

Article

Functional Cobalt-Based Biochar Activating Peracetic Acid for Sulfamethoxazole Degradation: Electron Shuttle Effect and Synergistic Oxidation Mechanisms

Zidu Yan ¹, Mengqi Liu ¹, Youcheng Luo ¹, Xiangjuan Yuan ^{1,*} and Lei Sun ^{1,2,*}

¹ School of Resources and Environment, Wuhan Textile University, Wuhan 430073, China; yanzidu99@163.com (Z.Y.); mqliu27@163.com (M.L.); lyc04104@163.com (Y.L.)

² State Key Laboratory of New Textile Materials and Advanced Processing Technologies, Hubei Key Laboratory of Biomass Fibers and Eco-Dyeing & Finishing, Wuhan Textile University, Wuhan 430073, China

* Correspondence: xjyuan@wtu.edu.cn (X.Y.); sunlei@wtu.edu.cn (L.S.)

Abstract

Advanced oxidation processes based on peracetic acid (PAA) have emerged as a sustainable strategy for water treatment; however, developing efficient, stable, and environmentally friendly catalysts remains challenging. In this study, a functional cobalt-based catalyst (CPBC_x) was fabricated by immobilizing cobalt ions onto phytic-acid-modified biochar to active PAA for the degradation of sulfamethoxazole (SMX). The effect of pyrolysis temperature on the catalytic performance was investigated, with CPBC₈ showing the highest SMX degradation efficiency, under the conditions of a CPBC₈ dosage of 200 mg/L, a PAA concentration of 0.2 mM, and an initial SMX concentration of 5 mg/L, and a 99.0% removal of SMX was achieved within 10 min. Moreover, the removal efficiency remained above 90% after five consecutive cycles. Mechanistic analysis revealed that biochar, acting as an efficient electron shuttle, enhanced electron transfer and accelerated the Co²⁺/Co³⁺ redox cycle, thereby shifting the SMX degradation pathway from a radical-dominated route to a non-radical one dominated by singlet oxygen (¹O₂). Density functional theory (DFT) calculations identified the vulnerable attack site (N11) on the SMX molecule. Transformation products and degradation pathways were elucidated using ultra-performance liquid chromatography coupled with time-of-flight mass spectrometry (UPLC-TOF-MS), and the identified intermediates exhibited low ecotoxicity. Furthermore, the CPBC₈ composite demonstrated sustained degradation rates, good stability, and environmental compatibility for practical application. This study provides a sustainable and efficient solution for applying biochar-based PAA advanced oxidation processes in water treatment.

Keywords: peroxyacetic acid; functional cobalt-based biochar; sulfamethoxazole; electron shuttle



Academic Editor: Qiulai He

Received: 2 June 2026

Revised: 29 June 2026

Accepted: 30 June 2026

Published: 3 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons](#)

[Attribution \(CC BY\)](#) license.

1. Introduction

Sulfamethoxazole (SMX), a broad-spectrum antibiotic, poses significant environmental and health risks due to its frequent detection and persistence in aquatic environments, where it resists complete degradation by conventional treatment processes [1–3]. Peracetic acid (PAA)-based advanced oxidation processes (AOPs) have attracted considerable attention because of their environmentally benign byproducts, high redox potential, and low O–O bond energy [4,5] and have become an important technological approach for efficient SMX removal [6]. These processes generate highly reactive radicals (e.g., •OH and R–O•),

which disrupt the SMX molecular structure via ring-opening and bond cleavage reactions, ultimately leading to complete mineralization into inorganic small molecules (e.g., CO₂ and H₂O) [7].

Studies have shown that the transition metal cobalt (Co) can efficiently activate PAA [8], exhibiting significantly superior performance compared to PAA oxidation alone [9,10]. For instance, Wang et al. constructed a homogeneous Co(II)/PAA system that achieved over 90% SMX degradation within 15 min under neutral conditions, with acetylperoxy radicals (CH₃C(O)OO•) identified as the primary reactive species [11]. However, the cobalt in homogeneous systems requires secondary recovery after the reaction, resulting in significantly increased costs. To address this issue, the immobilization of Co species has been widely investigated as an effective strategy to develop efficient and environmentally friendly catalytic systems [12].

Biochar, as a common supporting material, can immobilize or encapsulate Co species, thereby addressing the issue of secondary cobalt treatment in homogeneous systems [13]. Zhang et al. fabricated a biochar-supported cobalt nanoparticle composite using ZIF-67 as a precursor, in which Co retains the advantages of the precursor and enables morphology control through inheritance, while biochar provides dispersibility, stability, and facilitated electron transfer. Consequently, through the synergistic action of radical (R-O•) and non-radical (¹O₂) pathways, the system achieved 98.9% removal of carbamazepine (CBZ) within 30 min [14]. In addition, Xia et al. developed a CoFe₂O₄-BC composite that achieved 95.61% CBZ removal within 30 min; the introduction of biochar played a crucial role as an electron shuttle, accelerating the Co(II)/Co(III) cycle and shifting the degradation pathway from a conventional radical route to a non-radical pathway dominated by singlet oxygen (¹O₂) [15].

Among various biomass feedstocks, peanut shell, a common agricultural residue, exhibits advantages such as high carbon content and low cost [16]. However, biochar derived from direct pyrolysis of peanut shell suffers from disadvantages, including low specific surface area and uneven pore distribution. Phytic acid, a naturally occurring and environmentally benign saturated cyclic acid, can further tailor the porous structure of biochar through modification [17]. Deng et al. found that phytic acid modification dramatically increased the specific surface area of biochar from 1.89 (pristine BC) to 1376.39 m²/g (PABC) [18]. Furthermore, the calcination temperature could distinctly affect the morphology of biochar and cobalt valence (converting Co³⁺ to more active Co²⁺/Co⁰) [19], as well as the specific surface area, pore volume, and carbon content of the biochar [20]. To further extend the current understanding, this study will further examine how the morphological evolution of ZIF-67-derived cobalt-based biochar composites at different calcination temperatures affects catalytic activity—an aspect still lacking systematic investigation—and, moreover, the specific configuration of cobalt on phytic-acid-modified biochar, whose mechanistic function in PAA activation has yet to be fully clarified.

Therefore, to address the knowledge gaps concerning the configuration of cobalt species on modified biochar and the influence of calcination temperature on material morphology, this study synthesized a series of Co-based carbon composites (CPBC_x) for PAA activation toward SMX degradation, using phytic-acid-modified biochar and ZIF-67 as a precursor. The research focuses on four aspects: (i) to examine the effects of calcination temperatures on the morphology, structure, and catalytic performance of CPBC_x composites using multiple characterization techniques; (ii) to optimize the experimental parameters through comprehensive performance evaluation; (iii) to investigate the reaction mechanism and identify the dominant reactive species; and (iv) to analyze the toxicity changes during the reaction and evaluate the practical application performance.

2. Materials and Methods

2.1. Chemicals and Materials

Specific information of the chemical reagents used in this study can be found in the Text S1 [21,22].

2.2. Synthesis of CPBC_x Composites

The CPBC_x composites were synthesized via a two-step method. ZIF-67, prepared from 2-MeIM and Co(NO₃)₂·6H₂O according to Text S2 [14], was used as the precursor. Modified biochar (PBC) was prepared from commercially obtained peanut shells following the method in Text S3 [18]. ZIF-67 and PBC at a mass ratio of 1:4 (i.e., 0.1 g ZIF-67 and 0.4 g PBC) were dispersed in 45 mL of a 1:1 (*v/v*) methanol/water mixture. The mixture was vigorously stirred for 10 min, followed by sonication for 10 min, and then transferred into a Teflon-lined autoclave and maintained at 160 °C for 12 h. The resulting product was placed in a tube furnace and calcined under a nitrogen atmosphere at target temperatures of 600 °C, 700 °C, 800 °C, and 900 °C (with the corresponding products denoted as CPBC₆, CPBC₇, CPBC₈, and CPBC₉, respectively) for 2 h at a heating rate of 5 °C/min. After calcination, the material was centrifuged, washed twice with ethanol and three times with ultrapure water, and then dried at 80 °C for 3 h to obtain the final products, denoted as CPBC_x.

2.3. Experimental Procedure

The specific experimental procedures are detailed in Text S4. All experiments were performed in triplicate. A continuous fixed-bed column experiment was conducted using a mini-scale column (Figure S1), with the specific operational conditions detailed in Text S5.

2.4. Analytical Methods

The SMX concentration was quantified using liquid chromatography–mass spectrometry (LC-MS) under the operating conditions specified in Text S6. The screening and identification of SMX transformation products (TPs) were conducted, with detailed chromatographic and mass spectrometric parameters provided in Text S7.

The kinetic rate constant (*k*) and activation energy (*E_a*) for pollutant degradation was determined using the equation provided in Text S8 [23]. The reactive oxygen species (ROS) in the CPBC₈/PAA system were identified through inhibitor experiments, and the contribution of each ROS was calculated based on the inhibition rate according to the method described in Text S9.

The acute (LC50 or EC50) and chronic (ChV) toxicity of SMX and its TPs to fish, daphnid, and green algae were forecasted by the Ecological Structure–Activity Relationship (ECOSAR v2.0 USA) software [24]. The seed germination experiment was conducted in strict accordance with the method described in Text S10.

2.5. Characterization Methods and Theoretical Calculations

Material characterization for PBC and CPBC_x composites, including morphology, crystal structure, and surface properties, was performed as detailed in Text S11. Electrochemical measurements of the materials were conducted following the methods described in Text S12. In addition, density functional theory (DFT) calculations were employed to predict the susceptible attack sites on SMX at the atomic level, with computational details provided in Text S13 [25–28].

3. Results and Discussion

3.1. Characterizations and Catalytic Performance of CPBC_x

The influences of calcination temperatures on CPBC_x composites were systematically investigated. As depicted in Figure 1a of XRD patterns, the peak at $2\theta = 26.3^\circ$ corresponded to the (002) plane of graphitic carbon in biochar [14]. Meanwhile, peaks at $2\theta = 20.9^\circ$, 36.5° , 42.4° , 44.5° , 51.5° , and 76.2° were assigned to the (001), (111), (200), (002), (101), and (110) planes of CoO₂, CoO, and Co⁰, respectively [29]. Compared with pristine biochar (Figure S2), the CPBC_x composites exhibited distinct diffraction peaks of Co, confirming successful Co loading onto the biochar support. As the calcination temperature increased, the intensities of the CoO and Co⁰ peaks gradually increased, indicating that high temperature promotes the reduction of cobalt species to lower valence states (e.g., Co⁰). Since Co²⁺ is the primary active species, excessively high temperatures lead to further reduction of Co²⁺; in contrast, a more diverse cobalt speciation was obtained at 800 °C, which could be favorable for subsequent redox processes [19,30].

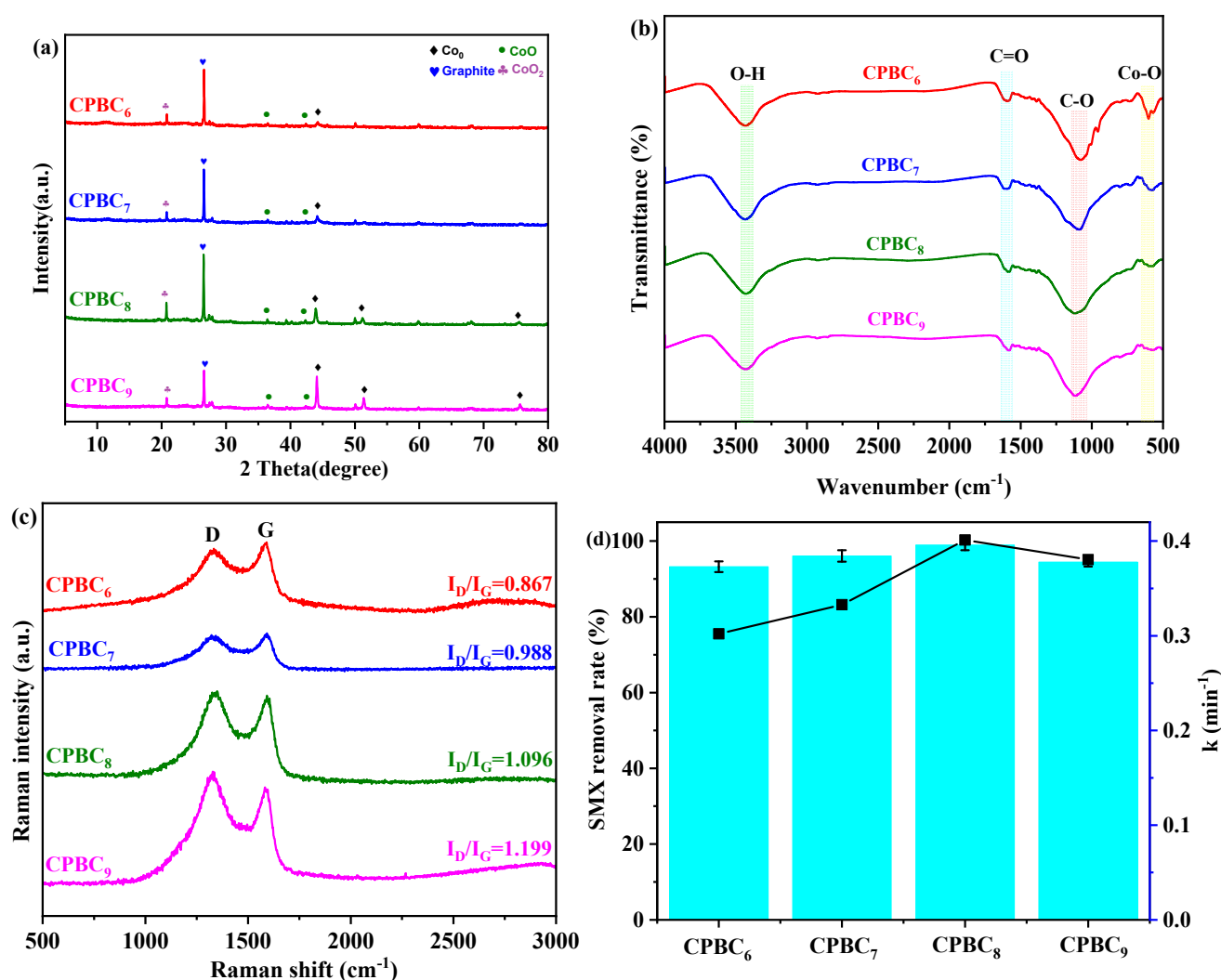


Figure 1. The characterizations of CPBC_x composites: XRD (a), FTIR (b), and Raman spectrum (c); the SMX degradation of CPBC_x (d). Reaction conditions: [Catalysts] = 200 mg/L, [PAA]₀ = 0.2 mM, [SMX]₀ = 5 mg/L, pH₀ = 6.8, T = 25 °C.

As shown in Figure 1b, the CPBC_x composites exhibited three characteristic FT-IR absorption bands of biochar structure at 3438, 1633, and 1091 cm⁻¹, corresponding to O-H, C=O, and C-O bonds, respectively [31]. An additional band appearing around 550 cm⁻¹

was attributed to the stretching vibration of the Co–O bond [32]. Notably, as the calcination temperatures increased from 600 °C to 900 °C, the intensity of Co–O band gradually diminished. This reduction can be ascribed to the reduction of Co^{3+} to lower-valence states (e.g., Co^0), which was consistent with the XRD results [19].

All isotherms of CPBC_x composites displayed typical type IV characteristics (Figure S3), confirming the existence of mesoporous structure [33]. As presented in Table S1, with the increment of calcination temperatures from 600 °C to 900 °C, the specific surface area increased from 636.1994 to 891.3164 m²/g, the pore volume from 0.5028 to 0.7181 cm³/g, and the pore diameter from 23.60 to 34.12 nm. A higher specific surface area could provide more active sites and reaction interfaces, while larger pore volume and diameter significantly enhance the diffusion efficiency of reactants toward active sites [34].

As the calcination temperature increased from 600 °C to 900 °C, the I_D/I_G ratio in Raman spectroscopy (Figure 1c), reflecting the degree of defects and disorder, increased from 0.867 to 1.199, indicating an increase in structural defects. This was primarily attributed to the release of volatile components from the precursor at high temperatures, leading to extensive etching of the carbonaceous framework and pore formation, thereby enhancing structural disorder [35]. Additionally, the loaded cobalt species may disrupt the graphitic microcrystalline structure of the biochar, further introducing additional structural defects [36].

Figure 2a illustrated the massive and bulk-like structure of PBC. The phytic acid modification process introduced abundant surface wrinkles, providing ample active sites for subsequent metal loading [18]. Meanwhile, the ZIF-67 precursor presented a well-defined polyhedral morphology (Figure 2b) [37]. As the calcination temperature increased from 600 °C to 900 °C (Figure 2c–f), numerous porous structures gradually developed on the surface, consistent with the trend of structural disorder indicated by Raman results (Figure 1c). The TEM image in Figure 2g further confirmed the presence of the layered structure in CPBC₈ composite. Additionally, HRTEM imaging (Figure 2h) revealed lattice fringes with spacings of 0.24 and 0.35 nm, corresponding to the (111) crystal plane of CoO and the (002) plane of graphitic carbon, respectively [38]. Furthermore, the EDS elemental mapping (Figure 2i–l) demonstrated homogeneous distribution of C, O, and Co throughout the CPBC₈ composite.

The XPS survey spectra (Figure S4) confirmed the presence of Co, C, and O, indicating the successful loading of Co onto the PBC substrate. In the high-resolution C 1s spectrum (Figure 3a), three peaks were deconvoluted at binding energies of 284.8, 286.39, and 288.94 eV, assigned to graphitic carbon, C–O, and C=O, respectively [39]. As the calcination temperature increased, the relative content of C–O gradually decreased from 37.68% to 18.15%, while that of graphitic carbon increased from 58.36% to 69.57% (Table S2). This indicates that oxygen-containing functional groups (e.g., epoxy and hydroxyl groups) were reduced by the thermal treatment [40]. For O 1s in Figure 3b, the peaks at 531.5, 532.0, 533.2, and 533.7 eV were attributed to adsorbed O–H, C=O, C–OH, and C–O bonds, respectively. A distinct peak at 530.0 eV was ascribed to lattice oxygen (O_{latt} , O^{2-}) from cobalt oxides [41,42]. Notably, as temperature increased, the C–OH content decreased from 33.38% to 20.77%, while the content of O_{lat} raised from 3.14% to 5.01%. This may be attributed to the thermal decomposition of surface oxygen-containing functional groups, which exposes the surface of cobalt oxides and promotes their crystallization [19]. For Co 2p in Figure 3c, the satellite peaks at 787.2 and 803.4 eV were characteristics of Co^{2+} [43]. The peak at 795.86 eV was assigned to Co^0 . The doublets at 781.0/797.1 and 783.4/798.3 eV were attributed to Co^{3+} and Co^{2+} species [44]. With increasing calcination temperature, the Co^{3+} content decreased from 31.99% to 18.20%, while the Co^{2+} content increased from 34.18% to 50.34%, and Co^0 appeared (increasing from 0% to 14.32%). These results indicated

that a substantial portion of Co^{3+} was reduced to Co^{2+} or even Co^0 , forming a multi-valent cobalt system [19].

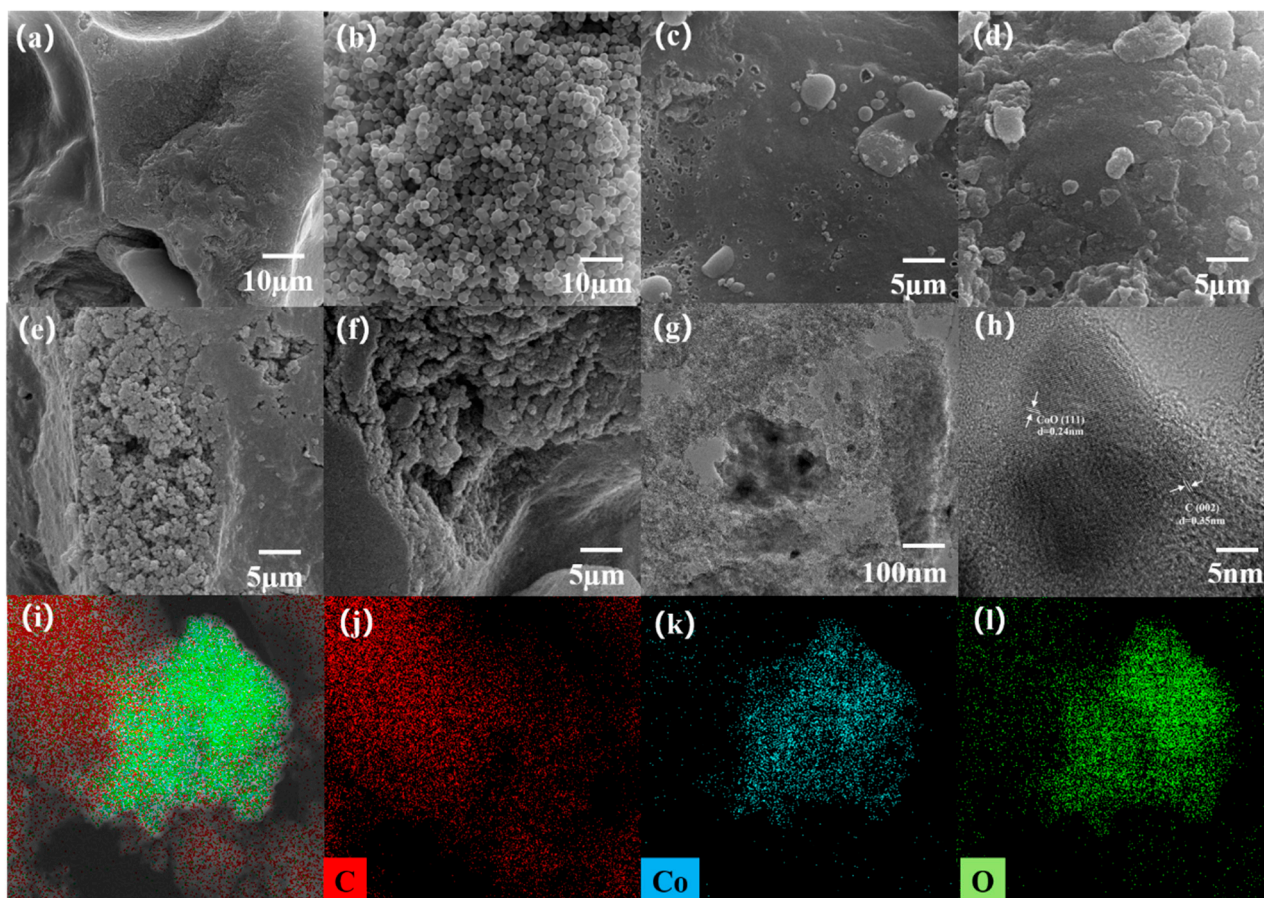


Figure 2. SEM images of PBC (a), ZIF-67 (b), and CPBC_x (c–f); TEM images (g,h) and EDS element mapping images (i–l) of CPBC₈.

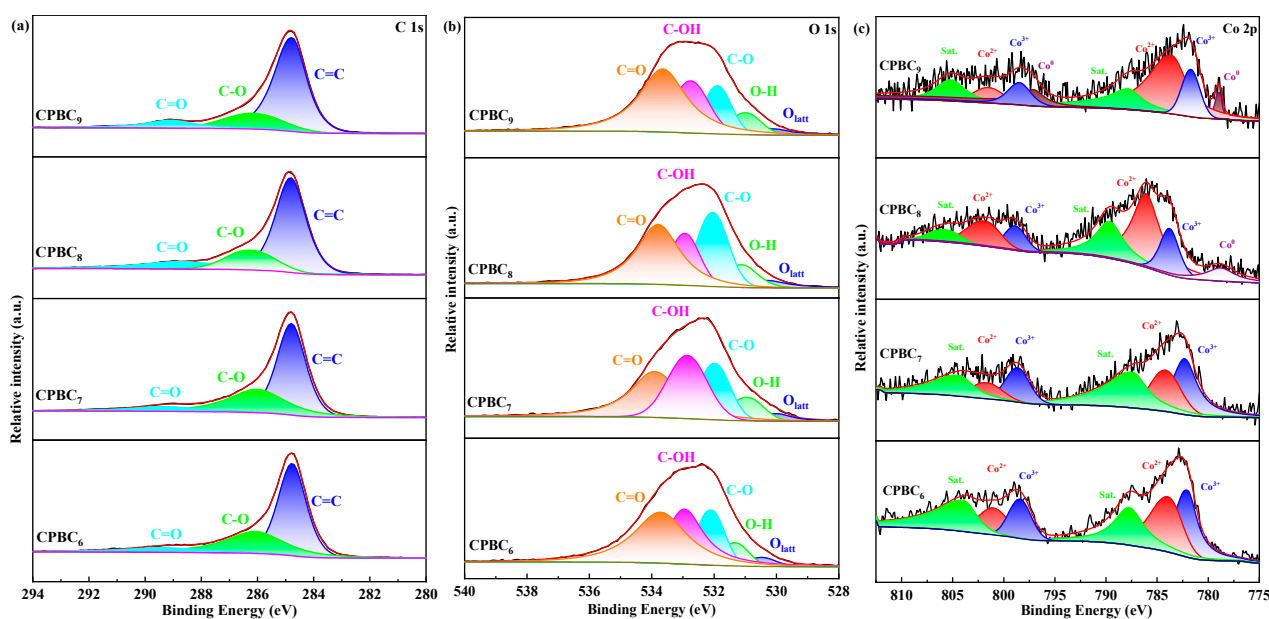


Figure 3. XPS analysis of CPBC_x: C 1s (a), O 1s (b), and Co 2p (c).

The performance of CPBC_x composites for activating PAA towards SMX degradation was evaluated (Figure 1d). As the temperature increased from 600 °C to 800 °C, the SMX

degradation efficiency markedly improved from 93.3% to 99.0%, with the corresponding pseudo-first-order kinetic constant (k_{obs}) increasing from 0.302 to 0.401 min^{-1} . This enhancement was primarily attributed to the increased specific surface area and improved accessibility of cobalt active sites. However, when the calcination temperature was further raised to 900 °C, both the SMX degradation efficiency and k_{obs} value slightly decreased to 94.5% and 0.312 min^{-1} , respectively. This decline likely resulted from partial collapse of the carbon skeleton and agglomeration or leaching of cobalt species at excessive high temperature (1.421 mg/L at 900 °C in Table S3), reducing the availability and stability of active sites. Therefore, the CPBC₈ composite (calcined at 800 °C) exhibited optimal overall performance, characterized by a high specific surface area, low metal leaching (0.648 mg/L), high catalytic reactivity, and favorable cost-effectiveness.

3.2. Effects of Different Experimental Parameters

Direct oxidation by PAA alone towards SMX was only 6.1% (Figure 4a). The adsorption efficiencies of SMX by BC, PBC, and CPBC₈ were 16.6%, 59.6%, and 59.8%, respectively. The similarly high adsorption efficiencies of PBC and CPBC₈ demonstrated the successful introduction of abundant surface functional groups and adsorption sites via phytic acid modification. With PAA addition, CPBC₈ exhibited remarkable synergistic catalytic superiority (0.401 min^{-1}) compared with ZIF-67 (0.382 min^{-1}) (Figure 4b) [45–50].

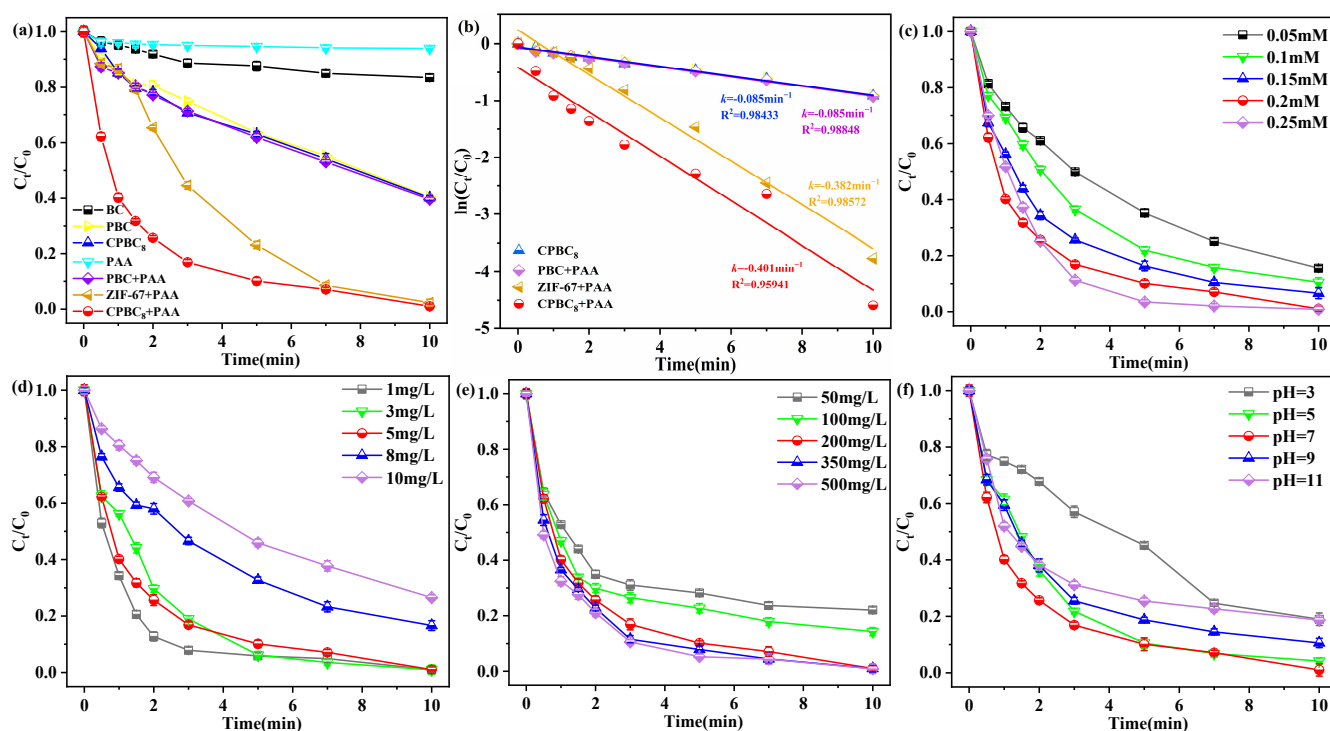


Figure 4. The SMX degradation in different systems (a), pseudo-first-order rate constant of SMX degradation in various reaction systems (b), the influence of different reaction conditions on SMX degradation: PAA concentration (c), SMX concentration (d), CPBC₈ dosage (e), initial pH (f). Reaction conditions: $[\text{PAA}]_0 = 0.2 \text{ mM}$ (except of (c)), $[\text{SMX}]_0 = 5 \text{ mg/L}$ (except of (d)), $[\text{Catalysts}]_0 = 200 \text{ mg/L}$ (except of (e)), $\text{pH}_0 = 6.8$ (except of (f)), $T = 25 \text{ }^\circ\text{C}$.

As shown in Figures 4c and S5a, when the PAA concentration increased from 0.05 to 0.2 mM, SMX degradation efficiency significantly improved from 84.6% to 99.0% (with the k_{obs} increasing from 0.180 to 0.401 min^{-1}). This enhancement was primarily attributed to increased PAA dosage promoting the generation of more reactive radical species. However, a further increase to 0.25 mM did not yield continued improvement, likely due to quenching

or coupling reactions among the surplus radicals [51,52]. Meanwhile, the increment of SMX concentration from 1 to 10 mg/L decreased its removal efficiency within 10 min from 99.8% to 83.5%, and k_{obs} value decreased from 0.459 to 0.128 min^{-1} (Figures 4d and S5b). This inhibitory effect was ascribed to competitive adsorption of SMX and its intermediates on the CPBC₈ surface, potentially covering or blocking some active sites, as well as their competition for the limited reactive species [39,53]. In addition, increasing the dosage of CPBC₈ from 50 to 200 mg/L led to a distinct increase in SMX degradation efficiency from 88.0% to 99.0%, with k_{obs} increasing from 0.126 to 0.401 min^{-1} (Figures 4e and S5c), owing to a greater number of available active sites. Nevertheless, no further enhancement was observed at 500 mg/L, likely due to agglomeration of excess catalysts in solution [46].

As illustrated in Figures 4f and S5d, the initial pH (3–11) significantly influenced SMX degradation efficiency in CPBC₈/PAA system, with efficiencies of 81.0%, 95.8%, 99.0%, 89.4%, and 81.3% at 3, 5, 7, 9, and 11, respectively. At pH 3, excessive H^+ ions may form hydrogen bonds with the O–O group of PAA molecules, thereby enhancing intermolecular forces, stabilizing the PAA structure, and consequently inhibiting its activation and decomposition [14]. The degradation efficiency did not differ much in the pH range of 5–7. Under neutral conditions, surface Co^{2+} sites on CPBC₈ dominated, and PAA remained largely undissociated, favoring their interaction to generate reactive species. In contrast, under alkaline conditions, the decline in SMX removal efficiency can be attributed to the negative surface charge of CPBC₈ (Figure S6) and the predominance of anionic PAA^- [54] and SMX^- [55] species, which could cause electrostatic repulsion and inhibit SMX degradation. Additionally, OH^- suppressed free radical generation, further reducing degradation efficiency of SMX [56].

The influences of common inorganic anions (Cl^- , CO_3^{2-} , HCO_3^- , NO_3^- , and SO_4^{2-}) on SMX degradation by CPBC₈/PAA system were also investigated (Figure S7). As the Cl^- concentration increased to 5 mM, the SMX degradation efficiency decreased to 80.1% (Figure S7a). The Cl^- exhibited an inhibitory effect due to its radical scavenging behavior [21]. When the CO_3^{2-} concentration increased to 5 mM, the degradation efficiency dropped to 32.2% (Figure S7b). The CO_3^{2-} can react with $\bullet\text{OH}$ and $\text{R-O}\bullet$ to generate $\text{CO}_3^{\bullet-}$, which has a lower reaction rate, thereby inhibiting SMX degradation [57]. The presence of HCO_3^- significantly suppressed SMX degradation. As its concentration increased from 0 to 5 mM, the removal rate declined from 99.0% to 74.8% (Figure S7c), which may be attributed to the inhibitory effect of HCO_3^- on PAA decomposition [58]. In contrast, the effects of NO_3^- (Figure S7d) and SO_4^{2-} (Figure S7e) were negligible, with SMX degradation efficiency remaining above 90%.

As the humic acid (HA) concentration (measured as TOC) increased from 0 to 10 mg/L, the SMX degradation efficiency decreased from 99.0% to 74.4% (Figure S7f). This inhibition was attributed to the ability of HA to consume organic radicals and compete with PAA for active sites on the catalyst [11,59]. Furthermore, rising the reaction temperature to 55 °C resulted in complete SMX removal within 3 min (Figure S8), a fivefold increase in k_{obs} , and the activation energy was 35.7207 kJ/mol, which is significantly lower than those reported for other cobalt-based composites (Table S4). This activation energy exceeded the diffusion-controlled range (10–13 kJ/mol), confirming kinetic control rather than mass transfer in CPBC₈/PAA system [60,61], while elevated temperatures enhanced molecular collisions to improve the degradation efficiency of SMX [62].

3.3. Mechanism Investigation in CPBC₈/PAA System

3.3.1. Identification of Reactive Species

Radical quenching experiments were conducted to identify the dominant reactive species in CPBC₈/PAA system (Figure 5a). Quenchers with different specificities were

employed: tert-butanol (TBA), a specific quencher for $\bullet\text{OH}$; methanol, a quencher for both $\bullet\text{OH}$ and organic oxygen radicals ($\text{R-O}\bullet$); 2,4-hexadiene (2,4-HD), a specific quencher for $\text{R-O}\bullet$ [11]; p-benzoquinone (p-BQ), a quencher for superoxide anion radical ($\text{O}_2^{\bullet-}$); and L-histidine (L-HD) and furfuryl alcohol (FFA), quenchers for $^1\text{O}_2$.

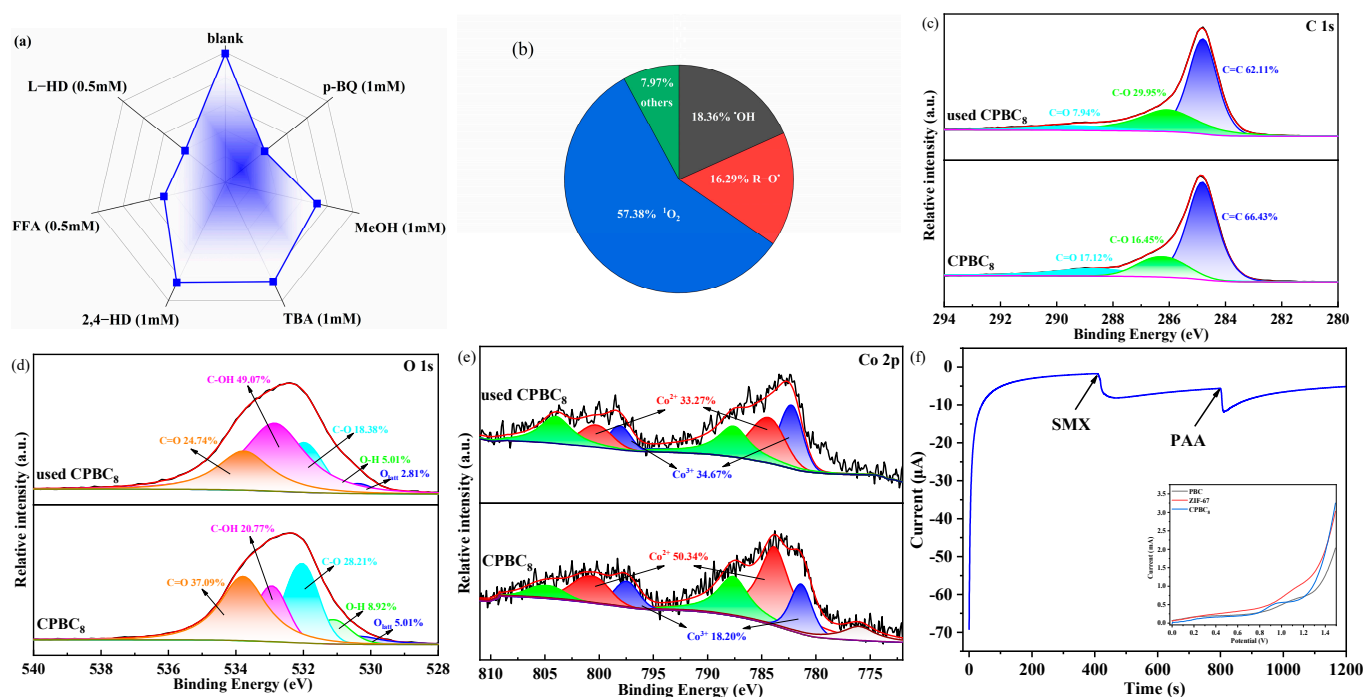


Figure 5. Quenching experiment (a); contribution of active species to SMX degradation in the CPBC₈/PAA system (b); XPS analysis of CPBC₈ and used CPBC₈: C 1s (c); O 1s (d); and Co 2p (e); I-t curve for SMX degradation by PAA activated with CPBC₈ (f) (inset: LSV curves of PBC, ZIF-67, and CPBC₈).

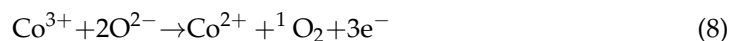
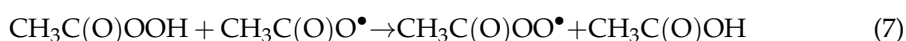
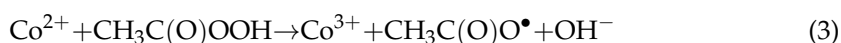
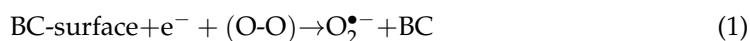
The addition of 1 mM methanol significantly suppressed the SMX degradation efficiency to 72.0%, suggesting the involvement of multiple reactive species such as $\bullet\text{OH}$, $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$, and $\text{CH}_3\text{C}(\text{O})\text{O}\bullet$. To further differentiate their roles, 1 mM TBA and 2,4-HD were added separately. TBA lowered the efficiency to 84.6%, confirming the role of $\bullet\text{OH}$, while 2,4-HD reduced it to 85.3%, providing direct evidence for the participation of $\text{R-O}\bullet$. In addition, the addition of 1 mM p-BQ drastically decreased the degradation efficiency to 38.6%, confirming that $\text{O}_2^{\bullet-}$ also played a significant role. Moreover, the addition of 0.5 mM L-HD or FFA strongly inhibited SMX degradation, reducing the efficiency to 39.3% and 48.1%, respectively, unequivocally indicating that $^1\text{O}_2$ played a crucial role in this system [14].

To further identify the dominant reactive species in SMX degradation, the relative contributions of the aforementioned ROS were calculated (Figure 5b and Text S9). The results showed that the contribution efficiencies of $^1\text{O}_2$, $\text{R-O}\bullet$, $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$ were 57.38%, 16.29%, 18.36%, and 7.97%, respectively. The discrepancy between the contribution of $\text{O}_2^{\bullet-}$ and the quenching experiment results can be attributed to the role of $\text{O}_2^{\bullet-}$ as a precursor of $^1\text{O}_2$, which can be further converted to $^1\text{O}_2$. This finding indicated a distinct mechanistic shift: the unmodified Co/PAA system degrades SMX primarily via a radical pathway dominated by $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$ and $\text{CH}_3\text{C}(\text{O})\text{O}\bullet$ species [63]; in contrast, upon the introduction of modified biochar into the CPBC₈/PAA system, the degradation pathway can be transformed into a non-radical pathway dominated by $^1\text{O}_2$. In summary, quenching experiments confirmed that SMX degradation in CPBC₈/PAA system involved multiple reactive species (including $^1\text{O}_2$, $\bullet\text{OH}$, $\text{R-O}\bullet$ and $\text{O}_2^{\bullet-}$), with $^1\text{O}_2$ being dominant.

3.3.2. Activation Mechanism Elucidation

The C 1s spectrum of used CPBC₈ in Figure 5c revealed that the C–O content increased from 16.45% to 29.95%, while the C=O content decreased from 17.12% to 7.94%, indicating the oxidation of C=O to C–O during the reaction. These oxygen-containing groups in biochar can activate PAA to generate ¹O₂ (Equations (1) and (2)) [64–66], which can be also demonstrated from the results of the O 1s spectra (Figure 5d). Additionally, the O–H content decreased from 8.92% to 5.01% (Figure 5d), suggesting the involvement of O–H in lowering the activation energy of PAA by increasing the electron density of CPBC₈ [67]. The O_{latt} content decreased from 5.01% to 2.81%, possibly due to the consumption of Co sites during ¹O₂ generation [68]. Moreover, after the reaction, the Co²⁺ content decreased from 50.34% to 33.27%, whereas Co³⁺ increased from 18.20% to 34.27% (Figure 5e), implying the Co³⁺/Co²⁺ cycle played a crucial role in the catalytic process (Equations (3)–(8)) [69]. The Co³⁺/Co²⁺ cycle established a synergistic degradation system involving both radical and non-radical pathways via electron transfer, further facilitated by the C=O/C–O interconversion and the electron-conducting biochar matrix [70].

The role of electron transfer in CPBC₈/PAA system was further investigated by electrochemical measurements. Chronoamperometry measurements (i-t, Figure 5f) displayed notable current responses upon addition of SMX and PAA, confirming electron transfer at the catalyst–SMX and catalyst–PAA–SMX interfaces. Here, PBC acted as an electron shuttle, further enhancing the electron transfer capability [71]. In addition, comparative analysis of linear sweep voltammetry (LSV, inset of Figure 5f), cyclic voltammetry (CV, Figure S9), and electrochemical impedance spectroscopy (EIS, Figure S10) demonstrated that the introduction of PBC effectively modulated the electrochemical properties of CPBC₈. Serving as an electron shuttle, PBC endowed CPBC₈ with a higher current density [72], enhanced electron storage and transfer capability [73], and lower charge transfer resistance compared to ZIF-67 [74]. These improved electrochemical characteristics facilitated efficient PAA activation for SMX degradation.



3.4. Degradation Pathways and Toxicity Evaluation

To predict the potential degradation pathways of SMX in the CPBC₈/PAA system, DFT calculations were performed to identify the vulnerable sites of SMX. The electrostatic potential (ESP) distribution of SMX (Figure 6a) indicated that the main negatively charged regions were located around S14, O15 and O16 atoms. Meanwhile, the highest occupied molecular orbital (HOMO) of SMX was concentrated around the electron-rich atoms N11, C1, and C5, while the lowest unoccupied molecular orbital (LUMO) was localized around the positively charged S14 atom and the electronegative N11 atom [75].

sensitive site for $^1\text{O}_2$ attack, this bond was broken through both non-radical and radical pathways, generating TP155, which was further oxidized to TP108 [79]. Pathway III involves cleavage of the S–C bond, which was susceptible to radical attack, leading to bond cleavage and formation of TP163. This intermediate was subsequently oxidized to smaller fragments, including TP99, TP115, and TP112 [80]. Pathway IV corresponded to hydroxylation. The carbon atoms on the benzene ring were readily attacked by hydroxyl radicals, ultimately being oxidized to TP253 [81]. As the reaction proceeds, all intermediates are eventually mineralized to CO_2 and H_2O .

As shown in Figure 7, acute toxicity (96 hr LC₅₀, 48 hr LC₅₀, and 48 hr EC₅₀) and chronic toxicity (ChV) of SMX and its intermediates to fish, daphnid, and green algae were assessed based on the ECOSAR model. The results indicated that the toxicity of all intermediates was reduced, demonstrating the system's effectiveness in mitigating environmental risks, highlighting the CPBC₈/PAA system as a safe and sustainable advanced oxidation process for water treatment.

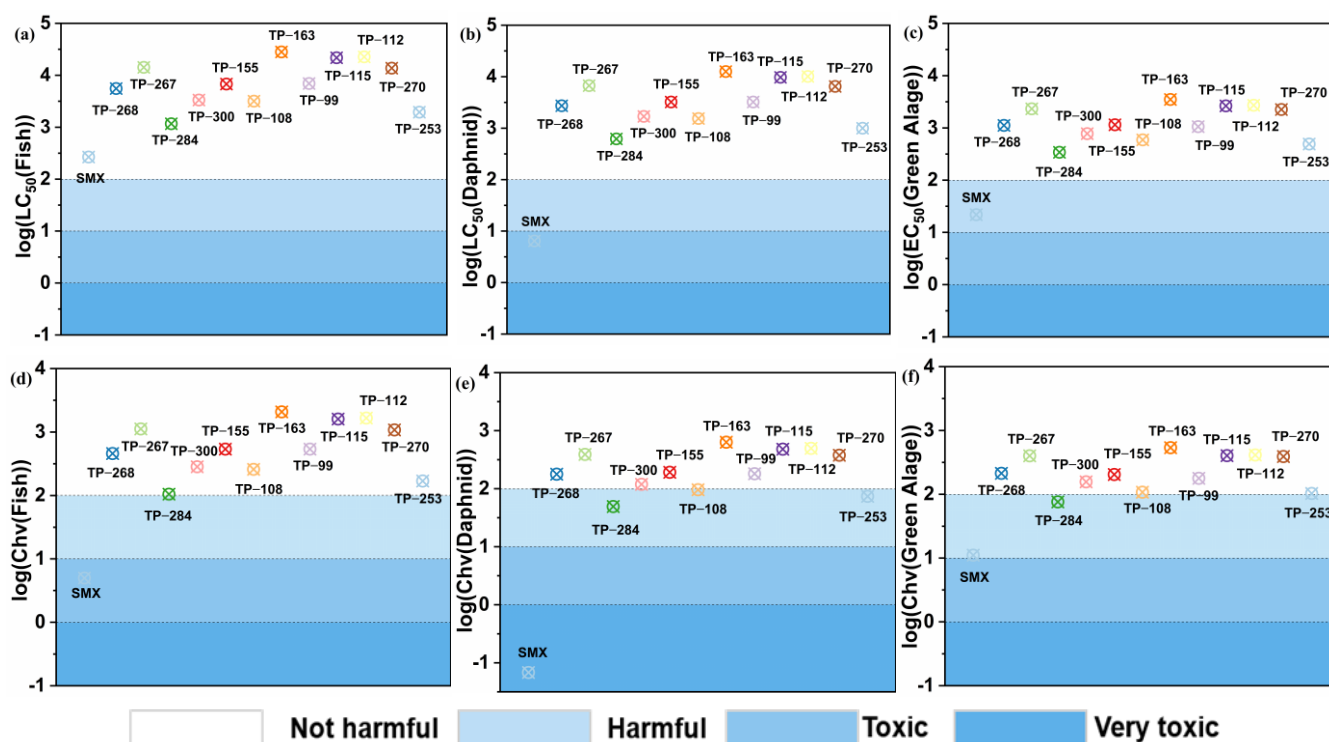


Figure 7. Ecotoxicity assessment of acute toxicity (a–c) and chronic toxicity (d–f) of SMX and its transformation products to fish, *Daphnia magna*, and green algae in the CPBC₈/PAA system. Reaction conditions: [CPBC₈] = 200 mg/L, [PAA]₀ = 0.2 mM, [SMX]₀ = 5 mg/L, pH₀ = 6.8, T = 25 °C.

3.5. Stability Investigation

To further evaluate the practical application potential of CPBC₈/PAA system, a hydroponic experiment was conducted using mung bean sprouts. Their growth lengths were recorded after cultivation in four solutions: ultrapure water, untreated SMX solution, SMX solution treated with ZIF-67/PAA for 15 min, and SMX solution treated with CPBC₈/PAA for 15 min (Figure 8a,b). In ultrapure water, the average sprout length was 9.58 cm. The untreated SMX solution severely inhibited growth (4.18 cm), confirming its toxicity, while treating with ZIF-67/PAA resulted in even shorter sprouts (2.31 cm) likely due to substantial Co^{2+} leaching from ZIF-67 (Table S3). In contrast, the CPBC₈/PAA-treated solution allowed significantly better growth (7.84 cm, Figure 8b), demonstrating effective toxicity reduction.

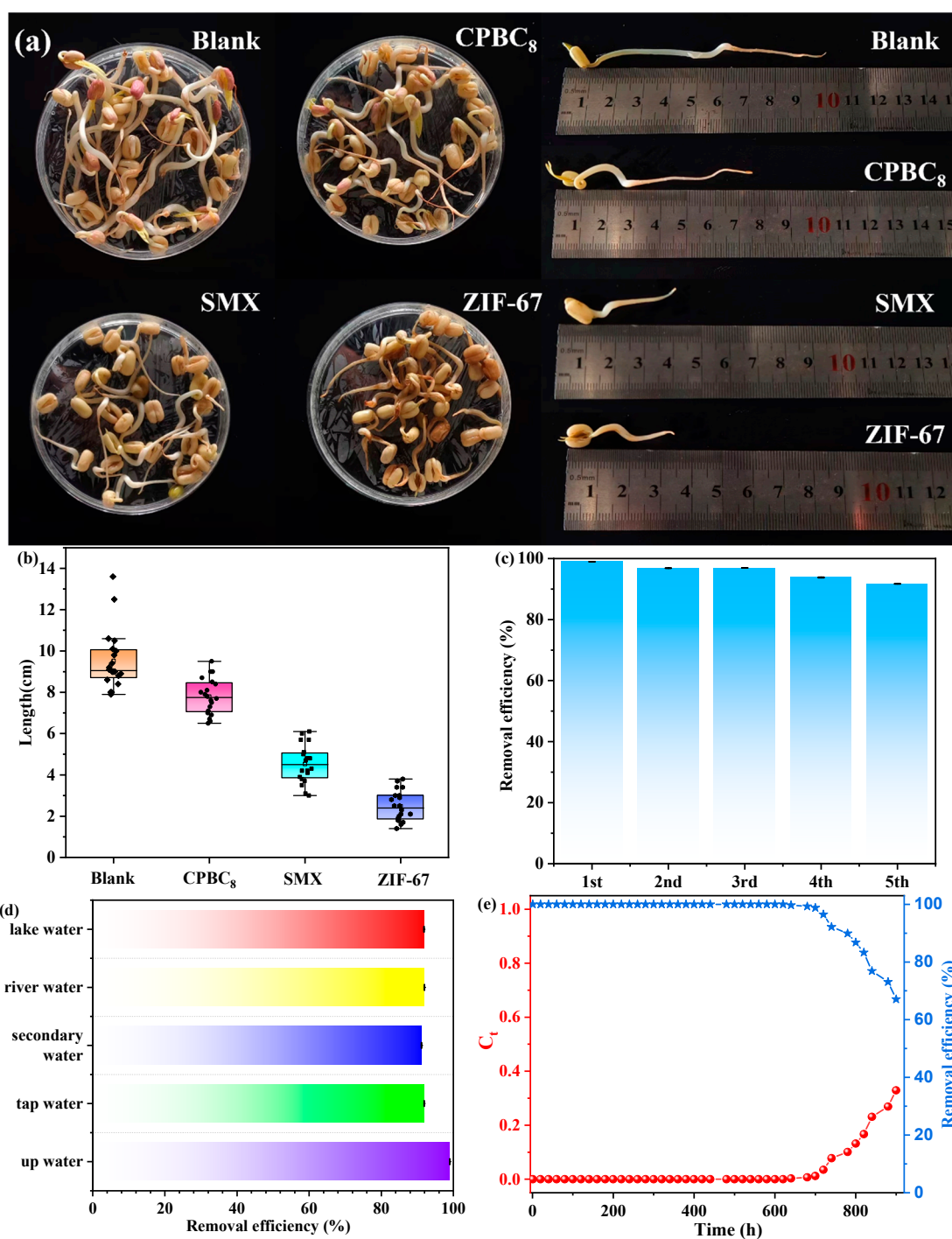


Figure 8. Practical application of CPBC₈/PAA system for efficient SMX degradation: seed growth status under different solution cultures (a), seed growth length (b), cyclic experiments (c), different water matrix (d) and continuous flow experiment (e). Reaction conditions: [Catalysts] = 200 mg/L, [PAA]₀ = 0.2 mM, [SMX]₀ = 5 mg/L, pH₀ = 6.8, T = 25 °C.

Recycling experiments (Figure 8c) showed that the SMX degradation efficiency remained above 95% over five consecutive cycles, and the cobalt ion leaching concentration in the solution after each cycle was below 0.5 mg/L (Table S3). Meanwhile, the comparison of XRD (Figure S11) and FTIR (Figure S12) patterns of CPBC₈ before and after the reaction revealed no significant structural changes. These results collectively demonstrate that CPBC₈ possesses excellent reusability and stability. To further explore its practical applicability, real water samples collected from local surface water sources were tested (Figure 8d). Al-

though degradation efficiency was somewhat reduced due to radical quenching by natural organic matter (particularly humic substances), the CPBC₈/PAA system still maintained the SMX removal efficiency exceeding 95%. This competitive performance in complex matrices underscores its potential for antibiotic-contaminated wastewater remediation. Furthermore, a continuous-flow column experiment was conducted (Figure 8e) under the conditions of a flow rate of 1 mL/min, a catalyst dosage of 1 g CPBC₈, and an initial SMX concentration of 5 mg/L. The system sustained the SMX removal efficiency of over 85% for 800 h, highlighting its long-term operational stability under dynamic conditions.

4. Conclusions

In this study, using ZIF-67 as a precursor, a composite material (CPBC₈) was successfully synthesized by integrating modified biochar with cobalt for the efficient activation of PAA toward SMX degradation. By investigating the physicochemical properties of the material at different pyrolysis temperatures, a comprehensive understanding of the influence of calcination temperature on degradation performance was obtained. Under the conditions of a CPBC₈ dosage of 200 mg/L, PAA concentration of 0.2 mM, and an initial pH of 6.8, the CPBC₈/PAA system achieved 99.0% removal of 5 mg/L SMX within 10 min, demonstrating remarkable performance, with optimal efficacy across pH 5–9. Quenching experiments confirmed the synergistic role of radical species ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and $\text{CH}_3\text{C}(\text{O})\text{OO}\bullet$) and non-radical pathways ($^1\text{O}_2$) in driving SMX oxidative degradation. Furthermore, DFT calculations identified N11 and N17 on the SMX molecule as the vulnerable atomic sites, consistent with intermediate product analysis. SMX degradation proceeded via pathways including oxidation of the aniline $-\text{NH}_2$ group and cleavage of the S–N bond. Ecotoxicity assessment using the ECOSAR model confirmed that the CPBC₈/PAA system effectively reduced the environmental hazard of the degradation intermediates. These findings demonstrate that incorporating modified biochar endows the composite with superior electron transfer efficiency, more diverse degradation pathways, and enhanced environmental compatibility compared to pristine ZIF-67. This study establishes a novel strategy for PAA activation based on engineered biochar, advancing its application in the treatment of antibiotic-contaminated water.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w18131617/s1>. Text S1: Reagents and chemicals; Text S2: Synthesis of ZIF-67; Text S3: Synthesis of PBC; Text S4: Batch Experimental Procedure; Text S5: A continuous fixed-bed column experiment; Text S6: LC-MS/MS conditions for SMX; Text S7: Identification of SMX Transformation Products (TPs); Text S8: Reaction kinetics and activation energy; Text S9: The contribution of ROS; Text S10: Seed germination experiment; Text S11: Characterization methods; Text S12: Electrochemical analysis; Text S13: DFT calculations; Table S1: The BET characterization results of CPBC_x composites; Table S2: Relative contents of C Co and O species on the surfaces of CPBC_x, derived from XPS spectra; Table S3: Co ions concentration in different systems; Table S4: Comparison of CPBC₈ with various reported cobalt-based catalysts in terms of E_a for pollutant degradation; Table S5: Fukui indexes of SMX; Table S6: Intermediate of SMX identified by UPLC-Q-TOF-MS; Figure S1: The schematic diagram of the mini-column experiments; Figure S2: XRD patterns of PBC; Figure S3: Nitrogen adsorption–desorption isotherms of CPBC_x; Figure S4: Survey scan of XPS spectra of CPBC_x; Figure S5: Pseudo-first-order rate constant of PAA concentration (a), SMX concentration (b), CPBC_x dosage (c), Initial pH (d); Figure S6: Zeta potential of CPBC₈; Figure S7: The effect of inorganic anion concentration on SMX degradation: Cl^- (a), CO_3^{2-} (b), HCO_3^- (c), NO_3^- (d), SO_4^{2-} (e) and HA (f); Figure S8: Reaction temperature on the degradation of SMX in the CPBC₈/PAA system; Figure S9: CV test of the PBC, ZIF-67 and CPBC₈; Figure S10: EIS test of the PBC, ZIF -67 and CPBC₈; Figure S11: XRD patterns of CPBC₈ and used CPBC₈; Figure S12: FTIR patterns of CPBC₈ and used CPBC₈.

Author Contributions: All authors contributed to the study conception and design. Z.Y.: Writing—original draft, Writing—review and editing, Investigation, Methodology, Data curation, Visualization. M.L.: Investigation, Software. Y.L.: Investigation, Software, Data curation. L.S.: Funding acquisition, Formal analysis, Resources, Supervision. X.Y.: Writing—review and editing, Conceptualization, Methodology, Validation. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by Joint Government-Enterprise Support Project of Hubei province (2024420619007390) and (2024420620000169) We appreciate the assistance in the identifying the transformation products by Jun Men from The Analysis and Testing Center of Institute of Hydrobiology, Chinese Academy of Sciences.

Data Availability Statement: The authors declare that the data supporting the findings of this study are available from the corresponding author on reasonable request.

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

References

1. Borsetto, C.; Raguideau, S.; Travis, E.; Kim, D.-W.; Lee, D.-H.; Bottrill, A.; Stark, R.; Song, L.; Cha, C.-J.; Pearson, J.; et al. Impact of sulfamethoxazole on a riverine microbiome. *Water Res.* **2021**, *201*, 117382. [\[CrossRef\]](#)
2. Mulla, S.I.; Hu, A.; Sun, Q.; Li, J.; Suanon, F.; Ashfaq, M.; Yu, C.-P. Biodegradation of sulfamethoxazole in bacteria from three different origins. *J. Environ. Manag.* **2018**, *206*, 93–102. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Formagini, L.; Ramirez, J.Z.R.; Corá, V.R.; Souza, D.M. Psychotropic pharmaceuticals in aquatic environments: Occurrence and analytical challenges. *Sci. Total Environ.* **2025**, *998*, 180269. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Luukkonen, T.; Pehkonen, S.O. Peracids in water treatment: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2017**, *47*, 1–39. [\[CrossRef\]](#)
5. Yao, G.; Zhou, X.; Gao, H.; Liu, T.; Zhang, Y.; Chen, J. Peracetic acid-driven advanced oxidation processes for wastewater treatment: Demystifying organic radicals and non-radical species. *Crit. Rev. Environ. Sci. Technol.* **2025**, *55*, 1124–1147. [\[CrossRef\]](#)
6. Honarmandrad, Z.; Sun, X.; Wang, Z.; Naushad, M.; Boczkaj, G. Activated persulfate and peroxymonosulfate based advanced oxidation processes (AOPs) for antibiotics degradation—A review. *Water Resour. Ind.* **2023**, *29*, 100194. [\[CrossRef\]](#)
7. Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* **2018**, *334*, 1502–1517. [\[CrossRef\]](#)
8. Gasim, M.F.; Bao, Y.; Elgarahy, A.M.; Osman, A.I.; Al-Muhtaseb, A.H.; Rooney, D.W.; Yap, P.-S.; Oh, W.-D. Peracetic acid activation using heterogeneous catalysts for environmental decontamination: A review. *Catal. Commun.* **2023**, *180*, 106702. [\[CrossRef\]](#)
9. Bux, N.; Tumrani, S.H.; Soomro, R.A.; Ma, Q.; Zhou, J.; Wang, T. Catalytic degradation of organic pollutants in aqueous systems: A comprehensive review of peroxyacetic acid-based advanced oxidation processes. *J. Environ. Manag.* **2025**, *373*, 123989. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Yuan, Q.; Xiao, L.; Gao, S.; Abdulkayum, A.; Kong, Q.; Hu, G.; Dubal, D.; Zhou, Y. From fundamentals to mechanisms: Peroxyacetic acid catalysts in emerging pollutant degradation. *Mater. Today* **2025**, *87*, 197–230. [\[CrossRef\]](#)
11. Wang, Z.; Wang, J.; Xiong, B.; Bai, F.; Wang, S.; Wan, Y.; Zhang, L.; Xie, P.; Wiesner, M.R. Application of cobalt/peracetic acid to degrade sulfamethoxazole at neutral condition: Efficiency and mechanisms. *Environ. Sci. Technol.* **2019**, *54*, 464–475. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Duan, X.; Kang, J.; Tian, W.; Zhang, H.; Ho, S.-H.; Zhu, Y.-A.; Ao, Z.; Sun, H.; Wang, S. Interfacial-engineered cobalt@ carbon hybrids for synergistically boosted evolution of sulfate radicals toward green oxidation. *Appl. Catal. B Environ.* **2019**, *256*, 117795. [\[CrossRef\]](#)
13. Zhao, Q.; Ni, X.; Wang, Z. Biochar matrix composites for persulfate-based advanced oxidation process: Preparation, performance and activation mechanism. *J. Ind. Eng. Chem.* **2025**, *152*, 1–17. [\[CrossRef\]](#)
14. Zhang, W.; Li, M.; Lin, L.; Li, M.; Sun, F. Peroxyacetic acid activation by cobalt-doped peanut shell biochar for efficient CBZ degradation: Role of organic radicals, singlet oxygen, and high-valent cobalt species. *Sep. Purif. Technol.* **2024**, *330*, 125592. [\[CrossRef\]](#)
15. Xia, L.; Li, X.; Wei, Z.; Liu, A.; Chen, J.; Shang, J. Biochar-mediated electron transfer in a spinel ferrite catalyst boosts peracetic acid activation for water decontamination. *Chem. Eng. J.* **2025**, *525*, 170068. [\[CrossRef\]](#)
16. Gao, Y.; Wang, Q.; Ji, G.; Li, A. Degradation of antibiotic pollutants by persulfate activated with various carbon materials. *Chem. Eng. J.* **2022**, *429*, 132387. [\[CrossRef\]](#)
17. Bloot, A.P.M.; Kalschne, D.L.; Amaral, J.A.S.; Baraldi, I.J.; Canan, C. A review of phytic acid sources, obtention, and applications. *Food Rev. Int.* **2023**, *39*, 73–92. [\[CrossRef\]](#)

18. Deng, Y.; Xiao, L.; Zhou, H.; Cui, B.; Zhang, L.; Chen, D.; Gu, C.; Zhan, Z.; Wang, R.; Mei, S.; et al. Phytic acid pre-modulated and Fe/N co-doped biochar derived from ramie fiber to active persulfate for efficient degradation of tetracycline via radical and non-radical pathways. *Sep. Purif. Technol.* **2024**, *342*, 126976. [\[CrossRef\]](#)
19. Shi, P.; Wang, X.; Zhou, X.; Min, Y.; Fan, J.; Yao, W. Influence of calcination temperature on the catalytic performance of Co₃O₄/GO nanocomposites for Orange II degradation. *Rsc Adv.* **2015**, *5*, 34125–34133. [\[CrossRef\]](#)
20. Tomczyk, A.; Sokołowska, Z.; Boguta, P. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Bio/Technol.* **2020**, *19*, 191–215. [\[CrossRef\]](#)
21. Shah, A.D.; Liu, Z.Q.; Salhi, E.; Höfer, T.; von Gunten, U. Peracetic acid oxidation of saline waters in the absence and presence of H₂O₂: Secondary oxidant and disinfection byproduct formation. *Environ. Sci. Technol.* **2015**, *49*, 1698–1705. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Xiao, J.; Li, Y.; Dong, H.; Pang, Z.; Zhao, M.; Huang, D.; Dong, J.; Li, L. Highly efficient activation of peracetic acid via zero-valent iron-copper bimetallic nanoparticles (nZVIC) for the oxidation of sulfamethazine in aqueous solution under neutral condition. *Appl. Catal. B Environ.* **2024**, *340*, 123183. [\[CrossRef\]](#)
23. Zhang, W.; Li, M.; Shang, W.; Wang, M.; Zhang, J.; Sun, F.; Li, M.; Li, X. Singlet oxygen dominated core-shell Co nanoparticle to synergistically degrade methylene blue through efficient activation of peroxymonosulfate. *Sep. Purif. Technol.* **2023**, *308*, 122849. [\[CrossRef\]](#)
24. Mayo-Bean, K.; Moran, K.; Meylan, B.; Ranslow, P. *Methodology Document for the Ecological Structure-Activity Relationship Model (Ecosar) Class Program*; United States Environmental Protection Agency: Washington, DC, USA, 2012; Volume 46.
25. Parr, R.G.; Yang, W. Density functional approach to the frontier-electron theory of chemical reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 4049–4050. [\[CrossRef\]](#)
26. Liao, W.; Liao, S.; Xu, S.; Li, Q.; Han, L. Non-radicals dominated degradation of sulfamethoxazole by a chemical-less microwave enhanced photolysis process. *J. Water Process Eng.* **2022**, *48*, 102854. [\[CrossRef\]](#)
27. Xie, Z.-H.; He, C.-S.; Pei, D.-N.; Zheng, Y.-Z.; Wu, X.-Y.; Xiong, Z.; Du, Y.; Pan, Z.-C.; Yao, G.; Lai, B. Efficient degradation of micropollutants in CoCaAl-LDO/peracetic acid (PAA) system: An organic radical dominant degradation process. *J. Hazard. Mater.* **2023**, *452*, 131286. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Xu, L.; Zhang, S.; Liu, W.; Du, Z. Vertically cobalt nanoplate arrays based on one-step electrochemical growth and their magnetic properties. *J. Phys. Chem. C* **2012**, *116*, 2801–2806. [\[CrossRef\]](#)
30. Sharifi, S.; Shakur, H.; Mirzaei, A.; Hosseini, M. Characterization of cobalt oxide Co₃O₄ nanoparticles prepared by various methods: Effect of calcination temperatures on size, dimension and catalytic decomposition of hydrogen peroxide. *Int. J. Nanosci. Nanotechnol.* **2013**, *9*, 51–58.
31. Abdel-Salam, M.; Yoon, T. Cobalt-ferrite/Ag-fMWCNT hybrid nanocomposite catalyst for efficient degradation of synthetic organic dyes via peroxymonosulfate activation. *Environ. Res.* **2022**, *205*, 112424. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Xie, M.; Tang, J.; Fang, G.; Zhang, M.; Kong, L.; Zhu, F.; Ma, L.; Zhou, D.; Zhan, J. Biomass Schiff base polymer-derived N-doped porous carbon embedded with CoO nanodots for adsorption and catalytic degradation of chlorophenol by peroxymonosulfate. *J. Hazard. Mater.* **2020**, *384*, 121345. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Kruk, M.; Jaroniec, M. Gas adsorption characterization of ordered organic–Inorganic nanocomposite materials. *Chem. Mater.* **2001**, *13*, 3169–3183. [\[CrossRef\]](#)
34. Pei, S.; Zhao, Y.; Li, W.; Qu, C.; Ren, Y.; Yang, Y.; Liu, J.; Wu, C. Critical impact of pyrolysis temperatures on biochars for peroxymonosulfate activation: Structural characteristics, degradation performance and mechanism. *Chem. Eng. J.* **2023**, *477*, 147274. [\[CrossRef\]](#)
35. Zhao, B.; Zhang, G.; Song, J.; Jiang, Y.; Zhuang, H.; Liu, P.; Fang, T. Bivalent tin ion assisted reduction for preparing graphene/SnO₂ composite with good cyclic performance and lithium storage capacity. *Electrochim. Acta* **2011**, *56*, 7340–7346. [\[CrossRef\]](#)
36. Liu, L.; Afzal, S.; Xu, L.; Ahmad, M.; Zhang, M.; Alshoaibi, A. Cobalt and nitrogen incorporated dendritic mesoporous carbon to activate peroxymonosulfate for degrading organic pollutants in water. *J. Environ. Chem. Eng.* **2025**, *13*, 117052. [\[CrossRef\]](#)
37. Foroutan, R.; Peighambaroust, S.J.; Mohammadi, R.; Peighambaroust, S.H.; Ramavandi, B. Cadmium ion removal from aqueous media using banana peel biochar/Fe₃O₄/ZIF-67. *Environ. Res.* **2022**, *211*, 113020. [\[CrossRef\]](#) [\[PubMed\]](#)
38. Li, G.; Cao, X.-q.; Meng, N.; Huang, Y.-m.; Wang, X.-d.; Gao, Y.-y.; Li, X.; Yang, T.-s.; Li, B.-l.; Zhang, Y.-z.; et al. Fe₃O₄ supported on water caltrop-derived biochar toward peroxymonosulfate activation for urea degradation: The key role of sulfate radical. *Chem. Eng. J.* **2022**, *433*, 133595. [\[CrossRef\]](#)
39. Lei, Y.; Guo, X.; Jiang, M.; Sun, W.; He, H.; Chen, Y.; Thumavichai, K.; Ola, O.; Zhu, Y.; Wang, N. Co-ZIF reinforced cow manure biochar (CMB) as an effective peroxymonosulfate activator for degradation of carbamazepine. *Appl. Catal. B Environ.* **2022**, *319*, 121932. [\[CrossRef\]](#)
40. Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co₃O₄ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nat. Mater.* **2011**, *10*, 780–786. [\[CrossRef\]](#) [\[PubMed\]](#)

41. Lee, J.-M.; Kim, J.-W.; Lim, J.-S.; Kim, T.-J.; Kim, S.-D.; Park, S.-J.; Lee, Y.-S. X-ray photoelectron spectroscopy study of cobalt supported multi-walled carbon nanotubes prepared by different precursors. *Carbon Lett.* **2007**, *8*, 120–126. [\[CrossRef\]](#)
42. Ahmed, F.; Rodrigues, D.F. Investigation of acute effects of graphene oxide on wastewater microbial community: A case study. *J. Hazard. Mater.* **2013**, *256*, 33–39. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Wang, Y.; Zhou, T.; Jiang, K.; Da, P.; Peng, Z.; Tang, J.; Kong, B.; Cai, W.B.; Yang, Z.; Zheng, G. Reduced mesoporous Co₃O₄ nanowires as efficient water oxidation electrocatalysts and supercapacitor electrodes. *Adv. Energy Mater.* **2014**, *4*, 1400696. [\[CrossRef\]](#)
44. Zhang, K.; Sun, D.; Ma, C.; Wang, G.; Dong, X.; Zhang, X. Activation of peroxymonosulfate by CoFe₂O₄ loaded on metal-organic framework for the degradation of organic dye. *Chemosphere* **2020**, *241*, 125021. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Gong, C.; Chen, F.; Yang, Q.; Luo, K.; Yao, F.; Wang, S.; Wang, X.; Wu, J.; Li, X.; Wang, D.; et al. Heterogeneous activation of peroxymonosulfate by Fe-Co layered doubled hydroxide for efficient catalytic degradation of Rhodamine B. *Chem. Eng. J.* **2017**, *321*, 222–232. [\[CrossRef\]](#)
46. Li, J.; Zhu, W.; Gao, Y.; Lin, P.; Liu, J.; Zhang, J.; Huang, T. The catalyst derived from the sulfurized Co-doped metal-organic framework (MOF) for peroxymonosulfate (PMS) activation and its application to pollutant removal. *Sep. Purif. Technol.* **2022**, *285*, 120362. [\[CrossRef\]](#)
47. Zeng, L.; Xiao, L.; Shi, X.; Wei, M.; Cao, J.; Long, Y. Core-shell Prussian blue analogues@ poly (m-phenylenediamine) as efficient peroxymonosulfate activators for degradation of Rhodamine B with reduced metal leaching. *J. Colloid Interface Sci.* **2019**, *534*, 586–594. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Chen, Y.; Huang, X.; Sun, D.; Ma, H.; Wang, G.; Ma, C.; Hao, J. Magnetic Co-Co Prussian blue analogue catalyst for peroxymonosulfate activation to degrade organic dye. *Sep. Purif. Technol.* **2021**, *277*, 119468. [\[CrossRef\]](#)
49. Song, Y.; Sun, D.; Liu, C.; Ma, H.; Ma, H.; Ma, C. Peroxymonosulfate activation through ferromagnetic bimetallic spinel sulfide composite (Fe₃O₄/NiCo₂S₄) for organic pollutant degradation. *Chemosphere* **2022**, *307*, 135682. [\[CrossRef\]](#) [\[PubMed\]](#)
50. Kang, S.; Hwang, J. CoMn₂O₄ embedded hollow activated carbon nanofibers as a novel peroxymonosulfate activator. *Chem. Eng. J.* **2021**, *406*, 127158. [\[CrossRef\]](#)
51. Xiong, Z.; Jiang, Y.; Wu, Z.; Yao, G.; Lai, B. Synthesis strategies and emerging mechanisms of metal-organic frameworks for sulfate radical-based advanced oxidation process: A review. *Chem. Eng. J.* **2021**, *421*, 127863. [\[CrossRef\]](#)
52. Chateaufneuf, J.; Luszyk, J.; Ingold, K. Spectroscopic and kinetic characteristics of aroyloxy radicals. 1. The 4-methoxybenzoyloxy radical. *J. Am. Chem. Soc.* **1988**, *110*, 2877–2885. [\[CrossRef\]](#)
53. Sun, W.; Pang, K.; Ye, F.; Pu, M.; Zhou, C.; Huang, H.; Zhang, Q.; Niu, J. Carbonization of camphor sulfonic acid and melamine to N, S-co-doped carbon for sulfamethoxazole degradation via persulfate activation: Nonradical dominant pathway. *Sep. Purif. Technol.* **2021**, *279*, 119723. [\[CrossRef\]](#)
54. Dong, J.; Xu, W.; Liu, S.; Gong, Y.; Yang, T.; Du, L.; Chen, Q.; Tan, X.; Liu, Y. Lignin-derived biochar to support CoFe₂O₄: Effective activation of peracetic acid for sulfamethoxazole degradation. *Chem. Eng. J.* **2022**, *430*, 132868. [\[CrossRef\]](#)
55. Wu, W.; Tian, D.; Liu, T.; Chen, J.; Huang, T.; Zhou, X.; Zhang, Y. Degradation of organic compounds by peracetic acid activated with Co₃O₄: A novel advanced oxidation process and organic radical contribution. *Chem. Eng. J.* **2020**, *394*, 124938. [\[CrossRef\]](#)
56. Liu, Y.; He, X.; Duan, X.; Fu, Y.; Dionysiou, D.D. Photochemical degradation of oxytetracycline: Influence of pH and role of carbonate radical. *Chem. Eng. J.* **2015**, *276*, 113–121. [\[CrossRef\]](#)
57. Wang, L.; Yan, T.; Tang, R.; Ping, Q.; Li, Y.; Wang, J. Motivation of reactive oxidation species in peracetic acid by adding nanoscale zero-valent iron to synergic removal of spiramycin under ultraviolet irradiation: Mechanism and N-nitrosodimethylamine formation potential assessment. *Water Res.* **2021**, *205*, 117684. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Dai, Y.; Qi, C.; Cao, H.; Wen, Y.; Zhao, Y.; Xu, C.; Yang, S.; He, H.J.S.; Technology, P. Enhanced degradation of sulfamethoxazole by microwave-activated peracetic acid under alkaline condition: Influencing factors and mechanism. *Sep. Purif. Technol.* **2022**, *288*, 120716. [\[CrossRef\]](#)
59. Li, X.; Liu, X.; Lin, C.; Zhang, H.; Zhou, Z.; Fan, G.; Ma, J. Cobalt ferrite nanoparticles supported on drinking water treatment residuals: An efficient magnetic heterogeneous catalyst to activate peroxymonosulfate for the degradation of atrazine. *Chem. Eng. J.* **2019**, *367*, 208–218. [\[CrossRef\]](#)
60. Ma, W.; Wang, N.; Fan, Y.; Tong, T.; Han, X.; Du, Y. Non-radical-dominated catalytic degradation of bisphenol A by ZIF-67 derived nitrogen-doped carbon nanotubes frameworks in the presence of peroxymonosulfate. *Chem. Eng. J.* **2018**, *336*, 721–731. [\[CrossRef\]](#)
61. Du, Y.; Ma, W.; Liu, P.; Zou, B.; Ma, J. Magnetic CoFe₂O₄ nanoparticles supported on titanate nanotubes (CoFe₂O₄/TNTs) as a novel heterogeneous catalyst for peroxymonosulfate activation and degradation of organic pollutants. *J. Hazard. Mater.* **2016**, *308*, 58–66. [\[CrossRef\]](#) [\[PubMed\]](#)
62. Feng, Y.; Wu, D.; Deng, Y.; Zhang, T.; Shih, K. Sulfate radical-mediated degradation of sulfadiazine by CuFeO₂ rhombohedral crystal-catalyzed peroxymonosulfate: Synergistic effects and mechanisms. *Environ. Sci. Technol.* **2016**, *50*, 3119–3127. [\[PubMed\]](#)
63. Kim, J.; Du, P.; Liu, W.; Luo, C.; Zhao, H.; Huang, C.-H. Cobalt/peracetic acid: Advanced oxidation of aromatic organic compounds by acetylperoxy radicals. *Environ. Sci. Technol.* **2020**, *54*, 5268–5278. [\[CrossRef\]](#) [\[PubMed\]](#)

64. Dai, C.; Li, S.; Duan, Y.; Leong, K.H.; Liu, S.; Zhang, Y.; Zhou, L.; Tu, Y. Mechanisms and product toxicity of activated carbon/peracetic acid for degradation of sulfamethoxazole: Implications for groundwater remediation. *Water Res.* **2022**, *216*, 118347. [[CrossRef](#)] [[PubMed](#)]
65. Lu, X.; Chen, Y.; Li, R.; Gao, J.; Pan, S. Insight into the activation of peracetic acid by cobalt-nitrogen-doped porous carbon for efficient norfloxacin degradation: Performance and mechanism. *Sep. Purif. Technol.* **2024**, *338*, 126572. [[CrossRef](#)]
66. Nguyen, T.-B.; Chen, C.-W.; Chen, W.-H.; Bui, X.-T.; Lam, S.S.; Dong, C.-D. Boosting acetaminophen degradation in water by peracetic acid activation: A novel approach using chestnut shell-derived biochar at varied pyrolysis temperatures. *Environ. Res.* **2024**, *252*, 119143. [[CrossRef](#)] [[PubMed](#)]
67. Huang, M.; Peng, S.; Xiang, W.; Wang, C.; Wu, X.; Mao, J.; Zhou, T. Strong metal-support interaction between carbon nanotubes and Mn-Fe spinel oxide in boosting peroxymonosulfate activation: Underneath mechanisms and application. *Chem. Eng. J.* **2022**, *429*, 132372. [[CrossRef](#)]
68. Lv, X.; Yu, M.; Guo, Y.; Sui, M. Weak magnetic field for enhanced degradation of sulfamethoxazole by the CoFe₂O₄/PAA system: Insights into performance and mechanism. *Sep. Purif. Technol.* **2025**, *357*, 130017. [[CrossRef](#)]
69. Wang, J.; Xiong, B.; Miao, L.; Wang, S.; Xie, P.; Wang, Z.; Ma, J. Applying a novel advanced oxidation process of activated peracetic acid by CoFe₂O₄ to efficiently degrade sulfamethoxazole. *Appl. Catal. B Environ.* **2021**, *280*, 119422. [[CrossRef](#)]
70. Niu, X.; Yang, Q.; Wang, Z.; Zhu, Y.; Zhang, C.; Liang, P.; Zhang, Z. Dealloyed nanoporous copper as a highly active catalyst in Fenton-like reaction for degradation of organic pollutants. *Chem. Eng. J.* **2022**, *431*, 133834. [[CrossRef](#)]
71. Zhang, D.; Li, Y.; Wang, P.; Qu, J.; Li, Y.; Zhan, S. Dynamic active-site induced by host-guest interactions boost the Fenton-like reaction for organic wastewater treatment. *Nat. Commun.* **2023**, *14*, 3538. [[CrossRef](#)] [[PubMed](#)]
72. Liu, L.; Chen, B.; Wu, T.; Li, M.; Chen, H.; Ge, Y.; Li, Z. Coordination reconstruction enhanced synergistic nonradical oxidation pathways in cobalt single-atom catalysts for sustained pollutant destruction. *Angew. Chem.* **2025**, *137*, e202508330. [[CrossRef](#)] [[PubMed](#)]
73. Zheng, J.; Lin, Q.; Wu, Y.; Liu, Y.; Zeng, C.; Luo, Y.; Chen, T. Key coordination of oxygen doping in Fe single-atoms enhances nonradical activation of peroxymonosulfate: The formation of high-valent Fe species and electron transfer. *Chem. Eng. J.* **2024**, *489*, 151307. [[CrossRef](#)]
74. Xie, M.; Yao, M.; Zhang, S.; Kong, L.; Zhao, L.; Zhan, J.; Zhao, R.-S. Single-atom Co-N₅ catalytic sites on carbon nanotubes as peroxymonosulfate activator for sulfamerazine degradation via enhanced electron transfer pathway. *Sep. Purif. Technol.* **2023**, *304*, 122398. [[CrossRef](#)]
75. He, J.; Huang, J.; Wang, Z.; Liu, Z.; Chen, Y.; Su, R.; Ni, X.; Li, Y.; Xu, X.; Zhou, W.; et al. The enhanced catalytic degradation of sulfamethoxazole over Fe@ nitrogen-doped carbon-supported nanocomposite: Insight into the mechanism. *Chem. Eng. J.* **2022**, *439*, 135784. [[CrossRef](#)]
76. Yanan, S.; Xing, X.; Yue, Q.; Gao, B.; Li, Y. Nitrogen-doped carbon nanotubes encapsulating Fe/Zn nanoparticles as a persulfate activator for sulfamethoxazole degradation: Role of encapsulated bimetallic nanoparticles and nonradical reaction. *Environ. Sci. Nano* **2020**, *7*, 1444–1453. [[CrossRef](#)]
77. Gao, X.; Chen, J.; Che, H.; Ao, Y.; Wang, P. Rationally constructing of a novel composite photocatalyst with multi charge transfer channels for highly efficient sulfamethoxazole elimination: Mechanism, degradation pathway and DFT calculation. *Chem. Eng. J.* **2021**, *426*, 131585. [[CrossRef](#)]
78. Cheng, Y.; Zheng, F.; Dong, H.; Pan, F.; Sun, L.; Aleksandr, N.; Yuan, X. Enhanced oxidation of micropollutants by ozone/ferrate (VI) process: Performance, mechanism, and toxicity assessment. *J. Water Process Eng.* **2023**, *55*, 104211. [[CrossRef](#)]
79. Qiu, J.; Yue, C.; Zheng, W.; Liu, F.; Zhu, J. Enhanced photocatalytic degradation of sulfamethoxazole by stable hierarchical Fe₂O₃/Co₃O₄ heterojunction on nickel foam. *Chin. Chem. Lett.* **2021**, *32*, 3431–3434. [[CrossRef](#)]
80. Liu, F.; Zhou, H.; Pan, Z.; Liu, Y.; Yao, G.; Guo, Y.; Lai, B. Degradation of sulfamethoxazole by cobalt-nickel powder composite catalyst coupled with peroxymonosulfate: Performance, degradation pathways and mechanistic consideration. *J. Hazard. Mater.* **2020**, *400*, 123322. [[CrossRef](#)] [[PubMed](#)]
81. Gardner, D.; Howard, J.; Ingold, K. The inhibition of autoxidation by 2, 4, 6-tri-tert-butyl substituted phenol, aniline, and thiophenol. *Can. J. Chem.* **1964**, *42*, 2847–2851. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.