

Article

Interfacial Electron Transfer-Assisted Activation of Peroxydisulfate by CuO/Biochar for Efficient Ciprofloxacin Degradation: Mechanistic Insights and Application in Permeable Reactive Barriers

Yingchun Wang ^{1,†} , Bang Li ^{1,†}, Jie Zhao ^{1,2}, Tong Zhou ^{1,3}, Xiaoxian Hu ¹, Xiang Guo ¹, Xinyu Li ¹, Shiqiang Yin ¹, Svyatoslav V. Fedorov ⁴, Xinhai Zhang ⁵ and Junfeng Wu ^{1,*}

¹ Henan Key Laboratory of Water Pollution Control and Rehabilitation Technology, Henan University of Urban Construction, Pingdingshan 467036, China; wangyc0628@163.com (Y.W.)

² School of Energy & Environmental, Zhongyuan University of Technology, Zhengzhou 450007, China

³ School of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450007, China

⁴ Faculty of Environmental Engineering and Municipal Services, Saint-Petersburg State University of Architecture and Civil Engineering, St. Petersburg 190005, Russia

⁵ College of Food and Chemical Engineer, Hebi Polytechnic, Hebi 458030, China

* Correspondence: wjf8047@163.com

† These authors contributed equally to this work.

Abstract

The efficient removal of antibiotic contaminants from aquatic systems remains a significant challenge due to their persistence and complex environmental matrices. In this study, a CuO-loaded biochar (CuO-BC) composite was developed as an efficient catalyst for peroxydisulfate (PDS) activation toward ciprofloxacin (CIP) degradation. The CuO-BC exhibited superior catalytic performance, achieving rapid CIP removal over a wide pH range with strong resistance to coexisting ions. Mechanistic investigations revealed that both radical ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) and non-radical pathways ($^1\text{O}_2$ and electron transfer) contributed to CIP degradation. Quenching experiments, electron paramagnetic resonance (EPR), and probe analyses confirmed the coexistence of multiple reactive oxygen species (ROS), with interfacial electron transfer between Cu species and biochar appearing to play a significant role. The synergistic coupling of $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling and the conductive biochar matrix facilitated efficient electron transport and selective ROS generation. Furthermore, the system was successfully applied in a simulated permeable reactive barrier (PRB), exhibiting stable degradation performance under continuous-flow conditions. This study provides new insights into interfacial PDS activation mechanisms and offers a promising strategy for designing efficient catalytic systems for antibiotic removal in complex water environments.



Academic Editor: Roberto Fiorenza

Received: 30 June 2026

Revised: 28 July 2026

Accepted: 30 July 2026

Published: 4 August 2026

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Keywords: copper oxide; biochar; persulfate; ciprofloxacin; PRB reactor

1. Introduction

The widespread occurrence of antibiotic contaminants in aquatic environments has raised increasing concerns due to their persistence, bioaccumulation potential, and contribution to the proliferation of antibiotic-resistant bacteria [1]. Among them, ciprofloxacin (CIP), a widely used fluoroquinolone antibiotic, is frequently detected in surface water, groundwater, and wastewater effluents owing to its extensive consumption and low

biodegradability [2–7]. The continuous release of CIP poses long-term ecological risks and challenges conventional water treatment technologies [8,9].

Advanced oxidation processes (AOPs), particularly sulfate radical-based systems, have emerged as promising strategies for degrading refractory organic pollutants [10–12]. Peroxydisulfate (PDS) activation can generate highly reactive species such as sulfate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals ($\bullet\text{OH}$), enabling efficient pollutant degradation. However, conventional PDS activation systems often suffer from limited catalytic efficiency, poor stability, and susceptibility to interference from complex water matrices [13,14]. More importantly, recent studies have highlighted that non-radical pathways, such as singlet oxygen ($^1\text{O}_2$) generation and direct electron transfer, can play critical roles in pollutant degradation, offering improved selectivity and resistance to background constituents [15–20]. Nevertheless, the mechanisms governing the coexistence and regulation of radical and non-radical pathways remain insufficiently understood.

Carbon-based materials, particularly biochar, have attracted increasing attention as catalyst supports due to their tunable surface chemistry, porous structure, and excellent electrical conductivity [21,22]. Incorporating transition metal oxides into biochar matrices is an effective strategy to enhance catalytic performance. In such systems, the interaction between metal active sites and conductive carbon frameworks can facilitate interfacial electron transfer and promote redox cycling of metal species, thereby improving oxidant activation efficiency [23]. Among various candidates, Cu-based catalysts are especially attractive due to their multiple valence states and strong redox capability [24,25].

While Cu-based biochar composites for persulfate activation have been extensively reported [26], most existing studies have focused on macroscopic performance evaluation and empirical optimization of reaction conditions [27]. The underlying mechanisms, particularly the precise role of interfacial electron transfer in regulating the balance between radical and non-radical pathways, remain insufficiently elucidated [28]. Furthermore, the specific contribution of the biochar matrix as an electron mediator in promoting $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling and its consequent influence on reactive oxygen species (ROS) selectivity are yet to be systematically investigated [29]. Recent studies have demonstrated that CuO/biochar composites can activate PDS via non-radical pathways involving outer-sphere interaction and singlet oxygen generation [30], and that electron transfer complexes can form in CuO/BC-PDS systems [28]. However, the interfacial interactions between Cu species and biochar, as well as their roles in regulating PDS activation pathways, remain unclear [31]. These mechanistic ambiguities hinder the rational design of more efficient and stable catalytic systems for practical applications [32].

In addition to mechanistic understanding, practical applicability is crucial for real-world environmental remediation. Permeable reactive barriers (PRBs) have been widely recognized as an effective in situ technology for groundwater treatment due to their low energy consumption and continuous operation capability [33–36]. However, integrating advanced oxidation processes into PRB systems remains challenging, particularly in maintaining long-term catalytic activity and stability under dynamic flow conditions [37,38]. Most reported studies utilizing Cu-based catalysts for persulfate activation have been limited to batch experiments, and the feasibility of continuous-flow operation in PRB configurations has rarely been demonstrated.

To address these knowledge gaps, the novelty of this work lies not merely in developing another Cu-based biochar catalyst, but rather in providing further understanding of the possible role of interfacial interactions between Cu species and biochar during PDS activation, together with a proof-of-concept application in a continuous-flow PRB system. Specifically, this study develops a CuO-loaded biochar (CuO-BC) composite as an efficient catalyst for PDS activation toward CIP degradation, with the following specific objectives:

(i) to evaluate the catalytic performance of CuO–BC under various environmental conditions and elucidate the key factors governing the degradation process; (ii) to systematically investigate the synergistic roles of radical and non-radical pathways, with particular emphasis on unraveling the interfacial electron transfer mechanism between Cu species and the biochar matrix, and how this interaction governs ROS generation and pathway regulation; and (iii) to assess, for the first time, the feasibility of integrating the CuO–BC/PDS system into a simulated PRB for continuous-flow water treatment, demonstrating its potential for practical groundwater remediation. This work provides new mechanistic insights into interfacial electron transfer-assisted PDS activation and proposes that this mechanism may play a key role in the CuO–BC/PDS system, offering a promising strategy for coupling advanced oxidation processes with PRB systems for in situ groundwater remediation.

2. Results and Discussion

2.1. Characterization of Catalysts

(1) SEM

The surface morphology of BC and CuO–BC was characterized by SEM (Figure 1). As shown in Figure 1a, pristine BC exhibited a relatively smooth and compact surface with limited porosity. After CuO loading (Figure 1b), the surface became rougher with the formation of interconnected grooves, providing more exposed active sites [39].

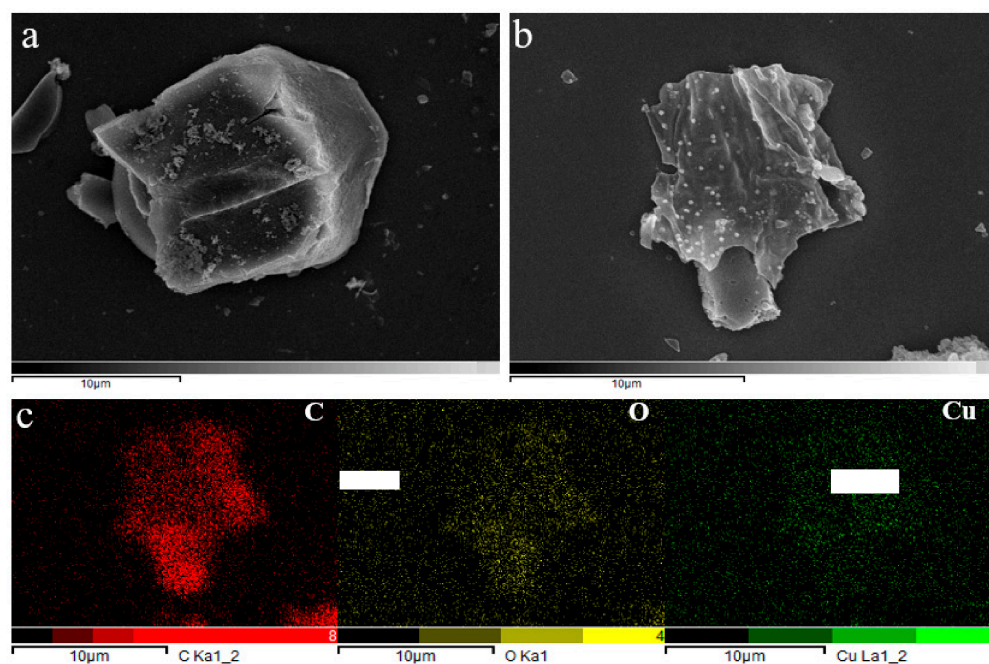


Figure 1. SEM photos of BC (a) and CuO-BC (b); (c) EDS mapping of CuO-BC.

In addition, CuO nanoparticles were uniformly distributed on the BC surface, which can be attributed to strong interactions between Cu species and oxygen-containing functional groups of biochar. This uniform dispersion effectively suppressed particle aggregation [23]. EDS mapping (Figures 1c and S1) further confirmed the homogeneous distribution of C, O, N, and Cu elements. It should be noted that EDS analysis in this study was mainly used to confirm the elemental distribution of Cu, C, O, and N within the catalyst, rather than to provide quantitative elemental composition. Since EDS is inherently semi-quantitative and the present work focuses on catalyst preparation, catalytic performance, and mechanistic investigation, quantitative elemental analysis was not included. The corresponding description has been revised to avoid implying quantitative interpretation.

(2) XRD

The crystalline structures of BC and CuO-BC were analyzed by XRD (Figure 2a). The diffraction peaks at 35.4° , 38.7° , 48.7° , and 61.5° correspond to the (0 0 2), (1 1 1), (2 0 2), and (1 1 3) planes of CuO (JCPDS No. 41-0254) [40,41], confirming the successful incorporation of CuO into the biochar matrix. Compared with BC, the CuO-BC sample exhibited stronger characteristic peaks of CuO, indicating improved crystallinity. In addition, the characteristic peaks of carbon were weakened or masked due to the presence of CuO species [42].

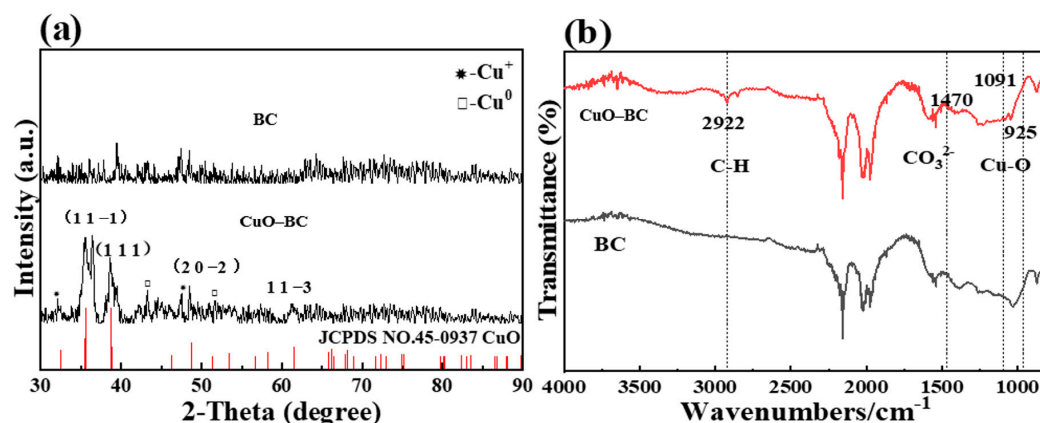


Figure 2. (a) XRD spectra of BC and CuO-BC; (b) FTIR spectra of CuO-BC and BC.

(3) FTIR

FTIR spectra of BC and CuO-BC are shown in Figure 2b. The peaks around 2922 cm^{-1} are attributed to the stretching vibrations of C-H bonds. The band near 1470 cm^{-1} corresponds to CO_3^{2-} vibrations [43]. Notably, the peaks observed at 925 cm^{-1} and 1091 cm^{-1} are assigned to Cu-O stretching vibrations, indicating the formation of Cu-O bonds and successful interaction between copper species and the biochar matrix [44–46].

(4) BET

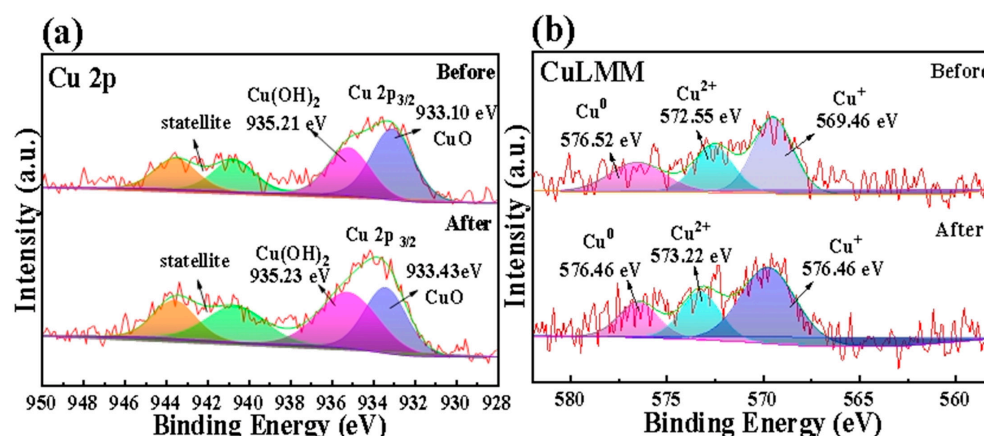
The surface area and pore structure of the samples were analyzed by N₂ adsorption-desorption measurements [47]. As summarized in Table 1, BC exhibited a specific surface area of $391.88\text{ m}^2/\text{g}$, while CuO-BC showed an increased value of $448.36\text{ m}^2/\text{g}$. Meanwhile, the total pore volume and average pore diameter also increased after CuO loading, indicating the formation of a more developed porous structure. This increase in specific surface area and porosity following CuO incorporation can be attributed to several factors. First, the impregnation of $\text{Cu}(\text{NO}_3)_2$ precursor and subsequent thermal decomposition during pyrolysis may generate additional pore structures through the release of gaseous species (e.g., NO_x , CO_2), which create new micropores and mesopores within the biochar matrix [48,49]. Second, the presence of CuO nanoparticles may act as a spacer or template, preventing the collapse of pore channels during carbonization and improving pore accessibility [50]. Third, the interaction between Cu species and oxygen-containing functional groups on the biochar surface may induce structural rearrangements that further enhance porosity [51]. It is obvious the pore size distributions of functionalized sample CuO-BC were larger than the unfunctionalized sample BC. In other words, CuO-modified biochar exhibits a richer pore structure which is conducive to providing more catalytic active sites and accelerate the mass transfer process between pollutants and PDS [48–50]. The isotherms of both samples were classified as type IV, characteristic of mesoporous materials (Figure S2) [51,52]. The enhanced porosity and surface area of CuO-BC are beneficial for exposing more active sites and facilitating mass transfer during PDS activation.

Table 1. Physical properties of the BC and CuO-BC.

Sample	S_{BET} (m^2/g)	TPV (cm^3/g)	BJH (Pore Diameter (nm))
BC	391.88	0.14	3.30
CuO-BC	448.36	0.19	6.22

(5) XPS

XPS analysis was conducted to investigate the surface elemental composition and chemical states of CuO-BC (Figure 3). The survey spectra confirmed the presence of C, O, and Cu elements in both fresh and used samples, indicating good structural stability [42]. The high-resolution C 1s spectrum showed peaks corresponding to C–C/C=C, C–O, and C=O bonds, suggesting abundant oxygen-containing functional groups on the biochar surface. These functional groups can enhance interactions between Cu species and PDS [53–57]. The Cu 2p spectrum exhibited characteristic peaks of Cu^{2+} , along with satellite peaks, confirming the dominant presence of CuO. Meanwhile, the Cu LMM Auger spectra further indicated the coexistence of Cu^0 , Cu^+ , and Cu^{2+} species [58–61]. The coexistence of multiple valence states of copper facilitates redox cycling ($\text{Cu}^{2+}/\text{Cu}^+$), which may contribute to PDS activation and electron transfer processes [62,63]. It should be noted that while XPS analysis qualitatively demonstrates the coexistence and variation of Cu species (Cu^0 , Cu^+ , and Cu^{2+}) before and after the reaction, accurate quantitative determination of the relative percentages of these species remains challenging. This is primarily because XPS is a surface-sensitive technique (with a typical sampling depth of 2–10 nm) that may not fully represent the bulk composition of the catalyst. Furthermore, the Cu $2p_{3/2}$ binding energies of Cu^+ and Cu^0 are nearly identical (approximately 932.5–932.7 eV), making it difficult to distinguish these species solely from the Cu 2p spectrum. Although Cu LMM Auger spectra can provide additional information for distinguishing Cu^+ from Cu^0 , precise quantification of the relative abundances of different Cu species is complicated by peak overlap and the need for appropriate sensitivity factors. Therefore, quantitative peak fitting analysis was not performed in this study, and the discussion of $\text{Cu}^+/\text{Cu}^{2+}$ redox cycling is limited to qualitative interpretation based on the observed spectral features. No quantitative conclusions regarding the relative proportions of different Cu species are drawn.

**Figure 3.** XPS spectra of CuO-BC before and after the reaction: (a) Cu 2p; (b) Cu LMM Auger spectrum.

2.2. Catalytic Degradation Performance of CIP

The catalytic performance of different systems for CIP removal is shown in Figure 4. Prior to oxidation, adsorption experiments indicated that BC exhibited a higher adsorption capacity (44.73%) compared to CuO-BC (14.31%). This decrease in adsorption capacity

after CuO loading can be attributed to the partial blockage or occupation of micropores by CuO nanoparticles, which reduces the accessible surface area and active adsorption sites for ciprofloxacin molecules [64]. Additionally, the introduction of CuO introduces a competitive balance between adsorption and catalytic degradation processes, where catalytic degradation becomes increasingly dominant. This is consistent with the significantly enhanced overall removal efficiency (91.71%) observed in the CuO–BC/PDS system, indicating that the removal mechanism shifts from adsorption-dominated to degradation-dominated upon PDS addition. In contrast, the CuO–BC/PDS system demonstrated significantly enhanced degradation efficiency, achieving 91.71% removal within 30 min, which was markedly higher than that of PDS alone, CuO, BC, CuO/PDS, and BC/PDS systems. This result indicates that the synergistic interaction between CuO and biochar is suggested to play an important role in PDS activation.

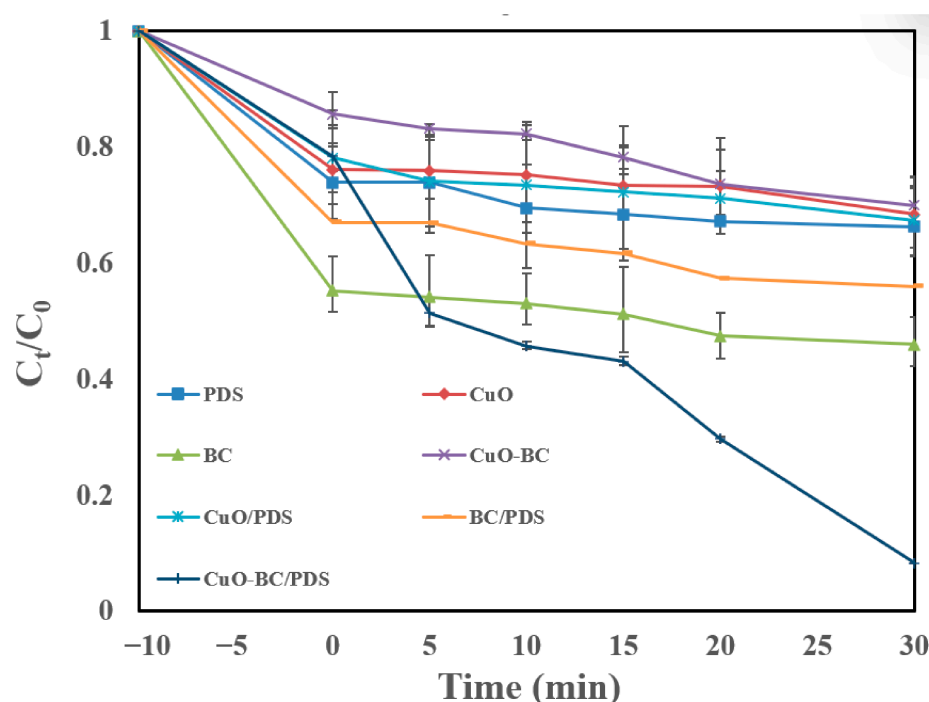


Figure 4. Degradation efficiency of CIP with different systems (catalyst dosage: 0.5 g/L, PDS: 0.8 g/L, CIP: 10 mg/L, pH: the initial pH (6.0)).

The superior performance of CuO–BC can be attributed to: (i) the presence of Cu active sites that promote PDS decomposition; (ii) the conductive biochar matrix that facilitates electron transfer; and (iii) the improved dispersion of CuO particles, providing more accessible reactive sites.

The degradation kinetics were further analyzed using a pseudo-first-order model. The apparent rate constant (k_{obs}) of the CuO–BC/PDS system reached 0.0830 min^{-1} , which was 6.92, 6.24, and 4.28 times higher than those of CuO–BC, CuO/PDS, and BC/PDS, respectively. The high correlation coefficients ($R^2 > 0.99$) indicate that the degradation process follows pseudo-first-order kinetics.

The pseudo-first-order kinetic model was adopted in this study because the PDS concentration (0.8 g L^{-1} , approximately 2.96 mmol L^{-1}) was maintained in large excess relative to the CIP concentration (10 mg L^{-1} , approximately 0.03 mmol L^{-1}), with a molar ratio of PDS to CIP exceeding 98:1. Under such conditions, the concentration of PDS can be considered approximately constant during the reaction, allowing the overall degradation rate to be expressed as first-order with respect to the target pollutant concentration [65,66]. This approach is widely employed in persulfate-based heterogeneous catalytic systems for

evaluating and comparing catalytic performance [67–70]. While alternative models such as pseudo-second-order or Langmuir–Hinshelwood kinetics may be applicable under certain conditions, they typically require additional assumptions regarding adsorption equilibria or surface reaction mechanisms that are beyond the scope of the present study [71,72]. The excellent linear fitting results ($R^2 > 0.99$) further justify the use of the pseudo-first-order model for describing the CIP degradation kinetics in the CuO–BC/PDS system.

These results demonstrate that the CuO–BC/PDS system exhibits outstanding catalytic activity for CIP degradation and highlight the importance of interfacial synergy in enhancing PDS activation.

To better highlight the novelty and advantages of the CuO–BC/PDS system, a comparison with recently reported Cu-based persulfate activation systems for antibiotic degradation is summarized in Table 2. As shown, the CuO–BC/PDS system achieves a CIP removal efficiency of 91.71% within 30 min with a k_{obs} of 0.0830 min^{-1} , which is competitive with or superior to many recently reported Cu-based catalysts. Notably, while some systems such as BC–Cu (1:4)/PMS achieve higher removal rates (99.99%) [73] or CuO/PS achieves 90.8% removal [74], the CuO–BC catalyst in this work offers several distinct advantages: (i) the use of agricultural waste (peanut shells) as a low-cost and sustainable biochar precursor; (ii) a simple one-step pyrolysis synthesis method without the need for additional modification or secondary treatment; (iii) excellent catalytic performance over a wide pH range (3.0–9.0) with strong resistance to coexisting ions; (iv) the coexistence of both radical ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) and non-radical ($^1\text{O}_2$ and electron transfer) pathways, with interfacial electron transfer playing a significant role; and (v) successful integration into a continuous-flow PRB system, demonstrating practical applicability for groundwater remediation. Compared with bimetallic systems such as $\text{CuFe}_2\text{O}_4\text{@BC}$ /PMS (97.8% removal in 30 min) [75] or CoO/CuO@CBC /PMS (99.3% in 5 min) [76], the CuO–BC catalyst utilizes a single metal oxide, which simplifies the synthesis process and reduces material costs while maintaining competitive performance. Furthermore, compared with CuCl_2 -modified biochar [77] or Cu_3P /biochar [78] systems that require specific chemical modifications or phosphorus doping, the present CuO–BC composite is prepared through a straightforward impregnation-pyrolysis method using widely available precursors. The combination of low-cost synthesis, excellent catalytic performance, mechanistic understanding of interfacial electron transfer, and successful PRB application distinguishes this work from previous studies and demonstrates the practical potential of CuO–BC for antibiotic-contaminated water treatment.

Table 2. Comparison of Cu-based persulfate activation systems for antibiotic degradation.

Catalyst	Oxidant	Target Pollutant	Conditions	Removal Efficiency	k_{obs} (min^{-1})	Radical/Non-Radical Pathways	Ref.
CuO–BC	PDS	CIP	0.5 g/L catalyst, 0.8 g/L PDS, pH 6.0	91.71% (30 min)	0.083	Radical + non-radical	This work
BC–Cu (1:4)	PMS	CIP	20 mg/L CIP, 40 min	99.99%	—	Non-radical ($^1\text{O}_2$)	[73]
CuO	PS	CIP	0.5 g/L CuO, 1.0 g/L PS	90.8% (60 min)	0.0196	Radical + non-radical (pH-dependent)	[74]
$\text{CuFe}_2\text{O}_4\text{@BC}$	PMS	CIP	0.4 g/L catalyst, 0.4 g/L PMS	97.8% (30 min)	—	Radical + non-radical	[75]
CoO/CuO@CBC	PMS	BPA	0.1 g/L catalyst, 0.2 g/L PMS	99.3% (5 min)	0.937	Radical + non-radical	[76]
Cu–BC (CuCl_2)	PDS	LFX	—	High efficiency	—	Radical ($\text{SO}_4^{\bullet-}$, $^1\text{O}_2$)	[77]
Cu_3P /biochar	PS	SMX	0.15 g/L catalyst, 3.0 mM PS	100% (30–180 min)	—	Radical ($\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$) + $^1\text{O}_2$	[78]

2.3. Effects of Operating Conditions

(1) Effect of CuO–BC dosage

The effect of catalyst dosage on CIP degradation is shown in Figure 5a. As the CuO–BC dosage increased from 0.1 to 0.5 g/L, the removal efficiency significantly improved from 38.39% to 91.71%, accompanied by an increase in k_{obs} from 0.0162 to 0.0830 min^{-1} (Figure S6a). This enhancement can be attributed to the increased number of active sites available for PDS activation. However, a further increase in catalyst dosage (0.7–0.9 g/L) led to a decline in degradation efficiency. This phenomenon may be due to the aggregation of catalyst particles at high concentrations, which reduces the effective surface area and limits mass transfer. In addition, excessive catalyst dosage may lead to unproductive consumption of reactive species, thereby inhibiting the degradation process [79]. These results suggest that an optimal catalyst dosage is essential to balance active site availability and reaction efficiency [80].

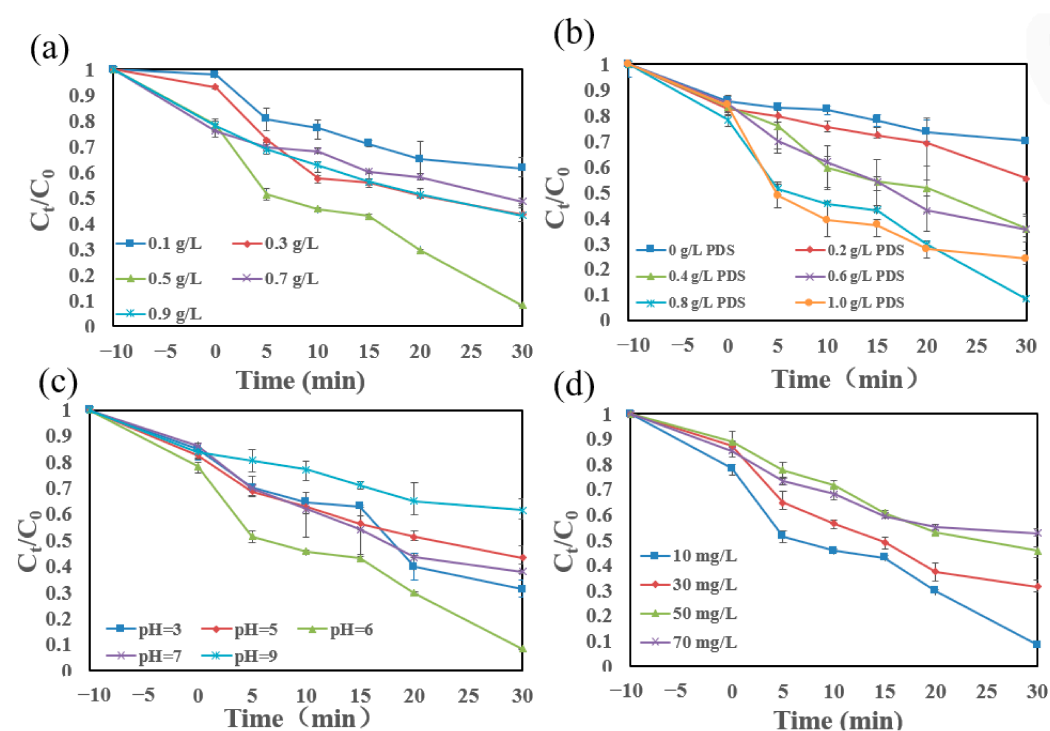


Figure 5. (a) Effect of different CuO–BC concentrations on CIP degradation. Experimental conditions: PDS: 0.8 g/L, CIP: 10 mg/L, pH: the initial pH (6.0). (b) Effect of different PDS concentrations on CIP degradation. Experimental conditions: CuO–BC: 0.5 g/L, CIP: 10 mg/L, pH: the initial pH (6.0). (c) Effect of different pH on CIP degradation. Experimental conditions: CuO–BC: 0.5 g/L, PDS: 0.8 g/L, CIP: 10 mg/L. (d) Effect of different CIP concentrations on CIP degradation. Experimental conditions: CuO–BC: 0.5 g/L, PDS: 0.8 g/L, pH: the initial pH (6.0).

(2) Effect of PDS concentration

As shown in Figures 5b and S6b, increasing the PDS concentration from 0 to 0.8 g/L significantly enhanced CIP degradation efficiency, indicating that higher oxidant availability promotes the generation of reactive oxygen species. However, further increasing the PDS concentration to 1.0 g/L resulted in a decrease in removal efficiency and k_{obs} . This can be attributed to the scavenging effect caused by excess sulfate radicals, as well as possible self-quenching reactions of PDS at high concentrations [81–83]. Therefore, an appropriate PDS dosage is critical to maximize the generation and utilization efficiency of reactive species.

(3) Effect of initial pH

The initial pH plays a crucial role in PDS activation and CIP degradation. As shown in Figures 5c and S6c, the highest degradation efficiency was achieved at near-neutral conditions ($\text{pH} = 6$), while both acidic and alkaline conditions led to reduced performance. Under acidic conditions, excessive protonation may suppress the interaction between PDS and catalyst surface [84,85]. In contrast, under alkaline conditions, Cu^{2+} may precipitate as $\text{Cu}(\text{OH})_2$, leading to the loss of active sites [81]. Moreover, electrostatic repulsion between negatively charged PDS ($\text{S}_2\text{O}_8^{2-}$) and the catalyst surface may further hinder the reaction [60]. The optimal performance at near-neutral pH suggests that the CuO-BC/PDS system is suitable for practical water treatment applications without the need for extensive pH adjustment.

(4) Effect of initial CIP concentration

The influence of initial CIP concentration on degradation performance is shown in Figures 5d and S6d. As the CIP concentration increased from 10 to 70 mg/L, the removal efficiency decreased from 91.71% to 47.32%, accompanied by a reduction. This decline can be attributed to the limited availability of reactive species at higher pollutant concentrations, leading to insufficient oxidation capacity [86]. In addition, higher CIP concentrations may occupy more active sites on the catalyst surface, thereby inhibiting PDS activation. These results indicate that the CuO-BC/PDS system is more effective for treating low to moderate concentrations of CIP-contaminated water.

It should be noted, however, that the initial CIP concentration of 10 mg L⁻¹ employed in this study is substantially higher than the typical concentrations found in real wastewater effluents and natural water bodies, which generally range from ng L⁻¹ to µg L⁻¹. The use of this elevated concentration was intended to facilitate kinetic analysis and intermediate identification for mechanistic elucidation. Nevertheless, the applicability of the proposed system under environmentally relevant trace concentrations remains to be validated. Future studies will therefore include degradation experiments at lower CIP concentrations (e.g., µg L⁻¹ or ng L⁻¹ levels) to confirm the effectiveness of the CuO-BC/PDS system under realistic conditions.

2.4. Mechanism of PDS Activation and CIP Degradation

The activation of peroxydisulfate (PDS) by heterogeneous catalysts typically involves the generation of reactive oxygen species (ROS), including sulfate radicals ($\text{SO}_4^{\bullet-}$), hydroxyl radicals ($\bullet\text{OH}$), and singlet oxygen ($^1\text{O}_2$) [87,88]. To elucidate the underlying mechanism of CIP degradation in the CuO-BC/PDS system, a combination of quenching experiments, electron paramagnetic resonance (EPR), and probe molecule analyses was employed.

It should be noted that while the combined evidence from quenching experiments, EPR, and XPS analysis suggests the involvement of interfacial electron transfer in the PDS activation process, direct electrochemical characterization (e.g., electrochemical impedance spectroscopy, linear sweep voltammetry, or chronoamperometry) would provide more definitive proof of electron mobility and transfer kinetics. Such measurements are planned for our future investigations. Therefore, the mechanistic interpretations presented below are proposed as plausible pathways based on the available evidence, rather than as conclusive proof.

Quenching experiments were first conducted to identify the dominant reactive species. Methanol (MeOH), which can scavenge both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, and tert-butanol (TBA), a selective scavenger for $\bullet\text{OH}$, were introduced into the system. As shown in Figure S7, the addition of MeOH and TBA significantly suppressed CIP degradation, indicating the involvement of both sulfate radicals and hydroxyl radicals [89]. In addition, the presence

of furfuryl alcohol (FFA), a well-known quencher for singlet oxygen ($^1\text{O}_2$), also led to a notable decrease in degradation efficiency [90]. This result suggests that $^1\text{O}_2$ plays an important role in the CuO-BC/PDS system.

The generation of ROS was further confirmed by EPR analysis. As shown in Figure 6a, characteristic signals corresponding to $\bullet\text{OH}$ (1:2:2:1 quartet) and $\text{SO}_4\bullet^-$ were clearly observed using DMPO as the spin-trapping agent, and their intensities increased over time, indicating continuous ROS generation. In addition, $\text{DMPO}\cdot\text{O}_2^-$ signals were detected (Figure 6b), suggesting the presence of superoxide radicals in the system. Furthermore, a typical triplet signal (1:1:1) of $\text{TEMP}\cdot^1\text{O}_2$ was observed (Figure 6c), confirming the generation of singlet oxygen. These results collectively demonstrate the coexistence of multiple ROS in the CuO-BC/PDS system.

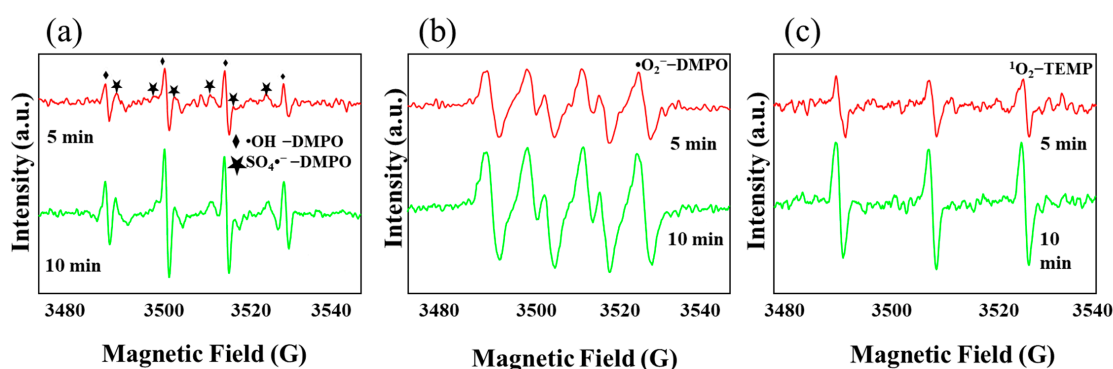


Figure 6. EPR pattern of (a) $\text{SO}_4\bullet^-$ –DMPO and $\bullet\text{OH}$ –DMPO, (b) $\bullet\text{O}_2^-$ –DMPO, (c) $^1\text{O}_2$ –TEMP.

The conductive biochar matrix acts as an electron mediator, facilitating electron transfer to Cu species and peroxydisulfate (PDS). The transferred electrons may facilitate the reduction of Cu^{2+} to Cu^+ and accelerate PDS activation, leading to the generation of reactive oxygen species ($\text{SO}_4\bullet^-$, $\bullet\text{OH}$, and $^1\text{O}_2$). Both radical and non-radical pathways contribute to ciprofloxacin (CIP) degradation. The possible interfacial electron transfer pathway is shown in Figure 7. Figure 7 provides an overview of the proposed interfacial electron transfer pathway and the generation of reactive oxygen species in the CuO-BC/PDS system, illustrating the interplay between the conductive biochar matrix, Cu redox species, and PDS activation.

This redox cycling accelerates PDS activation and sustains ROS production. The electrons supplied by the conductive biochar matrix reduce Cu^{2+} to Cu^+ , initiating the redox cycle. The Cu^+ species may participate in PDS activation to generate sulfate radicals ($\text{SO}_4\bullet^-$), while being oxidized back to Cu^{2+} . This continuous possible $\text{Cu}^{2+}/\text{Cu}^+$ cycling not only accelerate oxidant activation but also sustains reactive oxygen species production. The coupling of redox cycling and interfacial electron transfer is proposed to play a key role in regulating the balance between radical and non-radical pathways. While Figure 7 presents a comprehensive overview of the catalytic mechanism, Figure 8 specifically focuses on the detailed possible $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling, showing the sequential electron transfer steps between the biochar matrix, copper species, and PDS molecules. Together, these two figures provide complementary views of the overall mechanism at different levels of detail.

Specifically, Cu^{2+} species can be reduced to Cu^+ through electron donation from the biochar matrix. Subsequently, Cu^+ reacts with PDS to generate sulfate radicals ($\text{SO}_4\bullet^-$) while being oxidized back to Cu^{2+} , forming a continuous possible $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling. The proposed mechanistic illustration of the possible $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling during PDS activation is shown in Figure 8, which highlights the detailed electron transfer steps involved in this cycle.

Cu^{2+} species are reduced to Cu^+ by electrons transferred from the biochar matrix. The generated Cu^+ reacts with PDS, producing sulfate radicals ($\text{SO}_4^{\bullet-}$) and regenerating Cu^{2+} , thus forming a continuous redox cycle. This process facilitates sustained PDS activation and reactive oxygen species generation, enabling efficient degradation of ciprofloxacin. Interfacial electron transfer is suggested to play an important role in regulating PDS activation.

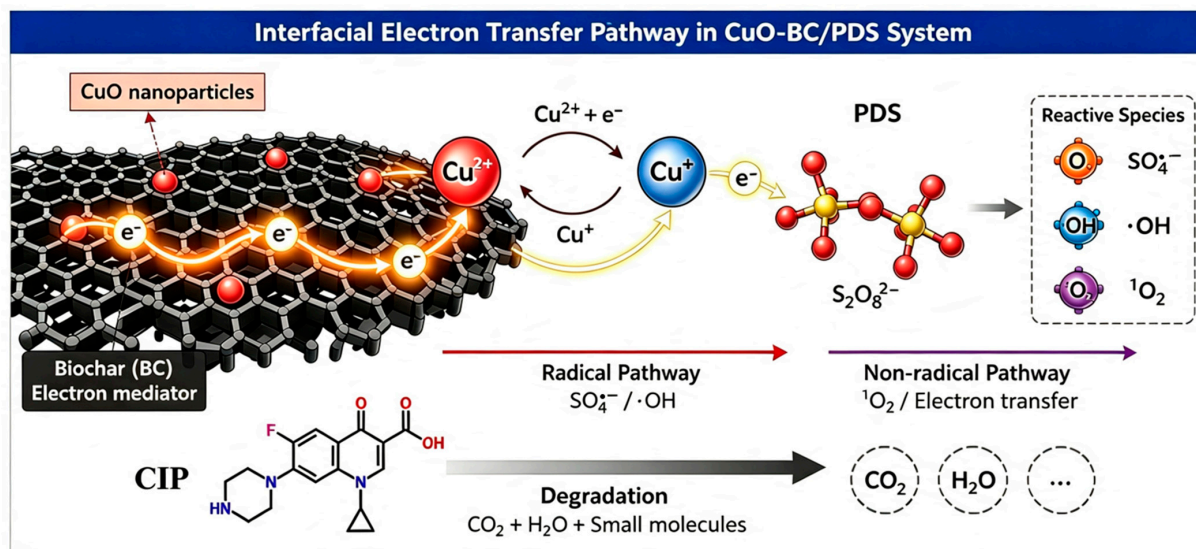


Figure 7. Schematic illustration of the interfacial electron transfer pathway in the CuO-BC/PDS system. This figure provides an overview of the proposed catalytic mechanism, showing the electron transfer from the conductive biochar matrix to Cu^{2+} species (forming Cu^+), the subsequent activation of PDS to generate reactive oxygen species ($\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, and $^1\text{O}_2$), and the contribution of both radical and non-radical pathways to CIP degradation.

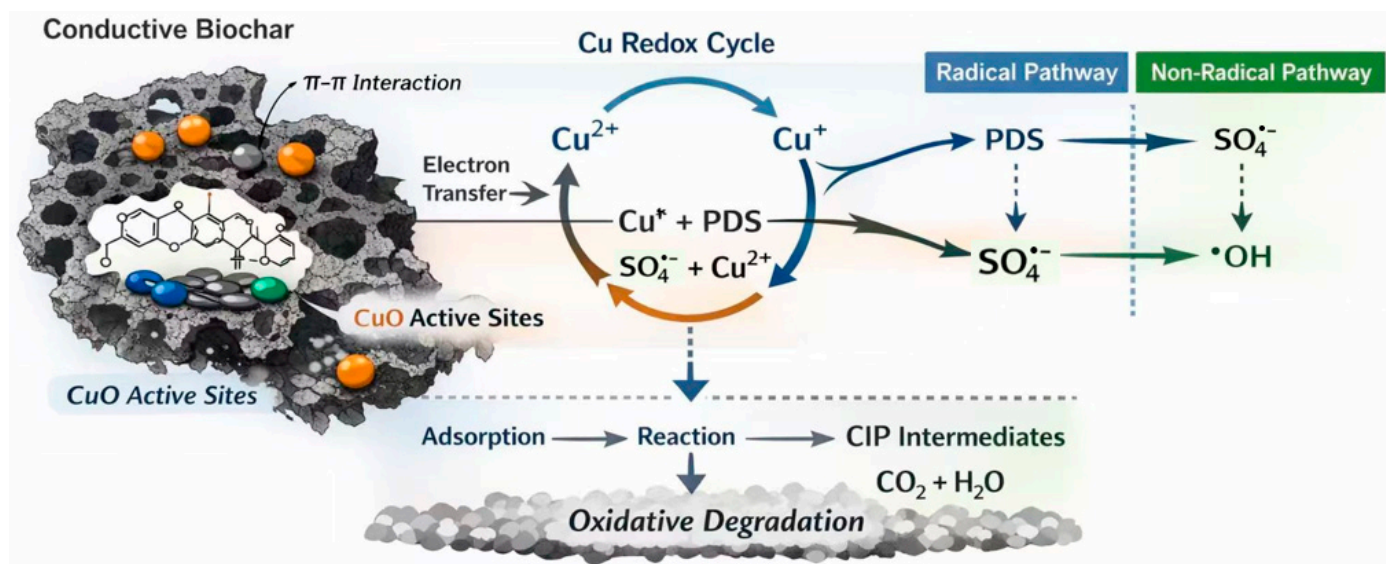


Figure 8. Proposed possible $\text{Cu}^{2+}/\text{Cu}^+$ redox cycle mechanism in the CuO-BC/PDS system. This figure focuses on the detailed redox cycling of copper species, illustrating the sequential electron transfer steps: Cu^{2+} is reduced to Cu^+ by electrons donated from the biochar matrix, Cu^+ reacts with PDS to generate $\text{SO}_4^{\bullet-}$ while being oxidized back to Cu^{2+} , and this continuous cycle sustains PDS activation and ROS generation. This figure provides complementary detail to the overall mechanism shown in Figure 7.

Based on these findings, a comprehensive mechanism is proposed (Figure 8). The CuO-BC catalyst integrates multiple functions: (i) Cu species act as active sites for PDS

activation through redox cycling; (ii) the biochar matrix facilitates interfacial electron transfer; and (iii) the synergistic interaction between radical and non-radical pathways enhances CIP degradation efficiency.

2.5. Stability and Reusability of CuO–BC

The stability and reusability of the CuO–BC catalyst were evaluated through consecutive cycling experiments. As shown in Figure 9, the CIP removal efficiency slightly decreased from 91.71% to 85.34% after five cycles, indicating good catalytic stability. Specifically, the removal efficiencies for the five consecutive cycles were 91.71%, 89.56%, 87.92%, 86.78%, and 85.34%, respectively, demonstrating that the catalyst retained approximately 93.1% of its initial activity after five cycles. The minor decline in performance may be attributed to partial loss of active sites or slight leaching of copper species during repeated use. Nevertheless, the overall degradation efficiency remained high, demonstrating the robustness of the catalyst.

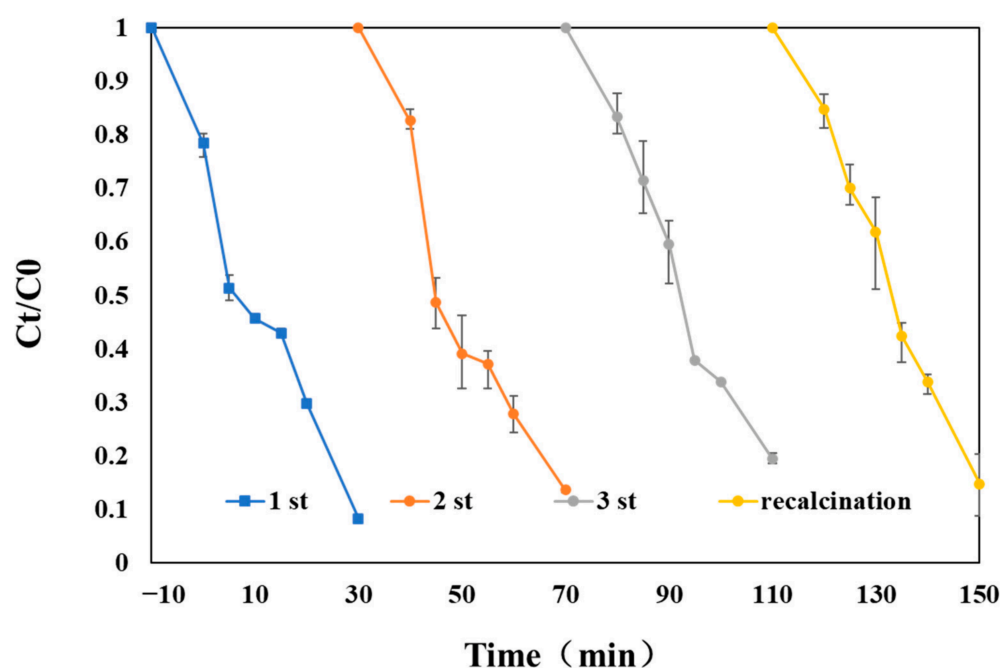


Figure 9. Recycle experiments for the CIP degradation by CuO–BC/PDS.

We acknowledge that quantitative analysis of copper leaching (e.g., by ICP-OES or ICP-MS) is important for both confirming the heterogeneous nature of the catalytic mechanism and assessing the environmental safety of the catalyst. Such analysis was not performed in the present study, as the primary focus was on catalyst preparation, catalytic performance, mechanistic investigation, and proof-of-concept PRB application. Nevertheless, the excellent stability observed during five consecutive cycling experiments (only ~6.4% decrease in removal efficiency) and the preserved Cu species in the used catalyst as confirmed by XPS analysis (Figure 3) indirectly suggest that copper leaching, if any, is limited under the investigated reaction conditions. Quantitative evaluation of copper leaching and its environmental implications will be systematically addressed in future studies.

To further assess structural stability, the used catalyst was characterized by XRD and XPS (Figures 2a and 3). The characteristic diffraction peaks of CuO remained largely unchanged after the reaction, suggesting that the crystalline structure was well preserved. In addition, XPS analysis revealed that the Cu²⁺/Cu⁺ redox pair was still present after cycling, indicating the persistence of active redox sites.

These results confirm that the CuO–BC catalyst possesses excellent structural stability and reusability, which are essential for practical applications.

2.6. Application in Permeable Reactive Barrier (PRB)

To evaluate the practical applicability of the CuO–BC/PDS system, a simulated permeable reactive barrier (PRB) was constructed, and continuous-flow experiments were conducted (Figures 10 and S8). It should be emphasized that this PRB experiment was designed as a laboratory-scale proof-of-concept study, intended to preliminarily assess the feasibility of integrating the CuO–BC/PDS system into a continuous-flow configuration. The column dimensions, packing ratio, and flow rate were selected to allow controlled evaluation of the catalytic performance under simulated groundwater flow conditions, rather than to fully replicate field-scale PRB engineering parameters. The groundwater experiment was intended as a preliminary demonstration to evaluate the feasibility of applying the CuO–BC/PDS system in a realistic water matrix, rather than to establish quantitative relationships between water chemistry and catalytic performance. As shown in Figure 11, the CuO–BC/PDS system maintained stable CIP removal performance over an extended operation period, with an average removal efficiency exceeding 90%. This result indicates that the catalytic system shows potential under laboratory-scale dynamic flow conditions.

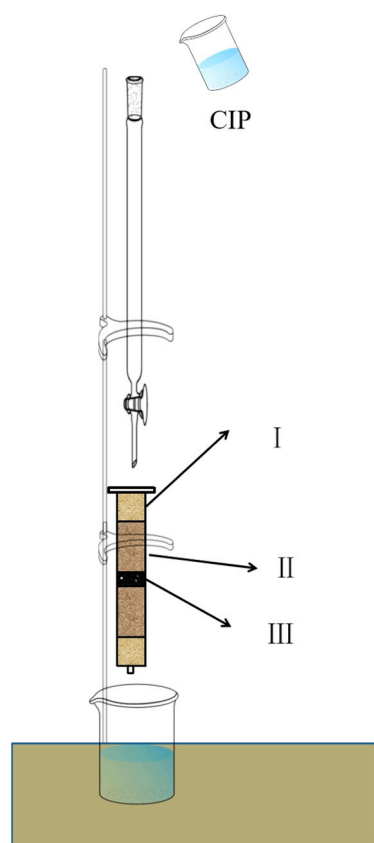


Figure 10. Experimental setup for PRB. Buffer layer I consisted of quartz sand with a particle size of 0.5–1 mm, simulated aquifer layer II was composed of quartz sand with a particle size less than 0.25 mm, and reactive medium III was made up of CuO–BC. The ratio of the three components was I:II:III = 2:7:1. The PRB column was constructed using a 50 mL plastic syringe with an inner diameter of approximately 2.5 cm. The reactive medium layer (III) was packed to a height of approximately 1 cm, and the total packing height (including buffer and aquifer layers) was approximately 10 cm. The flow rate was controlled at 1.0 mL min^{-1} using a peristaltic pump, corresponding to an empty bed contact time (EBCT) of approximately 10 min.

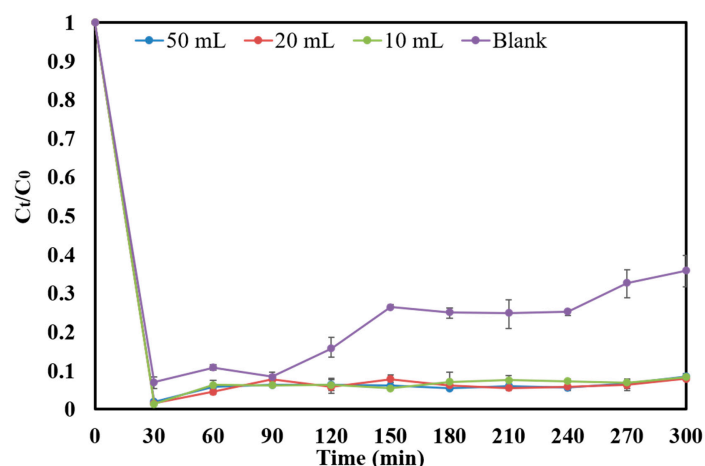


Figure 11. Removal of CIP from groundwater.

Compared with batch systems, the PRB configuration provides continuous treatment and better mimics real groundwater remediation scenarios. The sustained performance observed in the PRB can be attributed to the synergistic effects of continuous pollutant supply, stable catalyst packing, and efficient mass transfer within the porous medium.

In addition, the involvement of non-radical pathways, particularly singlet oxygen ($^1\text{O}_2$), may contribute to the improved resistance against interference from coexisting substances, thereby enhancing system stability in complex water matrices. We acknowledge that detailed physicochemical characterization of the groundwater sample (e.g., pH, conductivity, total organic carbon/dissolved organic carbon, and major inorganic ions such as Cl^- , HCO_3^- , SO_4^{2-} , Na^+ , Ca^{2+} , and Mg^{2+}) was not performed in this study. Such information is valuable for understanding the influence of water matrix components on PDS activation and for improving the reproducibility and practical relevance of the results. However, the primary objective of this experiment was to provide a preliminary proof-of-concept demonstration in a real water matrix rather than to systematically evaluate the effects of specific water quality parameters. Future studies will include comprehensive groundwater characterization to establish more quantitative correlations between water chemistry and catalytic performance. While the laboratory-scale PRB results are encouraging, several engineering parameters critical for field-scale implementation remain to be systematically evaluated. These include, but are not limited to: (i) hydraulic residence time optimization and its effect on degradation efficiency; (ii) long-term permeability evolution and potential pore clogging due to catalyst fouling or particle attrition; (iii) pressure drop across the reactive medium and its impact on operational energy consumption; (iv) catalyst stability and activity retention under prolonged continuous-flow operation; and (v) scale-up considerations such as reactor geometry and flow distribution uniformity. Future investigations will address these engineering aspects to facilitate the translation of this laboratory-scale proof-of-concept into practical PRB applications for in situ groundwater remediation.

It should be emphasized that the current PRB experiment was conducted over a relatively short operational period to validate the proof-of-concept. While the results demonstrate effective CIP removal during this period, long-term continuous-flow operation under practical conditions would require further investigation. Key aspects that remain to be addressed include: (i) long-term catalyst stability and activity retention over extended operation times (weeks to months); (ii) catalyst lifetime and regeneration strategies; (iii) performance under environmentally relevant pollutant concentrations ($\mu\text{g L}^{-1}$ to ng L^{-1}) and complex water matrices; and (iv) hydraulic performance including potential channeling, preferential flow paths, and pressure drop evolution over time. These aspects are critical for translating the current laboratory-scale proof-of-concept into

practical field-scale PRB applications and will be systematically investigated in future work. These findings highlight the feasibility of integrating advanced oxidation processes with PRB systems and demonstrate the potential of the CuO-BC/PDS system for in situ groundwater remediation.

2.7. Possible Degradation Pathways

In order to analyze the degradation process of antibiotics more effectively, potential intermediate degradation products and the degradation process and intermediate product formation during the catalytic degradation of CIP by the CuO/BC/PDS system are illustrated in Figure 12. Figures S9–S18 show the MS spectra of intermediates. The possible degradation pathways included oxidation, ring-opening, and defluorination steps [91]. In pathway I, P1 ($m/z = 334$) was obtained from CIP through hydroxylation and replacement of -F with -OH, with the cleavage of the C-F bond resulting from attack by free radicals [92]. Then, by removing the carboxyl and hydroxyl groups and breaking the C-N bond, P1 ($m/z = 334$) was converted into P2 ($m/z = 316$) and P3 ($m/z = 245$). In pathway II, the piperazine ring was gradually oxidized, possibly initiated by $^1\text{O}_2$. It has been reported that the 15 C and 16 C positions on the piperazine portion of CIP were susceptible to being attacked by electrophilic species $^1\text{O}_2$, leading to the cleavage and oxidation of the piperazine ring, resulting in the intermediate P4 ($m/z = 362$) and P5 ($m/z = 334$) [93]. P6 ($m/z = 263$) was formed after further oxidation, lost the “CH₂CH₂NH₂” group, and formed a carbonyl group. Both P7 ($m/z = 237$) and P10 ($m/z = 184$) were generated from P6 through the process of quinolone ring opening and hydroxylation, with P9 also losing the “NH₂” and “CH₂CH₂CH” moieties. In pathway III, the quinolone ring of CIP was attacked by activating agents to generate P8 ($m/z = 350$), which was then transformed into P9 ($m/z = 283$) by the addition of a hydroxyl group. Subsequently, P9 was converted to P10 by losing two carboxyl groups, an amide group, and the “CH₂CH₂CH” moiety. Finally, the above-mentioned intermediates were further transformed into smaller degradation products through different degradation pathways, or potentially further degraded into CO₂, H₂O, F[−], etc., according to different pathways [94,95].

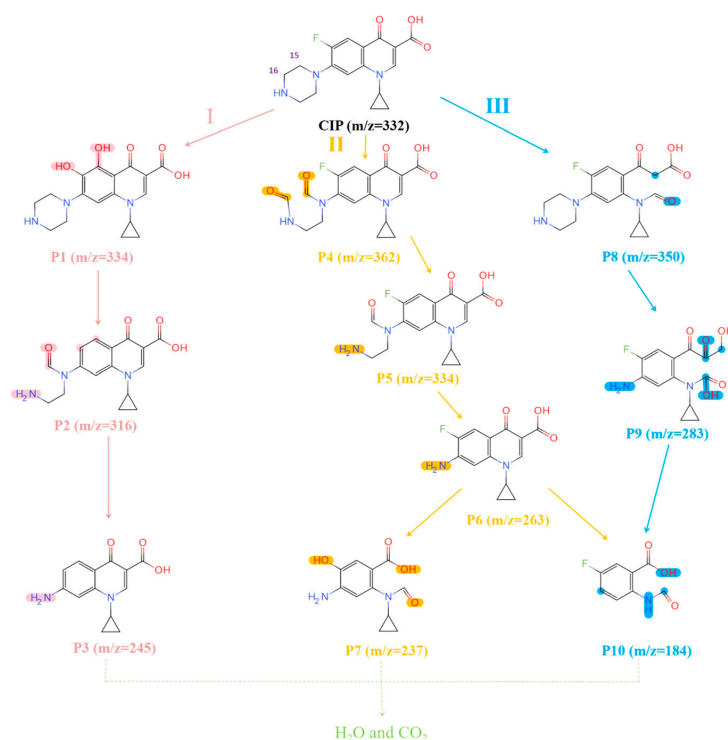


Figure 12. Possible degradation pathway of ciprofloxacin.

It is important to note that the proposed degradation pathways in Figure 12 are based on the identification of intermediate products by LC-MS analysis, which confirms the transformation of CIP into smaller organic fragments. However, the detection of these intermediates does not necessarily indicate complete degradation/transformation of the parent compound. The extent of degradation/transformation (i.e., conversion to CO_2 and H_2O) would require complementary analyses such as total organic carbon (TOC) or chemical oxygen demand (COD) measurements, which were not performed in the present study. It is worth noting that while the degradation intermediates of CIP have been identified in this study, their potential environmental implications and toxicity remain to be fully elucidated. Although the CuO-BC/PDS system effectively transforms CIP into smaller organic fragments, these intermediates may exhibit different toxicological profiles compared to the parent compound. Some studies have reported that certain degradation products of fluoroquinolone antibiotics, such as those retaining the quinolone core structure, may still possess antimicrobial activity or ecotoxicological effects [95]. In this study, several intermediates (e.g., P1, P2, P4, P5, P8) still contain the quinolone or piperazine ring structures, which could potentially retain some biological activity. However, comprehensive assessment of the toxicity, biodegradability, and environmental fate of these intermediates requires dedicated ecotoxicological studies using standardized bioassays (e.g., *Vibrio fischeri* luminescence inhibition, *Daphnia magna* immobilization, or algal growth inhibition tests), which were beyond the scope of the present investigation. Therefore, the environmental safety of the degradation products remains an important topic for future research. Nevertheless, the effective transformation of CIP into smaller fragments by the CuO-BC/PDS system represents a crucial first step toward mitigating the environmental risks associated with antibiotic contamination.

3. Material and Methods

3.1. Materials

Ciprofloxacin ($\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3$, $\geq 98.0\%$) and furfuryl alcohol ($\text{C}_5\text{H}_6\text{O}_2$, FFA, $\geq 98.0\%$) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\geq 99.0\%$) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, $\geq 99.5\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetonitrile (HPLC grade), methanol (HPLC grade), and tert-butanol (TBA, $\geq 99.0\%$) were also supplied by Sinopharm (Shanghai, China). Hydrochloric acid (HCl, 36–38%), acetic acid (CH_3COOH , $\geq 99.5\%$), and sodium hydroxide (NaOH, $\geq 96.0\%$) were purchased from Luoyang Chemical Reagent Factory (Luyang, China).

Groundwater samples were collected from Xinhua District, Pingdingshan City, China, at a depth of approximately 10 m. All chemicals were of analytical grade and used as received. Ultrapure water was used for the preparation of all solutions.

3.2. Catalyst Synthesis

Peanut shells were washed with deionized water, dried at $80\text{ }^\circ\text{C}$ for 4 h, and then crushed into powder. Subsequently, 15 g of the biomass was impregnated in 150 mL of 0.08 mol/L $\text{Cu}(\text{NO}_3)_2$ solution and stirred at $30\text{ }^\circ\text{C}$ and 150 rpm for 8 h. The mixture was then filtered, washed with deionized water until neutral pH, and dried at $80\text{ }^\circ\text{C}$ for 12 h.

The dried precursor was pyrolyzed in a muffle furnace at $600\text{ }^\circ\text{C}$ for 4 h with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under limited oxygen conditions (nitrogen was continuously introduced during pyrolysis to establish an oxygen-limited atmosphere). After pyrolysis, the sample was naturally cooled to room temperature under continuous nitrogen protection. The obtained product was ground and sieved (60–100 mesh), and denoted as CuO-BC.

3.3. Characterization of CuO-BC

The crystalline structure of the samples was analyzed using X-ray diffraction (XRD, Bruker D8 Advance, Karlsruhe, Germany). Surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR, Nicolet iS10, Thermo Scientific, Waltham, MA, USA). The surface morphology was observed using scanning electron microscopy (SEM, Regulus 8100, Hitachi, Tokyo, Japan). The elemental composition and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). The specific surface area and pore structure were determined by N₂ adsorption–desorption isotherms (BET, ASAP2460, Micromeritics, Norcross, GA, USA). Quenching experiments were observed using electron paramagnetic resonance (EPR, JEOL-JES-FA200, Tokyo, Japan). Detailed operating parameters for XRD, SEM, BET, XPS, and EPR are provided in Table S1 (Supplementary Materials).

3.4. CIP Degradation Experiments

Batch experiments were conducted in 100 mL CIP solution (10 mg/L). This initial concentration was selected to enable reliable kinetic evaluation and facilitate the identification of degradation intermediates via LC-MS, which is a common practice in mechanistic studies of advanced oxidation processes [86]. CuO-BC was added and stirred at 170 rpm in a thermostatic water bath at 35 °C for 10 min to reach adsorption–desorption equilibrium. Subsequently, PDS was added to initiate the reaction.

At predetermined time intervals, 5 mL of the reaction solution was withdrawn and immediately quenched with 40 µL methanol. A small amount of 0.01 mol/L NaOH solution was added to eliminate interference from dissolved copper ions. The samples were then centrifuged and filtered through a 0.22 µm membrane prior to analysis.

The residual CIP concentration was determined by high-performance liquid chromatography (HPLC).

For PRB experiments, the setup is illustrated in Figure 10.

All catalytic experiments were independently conducted in triplicate. The data presented in the figures represent the mean values, and the error bars indicate the standard deviation (SD) of three independent measurements. Statistical analysis was performed using standard methods, and the results are reported as mean ± SD.

3.5. Analytical Methods

CIP concentration was determined using an HPLC system equipped with a C18 column (4.6 × 150 mm, 5 µm). The column temperature was maintained at 30 °C, and the detection wavelength was set at 277 nm. The mobile phase consisted of acetonitrile and 0.1% acetic acid solution (25:75, v/v) at a flow rate of 1.0 mL/min. The injection volume was 20 µL.

The HPLC method employed in this study follows a previously established analytical protocol that has been extensively validated in our laboratory for CIP quantification in aqueous matrices. The calibration curve was constructed using standard solutions of CIP at concentrations ranging from 0.1 to 20.0 mg L^{−1}, yielding a linear regression equation of $y = 45,231x + 1256$ with a correlation coefficient (R^2) of 0.9996. The limit of detection (LOD) and limit of quantification (LOQ) were determined to be 0.03 mg L^{−1} and 0.10 mg L^{−1}, respectively, based on signal-to-noise ratios of 3:1 and 10:1. Since the primary objective of this study is catalyst evaluation rather than analytical method development, detailed method validation is not the focus of this work. However, the reliability of the analytical method is supported by the high linearity and reproducibility of the calibration standards.

4. Conclusions

In this study, a CuO-loaded biochar (CuO-BC) catalyst was successfully synthesized and applied for peroxydisulfate (PDS) activation toward ciprofloxacin (CIP) degradation. The CuO-BC/PDS system exhibited excellent catalytic performance, achieving rapid CIP removal over a wide pH range with strong resistance to coexisting substances. Mechanistic investigations revealed that CIP degradation proceeded via a synergistic pathway involving both radical ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) and non-radical ($^1\text{O}_2$ and electron-transfer) processes. Notably, interfacial electron transfer between Cu species and the conductive biochar matrix is suggested to play a key role in regulating PDS activation and ROS generation. The possible $\text{Cu}^{2+}/\text{Cu}^+$ redox cycling further enhanced catalytic efficiency by sustaining continuous oxidant activation. The catalyst also demonstrated excellent stability and reusability, with minimal structural changes after repeated cycles. Furthermore, the successful application of the CuO-BC/PDS system in a simulated permeable reactive barrier (PRB) highlights its potential for continuous water treatment under realistic conditions.

It should be emphasized that the proposed mechanistic interpretation regarding interfacial electron transfer is based on indirect evidence from quenching experiments, EPR, and XPS analysis, which collectively suggest the involvement of electron-transfer processes rather than conclusively prove them. Future work employing electrochemical characterization techniques (such as EIS and chronoamperometry) is warranted to provide more direct evidence for the proposed electron-transfer pathway. It should also be noted that the degradation pathways proposed in this study are based on LC-MS identification of intermediate products, which confirms the transformation and decomposition of CIP. However, further studies involving TOC or COD analysis are needed to verify the extent of complete degradation/transformation of the organic contaminants. In addition, while the experiments were conducted at a CIP concentration of 10 mg L^{-1} for mechanistic investigation, future work should include validation experiments under environmentally relevant trace concentrations (ng L^{-1} to $\mu\text{g L}^{-1}$) to confirm the practical applicability of the system in real water treatment scenarios. Moreover, the PRB application demonstrated in this work is currently at the laboratory proof-of-concept stage; systematic investigations of key engineering parameters—including residence time optimization, long-term permeability, pressure drop, and catalyst durability under continuous-flow conditions—are required before field-scale implementation can be considered. Furthermore, quantitative analysis of copper leaching (e.g., by ICP-OES or ICP-MS) during the reaction and long-term environmental safety assessment of the CuO-BC catalyst will be included in future investigations to further support its practical application. In addition, comprehensive physicochemical characterization of groundwater matrices (including pH, conductivity, TOC/DOC, and major inorganic ions) will be performed in future work to better understand the influence of water chemistry on PDS activation and to enhance the practical relevance of the findings. In particular, long-term continuous-flow experiments over extended operational periods are needed to evaluate catalyst lifetime, activity retention, and hydraulic performance under practical field-relevant conditions, which will be essential for assessing the true potential of the CuO-BC/PDS system for real-world groundwater remediation. Overall, this work provides new insights into interfacial PDS activation mechanisms and offers a promising strategy for coupling advanced oxidation processes with PRB systems for in situ groundwater remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16080706/s1>, Table S1 Operating parameters for the main characterization techniques. Figure S1 EDS mapping of CuO-BC. Figure S2 The adsorption/desorption isotherm of BC (a) and CuO-BC (b). Figure S3 XPS spectra of CuO-BC before and after the reaction: (a) survey scan, (b) C1s and (c) O1s. Figure S4 The observed pseudo first-order rate constant of Figure 4. Figure S5 Correlation coefficients R^2 . Figure S6 (a) The observed pseudo-first-order rate constant of Figure 5a; (b) The observed pseudo-first-order rate constant of Figure 5b; (c) The observed pseudo-first-order rate constant of Figure 5c; (d) The observed pseudo-first-order rate constant of Figure 5d. Figure S7 (a) Effect of different quenchers on the degradation efficiency of CIP; (b) The observed pseudo-first-order rate constant of (a). Figure S8 Recycle experiments for the CIP degradation by CuO-BC/PDS. Figure S9 Experimental setup for PRB. Figure S10 LC-MS spectra of CIP degradation intermediate P1 ($m/z = 334$). Figure S11 LC-MS spectra of CIP degradation intermediate P2 ($m/z = 316$). Figure S12 LC-MS spectra of CIP degradation intermediate P3 ($m/z = 245$). Figure S13 LC-MS spectra of CIP degradation intermediate P4 ($m/z = 362$). Figure S14 LC-MS spectra of CIP degradation intermediate P5 ($m/z = 334$). Figure S15 LC-MS spectra of CIP degradation intermediate P6 ($m/z = 263$). Figure S16 LC-MS spectra of CIP degradation intermediate P7 ($m/z = 237$). Figure S17 LC-MS spectra of CIP degradation intermediate P8 ($m/z = 350$). Figure S18 LC-MS spectra of CIP degradation intermediate P9 ($m/z = 283$). Figure S19 LC-MS spectra of CIP degradation intermediate P10 ($m/z = 184$).

Author Contributions: Y.W.: Conceptualization, Project administration, writing—review and editing. B.L., J.Z. and T.Z.: Investigation, Methodology, Data curation, Writing—original draft, Writing—review and editing. Investigation, Methodology. X.H., X.G. and S.Y.: Validation, Supervision. S.V.F., X.L. and X.Z.: Supervision, Resources. J.W.: Project administration, supervision, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Henan Provincial Natural Science Foundation (Grant Nos. 252300423371, Nos. 262300421911), Science and Technology Project of Henan Province (Grant Nos. 252102320112, Nos. 262102321171). Key Research and Development Projects of the Education Department of Henan Province (Grant Nos. 25A610016). Open Research Projects of Henan Key Laboratory of Water Pollution Prevention and Remediation (CJSZ2024016), Hebi Polytechnic (Grant Nos. 2024-KJZD-007). The APC was funded by Provincial Natural Science Foundation (Grant Nos. 252300423371).

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Acknowledgments: Provincial Natural Science Foundation (Grant Nos. 252300423371, Nos. 262300421911), Science and Technology Project of Henan Province (Grant Nos. 252102320112, Nos. 262102321171). Key Research and Development Projects of the Education Department of Henan Province (Grant Nos. 25A610016). Open Research Projects of Henan Key Laboratory of Water Pollution Prevention and Remediation (CJSZ2024016), Hebi Polytechnic (Grant Nos. 2024-KJZD-007).

Conflicts of Interest: The authors declare no conflicts of interest.

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