

Article

Enhanced Peroxydisulfate Activation by Co-Doping of Nitrogen, Chlorine, and Iron: Preparation, Synergistic Effects, and Application

Zhipeng Li ^{2,3}, Hao Zhang ^{1,*}, Wanjiang Guo ², Tan Meng ³, Hongru Cui ² and Chao Ma ^{1,*}

¹ School of Mechanical and Power Engineering, Tianjin Renai College, Tianjin 301636, China

² Shengli Oilfield Company, Sinopec, Dongying 257000, China; lizhipeng@tju.edu.cn (Z.L.); guowanjiang.slyt@sinopec.com (W.G.); cuihongru.slyt@sinopec.com (H.C.)

³ School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China; tanmeng@tju.edu.cn

* Correspondence: 15130248376@163.com (H.Z.); machao0412@163.com (C.M.)

Abstract

The continuous increase in solid waste poses a significant environmental challenge. Pyrolysis represents a crucial technology for the valorization of solid waste. As the primary product, biochar has found applications in numerous fields and garnered significant scientific interest. This study investigated the potential of NH_4Cl and FeCl_3 for modifying biochar. The resultant modified biochar achieved over 70% sulfamethoxazole (SMX) degradation within 30 min. The incorporation of NH_4Cl and FeCl_3 facilitated the formation of pyridinic nitrogen (N), graphitic nitrogen (N), and $\text{Fe(II)}\ 1/2p$, while the concomitant increase in persistent free radicals facilitated enhanced electron transfer rates. Notably, $\text{NH}_4\text{Cl}/\text{FeCl}_3$ -modified biochar demonstrated superior efficacy compared with alternative activation techniques for real wastewater treatment. This study presents a novel material for persulfate (PDS)-based advanced oxidation processes, while also offering a cost-effective strategy for solid waste disposal.

Keywords: biochar; persulfate; chlorine; nitrogen; iron



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1. Introduction

Currently, the continuous increase in solid wastes associated with agricultural and forestry development poses significant challenges [1]. As the world's largest developing agricultural economy, China generates substantial volumes of farming and forestry wastes annually [2]. The inadequate valorization of these solid wastes presents formidable challenges due to their bulk properties and limited reusability, exacerbating environmental impacts [3].

Among prevalent disposal methods, combustion remains widely adopted in several regions despite causing substantial air pollution and energy loss [4]. Consequently, numerous countries have implemented environmental policies aimed at fostering solid waste recycling while mitigating the environmental impacts of combustion [5,6]. Thus, developing environmentally sustainable and economically viable waste valorization techniques is imperative.

Pyrolysis, as a promising waste-to-energy conversion technology, has garnered increasing attention [7,8]. This process significantly reduces solid waste volume while concurrently yielding valuable gaseous and liquid fuels, along with biochar [9]. The gaseous and liquid products derived from pyrolysis serve as energy sources, whereas the residual biochar finds applications in diverse fields, including catalysis, adsorption, and soil enhancement [10–12].

On the other hand, owing to its abundant active sites, biochar serves as an excellent catalyst in advanced oxidation processes.

Advanced oxidation processes (AOPs) represent a practical approach for environmental remediation [13], with persulfate (PDS)-based technologies garnering significant scientific interest due to their distinct advantages in aquatic system restoration [14–16]. Compared to conventional hydrogen peroxide (H_2O_2)-based systems, PDS demonstrates superior aqueous solubility and stability [17]. The activated sulfate radicals ($\cdot\text{SO}_4^-$) exhibit an extended half-life (30–40 μs) and higher redox potential ($E^0 = +2.6\text{ V}$) [18,19]. PDS activation is a prerequisite for reactive oxygen species generation, with established methods including alkaline, radiation, thermal, transition metal, and UV activation [14,20,21]. Among these, heterogeneous catalysis has gained prominence owing to enhanced activation efficiency and structural stability.

Although metal-based catalysts demonstrate superior PDS activation efficacy, their practical implementation is constrained by heavy metal leaching risks [18,22]. Carbonaceous catalysts circumvent these limitations through environmental compatibility. Biochar, a carbon-rich pyrolysis product derived from solid waste, possesses a high specific surface area, exceptional adsorption capacity, abundant surface functionalities, and graphitic domains, positioning it as a promising remediation catalyst [23,24]. Recent studies implicate persistent free radicals (PFRs) on biochar surfaces as primary PDS activation sites, while structural defects facilitate the generation of $\cdot\text{OH}$ and $\cdot\text{SO}_4^-$ radicals [25].

Nevertheless, biochar exhibits comparatively lower oxidant activation and pollutant degradation kinetics relative to metal-based systems [18,26]. Consequently, modification strategies are increasingly employed to augment its catalytic performance [27–29]. Our prior research indicates chlorine incorporation promotes hierarchical pore formation and PFR generation, thereby modulating electron transfer kinetics and active site density [5]. Thus, synergistic modification of biochar with metallic species and chlorinated compounds presents a viable strategy for catalytic enhancement.

This study utilized sawdust-derived biochar modified with FeCl_3 and NH_4Cl to address four primary objectives: (1) characterize alterations in the physicochemical properties of biochar induced by $\text{FeCl}_3/\text{NH}_4\text{Cl}$ modification; (2) evaluate the efficacy of modified biochar in PDS activation and pollutant degradation; (3) elucidate the mechanistic pathways governing PDS activation and SMX degradation; (4) assess the environmental remediation potential of $\text{FeCl}_3/\text{NH}_4\text{Cl}$ -modified biochar. Collectively, this work aims to advance sustainable solid waste valorization strategies while contributing to the development of high-performance biochar materials for environmental applications.

2. Results and Discussion

2.1. Characterization of Biochars

To elucidate the physicochemical properties of biochar, comprehensive characterization was performed via Brunauer-Emmett-Teller (BET) and scanning electron microscope-energy dispersive spectrometer (SEM-EDS). BET results (Table S1) revealed that $\text{NH}_4\text{Cl}/\text{FeCl}_3$ co-modification increased biochar's specific surface area from 506.0 to 819.0 m^2/g . This enhancement might be attributed to HCl liberation during NH_4Cl pyrolysis, which facilitates porous structure development [5]. Notably, NH_4Cl -modified biochar (BCN) exhibited similarly elevated surface area (784.3 m^2/g), corroborating the pore-forming role of HCl .

Conversely, FeCl_3 modification (BCF) reduced surface area to 409.5 m^2/g , indicating Fe-induced pore blockage that compromised PDS activation efficacy. Furthermore, co-modified biochar (BCNF) demonstrated significantly reduced electrical resistivity (Table S2), potentially enhancing electron transfer for PDS activation and SMX degradation. Figure S1 showed that the Fe existed in the pores of biochar. The results of EDS indicated

that the modified biochar had more Fe content (Table S1), which stated that Fe had been successfully loaded on biochar. Meanwhile, the percentage of chlorine and nitrogen had increased significantly after the biochar was modified by NH_4Cl and FeCl_3 , followed by lower carbon and oxygen content.

2.2. Degradation of SMX and Decomposition of PDS by Biochar

The catalytic performance of biochar variants in PDS activation was evaluated as shown in Figure 1. Unmodified biochar (BCS) achieved 20% SMX degradation within 30 min. The enhanced catalytic activity of BCF over BCS is likely due to the iron doping effect [30]. Conversely, BCN demonstrated reduced efficacy (<20% SMX degradation), underperforming relative to BCS.

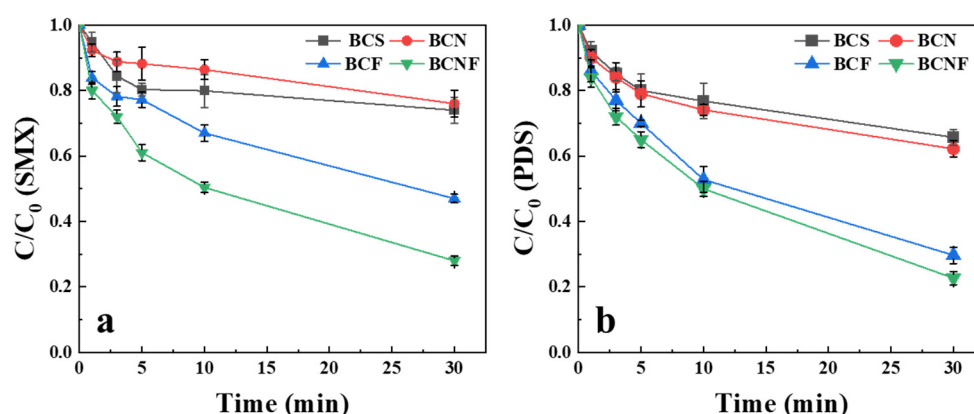


Figure 1. The SMX degradation (a) and PDS activation (b) by biochars. [Biochar] = 1 g/L, [PDS] = 1 mM, [SMX] = 10 μM , pH = 7.

Notably, the BCNF exhibited exceptional performance with 75% SMX removal within 30 min. This catalytic superiority was consistent in PDS activation kinetics, indicating synergistic effects from $\text{FeCl}_3/\text{NH}_4\text{Cl}$ incorporation that enhanced oxidant activation and subsequent pollutant degradation.

Comparatively, both BCS and BCN showed limited PDS activation (<30% within 30 min), resulting in lower SMX removal. These findings demonstrate that $\text{FeCl}_3/\text{NH}_4\text{Cl}$ modification may significantly alter physicochemical properties of biochar, thereby enhancing catalytic functionality. Given its superior performance, BCNF was selected for subsequent mechanistic investigations.

2.3. Elucidation of Reactive Oxygen Species

To identify the reactive oxygen species in the BCNF/PDS system, electron paramagnetic resonance (EPR) spectroscopy coupled with DMPO and TEMP as spin-trapping agents was performed. As depicted in Figure 2, distinguishable DMPO- $\cdot\text{O}_2^-$ signals were observed. Concurrently, the EPR spectrum employing TEMP displayed characteristic three-line signals of 1:1:1 intensity ratio (Figure 2, corresponding to the TEMP- $^1\text{O}_2$ adducts [5,25].

To elucidate reactive oxygen species (ROS) contributions to SMX degradation, radical quenching experiments were systematically conducted using specific scavengers. As presented in Figure 3, introduction of 0.1 M L-H significantly suppressed SMX degradation from 75% to 10% within 30 min ($\Delta 65\%$ inhibition), indicating singlet oxygen serves as a primary oxidative species in the BCNF/PDS system [30]. Benzoquinone quenching further revealed substantial $\cdot\text{O}_2^-$ involvement in SMX degradation (Figure 3). Previous studies had reported that $\cdot\text{O}_2^-$ cannot degrade SMX, but $\cdot\text{O}_2^-$ was a key intermediate medium in the generation of $^1\text{O}_2$ [25]. In order to make sure the role of $\cdot\text{O}_2^-$, the BCNF/PDS system

coupled with benzoquinone was used to detect the signal of $^1\text{O}_2$. Figure S2 found that no signal was observed. It indicated that $\cdot\text{O}_2^-$ was a key intermediate product, which was consistent with our previous research. Conversely, negligible degradation inhibition occurred with TBA and EtOH addition, demonstrating minimal contributions from $\cdot\text{OH}$ and $\cdot\text{SO}_4^-$. Collectively, these results establish $^1\text{O}_2$ as the dominant SMX-degrading species in the BCNF/PDS system, with $\cdot\text{O}_2^-$ functioning as the critical intermediate for $^1\text{O}_2$ formation [25].

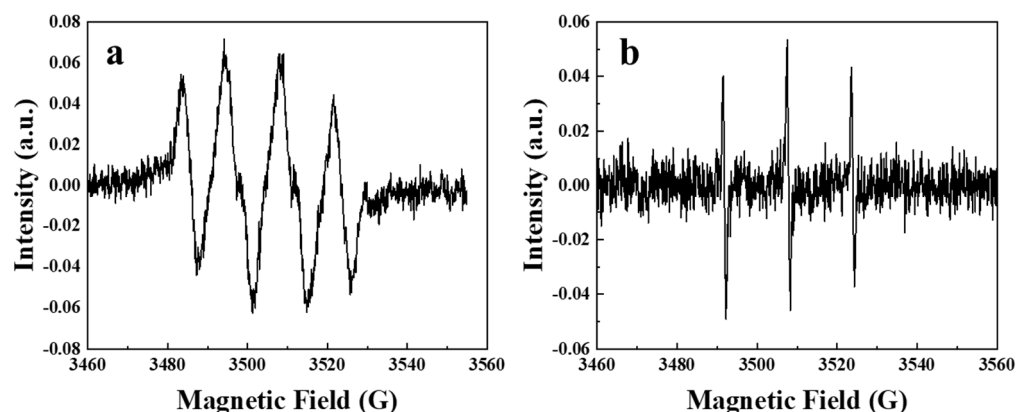


Figure 2. The EPR results of the BCNF/PDS system.

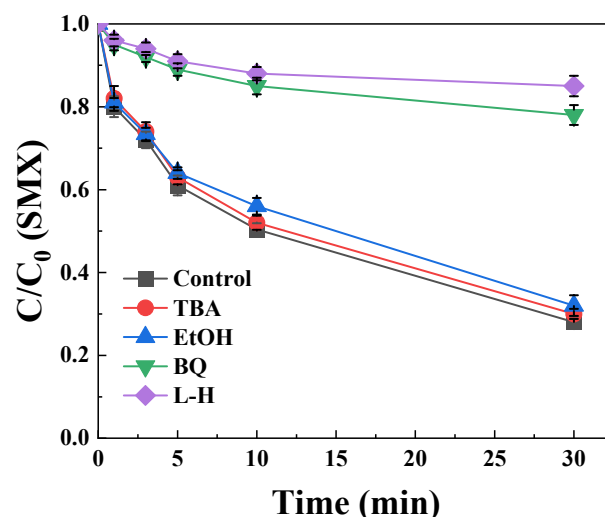


Figure 3. The effect of quenching agents in SMX degradation. [BCNF] = 1 g/L, [PDS] = 1 mM, [SMX] = 10 μM , [TBA] = 0.17 M, [EtOH] = 0.1 M, [BQ] = 1 mM, [L-H] = 0.1 M, pH = 9.

2.4. Possible Mechanism of PDS Activated by Biochar

Previous studies had established the doping of nitrogen as a critical modulator of material performance in oxidation activation [31]. Thus, to understand the activation mechanism of PDS by biochar, XPS analysis was performed in this study, and the corresponding results are depicted in Figure 4. The N 1s spectrum revealed that the proportion of pyridinic N and graphite N was initially as high as 16.8% and 47.3% before reacting with PDS, indicating a high surface graphitization degree and homogeneous nitrogen distribution structural features conducive to catalytic persulfate activation. After interacting with PDS for specific durations of time, the pyridinic N and graphite N content decreased to 12.96% and 44.73% after 30 min of reaction. This reduction in pyridinic N and graphite N content is an indication that these functional groups act as activators for PDS and are consumed during the reaction, resulting in an increase in the concentration of $^1\text{O}_2$. Concurrently, the content of Fe(II) 1/2p reduced from 43.53% at 0 min to 39.35% at 30 min, indicating a

decline in its abundance during the reaction. And the content of Fe(III) 3/2p increased from 30.1% to 32.33% after reacting with PDS. These redox transitions confirm iron's pivotal role in electron transfer processes during PDS activation.

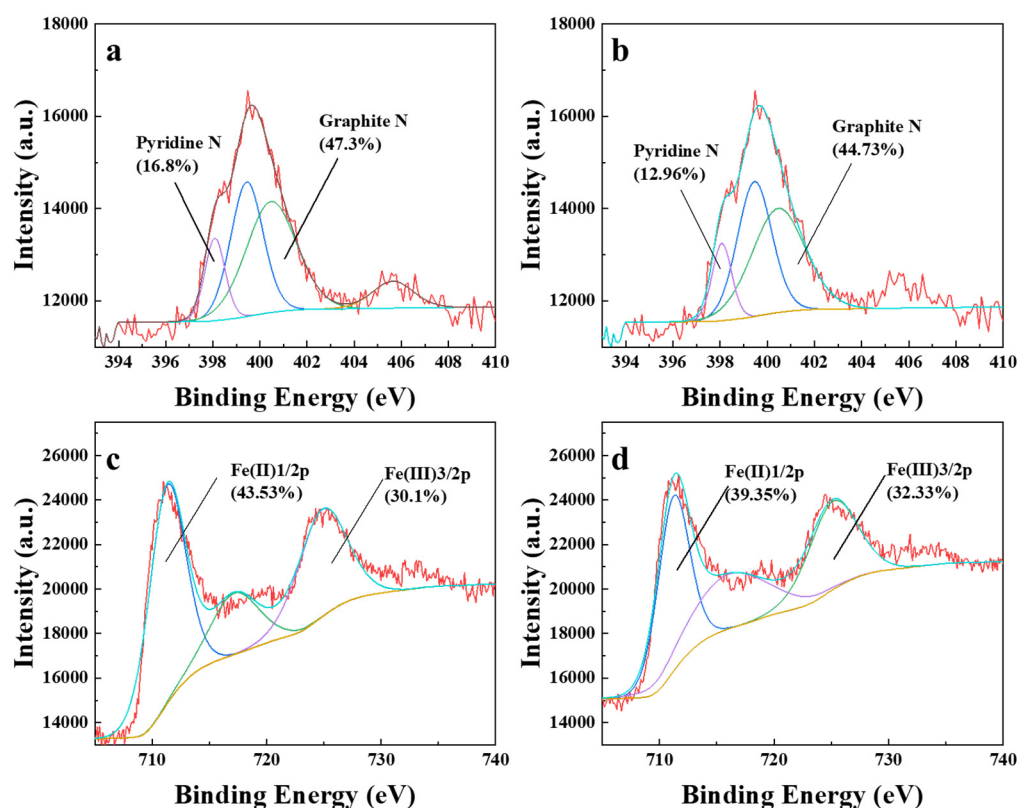


Figure 4. XPS (N 1s) spectra of BCNF before (a) and after (b) reacting with PDS; XPS (Fe 2p) spectra of BCNF before (c) and after (d) reacting with PDS.

Our previous study demonstrated that chlorine incorporation promotes PFRs formation. The PFRs had been verified to be reactive species that can directly transfer electrons and potentially contribute to the activation of PDS [5,31]. In order to measure its effect in the BCNF/PDS system, EPR spectroscopy was used to determine the presence of PFRs in BCNF. Based on the EPR results, the *g* factor of BCNF was 2.004, which indicated that PFRs of BCNF were mainly composed of carbon-centered radicals with an adjacent oxygen atom. EPR analysis revealed that the spin density of BCNF was 3.6×10^{16} spins/g. According to our previous studies, the PFRs with sufficient concentration could play a vital role in electron transfer. Thus, potassium iodide (KI) was used to quench the PFRs. After treatment with KI, the spin densities of the PFRs decreased to 1.1×10^{16} spins/g, and the electrical resistivity of BCNF increased from 2.578Ω to 3.89Ω , accompanied by a decrease in PDS activation and SMX degradation of BCNF (Figure 5). This triad of evidence established PFRs as critical electron transfer agents governing system reactivity.

Concurrently, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) was introduced to isolate the contribution of structural defects to PDS activation [32]. As shown in Figure S3, EDTA-2Na treatment exhibited a negligible impact on BCNF-mediated SMX degradation and PDS activation efficiency, effectively excluding defect-mediated mechanisms.

While prior studies implicate carbonyl (C=O) and carboxyl (-COOH) groups in carbonaceous materials as potential PDS activation sites, our Fourier Transform infrared spectrometer (FTIR) analysis revealed minimal alterations in biochar's functional group composition post-reaction (Figure S4). To explicitly probe these groups' roles, selective deactivation experiments were performed: Phenylhydrazine (PH) targeted ketonic C=O groups,

while 2-bromo-1-phenylethanone (BrPE) specifically quenched carboxyl functionalities without perturbing other structural elements [33,34]. Figure S5 demonstrates that neither C=O nor -COOH deactivation significantly impaired PDS activation or SMX degradation.

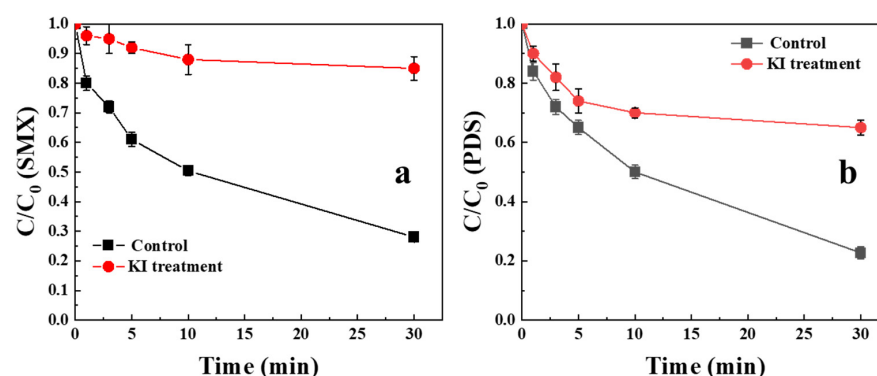


Figure 5. (a) The SMX degradation and (b) PDS activation after treatment with KI. [BCNF] = 1 g/L, [PDS] = 1 mM, [SMX] = 10 μ M, pH = 7.

Collectively, these findings establish that $\text{NH}_4\text{Cl}/\text{FeCl}_3$ modification modulates pyridinic N, graphitic N, iron species, and PFRs – the principal components governing PDS activation and contaminant degradation efficacy. It should be noted that the individual contributions of nitrogen, chlorine, and iron species were not decoupled in this study. The proposed synergistic effect, while supported by the enhanced performance and characterization, remains a mechanistic speculation and warrants further validation through more controlled experiments in future work.

2.5. Application in Wastewater Remediation

To evaluate the practical applicability of the BCNF/PDS system, comparative degradation experiments were conducted in pharmaceutical wastewater and chemical plant effluent matrices (Figure 6). Relative to ultrapure water performance (Figure 1), SMX degradation efficiency declined from 75% to approximately 30% within 30 min in these complex matrices, as depicted in Figure 6. This attenuation primarily stems from two mechanistic interferences: (i) competitive consumption of superoxide radicals ($\cdot\text{O}_2^-$) by background anions and natural organic matter (NOM), suppressing singlet oxygen generation; (ii) active-site masking through anion complexation, diminishing reactive species production [25].

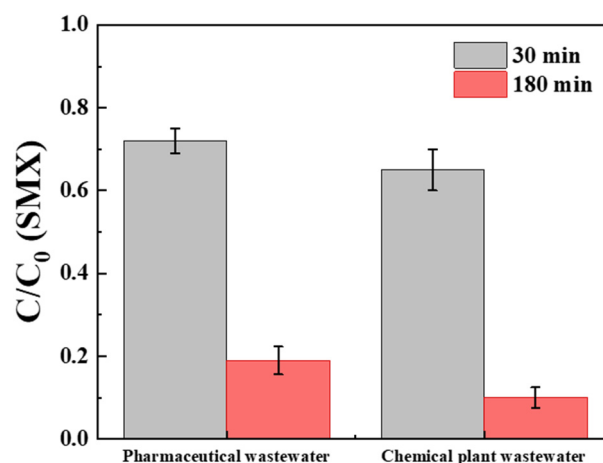


Figure 6. The SMX degradation by the BCNF/PDS system in real wastewater. [BCNF] = 1 g/L, [PDS] = 1 mM, [SMX] = 10 μ M, pH = 7.

Despite these inhibitory effects, the system achieved 80% SMX removal within 180 min, demonstrating notable resilience. This sustained efficacy is attributed to the inherent interference resistance of non-radical pathways (predominantly $^1\text{O}_2$ -mediated oxidation) [6], wherein overall catalytic performance remains uncompromised. These findings established BCNF/PDS as an effective advanced oxidation platform for wastewater remediation.

2.6. Comparison with Other Materials

Zero-valent iron (ZVI) and activated carbon (AC)—a benchmark carbonaceous catalyst—were comparatively evaluated against BCNF for SMX degradation via PDS activation.

As illustrated in Figure 7, ZVI exhibited moderate PDS activation and SMX degradation capacity, but its efficiency was lower than that of BCNF. Previous research indicated that the activation of PDS by ZVI could produce $\cdot\text{OH}$ and $\cdot\text{SO}_4^{2-}$ [35]. However, $\cdot\text{OH}$ and $\cdot\text{SO}_4^{2-}$ can be suppressed in the presence of interfering ions in the wastewater matrix, and ferric ions may become deactivated through hydroxide precipitate formation at high pH levels, ultimately hindering SMX degradation. Although AC demonstrated detectable PDS activation, its efficacy remained substantially lower than theoretical predictions. This might be attributed to the fact that the reactive oxygen species produced in the AC/PDS system were $\cdot\text{OH}$ and $\cdot\text{SO}_4^{2-}$, which can be quenched by the interfering ions and dissolved organic matter [36]. The superior performance of the BCNF/PDS system (75% SMX degradation within 30 min) established its catalytic advantage over conventional activation materials under identical reaction conditions.

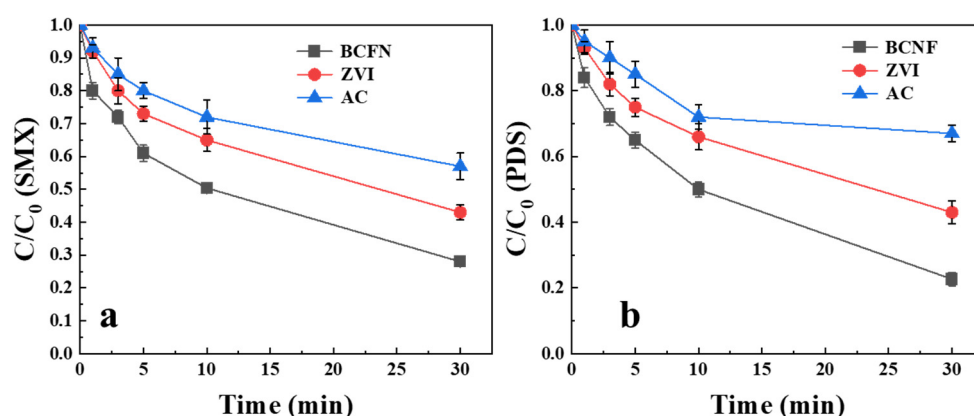


Figure 7. Comparison of different materials in (a) SMX degradation and (b) PDS activation. [BCNF] = 1 g/L, [PDS] = 1 mM, [SMX] = 10 μM , pH = 7.

2.7. Toxicity of Biochar

Due to the application of FeCl_3 in biochar modification, the potential risk of metal leaching should be considered. Analysis of reaction solutions (Table S2) detected no measurable iron content, precluding significant environmental hazards to soil or groundwater systems.

To comprehensively assess environmental impacts, bacterial bioluminescence assays were used to evaluate the toxicity of BCNF. Figure S6 demonstrated that biochar leachates enhanced luminescence by approximately 50% versus controls. Notably, despite iron and chlorine incorporation during synthesis, no luminescence inhibition occurred. Previous research demonstrated that the incorporation of chlorine-containing components during pyrolysis does not result in the formation of harmful substances, such as polycyclic aromatic hydrocarbons and dioxins [5,37]. This stimulatory effect suggests biochar releases growth-promoting constituents that support bacterial metabolic activity [37].

3. Experimental

3.1. Materials

Waste biomass was collected from the campus of Tianjin University in Tianjin, China. Sulfamethoxazole (SMX; purity: 99%), potassium persulfate, NaOH, and HCl were obtained from HEOWNS Co., Ltd. (Tianjin, China). Ultrapure water was acquired from a Merck Milli-Q Reference system (Darmstadt, Germany). Ferric chloride (FeCl_3) was obtained from Heowns Corporation (AR, 99.8%, Tianjin, China). Ammonium chloride (NH_4Cl) was purchased from Kermel Industrial Corporation (AR, 99%, Tianjin, China).

3.2. Pyrolysis Experiments

Pyrolysis was performed under oxygen-limited conditions using a muffle furnace (ZHX-G03183, Tianjin Zhonghuan Co., Ltd., Tianjin, China). The collected raw material was processed through a crusher to produce sawdust of uniform particle size. Sawdust feedstock was milled to particulate form, sequentially treated with aqueous FeCl_3 (biomass–Fe mass ratio = 10:1) for 24 h, and dry-mixed with NH_4Cl (biomass– NH_4Cl ratio = 10:1). All samples were prepared following an identical procedure. The mixture was transferred to a covered crucible without inert gas purging, heated to $700\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$, and maintained for 2 h. The resulting biochar was ground and stored under anhydrous conditions. Specimens were designated as: BCS (sawdust biochar), BCF (FeCl_3 -modified), BCN (NH_4Cl -modified), and BCNF (co-modified with $\text{FeCl}_3/\text{NH}_4\text{Cl}$).

3.3. Characterization of Biochar

Surface functional group evolution was characterized by Fourier transform infrared spectroscopy (FT-IR; HORIBA EMAX, Kyoto, Japan). Specific surface area analysis employed N_2 physisorption at 77 K (ASAP2020M, Micromeritics, Norcross, America). Raman spectra (Renishaw inVia plus, Gloucestershire, UK) were acquired at 532 nm excitation wavelength. Electrical conductivity measurements utilized a four-point probe system. X-ray photoelectron spectroscopy (XPS; Escalab 250Xi, Waltham, America) determined surface chemical compositions. Morphological features were examined by scanning electron microscopy (SEM; FEI Apreo S, Waltham, America). Charge transfer resistance was quantified via electrochemical impedance spectroscopy (EIS; CorrTestTM CS310H, Wuhan, China). Elemental composition (C, H, O, N, Cl, Fe) was analyzed by energy-dispersive spectroscopy (EDS; FEI Apreo S, Waltham, America). Electron spin resonance (ESR; Bruker EMXPLUS 10/12, Karlsruhe, Germany) monitored radical species under ambient conditions with the following parameters: 9.84 GHz resonance frequency, 20.00 mW microwave power, 100.00 kHz modulation frequency, 2.00 G modulation amplitude.

3.4. Experimental Procedures

In all batch experiments, a 100 mL screw-sealed bottle containing 50 mL of solution was placed on a magnetic stirrer at room temperature. To evaluate the catalytic performance of the prepared biochar in advanced oxidation processes, the solution pH was adjusted to 7.0 using NaOH (0.1 M) and HCl (0.1 M). Biochar and SMX were sequentially added to the bottles, followed by the introduction of a PDS solution to initiate the reaction. To terminate the reaction, 10 μL of ascorbic acid was immediately added, and the vial was used for quantifying the remaining concentrations of SMX and PDS. To eliminate the impact of adsorption, desorption experiments with 95% recovery were performed by utilizing methanol and 1 M NaHCO_3 in a 10:1 (*v/v*) ratio to desorb SMX from the biochar surface. Quenching experiments were conducted using tert-butanol (TBA; 0.17 M), ethanol (EtOH; 0.1 M), benzoquinone (BQ; 1 mM), and L-histidine (L-H; 0.1 M) to verify the presence of

hydroxyl radicals ($\cdot\text{OH}$), sulfate radical ($\cdot\text{SO}_4^-$), superoxide radical ($\cdot\text{O}_2^-$), and singlet oxygen ($^1\text{O}_2$).

3.5. Analytical Methods

PDS concentration was quantified by UV–Vis spectrophotometry using the potassium iodide chromogenic method [29]. SMX analysis employed high-performance liquid chromatography (HPLC; Shimadzu 2030C, Kyoto, Japan) with a Zorbax SB-C18 column (4.6×150 mm, $5 \mu\text{m}$) maintained at 30°C , coupled to a diode array detector. The mobile phase comprised methanol and 0.1% (*w/w*) phosphoric acid with the following gradient program: 10% methanol (0–1 min), linear increase to 50% (1–6 min), linear decrease to 10% (6–10 min), and isocratic elution at 10% (10–15 min). SMX quantification was performed at 254 nm based on peak area [30]. The post-reaction solution was filtered and analyzed for iron content using inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo iCAP Q, Waltham, America).

4. Conclusions

This study establishes that $\text{NH}_4\text{Cl}/\text{FeCl}_3$ co-modification significantly enhances biochar's physicochemical properties, enabling exceptional catalytic performance in PDS activation and SMX degradation. The introduced modifiers synergistically promote the following: (i) pyridinic N formation, (ii) graphitic N content, (iii) Fe(II) 1/2p species abundance, and (iv) persistent free radical generation, collectively augmenting electron transfer kinetics. These transformations render BCNF an efficient PDS-activating material for rapid SMX degradation.

Dominated by non-radical singlet oxygen with superoxide radicals as key precursors, the BCNF/PDS system demonstrated remarkable wastewater remediation potential. Crucially, negligible iron leaching and absence of ecotoxic compounds (as confirmed by bioluminescence assays) ensure minimal environmental hazards. These findings established waste-derived biochar as a sustainable, environmentally benign catalyst for persulfate-based advanced oxidation processes, while facilitating an integrated solid waste upcycling strategy.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15090880/s1>, Text S1. Materials and Methods. Surface functional groups elimination experiments; Text S2. The elimination of PFRs and defects; Table S1. The physical and chemical properties of CRs; Table S2. The change in components of CRs; Figure S1. The SEM results of BCNF; Figure S2. The EPR results of the BCNF/PDS system with BQ; Figure S3. The SMX degradation and PDS activation of BCNF after being treated with EDTA-2Na; Figure S4. The FTIR results of BCNF; Figure S5. The effects of surface groups elimination on (a) SMX degradation and (b) PDS activation; Figure S6. The bacterial luminescence results in BCNF solution.

Author Contributions: Z.L.: writing—review and editing, writing—original draft, methodology, investigation, funding acquisition. H.Z.: writing—review and editing, supervision. W.G.: writing—review and editing. T.M.: writing—review & editing. H.C.: writing—review and editing, methodology. C.M.: writing—review and editing, supervision. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data will be made available on request.

Conflicts of Interest: Author Zhipeng Li, Wanjiang Guo and Hongru Cui were employed by the company Shengli Oilfield Company, Sinopec. 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.

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