

Biochar supported zero valent iron activates peroxymonosulfate to degrade sulfamethoxazole through radical and nonradical pathways

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Abstract

Sulfamethoxazole (SMX) is poorly removed by conventional biological treatment, highlighting the need for more effective treatment strategies. In this study, a ball-milled biochar-supported zero-valent iron composite (BC-ZVI) was evaluated as an activator of peroxymonosulfate (PMS) for SMX degradation. Among BC mass ratios of 1:2, 1:5, 1:10, and 1:20, the 1:10 composite exhibited the highest catalytic performance. Under the baseline conditions, 98.0% of SMX was removed within 60 min, with an observed pseudo-first-order rate constant (k_{obs}) of 0.0628 min^{-1} , which was 3.69 times higher than that of the ZVI/PMS system. Arrhenius analysis over 15–35 °C yielded an apparent activation energy of 47.5 kJ mol^{-1} ($R^2=0.982$), whereas k_{obs} decreased by approximately 30-fold as the initial pH increased from 3 to 9, indicating strong pH dependence. Quenching experiments, electron paramagnetic resonance analysis, and solvent-isotope tests collectively indicated the coexistence of radical-mediated and $^1\text{O}_2$ -associated pathways. Five major transformation-product ions were identified, and a TOC removal of 62.7% indicated that SMX degradation was accompanied by only partial mineralization. The SMX removal efficiency decreased to approximately 69.0% after five reuse cycles, while dissolved-iron release measured during the first cycle suggested incomplete stabilization of the iron phase within the composite. Overall, ball milling promoted the formation of an effective biochar–iron interface for PMS activation and substantially enhanced SMX degradation, although strong acid dependence, matrix inhibition, catalyst deactivation, and iron release remain important limitations for application in complex aqueous systems.

Keywords Biochar · Zero-valent iron · Peroxymonosulfate · Sulfamethoxazole · Singlet oxygen

Introduction

Sulfonamide antibiotics, particularly sulfamethoxazole (SMX), have prompted investigations ranging from carbon-based remediation to photochemical and in situ persulfate oxidation^{1–3}. SMX is of particular concern because it can be incompletely removed by biological treatment and has consequently been examined using biodegradation and PMS-based catalytic processes^{4,5}. Its persistence can maintain selective pressure on microbial

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communities and contribute to the spread of antibiotic-resistance determinants. An effective treatment process must therefore do more than remove the parent compound in ultrapure water: it should provide measurable transformation or mineralization, retain activity in chemically complex water, and disclose material losses that could limit repeated use.

Persulfate-based advanced oxidation processes can transform refractory organic contaminants through radical and non-radical chemistry. PMS can be activated through transition-metal, carbon-based, and light-mediated routes^{5–7}, with non-radical carbon catalysts and iron-containing carbon composites further expanding heterogeneous activation strategies^{8,9}. Beyond $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, heterogeneous PMS activation can involve atomic H^* , preferential electron transfer, and biochar-mediated reaction pathways^{10–12}. High-valent metal–oxo species and singlet oxygen ($^1\text{O}_2$) have also been identified^{13,14}. These routes differ in substrate selectivity and sensitivity to pH, dissolved organic matter, and inorganic ions. Mechanistic interpretation therefore requires consistent results from multiple experiments and should distinguish pathway-sensitive evidence from a quantitatively resolved reaction network.

Zero-valent iron (ZVI) can donate electrons, generate Fe(II) , and promote Fe-mediated PMS decomposition^{15,16}. Its reactivity is nevertheless dynamic rather than constant. Particle aggregation reduces accessible surface area, while iron oxide and hydroxide layers restrict transport from the Fe(0) core to solution-phase or surface-associated reactants^{17–19}. Iron dissolution can sustain homogeneous Fe chemistry but simultaneously represents loss of the solid active phase. Consequently, high initial removal does not by itself establish stable heterogeneous catalysis; formulation, deactivation, and dissolved-iron release must be considered together. Interface design can enhance corrosion resistance and regulate transport across multiphase surfaces²⁰, highlighting the importance of controlling the reactive boundary in ZVI-based composites.

Biochar (BC) offers a porous carbon matrix with tunable surface chemistry and potential electrical conductivity^{21–23}. Coupling BC with ZVI may distribute iron-containing domains, moderate severe aggregation, and create carbon–iron interfaces that affect adsorption and contaminant transformation²⁴. The same carbon phase can also compete for oxidants or retain SMX without degrading it. Therefore, a comprehensive consideration of the interplay between BC and ZVI is required. Ball milling is an established mechanochemical route for preparing carbon–metal composites^{23,25}. Repeated collision, compression, and shear can reduce particle size, expose reactive surfaces, disrupt passivation layers, and increase contact between carbon and iron^{18,25}. It therefore remains necessary to determine whether optimization of the BC formulation can provide a reproducible kinetic improvement over the individual components and retain this advantage across operating conditions and complex water matrices. This framing treats the preparation method as a means of constructing the reactive interface rather than as the principal novelty. Engineered heterointerfaces can promote charge redistribution and mass transport in catalytic materials²⁶, supporting the design of intimate carbon–iron contact in BC-ZVI.

This study addressed three linked questions. First, BC: ZVI mass-ratio screening and component controls were used to determine whether the composite response was composition-dependent and exceeded that of pristine ZVI or an unmilled mixture. Second, quenching tests, EPR measurements, solvent-isotope experiments, transformation-product analysis, and TOC removal were integrated to establish an evidence-based reaction network. Third, pH, PMS and catalyst dosages, SMX concentration, temperature, selected anions, real-water matrices, catalyst reuse, and total dissolved iron were evaluated to assess the performance of BC-ZVI/PMS under different operating and water-matrix conditions.

Materials and methods

Chemicals and materials

Peroxymonosulfate (PMS; $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, analytical grade), zero-valent iron powder (Fe(0) , >98%), and sulfamethoxazole (SMX, 99%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China).

Furfuryl alcohol (FFA, $\geq 98\%$), tert-butanol (TBA, $\geq 99.5\%$), methanol (HPLC grade), L-histidine ($> 99\%$), and p-benzoquinone (p-BQ, $> 99\%$) were purchased from Macklin Chemical Reagent Co., Ltd. (Shanghai, China). Reagents were used as received, and ultrapure water ($18.25 \text{ M}\Omega \text{ cm}$) was used for solution preparation and laboratory batch experiments unless otherwise specified.

Preparation of BC-ZVI composite

Coconut shell powder was dispersed in ultrapure water and mixed under stirring, followed by freeze-drying. The dried powder was pyrolyzed at 600°C for 1 h under an N_2 atmosphere in a vacuum box furnace at a heating rate of 5°C min^{-1} . After cooling to room temperature, the biochar (BC) was washed three times with ultrapure water, collected by filtration, freeze-dried, and stored at -10°C until use.

BC (3.0 g), zero-valent iron powder (30.0 g), and approximately 200 g of stainless-steel milling balls were placed in a milling jar. The jar was purged with N_2 , and the mixture was ball-milled at 500 rpm for 6 h. The resulting BC-ZVI composite had a BC: ZVI mass ratio of 1:10. Composites with mass ratios of 1:2, 1:5, and 1:20 were prepared using the same procedure for formulation comparison. After cooling, the composites were collected and stored in sealed containers.

Batch degradation experiments

Batch reactions were conducted in 200 mL SMX solutions. Unless otherwise stated, the baseline conditions were $[\text{SMX}]_0 = 5 \text{ mg/L}$, $[\text{PMS}]_0 = 0.5 \text{ mM}$, BC-ZVI = 500 mg/L, initial pH = 3.0, and $25 \pm 2^\circ\text{C}$. The initial pH was adjusted with dilute HCl or NaOH before catalyst addition. PMS was introduced before BC-ZVI addition, which defined reaction time zero. At predetermined intervals, aliquots were withdrawn, filtered through $0.22 \mu\text{m}$ membranes, and analyzed for residual SMX. The tested variables included initial pH (3, 5, 7, and 9), PMS concentration (0.05–1.0 mM), BC-ZVI dosage (0–1.0 g/L), SMX concentration (1–10 mg/L), temperature ($15\text{--}35^\circ\text{C}$), BC: ZVI mass ratio (1:2–1:20), and selected inorganic anions (5 mM). Each condition was tested at least in duplicate.

Characterization and analytical methods

Surface morphology was examined by scanning electron microscopy (SEM; SU5000, Hitachi, Tokyo, Japan), and elemental distributions were measured by SEM–energy-dispersive X-ray spectroscopy (EDS). Water contact angles were measured at room temperature with a contact-angle goniometer (DataPhysics Instruments GmbH, Filderstadt, Germany). Surface composition and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, Waltham, MA, USA). Crystalline phases were examined by X-ray diffraction (XRD; D8 ADVANCE, Bruker) using $\text{Cu K}\alpha$ radiation.

SMX was quantified using an HPLC system (LC-16, Shimadzu, Kyoto, Japan) equipped with a UV detector and a C18 column ($4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$). The mobile phase was methanol/water (40:60, v/v) at 1.0 mL min^{-1} . Transformation products were examined by UPLC-MS/MS (Agilent Technologies, Santa Clara, CA, USA). Three-dimensional excitation–emission matrix fluorescence spectroscopy (F-7000, Hitachi High-Technologies, Japan) was used to characterize fluorescent natural organic matter. Total dissolved iron was measured by ICP-OES (iCAP 6500 Series, Thermo Fisher Scientific, Waltham, MA, USA) after filtration through $0.22 \mu\text{m}$ membranes.

Quenching experiments

Quenching tests were performed under the baseline conditions. TBA (10 mM) was used primarily as an $\cdot\text{OH}$ probe because it reacts much faster with $\cdot\text{OH}$ than with $\text{SO}_4^{\cdot-}$. Methanol (10 mM) was used as a nonselective alcohol scavenger for both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. p-BQ (1 mM; prepared in water to avoid an organic-solvent effect) was used to probe $\text{O}_2^{\cdot-}$ -associated reactions, and L-histidine (5 mM) was used to probe $^1\text{O}_2$ -associated oxidation²⁷.

Because these compounds may also affect surface reactions, iron complexation, PMS consumption, or electron transfer, inhibition was interpreted qualitatively and not converted into reactive-species contribution percentages.

EPR measurements

EPR spectroscopy was used to detect transient reactive species. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 100 mM) and 2,2,6,6-tetramethylpiperidine (TEMP, 100 mM) were used as spin-trapping agents for radical species and $^1\text{O}_2$, respectively²⁸. Samples were collected during the initial rapid-reaction period and analyzed immediately. Spectra were interpreted qualitatively from characteristic signal patterns and relative intensities; no absolute reactive-species yields were calculated.

Real-water test and reusability protocol

Real-water sample was collected from a natural spring outlet in Dalingshan Forest Park, Dongguan, Guangdong, China. The measured pH, total organic carbon (TOC), chemical oxygen demand (COD), dissolved oxygen, and major-ion concentrations are summarized in Table S2. The collected water was spiked with SMX and used without adjustment to the baseline pH. For reuse tests, the catalyst was magnetically recovered after each reaction, washed three times with ultrapure water and three times with ethanol, and reused with freshly prepared PMS and SMX solutions. Total dissolved iron was measured during the first reuse cycle in ultrapure water. Samples were collected at predetermined times, filtered through 0.22 μm membranes, and analyzed by ICP-OES.

Results and discussion

Catalyst characterization and interfacial implications

SEM showed an irregular, rough BC-ZVI surface containing fine particles and larger aggregates after ball milling (Fig. 1a). The morphology therefore contained both potentially exposed interfacial domains and agglomerated regions that could restrict access to some of those domains. SEM-EDS maps detected C, O, N, and Fe in the same imaged region, with Fe signals spatially associated with the carbon-containing matrix. This co-location confirms that the recovered material contained supported iron-rich domains rather than carbon alone, although EDS does

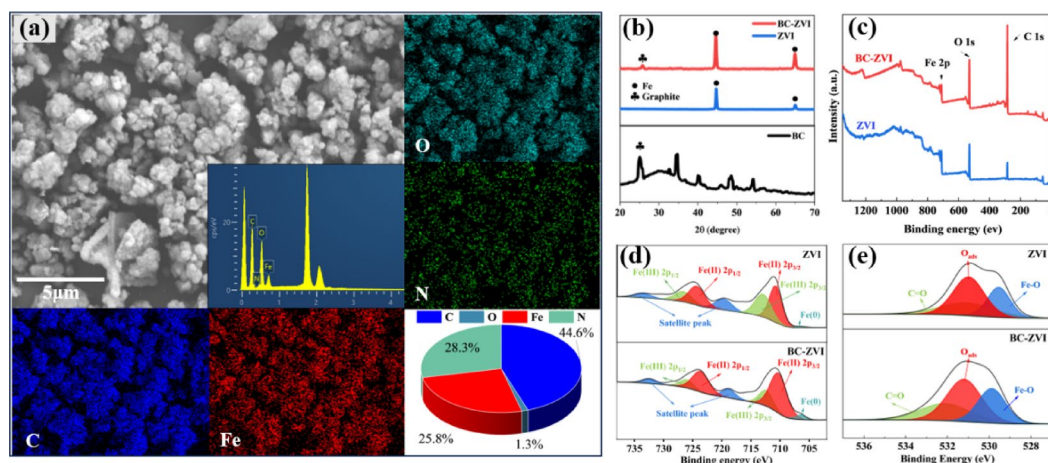


Fig. 1 Physicochemical characterization of BC-ZVI. (a) SEM image, EDS spectrum, elemental mapping, and elemental composition of BC-ZVI; (b) XRD patterns of pristine ZVI, BC-ZVI and BC; (c) XPS survey spectra of ZVI and BC-ZVI; (d) high-resolution Fe 2p spectra; and (e) high-resolution O 1s spectra.

not resolve chemical bonding or nanoscale interfacial structure. The structural interpretation is consequently based on the combined microscopy, diffraction, and surface-spectroscopy evidence.

XRD showed that BC-ZVI retained the characteristic diffraction peaks of metallic Fe(0) after ball milling (Fig. 1b). Standalone BC displayed a broad feature at approximately 22° – 35° , consistent with the (002) reflection of disordered aromatic carbon, together with sharper peaks attributable to crystalline inorganic constituents of the ash fraction. The BC-ZVI pattern combined the broad carbon-associated background with iron- and mineral-phase signals. Thus, milling produced intimate physical integration without eliminating the crystalline Fe(0) phase required for Fe-mediated PMS activation.

XPS detected Fe, C, and O on the composite surface (Fig. 1c–e). Components assigned to Fe(0), Fe(II), and Fe(III), together with satellite features, indicate that metallic and oxidized iron states coexisted within the surface-sensitive sampling depth. Quantitative deconvolution of the Fe 2p envelope showed that Fe(0), Fe(II), and Fe(III) accounted for 1.8%, 51.1%, and 47.1% of the fitted surface Fe components in ZVI, and for 3.8%, 68.5%, and 27.7% in BC-ZVI, respectively (Table S3). The higher Fe(0)/Fe(II) fraction and lower Fe(III) fraction in BC-ZVI indicate that BC incorporation partially suppressed surface oxidation of ZVI. O 1s components were assigned to metal–oxygen bonds, carbonyl oxygen groups, and adsorbed oxygen-containing species or water. Contact angles of 25.05° for ZVI and 30.86° for BC-ZVI (Supplementary Fig. S1) show that both materials were readily wetted, although the composite was not more hydrophilic than pristine ZVI by this measurement.

Taken together, the characterization establishes a carbon-supported material that retains Fe(0), contains surface oxidized iron, and presents close carbon–iron contact. These features provide a physically plausible basis for adsorption and interfacial PMS activation. The functional significance of the interface is instead evaluated by comparison with pristine ZVI, BC, and the unmilled BC + ZVI mixture. Surface functionalization can strengthen coupling between dissimilar phases²⁹, consistent with the role of close carbon–iron contact in interfacial PMS activation.

Degradation performance and kinetic behavior

SMX removal depended non-monotonically on the BC: ZVI mass ratio. After 60 min, removal was 47.4%, 64.9%, 97.9%, and 82.7% for ratios of 1:2, 1:5, 1:10, and 1:20, respectively (Supplementary Fig. S3). The decrease on either side of 1:10 shows that performance was not controlled simply by increasing the fraction of BC or ZVI. The 1:10 formulation was therefore selected as the best-performing composition among those tested, while the absence of surface-area, accessible-Fe, and interfacial-site measurements prevents attribution of the maximum to a single structural variable. Under the baseline conditions, SMX-only and PMS-only controls changed minimally, whereas BC and BC/PMS removed 26.3% and 23.2%, respectively (Fig. 2a). ZVI/PMS achieved 69.0% removal and the unmilled BC + ZVI + PMS mixture achieved 44.3%, compared with 98.0% for ball-milled BC-ZVI/PMS. Multiscale architecture can generate synergistic composite performance³⁰, supporting systematic optimization of the BC: ZVI mass ratio.

Pseudo-first-order fitting gave k_{obs} values of 3.70×10^{-4} , 6.10×10^{-4} , 0.00410, 0.00370, 0.00770, 0.0170, and 0.0628 min^{-1} for SMX only, PMS only, BC, BC/PMS, BC + ZVI + PMS, ZVI/PMS, and BC-ZVI/PMS, respectively (Fig. 2a and Supplementary Fig. S4a). The BC-ZVI/PMS rate constant was 3.69 times that of ZVI/PMS, 8.16 times that of the unmilled mixture, and 17.0 times that of BC/PMS. BC/PMS did not outperform BC alone, whereas the ball-milled composite exceeded both component controls. The superior performance of BC-ZVI over the individual components indicates that ball milling enhanced the catalytic activity of the composite, although the relative contributions of improved ZVI dispersion, Fe cycling, surface adsorption, and their combined effects could not be distinguished. Approximately 55% of SMX was removed within the first 5 min, followed by a slower phase, consistent with rapid consumption of initially accessible reactive capacity followed by a regime increasingly influenced by oxidant depletion, product competition, or surface evolution.

Increasing the reaction temperature from 15 to 35 $^{\circ}\text{C}$ progressively increased k_{obs} from 0.0343 to 0.114 min^{-1} , demonstrating a pronounced temperature dependence of SMX degradation (Fig. S2). The temperature-dependent

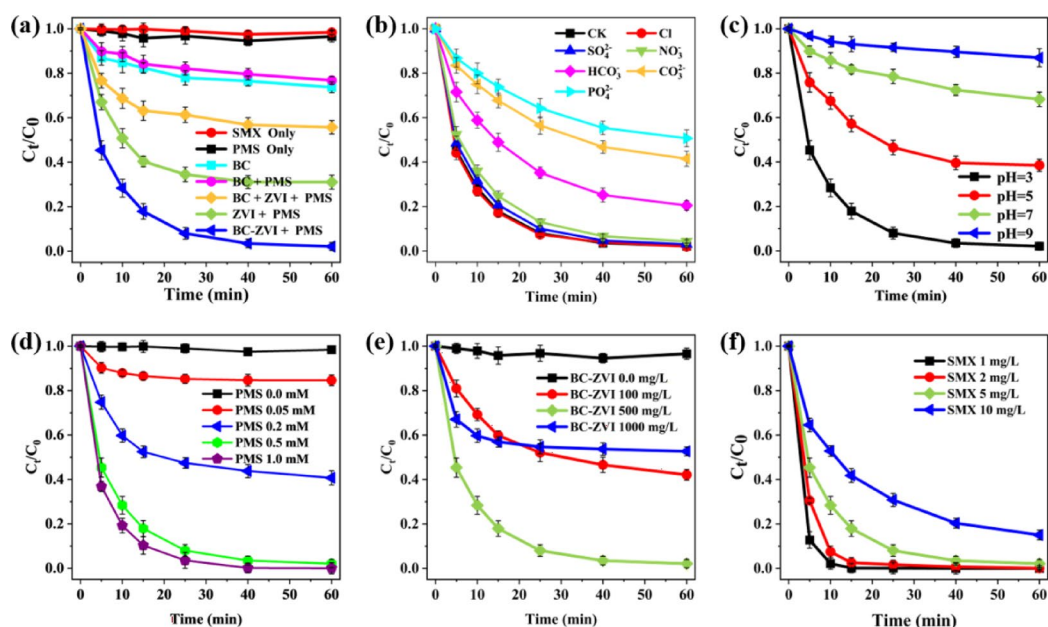


Fig. 2 SMX removal and kinetic behavior under the tested conditions. (a) System comparison; (b) effect of coexisting anions; (c) initial pH; (d) PMS concentration; (e) BC-ZVI dosage; and (f) initial SMX concentration. Unless otherwise stated, $[\text{SMX}]_0 = 5 \text{ mg/L}$, $[\text{PMS}]_0 = 0.5 \text{ mM}$, BC-ZVI = 500 mg/L, initial pH = 3.0, reaction volume = 200 mL, and temperature = $25 \pm 2 \text{ }^\circ\text{C}$.

rate constants were analyzed using the Arrhenius equation, $k_{\text{obs}} = A \cdot \exp(-E_a/RT)$, which can be linearized as $\ln k_{\text{obs}} = \ln A - (E_a/RT)$. Linear regression of $\ln k_{\text{obs}}$ against $1/T$ gave $\ln k_{\text{obs}} = -5709.95(1/T) + 16.3915$, with $R^2 = 0.9823$. Accordingly, the apparent activation energy calculated from the slope ($-E_a/R$) was 47.5 kJ mol^{-1} . The marked increase in k_{obs} demonstrates a strong temperature dependence of SMX degradation in the BC-ZVI/PMS system. Higher temperature facilitates PMS activation and Fe-mediated interfacial reactions, thereby accelerating the generation and utilization of reactive species and enhancing SMX degradation. The good linearity of the Arrhenius relationship further indicates that the observed temperature dependence follows Arrhenius behavior over the investigated range.

Effects of operational parameters

Effect of coexisting anions

The selected anions produced a clear hierarchy of kinetic inhibition at 5 mM (Fig. 2b and Fig. S4b). Relative to the control k_{obs} of 0.0628 min^{-1} , Cl^- caused no meaningful change (0.0630 min^{-1}), while SO_4^{2-} and NO_3^- reduced k_{obs} by 12.1% and 21.8%, respectively. HCO_3^- , CO_3^{2-} , and PO_4^{3-} produced much stronger reductions of 61.5%, 78.3%, and 83.0%, corresponding to k_{obs} values of 0.0242, 0.0136, and 0.0107 min^{-1} . The response therefore separates weakly interfering chloride from oxyanions that strongly suppress the observed rate under the tested conditions.

This inhibition cannot be assigned to a single scavenging reaction. Added salts can alter radical exposure and PMS speciation⁶, while ligand- and corrosion-dependent changes in Fe dissolution and Fe(II) generation can modify Fe complexation, precipitation, and surface reactivity^{31,32}. The particularly strong phosphate and carbonate responses are consistent with combined solution-phase and surface effects. Accordingly, the 5 mM experiments are interpreted as comparative single-anion challenge tests rather than quantitative reconstructions of the spring-water matrix.

Effects of pH and PMS concentration

Initial pH was the strongest operating constraint identified in the parameter study (Fig. 2c and Supplementary Fig. S4c). k_{obs} decreased from 0.0628 min⁻¹ at pH 3 to 0.0151, 0.00575, and 0.00209 min⁻¹ at pH 5, 7, and 9, respectively. The pH 3 rate was therefore 4.16, 10.9, and 30.0 times the rates at pH 5, 7, and 9. This nonlinear loss is consistent with reduced Fe(0) corrosion and Fe(II) availability, increased iron-(oxyhydr)oxide passivation, and altered PMS chemistry as pH increased^{31,32}. The result identifies acidic operation as a condition on which the reported high rate depends, rather than a minor optimization variable.

Increasing PMS concentration from 0.05 to 1.0 mM increased k_{obs} from 0.00196 to 0.142 min⁻¹, a 72.4-fold change across the tested range (Fig. 2d and Supplementary Fig. S4d). At 0.5 mM, k_{obs} was 0.0628 min⁻¹ and removal approached completion within 60 min. This concentration was retained as the baseline because it provided a high measurable rate without using the maximum PMS dose. Increasing the PMS concentration enhanced SMX degradation over the tested range, although the corresponding oxidant utilization efficiency and treatment cost were not evaluated.

Effects of catalyst dosage and initial SMX concentration

BC-ZVI dosage produced a non-monotonic kinetic response (Fig. 2e and Supplementary Fig. S4e). k_{obs} values were 6.10×10^{-4} , 0.00133, 0.0628, and 0.00728 min⁻¹ at 0, 0.1, 0.5, and 1.0 g/L, respectively. Increasing the dose from 0.1 to 0.5 g/L sharply increased the rate, but a further increase to 1.0 g/L lowered k_{obs} by 8.63-fold. Thus, additional solid did not translate directly into additional productive sites. Nonproductive PMS decomposition, reactive-species scavenging by excess surface, and particle aggregation are plausible coupled explanations, but the relative contributions of these processes could not be distinguished experimentally. Optimized incorporation of a nanoscale secondary phase can synergistically enhance composite properties³³, underscoring the importance of catalyst-loading optimization.

Increasing the initial SMX concentration from 1 to 10 mg/L decreased k_{obs} from 0.217 to 0.0299 min⁻¹ (Fig. 2f and Supplementary Fig. S4f). Although the apparent first-order constant decreased 7.26-fold, the model-based initial rate $k_{\text{obs}C_0}$ remained within approximately 0.217–0.314 mg/L min⁻¹ across 1, 2, 5, and 10 mg/L. The near-plateau in this absolute-rate estimate indicates that oxidant activation or accessible surface capacity became limiting as the pollutant loading increased, while competition from transformation products may have reinforced the decline in k_{obs} ³⁴.

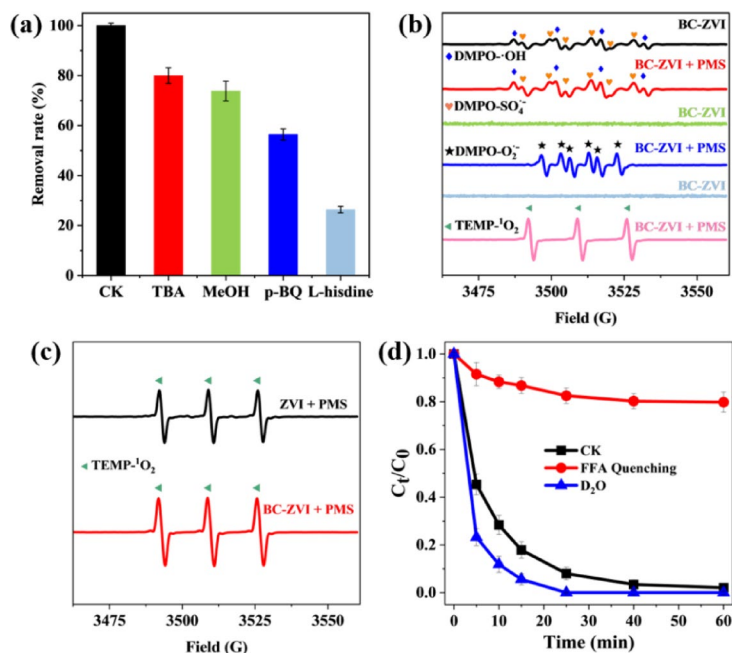
Reactive species identification: quenching and EPR evidence

Probe experiments first tested whether the system could be described as radical-only (Fig. 3a). TBA and methanol caused weaker inhibition than p-BQ and L-histidine, whereas p-BQ and L-histidine decreased 60-min SMX removal to 56.4% and 26.4%, respectively. The much stronger response to p-BQ and L-histidine is inconsistent with exclusive control by freely diffusing $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ and supports $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ associated chemistry^{35,36}. Because every probe can also alter adsorption, PMS consumption, iron complexation, or surface reactions, the inhibition magnitudes are treated as pathway sensitivities rather than species-contribution fractions.

EPR supplied a second, spectroscopically independent line of evidence (Fig. 3b, c). BC-ZVI without PMS produced no detectable trapped-species signal. After PMS addition, signals assigned to DMPO- $\cdot\text{OH}$ /DMPO- $\text{SO}_4^{\cdot-}$ and DMPO- $\text{O}_2^{\cdot-}$ adducts were observed^{37,38}. TEMP produced a triplet signal consistent with $^1\text{O}_2$, and its intensity was higher for BC-ZVI/PMS than for ZVI/PMS. Comparable PMS systems have combined EPR with complementary tests to distinguish radical, electron-transfer, and other non-radical pathways^{39,40}. Relative EPR intensities, however, are not direct concentration measurements across different spin adducts.

Solvent-isotope and furfuryl-alcohol experiments provided a third evidence class (Fig. 3d). Faster SMX removal in D₂O than in H₂O, together with inhibition by furfuryl alcohol, was consistent with a longer-lived

Fig. 3 Qualitative reactive-species evidence for the BC-ZVI/PMS system. **(a)** SMX removal in the presence of probe compounds; **(b)** DMPO-EPR spectra assigned to oxygen-centered radical adducts; **(c)** TEMP-EPR spectra consistent with $^1\text{O}_2$ in ZVI/PMS and BC-ZVI/PMS; and **(d)** SMX removal in D_2O and with furfuryl alcohol. Probe and spin-trapping results are interpreted as pathway-sensitive evidence, not as quantitative reactive-species contributions.



$^1\text{O}_2$ -associated oxidation channel. Agreement among the L-histidine response, TEMP-EPR signal, D_2O acceleration, and furfuryl-alcohol inhibition makes the $^1\text{O}_2$ assignment less dependent on any single probe. The combined dataset therefore supports coexisting pathways, but not quantitative dominance by one reactive species.

Representative reactions consistent with the observed radical and $^1\text{O}_2$ -associated chemistry are:

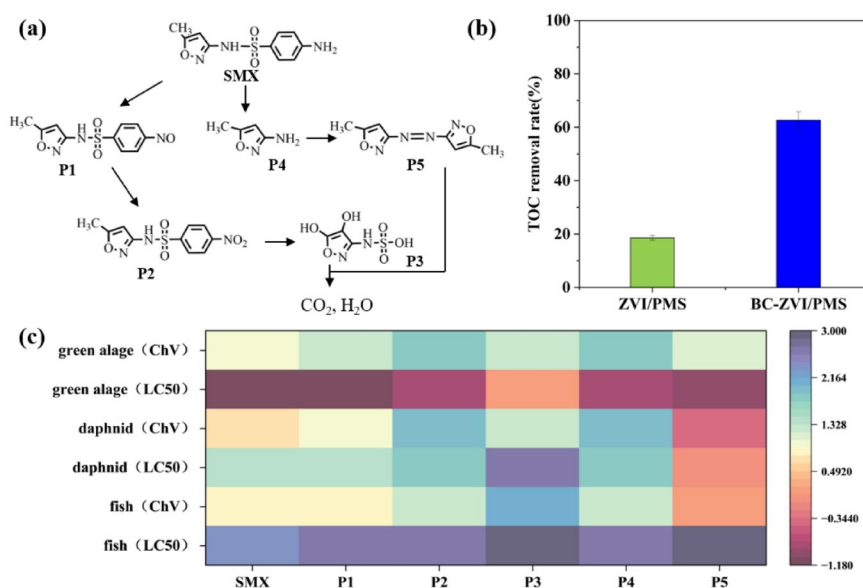


The combined characterization and kinetic results further indicate an important role of the BC-Fe interface in PMS activation. Ball milling produced intimate contact between the carbon and iron phases while retaining Fe(0) and generating surface Fe(II)/Fe(III) species. Consistent with this interfacial structure, the k_{obs} of the BC-ZVI/PMS system was 3.69 times that of ZVI/PMS and 8.16 times that of the unmilled BC + ZVI + PMS system. The BC-Fe interface therefore facilitated PMS activation and Fe redox cycling, leading to the formation of $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$, together with the experimentally supported $^1\text{O}_2$ -associated pathway. These coupled radical and non-radical processes collectively contributed to SMX transformation in the BC-ZVI/PMS system.

Transformation products and proposed degradation pathways

UPLC-MS/MS detected five transformation-product ions, P1–P5, at m/z 268.03, 283.03, 199.00, 99.05, and 193.07 (Fig. 4a and Supplementary Table S1 and Figure S5). The mass changes and tentative formula/structure assignments were consistent with amino-group oxidation followed by S–C cleavage (P1–P3) and S–N cleavage followed by further transformation (P4–P5)^{23,42}. TOC removal after 60 min was 62.7% for BC-ZVI/PMS

Fig. 4 Transformation and mineralization assessment. **(a)** Proposed SMX transformation pathways; **(b)** TOC removal in ZVI/PMS and BC-ZVI/PMS after 60 min; and **(c)** ECOSAR screening estimates for SMX and the proposed products.



and 18.6% for ZVI/PMS (Fig. 4b), a 3.37-fold difference. The gap between parent-SMX removal and TOC removal was 35.3% points for BC-ZVI/PMS, compared with 50.4% points for ZVI/PMS. The composite therefore promoted oxidation beyond disappearance of the parent chromophore, but 37.3% of the initial organic carbon remained. This balance is consistent with substantial, yet incomplete, mineralization and the persistence of soluble transformation products.

The predicted toxicities of most proposed products were lower than that of SMX, whereas P5 retained predicted toxicity (Fig. 4c). Because the predictions depend on tentative structures and do not measure mixture effects, they cannot establish detoxification. Their value is to identify products that warrant targeted confirmation. Considered together with incomplete TOC removal, the screening shows why parent-compound removal alone is an insufficient endpoint for assessing treatment outcome. Integrated network toxicology and experimental validation have been used to characterize the molecular effects of emerging contaminants and their transformation products⁴³, providing a complementary basis for product-level toxicity assessment.

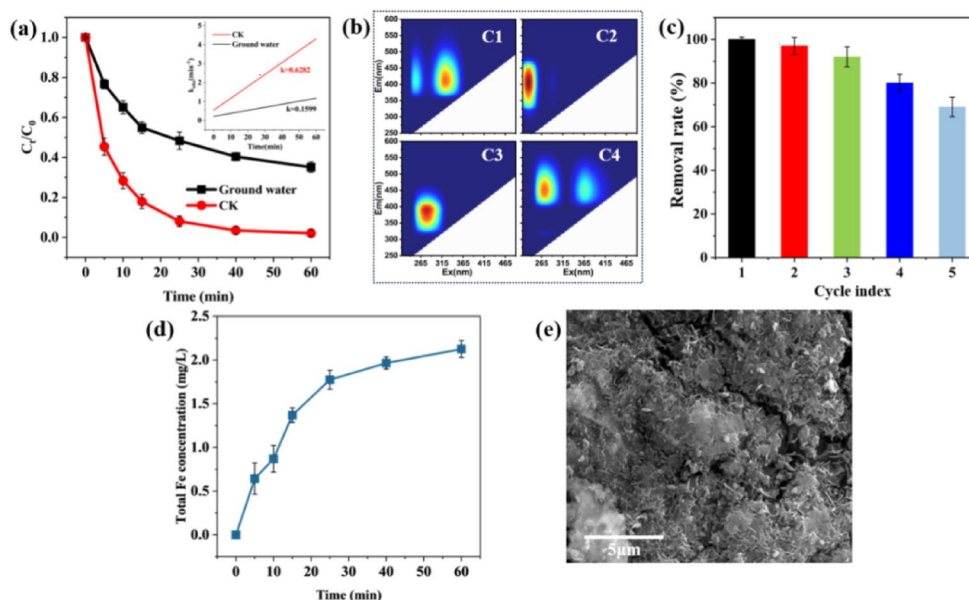
Application in real-water matrices

Spring-water performance and natural organic matter response

In SMX-spiked real-water matrices, 60-min removal decreased from 98.0% in the pH 3 ultrapure-water control to 65.34% without pH adjustment (Fig. 5a). This represents a 32.66-percentage-point loss while retaining 66.7% of the control endpoint. The spring water had pH 6.36, TOC of 11.83 mg/L, COD of 13.64 mg/L, dissolved oxygen of 7.28 mg/L, and the major-ion composition in Supplementary Table S2. The result therefore measures the integrated response to a less acidic and chemically more complex matrix, rather than an isolated real-water constituent effect. The EEM spectral component diagram obtained through the PARAFAC method further resolved four fluorescent components in the spring-water sample (Fig. 5b), including terrestrial humic-like (C1), marine humic-like (C2), microbial-derived humic-like components (C4), and wetland-derived-like components (C3), indicating the presence of compositionally diverse fluorescent organic matter. Natural organic matter can compete for reactive species, occupy carbon or iron surface sites, and alter oxidant exposure^{44–46}.

The pH series provides an important reference for interpreting the spring-water result. k_{obs} decreased approximately 30-fold between pH 3 and pH 9, and the spring water was used at pH 6.36. Loss of acid-promoted Fe reactivity can therefore account for part of the performance decrease, while the measured TOC and ions provide

Fig. 5 Spring-water performance, catalyst reusability, and iron release. **(a)** SMX removal in real-water matrices compared with the ultrapure-water control (CK), with apparent pseudo-first-order rate constants shown in the inset; **(b)** EEM-PARAFAC components (C1–C4) of fluorescent natural organic matter; **(c)** SMX removal over five consecutive cycles in ultrapure water; **(d)** total dissolved iron during the first reuse cycle in ultrapure water; and **(e)** SEM image of BC-ZVI after five cycles.



additional competitive and surface-chemical constraints. The relative contributions of pH, natural organic matter, and inorganic ions could not be quantified from the current experiments, but the results identify pH and matrix composition as coupled application variables.

The 5 mM single-anion tests further clarify this boundary without reproducing the real-water. Chloride had little effect at the challenge concentration, whereas nitrate, sulfate, bicarbonate, carbonate, and phosphate progressively suppressed k_{obs} . In contrast, the spring water contained multiple ions at their measured concentrations together with natural organic matter. The single-anion and spring-water experiments therefore serve different purposes: the former ranks potential interferents under a common concentration, while the latter tests their combined consequence in one environmental matrix.

Reusability and iron leaching

Across five consecutive cycles in ultrapure water, SMX removal decreased from the high initial response to 69.0% in the fifth cycle (Fig. 5c). Total dissolved iron increased during the first cycle (Fig. 5d), demonstrating incomplete retention of the iron phase, while post-use SEM showed particle aggregation and surface coverage after five cycles (Fig. 5e). The concurrence of activity loss, dissolved-iron release, and morphological evolution supports a coupled deactivation picture involving Fe(0) consumption, oxide or hydroxide accumulation, aggregation, site blockage, and physical material loss during recovery and washing⁴⁷. The measurements do not separate the fractional contribution of each process. The spring-water and reuse tests define complementary but distinct boundaries. The former measured a single-cycle matrix response without pH adjustment; the latter isolated five-cycle material durability in ultrapure water. The reuse series therefore demonstrates partial retention of intrinsic activity under controlled recovery conditions, whereas the spring-water test demonstrates matrix sensitivity. Organic ligands can regulate Fe-(oxyhydr)oxide dissolution kinetics and phase selection⁴⁸, while carboxyl–Fe and phosphonate–Fe interactions govern organic-phosphate redistribution during ferrihydrite transformation⁴⁹. These processes provide a mechanistic basis for considering natural organic matter and phosphate in the surface evolution of reused BC-ZVI.

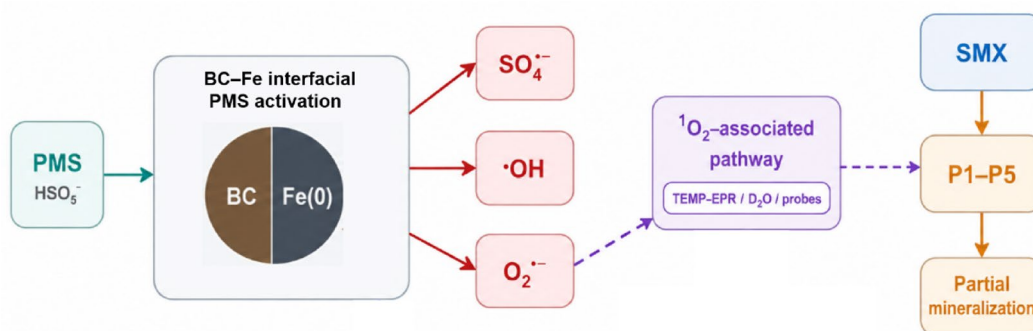


Fig. 6 Evidence-based reaction network in the BC-ZVI/PMS system.

Mechanistic synthesis and evidence boundaries

The combined results support a coupled reaction network involving radical and non-radical pathways (Fig. 6). Fe(0) retained in BC-ZVI and the enhancement over ZVI/PMS are consistent with Fe-mediated PMS activation, while EPR identified $\text{SO}_4^{\bullet-}/\cdot\text{OH}$ and $\text{O}_2^{\bullet-}$ -associated signals. Quenching, TEMP-EPR, D_2O , and furfuryl-alcohol responses converged on an additional $^1\text{O}_2$ -associated pathway. Transformation-product ions and TOC removal show that these pathways produced both selective bond cleavage and broader oxidation. The data support coexistence of these processes, but not a unique percentage contribution for each pathway. A self-powered galvanic PMS system for levofloxacin identified a $^1\text{O}_2$ -dominant non-radical route through combined quenching, EPR, and probe experiments⁵⁰, supporting the multi-evidence approach used here. Studies of reactive-water chemistry further demonstrate that identifying reactive species and their formation sequence is essential for resolving treatment pathways⁵¹. Together, these results provide a consistent interpretation of the reactive-species pathways in the BC-ZVI/PMS system.

The role of the ball-milled BC-Fe interface is supported by the 3.69-fold k_{obs} enhancement over ZVI/PMS and the 8.16-fold enhancement over the unmilled BC + ZVI + PMS system. Combined with the preservation of Fe(0), the coexistence of Fe(II)/Fe(III) surface species, and the close spatial association between carbon and iron, these results indicate that ball milling promoted interfacial PMS activation. In the revised Fig. 6, the BC-Fe interface is therefore positioned as the activation center connecting PMS decomposition with the experimentally identified $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$ -associated pathways. Solid arrows represent relationships supported by material characterization, control kinetics, quenching experiments, EPR analysis, solvent-isotope experiments, transformation-product identification, and TOC measurements.

Conclusions

Ball-milled BC-ZVI activated PMS and removed 98.0% of SMX within 60 min under the acidic baseline conditions. The BC: ZVI response was non-monotonic: the 1:10 formulation gave the highest removal among the four compositions tested, showing that neither increasing BC nor increasing ZVI alone controlled performance. Its k_{obs} of 0.0628 min^{-1} was 3.69 times that of ZVI/PMS and 8.16 times that of the unmilled BC + ZVI + PMS mixture. Together with the component controls, this kinetic enhancement indicates that the carbon-iron interface contributed to PMS activation.

The mechanistic conclusion rests on convergence rather than on a single scavenger experiment. Quenching, EPR, D_2O , and furfuryl-alcohol experiments consistently supported the coexistence of $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$ -associated pathways. Together with the enhanced kinetics of BC-ZVI relative to ZVI and the unmilled

BC+ZVI system, these results show that the ball-milled BC–Fe interface promoted PMS activation and coupled radical/non-radical oxidation.

Five transformation-product ions were consistent with amino-group oxidation and S–C/S–N bond cleavage. TOC removal reached 62.7%, 3.37 times that of ZVI/PMS, but remained below parent-SMX removal, demonstrating substantial yet incomplete mineralization.

The same dataset defines three limitations that constrain application. First, k_{obs} decreased 30-fold from pH 3 to pH 9, and spring-water removal was only 65.34% without acidification; high performance therefore depended on acidic operation and was further reduced by the real-water matrix. Second, fifth-cycle removal decreased to approximately 69.0%, while post-use SEM showed aggregation and surface coverage, indicating progressive catalyst deactivation under the tested recovery protocol. Third, total dissolved iron increased during the first cycle, showing incomplete iron retention. ICP-OES quantified the released iron pool but did not resolve Fe(II) and Fe(III) fractions, so catalytic Fe cycling and net material loss cannot yet be separated quantitatively.

Future studies should address these limitations using clearly defined and quantifiable performance targets. Circumneutral activity should be pursued by tuning biochar surface chemistry and Fe–carbon interfacial sites while reporting PMS utilization rather than removal alone. Durability should be tested with regeneration protocols that suppress passivation and aggregation and restore activity across repeated cycles in real-water. Iron retention should be strengthened through improved immobilization and evaluated with dissolved-iron speciation, total iron mass balances, and post-cycle solid characterization. These experiments would determine whether the kinetic benefit of the present formulation can be maintained under circumneutral, application-relevant conditions.

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Data availability Data are available from the corresponding author upon reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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