

## Article

# Activation of Peroxymonosulfate by Fe, O Co-Embedded Biochar for the Degradation of Tetracycline: Performance and Mechanisms

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**Abstract:** In recent years, pollution stemming from pharmaceuticals has garnered widespread global concern, which exacerbates the ecological risk to both surface and groundwater. In the current study, Fe and O co-embedded biochar (Fe-O-BC) was synthesized through a one-step pyrolysis procedure with corncob serving as the feedstock. The fabricated Fe-O-BC catalysts were characterized by various techniques and were employed for the activation of peroxymonosulfate (PMS) to degrade tetracycline (TC). TC was rapidly degraded within 40 min, with a degradation rate of  $0.1225 \text{ min}^{-1}$ , which was much higher than those for O-BC/PMS ( $0.0228 \text{ min}^{-1}$ ) and Fe-BC/PMS ( $0.0271 \text{ min}^{-1}$ ) under the same conditions. The effects of PMS dosage, Fe-O-BC dose, initial pH value and coexisting anions for TC degradation were investigated. Finally, the mechanism of TC oxidation in the catalytic system was implored through experiments of determining the active sites and radical scavenging experiments. The C-O-Fe bond in the catalyst was confirmed to be the dominant active sites accelerating TC degradation. Free diffused  $\text{HO}^\bullet$ , the surface-bound  $\text{HO}^\bullet$  and  $\text{SO}_4^{\bullet-}$  and  $\text{O}_2^{\bullet-}$  participated in the reaction and absorbed  $\text{SO}_4^{\bullet-}$ , and  $\text{HO}^\bullet$  predominantly contributed to TC degradation. This study provides an efficient and green alternative for pharmaceutical wastewater treatment by Fe and O co-doped catalyst-induced heterogeneous process.

**Keywords:** pharmaceuticals; Fe and O co-embedded catalyst; peroxymonosulfate; biochar; heterogeneous catalysis



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## 1. Introduction

In the latest decades, pollution by emerging pollutants (EPs) such as personal care products, pesticides, pharmaceuticals, household products, endocrine disruptors, illegal drugs and microplastics have globally occurred in both surface and subsurface aquatic systems [1,2]. EPs are considered a latent negative effect on both ecosystems and human health since they are not commonly regulated by any regulatory framework and environmental legislation so far. Among myriad EPs, pharmaceuticals represented by tetracyclines (TCs) have been widely detected in wastewater, groundwater and even potable water [3,4]. Exposure to TCs pollution was found to arouse growth inhibition, cell permeability and oxidative stress variation to aquatic organisms and variable hazard quotients regarding age to human health [5,6]. Due to the stable chemical structure and low biodegradability of TCs, conventional treatments exhibited some limitations such as low efficacy and as being time-consuming in removing TCs [7,8]. Hence, there is a great significance and necessity to develop a green friendly and cost-effective technique to eliminate TCs from aquatic environments.

Persulfate based advanced oxidation processes (PS-AOPs), which produce reactive oxygen species, such as sulfate radical ( $\text{SO}_4^{\bullet-}$ ), hydroxyl radical ( $\text{HO}^{\bullet}$ ) and singlet oxygen ( $^1\text{O}_2$ ) via activation of Peroxymonosulfate (PMS) or Peroxydisulfate (PDS), have been identified as efficient and economical strategies for TCs removal [9,10]. Compared with traditional popular oxidants, e.g.,  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , PS has garnered increasing interest due to its energy saving of activation, security of transportation and convenience of storage as well as superior performance of dominant  $\text{SO}_4^{\bullet-}$  [11,12]. The activation of PS by carbonous materials, especially biochar (BC) is recognized as a relatively inexpensive, green and practical process [13,14]. BC is a pyrolysis byproduct from organic wastes under oxygen deprived conditions. The abundant functional groups on the BC surface including hydroxyl, carboxyl and quinone ones were identified to be reactive for  $\text{SO}_4^{\bullet-}$  generation in PS-involved processes [14]. Large numbers of studies have emphasized the potential of BC for activating PS. Cai et al. unveiled that biochar pyrolyzed from biogas residue exhibited superior catalytic activity of PMS activation for the oxidation of TC with 97.9% of removal efficiency [15]. To enhance the effectiveness of the produced biochar as catalytic materials, there have been many attempts at embedding organic or inorganic components into the BC matrix [16]. Iron, benefiting from its low cost, abundant availability on earth and insignificant secondary pollution, has emerged as the preeminent inorganic metal incorporated into biochar [17]. For instance, Zuo et al. reported that iron-incorporated biochar (Fe-BC) obtained from peanut shells indicated a significant catalytic efficacy for PMS activation to degrade TC in the natural pH [18]. Heteroatoms including N, O, S and B atoms have also been employed as intriguing dopants for enhancing BC properties [16]. Among the various dopants, O ones were observed to positively improve the reactivity for persulfate activation. Huang et al. demonstrated that the incorporation of O atoms into the coconut shell derived biochar (CSBC) increased the catalytic activity of PMS for sulfathiazole degradation [19]. More importantly, the co-doping of iron and heteroatoms was proved to have more flexibility and better performance for removal of refractory organic pollutants [20]. For example, Chen et al. found that iron and nitrogen co-doped biochar (Fe-N-BC) using peanut shells as feedstocks showed higher catalytic activity than iron or nitrogen single-doped biochar, and Fe-N-BC had a 12 times higher removal rate compared to the pristine biochar [21]. Notably, Huang et al. indicated that the catalytic efficiency of O embedded biochar (O-BC) materials was superior to the N doped ones (N-BC) for the activation of PMS to oxidize antibiotics [19]. Motivated by these earlier discoveries, one can postulate that co-assembling biochar with Fe and O may achieve a better PS activation and a more effective contaminant degradation.

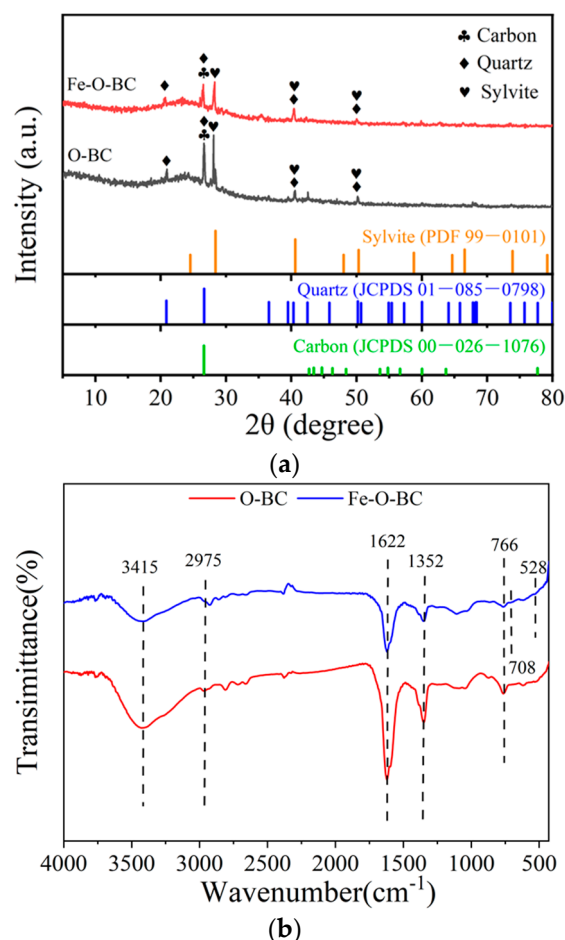
Hereon, this study explored the co-doping of Fe and O into corncob-derived BC for the oxidative elimination of EPs using TC as the representative. Iron and oxygen singly doped or co-doped BC named Fe-BC, O-BC and Fe-O-BC were synthesized via one step calcination and applied to activate PMS for TC oxidation. Moreover, the factors that influence the rate of TC degradation were examined, such as the dose of PMS, the amount of catalyst used, the initial pH of the solution and the presence of coexisting anions. Additionally, the active sites of the catalysts were elaborated through comparative experiments using different catalysts. Finally, the contributions of the active species and the degradation mechanism were elucidated by scavenging experiments.

## 2. Results and Discussion

### 2.1. Characterization of the Catalysts

The XRD pattern of O-BC and Fe-O-BC are displayed in Figure 1a. The distinct peak near  $27^\circ$  of O-BC and Fe-O-BC can be attributed to the graphite structure of carbon (JCPDS 00-026-1076) [22]. The small diffraction peaks at  $20.6^\circ$ ,  $26.5^\circ$ ,  $40.4^\circ$  and  $50.1^\circ$  for both O-BC and Fe-O-BC indicate the presence of Si-containing phase, named quartz, (JCPDS 01-085-0798) was confirmed, which can be generally found in BC-based materials [18]. The diffraction peaks at  $28.2^\circ$ ,  $40.4^\circ$  and  $50.1^\circ$  for both O-BC and Fe-O-BC are attributed to sylvite [23,24]. In addition, no obvious peak corresponding to iron oxides was observed in

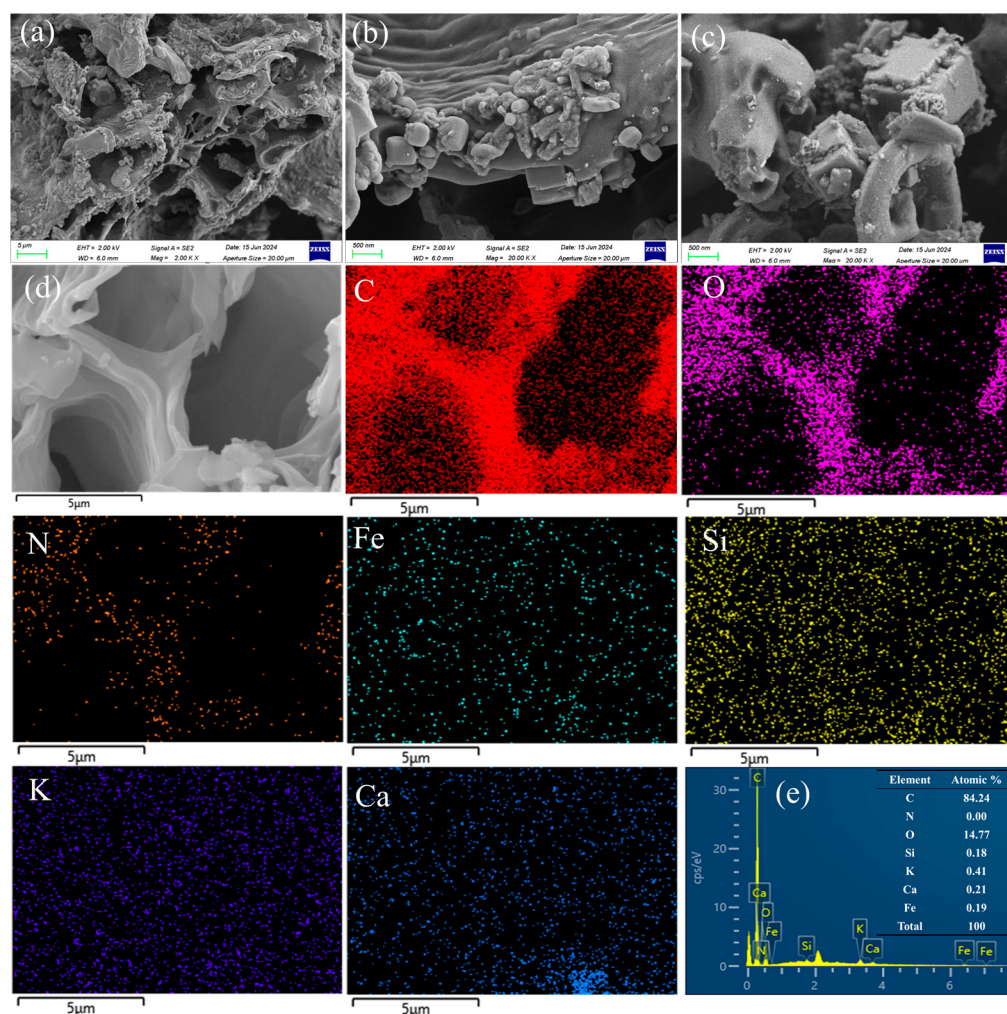
the spectrum of Fe-O-BC, indicating that the doped Fe probably present in the form of Fe complexes or the formed iron oxides can be neglected.



**Figure 1.** (a) XRD pattern of O-BC and Fe-O-BC; (b) FTIR spectra of O-BC and Fe-O-BC.

The FTIR spectra are depicted in Figure 1b. The peaks at  $766\text{ cm}^{-1}$  and  $1352\text{ cm}^{-1}$  responded to the out-of-plane deformation vibration of aromatic C-H and the C-H bending vibration peak corresponding to  $\text{CH}_2$ , respectively [25]. The peaks of C=O tensile vibration ( $1622\text{ cm}^{-1}$ ) and C-O bending vibration ( $2975\text{ cm}^{-1}$ ) were also observed for both O-BC and Fe-O-BC [26,27]. The characteristic peak at  $3415\text{ cm}^{-1}$  corresponded to the stretching vibration of -OH [21]. Meanwhile, the new adsorption wave for Fe-O-BC at near  $528$  and  $708\text{ cm}^{-1}$  was associated with the tensile vibration of Fe-O, further substantiating the potential existence of Fe complexes on the Fe-O-BC surface [18,28].

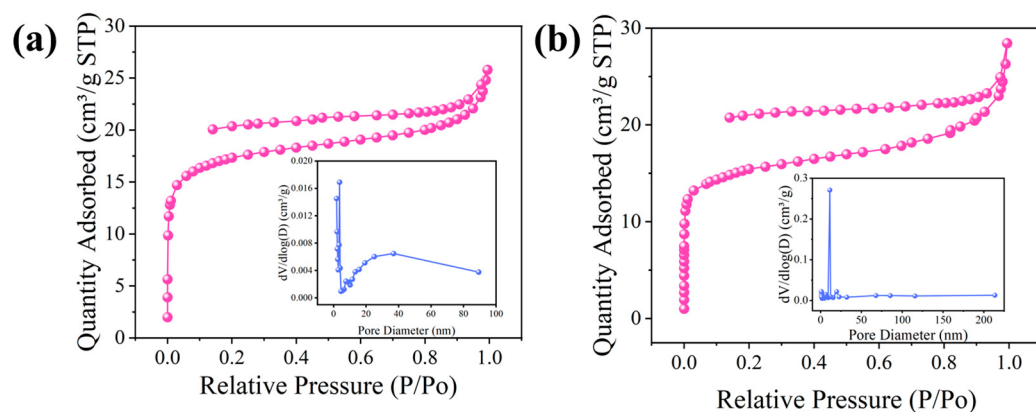
The SEM images of Fe-O-BC are indicated in Figure 2a–d. As shown in Figure 2a, a porous structure was observed for Fe-O-BC, and the pores were irregularly distributed with different diameters. In addition, a pronounced gully morphology like rolling hills was found on the outer wall of the pores from Figure 2b. It can be seen from Figure 2c,d that the surface of Fe-O-BC is shaggy and unsmooth with bits of small particles presented on it. In addition, the EDS-mapping images of the elements C, O, N, Fe, Si, K and Ca were recorded via the surface scanning of Fe-O-BC (Figure 2d). The elemental images indicated that Fe and O were successfully embedded into the biochar. The actual chemical composition of the sample obtained from the EDS analysis is shown in Figure 2e, and the atomic ratios of C, N, O, Si, K, Ca and Fe were 84.24%, 0.00%, 14.77%, 0.18%, 0.41%, 0.21% and 0.19%, respectively.



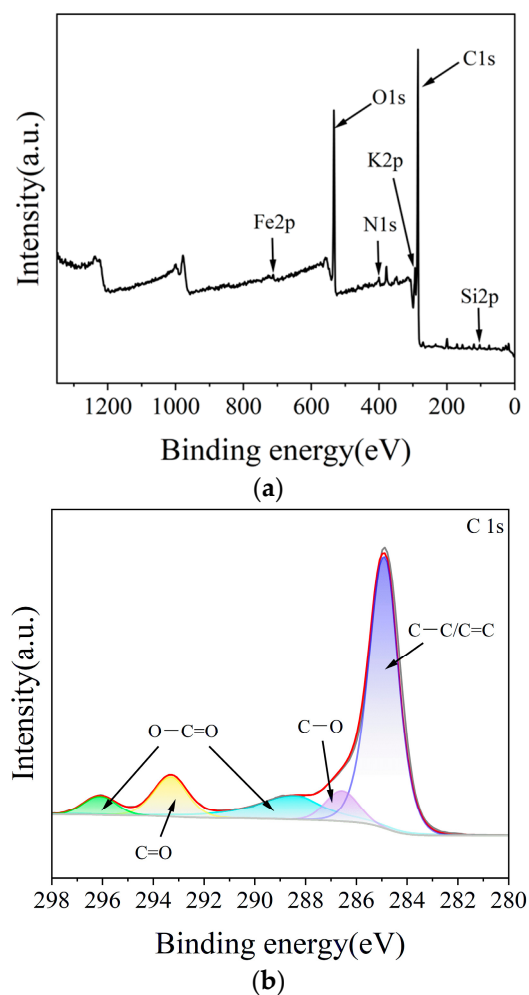
**Figure 2.** SEM images (a–c) and the EDS analysis (d,e) of Fe-O-BC.

The  $N_2$  adsorption desorption curve and pore size distribution of Fe-O-BC and BC are shown in Figure 3. The surface areas of BC and Fe-O-BC were  $56.47 \text{ m}^2 \text{ g}^{-1}$  and  $63.82 \text{ m}^2 \text{ g}^{-1}$ , respectively. The larger surface area of Fe-O-BC was attributed to the abundant porosity [29]. According to the IUPAC classification, both BC and Fe-O-BC exhibited Type IV isotherms, indicative of a mesoporous structure. The pore size distribution (the insets of Figure 3) also confirmed that the majority of pores in both Fe-O-BC and BC were within the mesopore range (2–50 nm) [30]. In addition, the average pore diameters of BC and Fe-O-BC were 5.77 nm and 6.79 nm, respectively. The adsorption and desorption curves of  $N_2$  were not closed, which might be attributed to the fact that the pores of the carbon material tended to shrink during gas adsorption, making it difficult for the adsorbed gas to desorb. [31,32] The little difference of surface area and pore size distribution between Fe-O-BC and BC revealed that the structure of biochar was not significantly altered by Fe and O co-embedding.

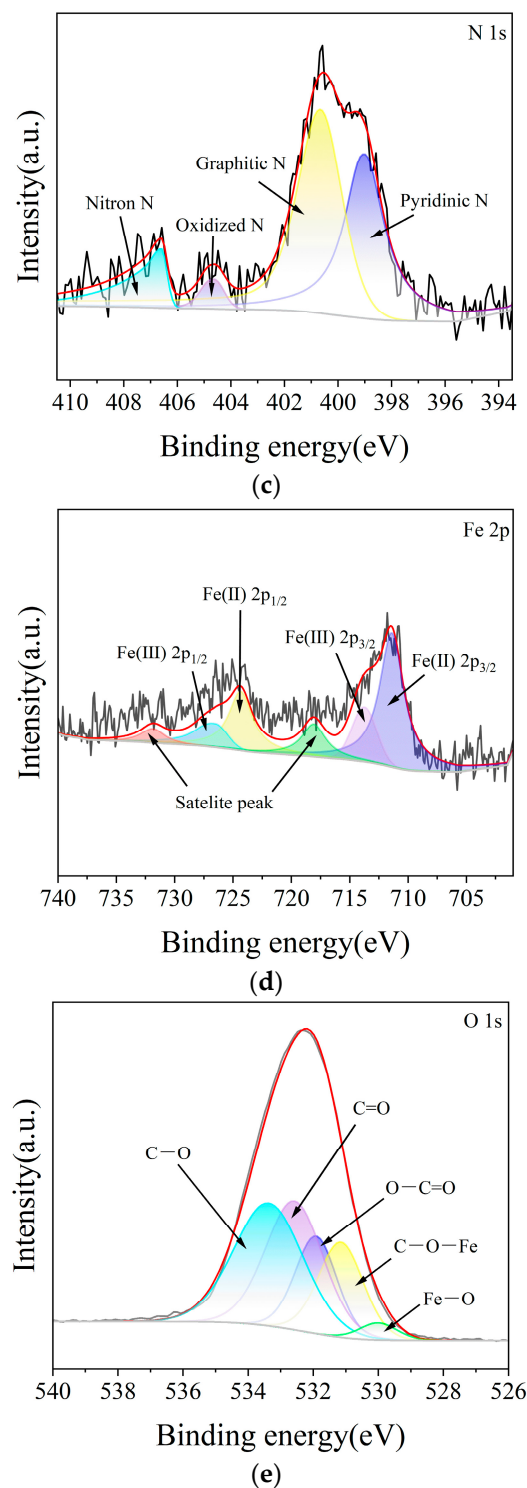
The XPS analyses of Fe-O-BC are manifested in Figure 4. The comprehensive scan spectra revealed that the primary elements in Fe-O-BC are Fe, N, O, Si, K and C. The C 1s spectra are shown in Figure 4b. The peaks at 286.6, 293.3, 288.4, 296.1 and 284.8 eV were attributed to C-O, C=O, O-C=O and C-C/C=C in the aromatic rings, respectively [28,33]. This suggests that the surface of the BC was enriched with oxygen-containing functional groups (OFGs),  $\pi$ -electron clouds and aromatized structures. The OFGs on the surface of BC-based materials were frequently claimed as reactive sites for PMS activation in the wastewater treatment [14,34].



**Figure 3.** Nitrogen adsorption-desorption isotherms and pore size distribution curves (inserts) of Fe-O-BC (a) and BC (b).



**Figure 4.** Cont.



**Figure 4.** The full-scale XPS spectrum (a), C 1s (b), N 1s (c), Fe 2p (d) and O 1s (e), of Fe-O-BC.

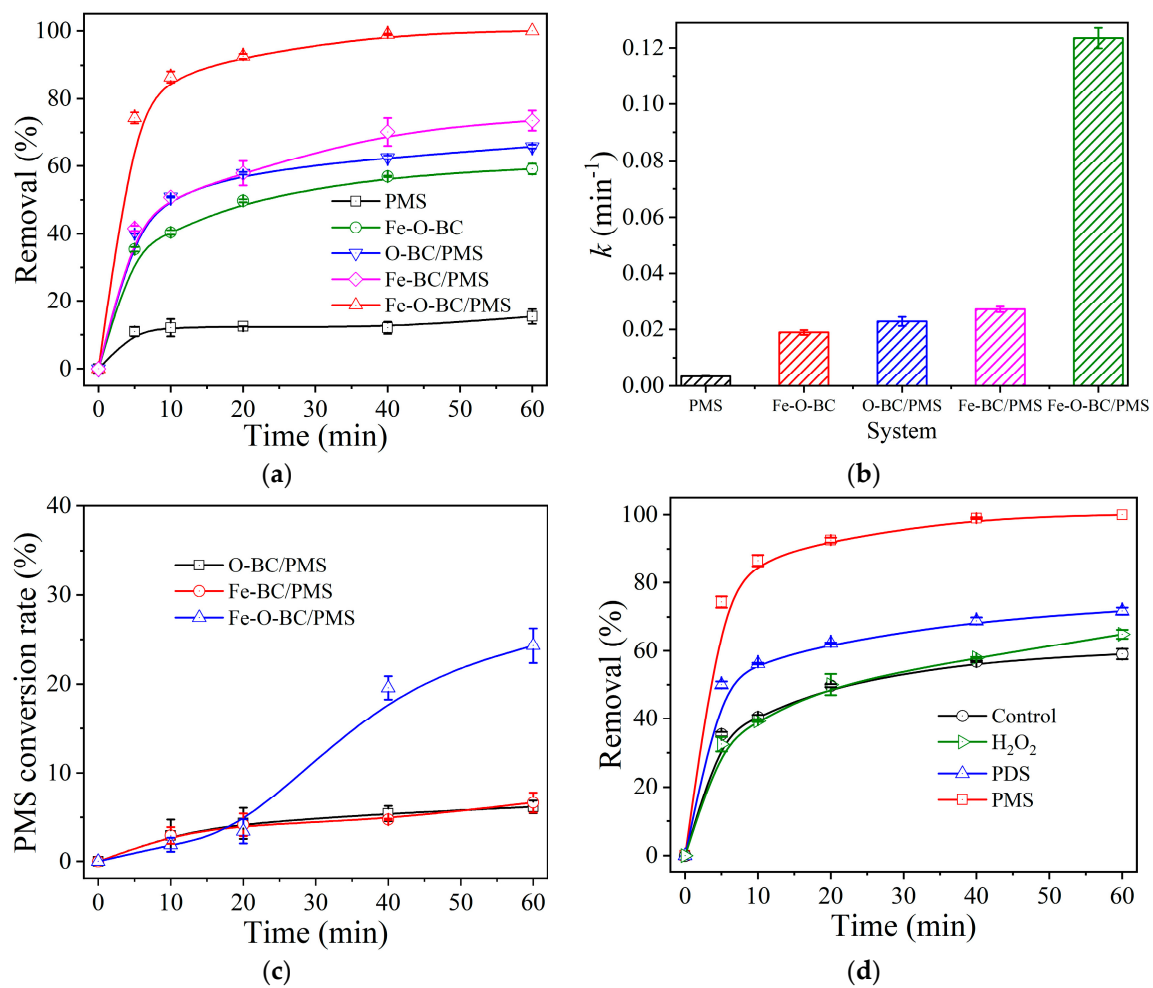
In the N1s spectrum (Figure 4c), the peaks at 399.0, 400.7, 404.6 and 406.6 eV correspond to pyridinic N, graphitic N, oxidized N and Nitron N, respectively [35,36]. Pyridine N and graphite N are reported to induce catalytic reactions for activation of PMS through Lewis alkaline sites or electron transformation [37,38]. As shown in Figure 4d, the peaks of Fe (II) (711.4 and 722.4 eV) and Fe (III) (713.9 and 726.7 eV) appeared in the Fe 2p spectrum. The peaks at 718.0 and 731.8 eV were dedicated to the satellite peaks of Fe (II) and Fe (III) [21]. The Fe-C peak was not observed around 707.6 eV, suggesting that Fe was not directly incorporated into the BC layer but was instead complexed on the BC surface through

functional groups [39]. The above findings indicated that both Fe (III) and Fe (II) were prevalent in the Fe-O-BC, serving as potential active sites for PMS activation. The O 1s spectra of Fe-O-BC are depicted in Figure 4e. The peaks located at 530.0, 531.9, 532.6 and 533.4 eV correspond to Fe-O, O-C=O, C=O and C-O [22,40]. The finding of the Fe-O peak was consistent with the observation in FTIR in Figure 1b. The peak at 531.2 eV was ascribed to C-O-Fe, serving as direct evidence for the existence of iron complexes on the Fe-O-BC surface [28].

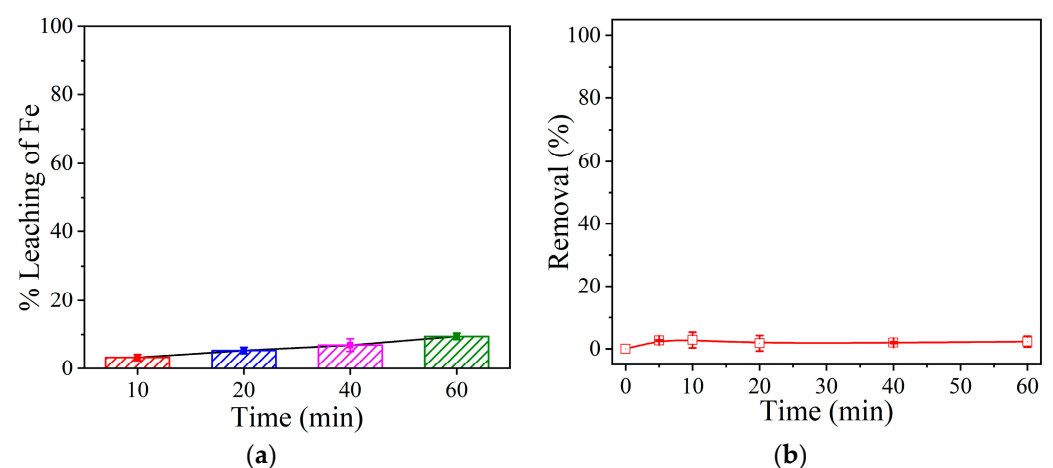
## 2.2. Catalytic Performance of the Materials

The prepared BC-based catalysts were applied to activate PMS for the oxidation of TC. As illustrated in Figure 5a, 15.4% of the TC decomposed by PMS alone after 60 min with a rate constant of  $0.0034 \text{ min}^{-1}$ , which can be ascribed to the self-decomposition of PMS. The single doped materials Fe-BC and O-BC exhibited moderate removal efficiencies of respectively 73.5% and 65.8% for TC after 60 min. With the addition of Fe-O-BC, TC degradation efficiency observably reached 99.1% within 40 min under the same condition. The reaction rate of TC degradation by Fe-O-BC/PMS ( $0.1225 \text{ min}^{-1}$ ) was 5.4 folds that by O-BC/PMS ( $0.0228 \text{ min}^{-1}$ ) and 4.5 folds that by Fe-BC/PMS ( $0.0271 \text{ min}^{-1}$ ) as displayed in Figure 5b. To determine the role of advanced oxidation in TC removal in the Fe-O-BC/PMS system, an adsorption experiment was carried out using Fe-O-BC without the presence of the oxidant (PMS). It can be seen that Fe-O-BC exhibited an adsorption efficiency of 59.1% for TC in 60 min, suggesting that the degradation of TC was the synergistic effect of adsorption and PMS activation by Fe-O-BC. Additionally, to further confirm that TC was oxidized but not adsorbed by the materials, the Fe-O-BC was separated by centrifugalizing after the reaction of Fe-O-BC/PMS and Fe-O-BC alone systems. Then, methanol was used to extract the adsorbed TC on the separated materials twice followed by monitoring the TC in the obtained methanol solution. No TC was detected in the solution obtained after the Fe-O-BC/PMS system, but TC was found after the Fe-O-BC alone systems, indicating that TC was completely oxidized in the Fe-O-BC/PMS process. The superior degradation efficiency of TC induced by Fe-O-BC was mainly due to the acceleration of PMS activation by the oxygen and iron containing functional groups of Fe-O-BC, leading to the production of sufficient active species. To verify this point, PMS decomposition by O-BC, Fe-BC and Fe-O-BC was compared in Figure 5c. PMS was decomposed less than 6.5% within 60 min by O-BC and Fe-BC; however, it was rapidly consumed by 24.3% by Fe-O-BC, which was in accordance with the dramatic degradation of TC within 60 min. The above results revealed that Fe and O co-embedded biochar was advantaged over Fe or O single-doped biochar for PMS activation and TC oxidation. Comparison experiments were further conducted using the common oxidants  $\text{H}_2\text{O}_2$  and PDS. As illustrated in Figure 5d, TC degradation followed the order of  $\text{PMS} > \text{PDS} > \text{H}_2\text{O}_2$ , which probably can be ascribed to the asymmetrical structure of PMS resulting in its being activated more easily [12].

To assess the environmental friendliness of the present advanced process, the monitor of iron leaching in the oxidative system was employed. As recorded in Figure 6a, the leaching of Fe ions was less than 9% at the end of the reaction, which was far less than some of the reported materials [41,42], indicating the friendliness of the Fe-O-BC/PMS system. In addition, a control experiment was conducted using the maximum leaching of Fe to verify the contribution of the leached Fe to the performance of the material. As shown in Figure 6b, the TC removal was less than 3% within 60 min in the PMS activation process by the leached Fe, revealing that the contribution of the leached Fe to the performance of the material could be neglected.



**Figure 5.** (a) TC removal in various systems, (b) observed rate constants of TC removal in various systems, (c) PMS decomposition in different systems and (d) TC degradation with different oxidants. Conditions: [TC] = 0.2 mM, [PMS] = 5 mM, [Catalyst] = 2 g L<sup>-1</sup>.

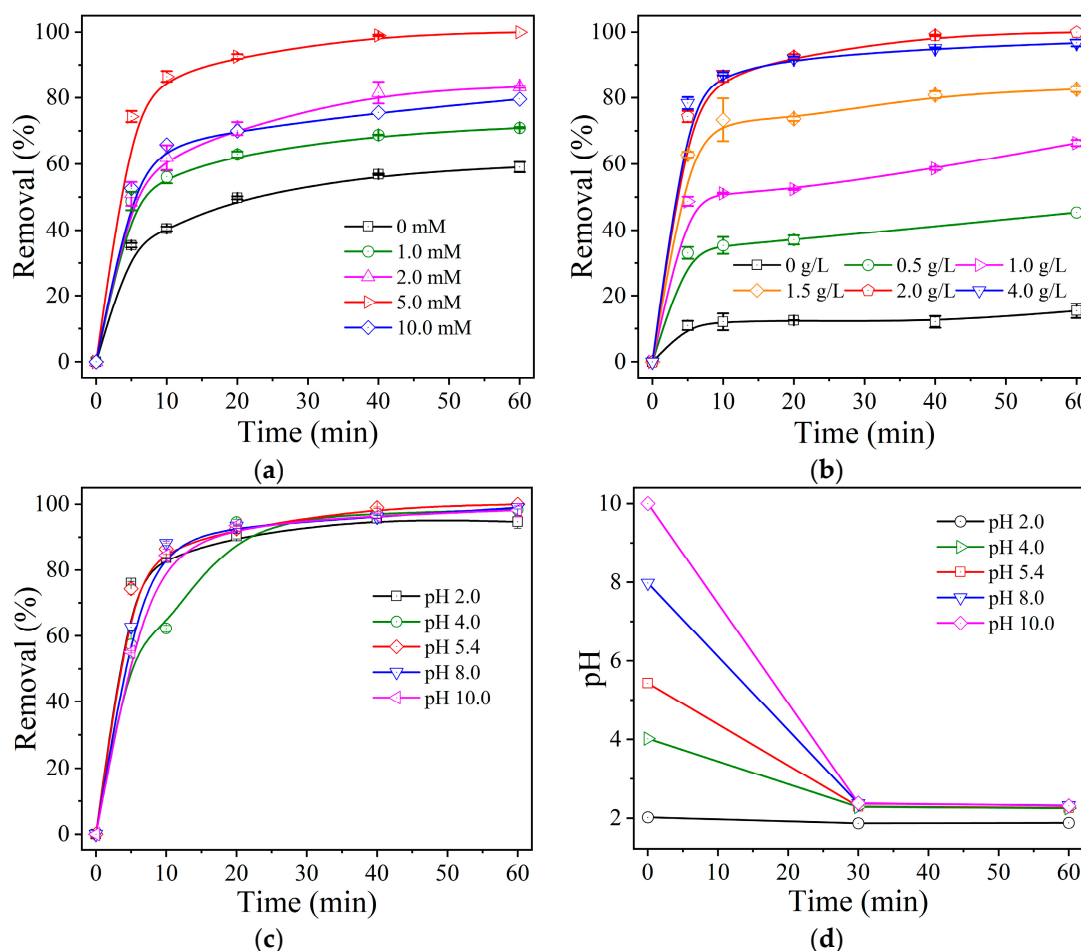


**Figure 6.** The leaching of Fe with time in the Fe-O-BC/PMS process (a), TC degradation in the catalytic process using the leached Fe (b).

### 2.3. Effects of Parameters

The impact of PMS dosage on TC oxidation is depicted in Figure 7a. Fe-O-BC led to a removal efficiency of 59.1% of TC in 60 min without PMS, which can be attributed to the

adsorption of organics by the prepared materials. With the addition of PMS from 1 mM to 5 mM, the oxidation efficiency of TC obviously increased to 100.0% in 60 min under the same conditions as for Fe-O-BC alone. This is due to the reactive species yielded in the system activating of PMS by Fe-O-BC. However, the TC removal decreased to 79.6% in 60 min with further addition to 10 mM, implying that overdosed PMS can quench the produced reactive species (e.g.,  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^\bullet$ ) in the processes, which was the reason for the decrease of TC removal [43]. Xue et al. also reported comparable findings when employing an Fe, N-BC/PMS system for the removal of sulfamethoxazole [26].



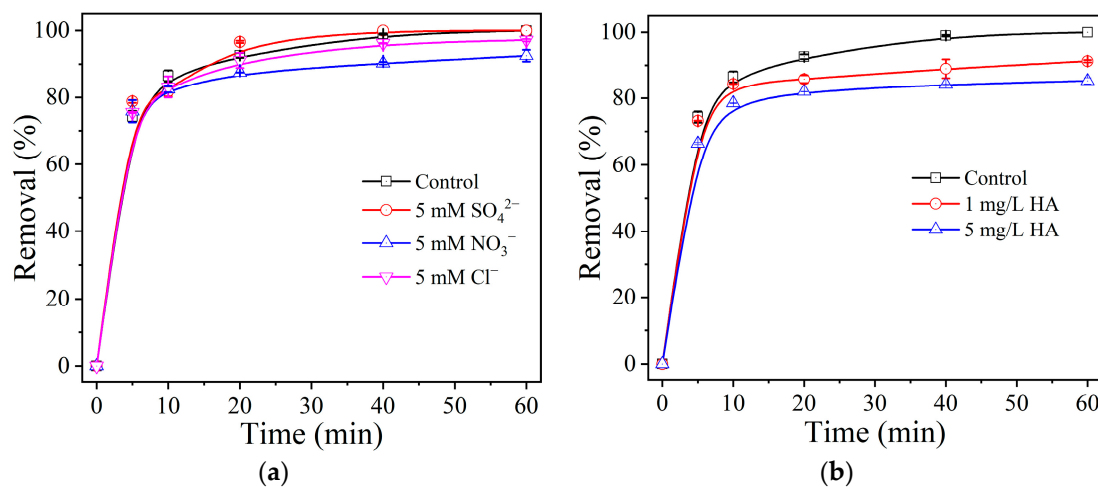
**Figure 7.** The effects of (a) PMS dosage, (b) catalyst dosage, (c) initial pH for TC degradation, (d) the evolution of pH value with reaction time in the systems of various initial pH. Conditions:  $[\text{TC}] = 0.2 \text{ mM}$ ,  $[\text{PMS}] = 5 \text{ mM}$ ,  $[\text{Catalyst}] = 2 \text{ g L}^{-1}$ .

The impact of the catalyst dose on TC oxidation is also displayed in Figure 7b. The TC removal efficiency of Fe-O-BC was elevated from 15.4% to 100% as the catalyst amount rose from 0 mg/L to 2 g/L. This is primarily attributed to the increased availability of active sites for PMS activation with higher catalyst doses. In addition, a decreasing trend of TC oxidation efficiency was observed as the catalyst dose was further elevated to 4 g/L. This can be explained by the fact that as the concentration of the catalyst increases, the distance between nanoparticles diminishes. Consequently, there is an elevated possibility of oxidative species produced on the material surface interacting with one another or with PMS prior to encountering the pollutants. A similar finding was also observed by Yu et al. whereby the contaminant degradation efficiency was reduced slightly as the catalyst amount rose from 0.45 g/L to 0.6 g/L in a P-Fe/Co/N@BC-PMS system, which was mainly caused by the self-quenching of the produced reactive species [41].

The influence of the initial pH values on TC oxidation was examined in the Fe-O-BC/PMS system with pH values ranging from 2 to 10. As illustrated in Figure 7c.

TC could be effectively degraded and almost effect-free with pH variation by the Fe-O-BC/PMS system within the pH range of 2–10, revealing the good adaptability to pH of the Fe-O-BC/PMS process. This can be attributed to the findings that the pH value of the solution quickly decreased to a similar acidic condition although the initial pH value varied in the range of 2–10 (Figure 7d). The decrease of the pH value in the process can be possibly ascribed to the generation of  $H^+$  from activation of PMS and the production of acidic intermediates of TC. Ren et al. also reported that TC degradation was negatively impacted as the initial pH ranged from 2.97 to 11.02 in a PMS activation process by sepiolite/ $Fe_3O_4$  [10].

Various anions and organic matter are ubiquitously concomitant in wastewater, and those substances have been identified to affect the degradation of organic contaminants [44]. In this work, the effects of  $SO_4^{2-}$ ,  $Cl^-$ ,  $NO_3^-$  and humic acid (HA) as the representatives of anions and natural organic matter on the removal of TC were also examined. As depicted in Figure 8a, the addition of  $SO_4^{2-}$  scarcely affects the removal of TC. As the main byproduct of persulfate activation,  $SO_4^{2-}$  was also found to have no effect on TC degradation in PMS activation processes by Fe-N/BC and sepiolite/ $Fe_3O_4$  [10,45]. Contrarily, the presence of  $Cl^-$  and  $NO_3^-$  was found to exert a slight inhibitory effect on TC degradation in the order  $Cl^- < NO_3^-$ . This probably can be explained by the fact that  $Cl^-$  would react with  $SO_4^{\bullet-}$  and  $HO^{\bullet}$  to produce  $Cl^{\bullet}$  and  $ClOH^{\bullet-}$  with less reactivity, and  $NO_3^-$  exhibits scavenging effect on  $SO_4^{\bullet-}/HO^{\bullet}$  [45,46]. The inhibitory effects of  $Cl^-$  and  $NO_3^-$  on TC oxidation were also observed in PMS activation by sepiolite/ $Fe_3O_4$  [10], walnut shell derived, carbon supported nano zero-valent iron (WS-AC/nZVI) [46] and magnetic rape straw biochar [47].



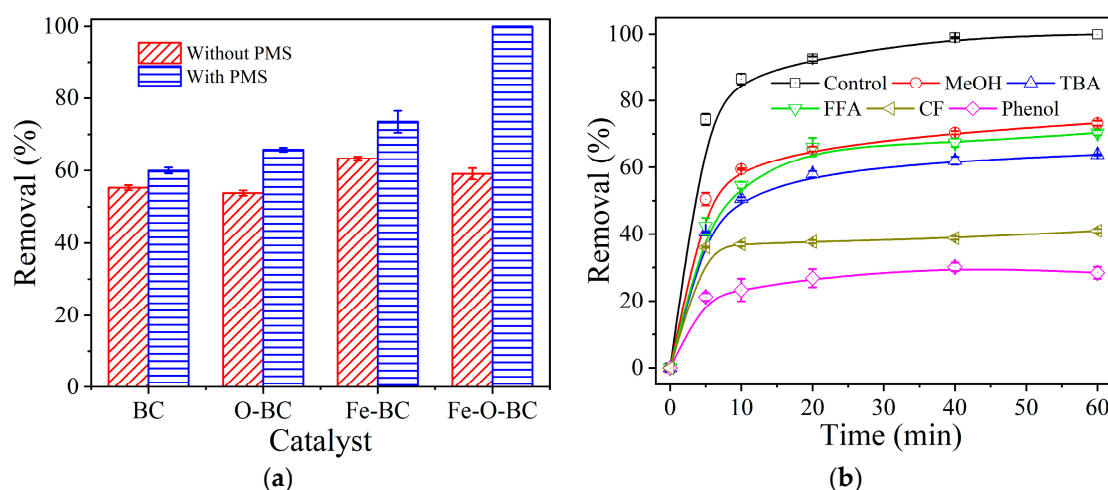
**Figure 8.** The effects of coexisting ions (a) and HA (b) for the degradation of TC. Conditions:  $[TC] = 0.2$  mM,  $[PMS] = 5$  mM,  $[Catalyst] = 2$  g  $L^{-1}$ .

As shown in Figure 8b, with the addition of HA from 0 to 5 mg/L, TC removal decreased from 100% to 85.3%. HA was believed to consume active species (e.g.,  $SO_4^{\bullet-}$ ) and occupy the active sites on the catalyst surface. Thereby, HA was frequently reported to exert a negative influence on the catalytic process [28,46,48].

#### 2.4. Mechanism Investigation

To ascertain the mechanism of TC degradation, the active sites identification experiments using different catalysts and the quenching experiments for active species conformation were conducted in an Fe-O-BC/PMS system. As illustrated in Figure 9a, the adsorption efficacies for TC by the BC-based materials were in the range of 53.8% and 63.3%, implying good adsorption ability of the prepared catalysts, which was beneficial for the mass transfer of reactants towards the active sites. In addition, the adsorption

capacity of Fe-O-BC was calculated to be 36.38 mg/g after the adsorption equilibrium of TC for 24 h. The 59.1% adsorption efficiency of Fe-O-BC can be explained by two factors. First, the porous structure of the materials as observed in SEM facilitates the adsorption of contaminants. Secondly, Fe-O-BC possesses a substantial aromatic ring structure as recorded by XPS that favors TC adsorption due to its analogous aromatic ring structure through  $\pi$ - $\pi$  interactions. With the presence of PMS, BC, O-BC and Fe-BC exhibited a catalytic performance improvement of 4.7%, 12.0%, 10.2%, respectively in 60 min compared with their adsorption compacity in the absence of PMS. Notably, 42.1% of improvement for TC degradation by Fe-O-BC/PMS in comparison with Fe-O-BC adsorption was achieved within 40 min, which was almost two folds the improvement summation of Fe-BC and O-BC. The above results indicated that specific active sites except for general reactive sites of iron species (e.g.,  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) found in Fe-embedded BC and OFGs (e.g.,  $-\text{C}=\text{O}$ ,  $-\text{OH}$ ,  $-\text{OOH}$  and quinone ones) in heteroatom doped BC [14] dominated PMS activation with the Fe and O co-embedded BC materials. In the study of Zubir et al., the C-O-Fe bonds in graphene oxide- $\text{Fe}_3\text{O}_4$  nanocomposites were found leading to a 20% higher degradation of contaminant in the Fenton-like process [49]. What is more, Kang et al. revealed that the C-O-Fe bonds in Fe containing BC derived from sewage sludge played the dual role of PDS activation and as a bridge for electron transfer [28]. Therefore, the exceeding improvement of TC degradation in the Fe-O-BC/PMS process can be attribute to the observed C-O-Fe bonds by XPS characterization in this study. Overall, in the present work, traditional iron species, OFGs and the C-O-Fe bonds were the active sites for PMS activation.

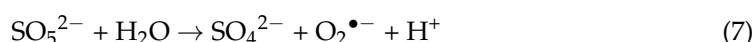
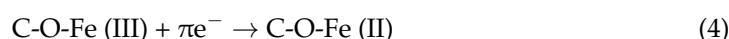
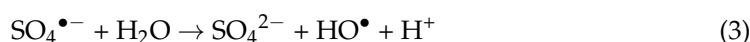
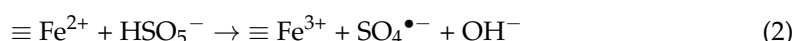
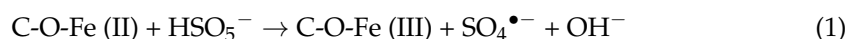


**Figure 9.** TC removal by various catalysts (a), TC degradation with various scavengers (b). Conditions:  $[\text{PMS}] = 5 \text{ mM}$ ,  $[\text{TC}] = 0.2 \text{ mM}$ ,  $[\text{PMS}] = 5 \text{ mM}$ ,  $[\text{Catalyst}] = 2 \text{ g L}^{-1}$ .

To clarify the active species in the Fe-O-BC/PMS system, quenching experiments were performed by introducing different radical scavengers. As a hydrophilic scavenger, methanol (MeOH) is routinely employed to simultaneously suppress the freely diffused  $\text{SO}_4^{\bullet-}$  ( $\text{SO}_4^{\bullet- \text{free}}$ ) and  $\text{HO}^{\bullet}$  ( $\text{HO}^{\bullet \text{free}}$ ) present in the solution. In contrast, tert-butyl alcohol (TBA) exhibits a preferential affinity for quenching  $\text{HO}^{\bullet}$  [50]. As displayed in Figure 9b, with the addition of TBA, TC removal decreased to 63.8%, suggesting that the  $\text{HO}^{\bullet \text{free}}$  in the solution played a role in TC oxidation. It is notable that the suppressive influence of MeOH for TC oxidation was weaker than that of TBA, which could stem from the tradeoff between sweeping the surface of the catalysts and scavenging the radicals by MeOH [51]. Moreover, due to the hydrophilicity, MeOH is difficult to trap the surface-bound/adsorbed  $\text{SO}_4^{\bullet-}$  ( $\text{SO}_4^{\bullet- \text{ads}}$ ) and  $\text{HO}^{\bullet}$  ( $\text{HO}^{\bullet \text{ads}}$ ), and phenol is frequently used to capture the bound radicals [46]. In the presence of phenol, TC degradation was dramatically restricted to 28.4%, implying  $\text{SO}_4^{\bullet- \text{ads}}$  and  $\text{HO}^{\bullet \text{ads}}$  were contributed to TC degradation. Additionally, with the involvement of furfuryl alcohol (FFA), a documented scavenger of  $^1\text{O}_2$ ,  $\text{HO}^{\bullet}$  and  $\text{SO}_4^{\bullet-}$ , TC degradation was suppressed to 70.3%. The weaker suppression of FFA than that

of TBA revealed that  $^1\text{O}_2$  was not the active species in the present system. Moreover,  $\text{O}_2^{\bullet-}$  was scavenged by chloroform (CF), and the obvious inhibition of TC removal obtained with the addition of CF indicated the important contribution of  $\text{O}_2^{\bullet-}$  to the oxidation of TC. To conclude, the above results revealed that  $\text{HO}^{\bullet}_{\text{free}}$ ,  $\text{HO}^{\bullet}_{\text{ads}}$ ,  $\text{SO}_4^{\bullet-}_{\text{ads}}$  and  $\text{O}_2^{\bullet-}$  participated in the TC degradation, and  $\text{SO}_4^{\bullet-}_{\text{ads}}$  and  $\text{HO}^{\bullet}_{\text{ads}}$  were the predominant contributors.

Based on the preceding discussion, the mechanism of PMS activation by Fe-O-BC for the oxidation of TC is proposed. The PMS molecules were specifically adsorbed to Fe-O-BC followed by PMS activation with Fe (II) in C-O-Fe,  $\equiv \text{Fe}^{2+}$  and the OFGs present on the materials (Equations (1) and (2)) [28]. In this process, the generated  $\text{SO}_4^{\bullet-}$  partially transformed to  $\text{HO}^{\bullet}$  for TC degradation (Equation (3)). Then C-O-Fe (III) can be reduced to C-O-Fe (II) through  $\pi$  electrons on the catalyst layer and electrons transferred through the C-O-Fe bridge (Equations (4) and (5)). The formation of  $\text{O}_2^{\bullet-}$  can be accomplished through the interaction of water molecules with  $\text{SO}_5^{2-}$  resulting from decomposition of PMS within the system (Equations (6) and (7)). The presence of  $\equiv \text{Fe}^{2+}$  on the surface of the materials also facilitated the generation of  $\text{O}_2^{\bullet-}$  via Equation (8). Ultimately, the generated  $\text{SO}_4^{\bullet-}$ ,  $\text{HO}^{\bullet}$  and  $\text{O}_2^{\bullet-}$  were involved and responsible for the oxidation of TC.



### 3. Materials and Methods

#### 3.1. Chemicals and Reagents

Tetracycline (TC,  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$ ), sodium peroxydisulfate (PS,  $\text{Na}_2\text{S}_2\text{O}_8$ ), peroxymonosulfate (PMS,  $\text{KHSO}_5 \bullet 0.5\text{KHSO}_4 \bullet 0.5\text{K}_2\text{SO}_4$ ), furfuryl alcohol (FFA) and phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) were purchased from the Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) Ferric chloride hexahydrate ( $\text{FeCl}_3 \bullet 6\text{H}_2\text{O}$ ), tert-butyl alcohol (TBA) and sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) were obtained from the Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China) Oxalic acid dihydrate ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2(\text{H}_2\text{O})$ ) and sodium chloride ( $\text{NaCl}$ ) were bought from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) Methanol ( $\text{MeOH}$ ) was purchased from the Tianjin ZhiYuan Reagent Co., Ltd. (Tianjin, China) Trichloromethane (CF) was purchased from the Chengdu Colon Co., Ltd. (Chengdu, China).

#### 3.2. Synthesis of Fe-O-BC

The Fe,O co-doping of biochar (Fe-O-BC) catalysts were obtained by one step pyrolysis using corncob as feedstocks, iron (III) chloride as the Fe source and oxalate as the O source. Briefly, 10 g of corncob, 11.2 g of oxalate and 0.1 g of Ferric chloride were fully ground with a mortar for 30 min followed by vigorously shaking in water for 10 min. The dried solids were filled in a lidded crucible followed by wrapping the crucible in tinfoil, and then anoxically pyrolyzed at 500 °C for a duration of 2 h, with the heating rate setting at 5 °C/min. The black powder was allowed to cool naturally to 25 °C before being sieved through a 40-mesh screen for future use. Fe-BC and O-BC materials were fabricated under the same conditions except with the absence of O or Fe source.

### 3.3. Experimental Procedures

Batch experiments of TC degradation were performed in a 100 mL bottle filled with 50 mL of TC solution. A measured amount of the prepared BC-based catalysts was added to the bottle, and then the PMS solution was injected while stirring in a thermostatic shaker at 100 rpm and 25 °C. At predetermined time intervals, an approximately 1 mL sample was extracted, filtered with a 0.22 µm membrane and analyzed. The initial pH of TC solution was regulated with diluted H<sub>2</sub>SO<sub>4</sub> and NaOH if needed.

### 3.4. Characterizations and Analytic Methods

Characterizations of scanning electron microscopy (SEM) were used to capture the morphology of the samples. The sample was stuck to a conductive adhesive, sprayed with gold and tested. Fourier transform infrared spectroscopy (FTIR) was used to detect functional groups in the wave number range of 400–4000 cm<sup>−1</sup>. The crystal structure of the material was recorded using an X-ray diffractometer (XRD) at a scanning range of 5 to 80°. In this experiment, we used a copper target (Cu-Kα) ray source at a scanning rate of 10 °/min. The specific surface area and aperture were measured by an automatic specific surface area meter (BET). Before adsorption, the sample was degassed at 200 °C for 11 h, and the nitrogen adsorption isotherm was conducted at 77 K. The elemental valence states of the samples were analyzed by an X-ray photoelectron spectroscopy (XPS) using an Al Kα X-ray source (1486.6 eV) at 12 kV and 6 mA [52]. The TC was monitored by an HPLC system with a mobile phase of the mixture of acetonitrile and ultrapure (v:v, 80:20) at 350 nm. The PMS concentration was quantified using spectrophotometry with potassium iodide serving as the chromogenic agent. The dosage of leached iron was ascertained using the o-phenanthroline spectrophotometric method.

### 3.5. Calculation Method

The removal efficiency of TC was calculated by the following formula,

$$\text{Removal efficiency} = \frac{C_0 - C}{C_0} \times 100\% \quad (9)$$

where  $C_0$  and  $C$  represent the TC concentration at the initial state and time  $t$  (min), respectively, mg/L.

The adsorption capacity was calculated as follows [53],

$$Q_e = (C_0 - C_e) \frac{V}{m} \quad (10)$$

where  $Q_e$  is the adsorption capacity of Fe-O-BC at adsorption equilibrium, mg/g;  $C_0$  and  $C_e$  represent the initial and equilibrium concentrations of TC, respectively, mg/L;  $V$  is solution volume, L;  $m$  is the Fe-O-BC dosage, g.

## 4. Conclusions

In conclusion, the present study reported an iron and oxygen co-embedded biochar catalyst (Fe-O-BC) synthesized by one step pyrolysis, which exhibited an excellent ability to activate PMS for TC oxidation. The series of characterizations revealed the porous structure of the catalyst and the enrichment of iron species, oxygen containing groups and the specific C-O-Fe bonds on the surface of the materials. The experimental findings illustrated that the PMS activation by Fe-O-BC resulted in the complete elimination of TC, outperforming Fe-BC (73.5%) and O-BC (65.8%). The TC degradation was affected by the concentration of PMS and dose of catalyst, however little influenced by the initial pH. The co-existence of anions exerted influence on TC degradation in the order of  $\text{SO}_4^{2-} < \text{Cl}^- < \text{NO}_3^-$ , and HA also had a negative impact on TC oxidation. The experiments of active sites identification implied that traditional iron species and the oxygen containing groups were the potential active sites while the specific C-O-Fe bonds dominated PMS activation. Quenching experiments

showed that  $\text{HO}^{\bullet}_{\text{free}}$ ,  $\text{HO}^{\bullet}_{\text{ads}}$ ,  $\text{SO}_4^{\bullet-}_{\text{ads}}$  and  $\text{O}_2^{\bullet-}$  participated in the reaction, and  $\text{SO}_4^{\bullet-}_{\text{ads}}$  and  $\text{HO}^{\bullet}_{\text{ads}}$  were the predominant contributors to TC degradation. Based on the greenness analysis of the analytic method and the measurement of iron leaching, the Fe-O-BC system was found to be environmentally friendly. This work provided a high-effective catalyst for PMS activation and an eco-friendly process for TC degradation.

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