated ROS, the proposed degradation paths were determined. As shown in Figure 4a, the characteristic peak at $m/z = 138$ corresponded to o-HBA, which firstly generated 2,5-dihydroxybenzoic acid ($m/z = 161$) and other isomers with similar structures through a hydroxylation reaction with •OH, or formed benzoquinone ($m/z = 127$) through decarboxylation, hydroxylation and hydrogen extraction [34]. Then, the ring of benzoquinone could be opened and further converted into catechol ($m/z = 116$) through decarboxylation and hydroxylation. Subsequently, after being hydroxylated by •OH, various small-molecule substances such as glycerol ($m/z = 102$) and fructose ($m/z = 152$) were produced. These small-molecule compounds were eventually degraded into CO₂ and H₂O through further mineralization. Regarding the degradation path of p-HBA, the peak at $m/z = 137$ in the HPLC-MS spectrum corresponded to the deprotonated molecule of p-HBA. Some additional fragment ions peak existed in this vicinity, possibly corresponding to the acetate adduct or dimer of p-HBA. A peak at $m/z = 109$ belonging to hydroquinone confirmed the -COO[−] loss from p-HBA. Then, a ring-opening reaction might occur in hydroquinone due to the attack of •OH on the aromatic ring [35]. Another possible degradation path involved •OH preferring to attack the ortho position of the benzene ring to generate the possible by-product of 3,4-dihydroxybenzoic acid ($m/z = 153$). •OH continued to attack the benzene ring to undergo a second addition and hydroxylation reaction of the aromatic ring to generated the compounds with a main peak at $m/z = 169$. The MS2 mass spectra of these molecules showed the loss of a neutral CO₂ fragment or dehydration, suggesting that they might be 3,4,5-trihydroxybenzoic acid ($m/z = 151$). The other two substances had similar structures and might belong to 2,4,5-trihydroxybenzoic acid ($m/z = 118$) and 2,3,4-trihydroxybenzoic acid ($m/z = 125$). All of them were formed by the continuous hydroxylation of activated sites on the benzene ring.

According to the HPLC-MS spectra of p-CBA, the peaks at m/z of 155, 127, 93, 109, 115, 137, 141, 89, and 59 corresponded to the target substances p-CBA, p-chlorophenol, phenol, p-phenylenedialdehyde, cis-butyric acid, p-hydroxybenzoic acid, trans-hexadialdehyde acid, oxalic acid, and acetic acid. Hence, it could be inferred that •OH would react with p-CBA through electrophilic behavior, thereby initiating a series of addition reactions and leading to dechlorination and dehydroxylation reactions to form various aromatic compounds and

even smaller molecular organic substances [36]. Firstly, chlorobenzoic acid was oxidized by $\bullet\text{OH}$ and the single bond connecting the Cl group and benzene ring was broken. Then, $\bullet\text{OH}$ underwent an addition reaction with the benzene ring to form p-hydroxybenzoic acid. Subsequently, the generated p-hydroxybenzoic acid further reacted with $\bullet\text{OH}$ and underwent dehydroxylation to form benzenediol. With the continuous attacking of $\bullet\text{OH}$ towards the benzene ring, dihydroxybenzoic acid and p-phenylenedialdehyde were further oxidized to cause C-C cleavage and the ring-opening reaction to form trans-hexadecadienoic acid, which was subsequently oxidized to cis-butenedioic acid and finally into small-molecule organic compounds such as oxalic acid, formic acid, and acetic acid [37]. As for m-HBA, the initial addition reaction of $\bullet\text{OH}$ showed a characteristic peak at $m/z = 161$, belonging to 2,5-dihydroxybenzoic acid. Then, the benzene ring was attacked to undergo a ring-opening reaction to generate cis-butenedioic acid-monoacyl pyruvic acid [38]. Subsequently, an isomerization reaction occurred to generate fumaric acid-monoacyl pyruvic acid, which further hydrolyzed to generate fumaric acid and pyruvic acid. Although the degradation paths of benzoic acids varied with their substituent groups and structures, some certain commonalities were observed during the degradation process; for example, $\bullet\text{OH}$ played the most important role, especially during the first addition reaction of the degradation process.

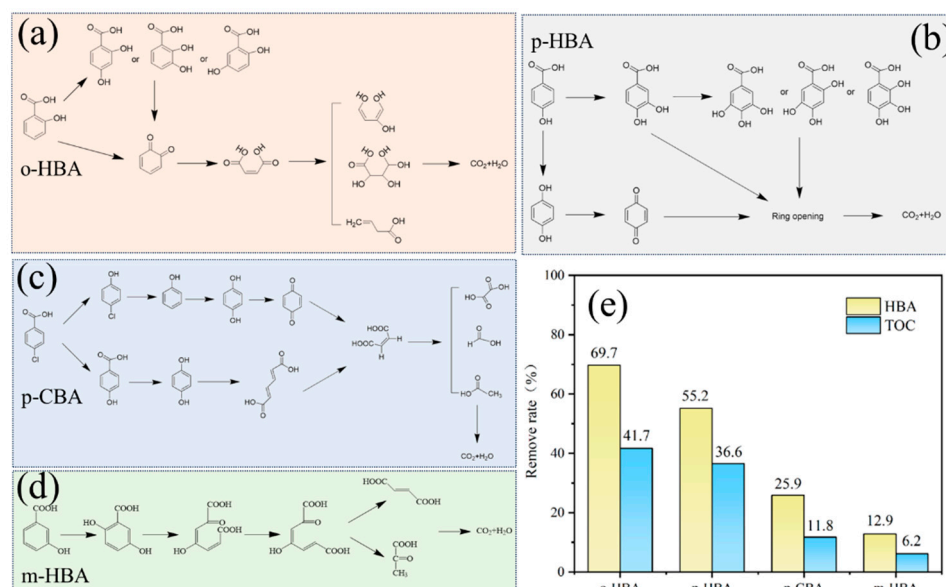


Figure 4. Proposed degradation paths for (a) o-HBA, (b) p-HBA, (c) p-CBA, and (d) m-HBA; (e) removal efficiencies of different benzoic acids and TOC.

3.3.2. Proposed Mechanisms for the Effect of Benzoic Acids on Cr(VI) Removal

As discussed above, the degradation extent of different benzoic acids determined their influence on Cr(VI) reduction, which was dependent on the structure, position and electronegativity of their substituent groups. Hence, the ability of electron withdrawing or electron donating for different substituent groups at different positions of the benzene ring was firstly analyzed, as shown in Figure 5a. The color and direction of the arrows in the substituent groups of the ball-and-stick models represented the electron-withdrawing group (EWG, the blue arrow pointed outside the benzene ring) or the electron-donating group (EDG, the red arrow pointed inside the benzene ring). The thickness of the arrows represented the strength of EWG or EDG. Totally speaking, a higher electron-donating degree of EDG has a more significant promoting effect on Cr(VI) reduction. -OH belonged to a strong conjugated electron-donating group and could activate the benzene ring. However, -COOH had a strong electron-withdrawing ability and would inactivate the benzene ring [39]. Because the activation effect of -OH on the meta-position of the benzene ring

would enhance, the -OH groups in o-HBA possessed a greater electron-donating degree and its -COOH had a relatively lesser electron-withdrawing ability as compared to other benzoic acids, making it more reactive, especially for the attacking of electrophilic $\bullet\text{OH}$. The electronegativity of halogen atoms in p-CBA made it have an electron-withdrawing effect. However, the p orbital of the halogen atom overlapped parallelly with the p orbital of carbon in the benzene ring, generating an electron-donating conjugation effect. Overall, the electron-withdrawing induction effect in p-CBA was greater than the electron-donating conjugation effect [40]. Therefore, halogen in p-CBA was a weak electron-withdrawing group. In addition, the inactivation effect of -COOH would be enhanced in the meta-position of the benzene ring, thereby suppressing the activity of m-HBA and making m-HBA recalcitrant to degradation.

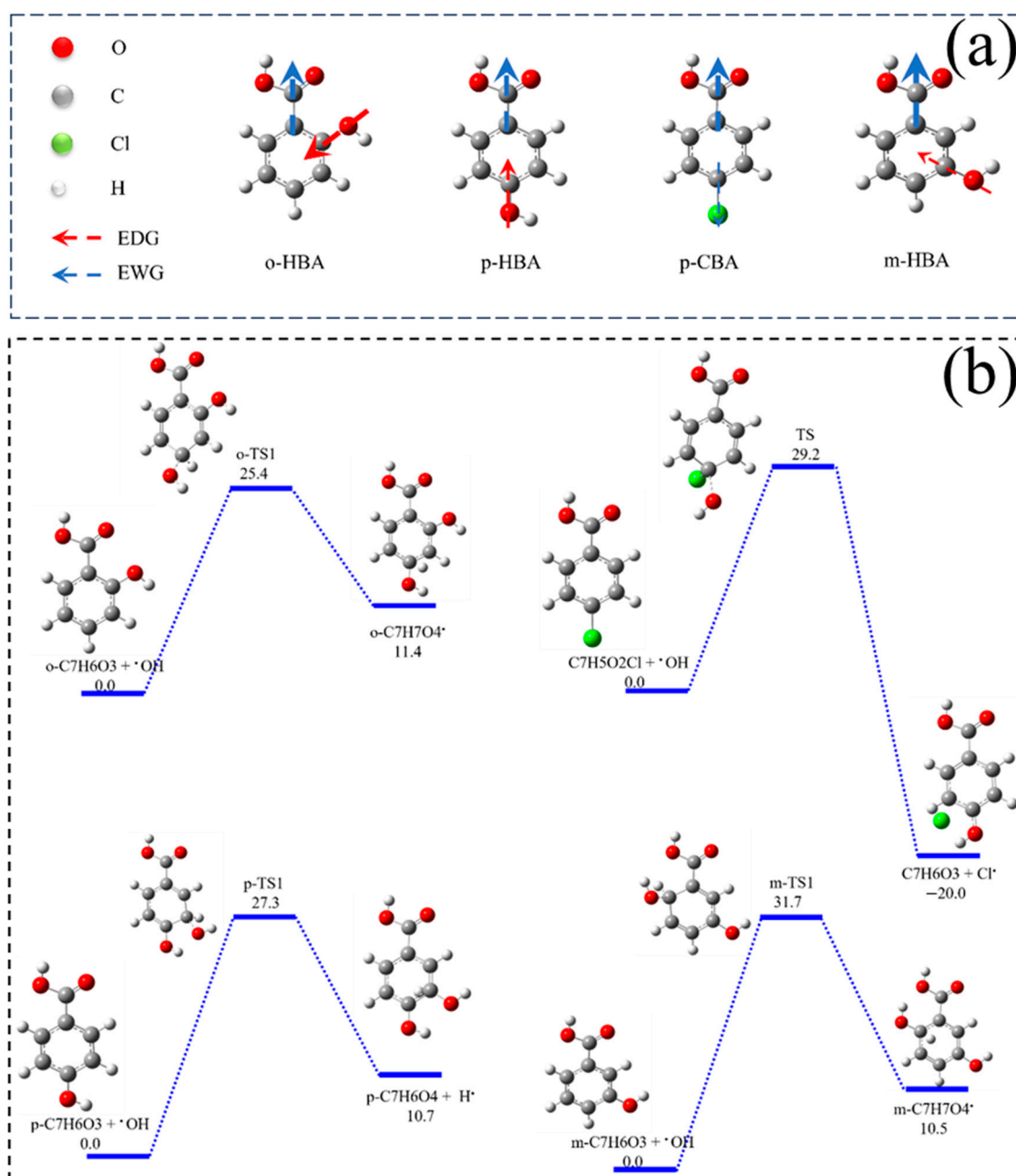


Figure 5. (a) Ball-and-stick model of different benzoic acids; (b) the calculated energy barrier diagrams for addition reactions between benzoic acids and $\bullet\text{OH}$.

Furthermore, theoretical calculations were conducted to further verify the above inference. Based on the degradation pathways of different benzoic acids, the first degradation step for all four benzoic acids was the addition reaction of $\bullet\text{OH}$. Hence, primarily considering the addition reaction between benzoic acid and $\bullet\text{OH}$, the potential energy change curve of the first addition reaction was calculated, as shown in Figure 5b [41]. The activation energy barriers for the reaction between different benzoic acids and $\bullet\text{OH}$ followed the order $\text{o-HBA} < \text{p-HBA} < \text{p-CBA} < \text{m-HBA}$ ($25.4 < 27.3 < 29.2 < 31.7$ kcal/mol). This phenomenon further proved a positive correlation between the degradability of organic substances and their accelerating effect on Cr(VI) reduction. o-HBA, with the best electron-donating effect, had a lower reaction energy barrier for reacting with $\bullet\text{OH}$ during the oxidation reaction, which could more quickly consume $\bullet\text{OH}$ and associated photogenerated h^+ to further promote the separation and generation of photogenerated carriers in the photocatalysis process. In this way, the reduction of Cr(VI) in the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible light}$ system was apparently increased. Overall, only the timely consumption of photogenerated h^+ and its derived oxidative species via organic pollutants could accelerate Cr(VI) reduction. A synergistic effect would simultaneously occur under this condition.

3.4. Influence of Typical Operation Conditions on Cr(VI) Reduction and Benzoic Acid Degradation

3.4.1. Initial Concentration

Because the initial contaminants' concentration usually varies in real wastewater, the influence of the initial Cr(VI) and o-HBA concentration on their removal performance was determined. Firstly, due to the strong reduction ability of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$, all the Cr(VI) could be removed within 60 min. However, the results in Figure 6 indicate that the k_{obs} of Cr(VI) firstly increased and then decreased as the o-HBA concentration increased from 0 to 20 mg/L. When the initial o-HBA concentration was 5 mg/L, the promotion effect for Cr(VI) removal was the highest. According to the proposed synergistic mechanism, photogenerated h^+ and its derived oxidative species, especially for $\bullet\text{OH}$, were consumed in a timely fashion when the o-HBA concentration was relatively lower, which further accelerated the separation of photogenerated carriers during photocatalysis to produce more e^- for Cr(VI) reduction. However, the degradation of o-HBA could also consume partial $\bullet\text{O}_2^-$, although $\bullet\text{O}_2^-$ was not the main oxidative reactive species. Consequently, a competition for $\bullet\text{O}_2^-$ would happen between Cr(VI) and o-HBA under the higher o-HBA concentration, resulting in the inhibition of Cr(VI) reduction. As for the influence of the initial Cr(VI) concentration on o-HBA degradation, a similar influence rule was found. When the initial Cr(VI) concentration was increased from 0 to 10 mg/L, the o-HBA removal efficiencies were apparently increased from 37% to 70%. The k_{obs} was increased by 2.7 times to 0.019 min^{-1} . This was because a suitable amount of Cr(VI) reacted with photogenerated e^- and facilitated the photocatalysis reaction to generate more h^+ for o-HBA degradation. However, both the o-HBA removal efficiency and rate constant decreased when the initial Cr(VI) concentration was further increased. According to our previous studies, the reduced Cr(III) would form a precipitate or coordinate with Fe-OH through a complexation reaction [9,17], covering the surface and consuming synthesized functional groups to influence the photocatalysis efficiency. Additionally, under suitable operation conditions, as compared to other similar photocatalysts for simultaneous removal of Cr(VI) and organic pollutants in Table S1, $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ seemed to possess relatively high Cr(VI) and organic pollutant removal performance. Overall, a suitable amount of Cr(VI) and o-HBA would promote their mutual elimination.

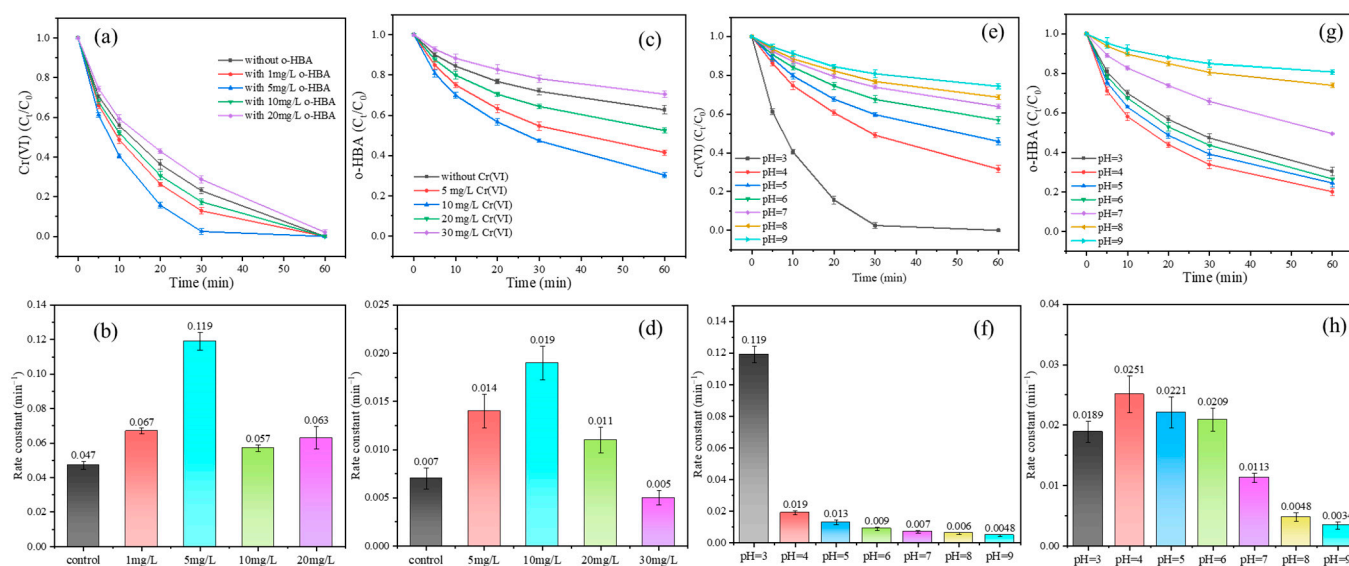
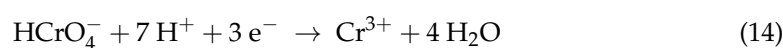
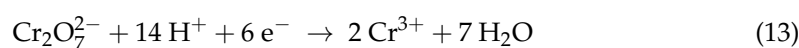


Figure 6. (a,b) Influence of initial o-HBA concentration on Cr(VI) removal and their removal rate constants; (c,d) influence of initial Cr(VI) concentration on o-HBA removal and their removal rate constants; (e,f) influence of pH on Cr(VI) removal and their removal rate constants; (g,h) influence of pH on o-HBA removal and their removal rate constants.

3.4.2. Initial pH

In real electronic industry wastewater, pH often influences the surface property of catalysts and changes the pollutant removal process. The results in Figure 6e–h show the effect of pH from 3 to 9 on Cr(VI) and o-HBA removal. With the increased pH, the Cr(VI) removal efficiency and k_{obs} were decreased. According to the Zeta potential test in our previous study [9], the isoelectric point (pH_{IEP}) of the $FeS_2/\alpha-FeOOH/C$ composite was about 4.2. When pH was less than 4.2, the surface of $FeS_2/\alpha-FeOOH/C$ was electropositive to adsorb Cr(VI) through electrostatic attraction, beneficial for the direct contact and reduction of Cr(VI) via Fe^{2+} , S_2^{2-} , e^- , etc. [9,17]. However, when pH was more than 4.2, the surface potential of $FeS_2/\alpha-FeOOH/C$ became negative to repel $Cr_2O_7^{2-}$ and $HCrO_4^-$, retarding the contact of Cr(VI) with $FeS_2/\alpha-FeOOH/C$, unfavorable for Cr(VI) reduction [42]. Additionally, H^+ would be consumed in the Cr(VI) reduction reaction according to Equations (13) and (14). The oxidizability of Cr(VI) would be decreased with increased pH. All these reasons resulted in decreased Cr(VI) removal efficiency with increased pH [43]. As for o-HBA, the degradation rate of o-HAB was gradually increased in the pH range of 3.0–4.0. When pH was further increased to 6.0, although the degradation rate constant of o-HAB decreased, a certain of promoting effect still existed on the removal efficiency of o-HAB. However, when the pH was higher than 7.0, the removal efficiency and k_{obs} of o-HAB were apparently inhibited. o-HAB was hardly degraded under alkaline conditions. This might be because the chemical properties of carboxylic acid made o-HAB have a highly active nature under acidic conditions. Additionally, o-HAB could be easily adsorbed onto the positively charged surface of a catalyst. However, as the pH was increased from neutral to alkaline, the potential of both o-HAB and $FeS_2/\alpha-FeOOH/C$ gradually became negative. Electrostatic repulsion dominated and prevented the adsorption of anionic o-HAB on the catalyst surface, adverse to o-HAB degradation [44].



3.5. Comprehensive Evaluation for Real Electronic Industry Wastewater Treatment

To comprehensively evaluate the practical applicability of the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible}$ light system, two types of real electronic industry wastewater from the Yangtze River Delta area of China were treated. The basic water index of the real wastewater is shown in Table S2. The results in Figure 7 indicate that most of the Cr(VI) could be reduced within about 30 min for the two wastewaters despite their complex components. For the removal of total Cr, about 97% and 99% of total Cr were removed from the first and second wastewaters within about 12 h. Both the effluent Cr(VI) and total Cr concentration for the two types of wastewaters after treatment via the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible}$ light system could steadily meet the emission standards of China (Cr(VI) < 0.5 mg/L and total Cr < 1.5 mg/L, GB 21900-2008) [45]. Additionally, 88% and 92% of total o-HAB were degraded within about 60 min, proving the strong photocatalysis ability for simultaneous removal of Cr and organic pollutants. The test on the dissolution rate of Fe indicated that only about 0.3–0.4 mg/L of Fe was leached, showing the relatively strong stability of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$. All these phenomena indicated the strong applicability and sustainability of synthesized $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ for synergetic removal of Cr(VI) and coexisting organic pollutants in real electronic industry wastewater.

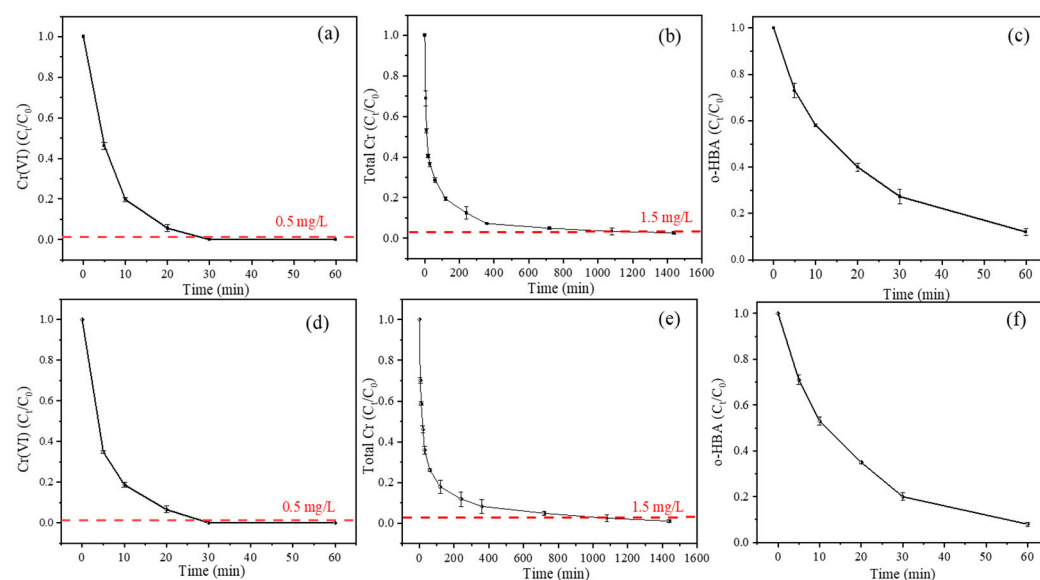


Figure 7. Cr(VI) and organic pollutant removal performance in real mixed electroplating wastewater via $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible}$ light system: (a–c) first wastewater for manufacturing copper and aluminum circuit board and (d–f) second wastewater for manufacturing palladium and nickel circuit board (addition dosage of catalyst: 1.5 g/L).

4. Conclusions

In this study, the simultaneous removal of different benzoic acids and Cr(VI) via the $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}/\text{visible}$ light system was performed to study the influence of benzoic acid degradation on Cr(VI) reduction. The results showed the efficacy of different benzoic acids in accelerating Cr(VI) reduction in the order o-HBA > p-HBA > p-CBA > blank > m-HBA. Under the addition of o-HBA, the Cr(VI) removal rate constant was increased by 1.5 times (0.047 to 0.119 min^{-1}). Quenching experiments indicated that photogenerated e^- and $\bullet\text{O}_2^-$ played an important role in Cr(VI) reduction. Additionally, photogenerated h^+ and its derived $\bullet\text{OH}$ contributed to o-HBA degradation. Because $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ were separately ascribed to photogenerated e^- and h^+ , the timely consumption of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ further accelerated the separation and generation of photogenerated carriers, resulting in synergetic improved removal performance for both Cr(VI) and o-HBA. Naturally, the

light utilization and environmental sustainability were further improved. Theoretical calculations indicated that the electron-donating ability of hydroxy groups in o-HBA was better than other benzoic acids, making the activation energy for the addition reaction with $\bullet\text{OH}$ lower. Hence, $\bullet\text{OH}$ would be consumed more quickly, leading to a greater promoting effect of o-HBA on Cr(VI) reduction. The real wastewater treatment experiment indicated the relatively strong applicability of $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ for synergetic removal of Cr(VI) and coexisting organic pollutants in real electronic industry wastewater. This study supplied a novel photo-assisted technology for synergistic and sustainable removal of typical heavy metal and organic contaminants in electronic industry wastewater.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su17209239/s1>, Text S1: Preparation method for optimal $\text{FeS}_2/\alpha\text{-FeOOH}/\text{C}$ [9]; Text S2: The specific test methods for different benzoic acids; Text S3: The specific steps for theoretical calculation performed on Gaussian 16 software package; Text S4: The equations for calculating the specific contribution rate of different ROS on Cr(VI) reduction and benzoic acid degradation [31]; Figure S1: Structural diagrams of different benzoic acids; Figure S2: The EPR spectra of (a) $\text{DMPO}\cdot\text{O}_2^-$ and (b) $\text{DMPO}\cdot\text{OH}$; Table S1: Comparison of simultaneous removal ability for Cr(VI) and organic pollutants via similar catalysts in this study and previous studies [33,46–49]; Table S2: The main water quality indicators of real electronic industry wastewater.

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Conflicts of Interest: Authors Jinqun Zhou, Qinghui Liu and Gang Chen were employed by the company Shennan Circuits Co., Ltd. Authors Wei Zhang and Mengbo Yan were employed by the company Wuxi Shennan Circuits Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

p-HBA	p-hydroxybenzoic acid
o-HBA	o-hydroxybenzoic acid
m-HBA	m-hydroxybenzoic acid
p-CBA	parachlorobenzoic-acid

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