

ORIGINAL RESEARCH

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Tailored co-doped biochar by varying the N:B ratio as peroxymonosulfate activator for sulfamethoxazole degradation

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Abstract

Biochar doped with heteroatoms showed superior performance in activating peroxymonosulfate (PMS) for contaminant degradation. The incorporation of nitrogen (N) enhanced surface functional groups and defects, while boron (B) improved pore structure; however, uncertainties remain regarding the identification of key active sites and reaction mechanisms under different N:B ratios. To address this issue, a series of co-doped biochar derived from waste sawdust was investigated in this work. Decreasing the N:B ratio (from 4 to 0.25) led to a significant enhancement of sulfamethoxazole (SMX) degradation (from 0.20 to 0.47 min⁻¹) in the PMS system. Specifically, the contribution of catalysis was limited compared to that of adsorption at higher N:B ratios (> 1). Linear fitting analysis indicated that catalytic efficiency was primarily regulated by specific surface area. Additionally, C–OH groups acted as electron donors for generating radicals, while C=O groups were active sites for singlet oxygen (¹O₂). In contrast, the catalytic rate increased substantially at lower N:B ratios (0.25–1), suggesting that catalytic sites prevalent under boron-rich conditions became the dominant active centers. Correlation analysis revealed that decreasing N:B ratio (from 2 to 0.25) enhanced SMX degradation by elevating defect density (I_D/I_G from 1.40 to 1.46) and graphitic N content, thereby enhancing electron transfer and ¹O₂ formation for faster SMX degradation. The promotion of nonradical ¹O₂ pathway was further validated by theoretical calculations. Collectively, this study provides new insights into the mechanisms of PMS activation by biochar with varying N:B ratios, underscoring the potential of tailored biochar for efficient pollutant degradation.

Highlights

- A low N:B ratio increases SSA, defect sites, and graphitic N, markedly improving SMX removal.
- Defects and graphitic N boost ¹O₂ generation, and DFT confirms ¹O₂ route.
- Optimized ratio shifts SMX degradation from adsorption- to catalysis-dominated.

Keywords Sulfamethoxazole degradation, Peroxymonosulfate activation, Defects, N and B co-doped biochar

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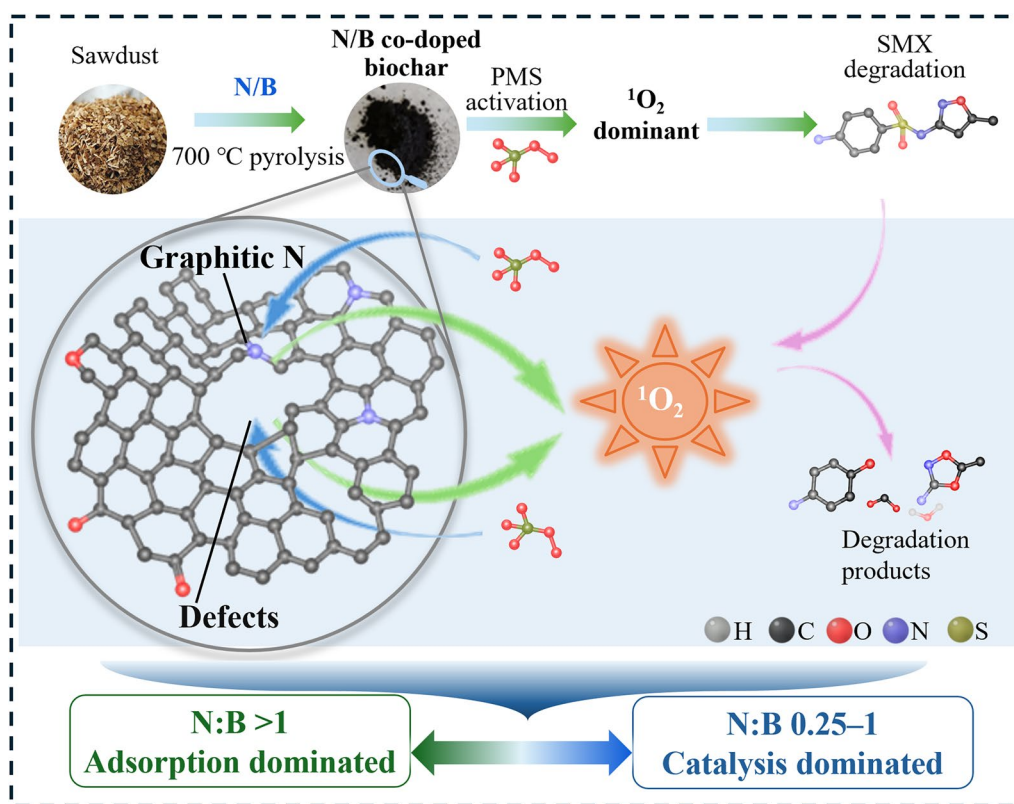
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Graphical Abstract



1 Introduction

Advanced oxidation processes based on peroxymonosulfate (PMS) activation have attracted considerable interest in wastewater treatment due to their broad pH adaptability (2–9), low catalyst demand, and selectivity toward organic pollutants (Zhao and Zhang 2025). PMS activation is typically achieved through transition metal catalysts, carbon-based materials, or external energy inputs like heat, UV irradiation, or ultrasound, to generate reactive oxygen species (ROS). Particularly, carbon-based catalysts (e.g., graphene (Zhang et al. 2024), nanoporous carbon (Li et al. 2025) and biochar (Shin et al. 2026)) stand out for their environmental compatibility and their tunable electronic and physicochemical properties. Unlike metal-based catalysts, they circumvent concerns related to metal scarcity, toxicity, and leaching, offering a more sustainable alternative for advanced oxidation processes (Wang et al. 2025).

Among carbon-based catalysts, biochar stands out as a sustainable and cost-effective option due to its abundant feedstock sources, low production cost, high surface area, and tunable surface chemistry through activation

and heteroatom doping (Chu et al. 2025; Lu et al. 2024; Zhao et al. 2025). As pristine biochar often exhibits limited active sites that affect catalytic activity (Chen et al. 2024), heteroatoms such as nitrogen (N), boron (B), sulfur (S), and phosphorus (P) are often employed to alter electronic structures (Choong et al. 2023a; Fang et al. 2025) and physicochemical properties of biochar and to enhance the catalytic performance (Dou et al. 2022); moreover, tailoring the carbon framework toward nanosheet-like morphologies and graphitic/graphite-phase domains facilitates electron transport and exposes abundant active sites (Dong et al. 2025). For example, N incorporation increases electron cloud density, introduces structural defects, and can increase the specific surface area (SSA) of biochar (Song et al. 2026). As a result, N-doped biochar generally exhibits substantially enhanced PMS-activated oxidation of dyes and antibiotics, compared with pristine materials (Wen and Wang 2025). B-related modification has also been reported to promote pore development, local charge redistribution, defect formation, and electron-transfer pathways (Hayat et al. 2025; Pan et al. 2023). Thus, combining N and B is

not simply an additive strategy: N primarily contributes to electronic regulation and N-containing active sites, whereas B-related modification favors pore development and local electronic redistribution. Compared with single heteroatom doping, this dual modification is expected to simultaneously increase the density of reactive sites, improve PMS accessibility, and facilitate $^1\text{O}_2$ -dominated oxidation pathways.

Consistent with these complementary effects, N and B co-doped biochar derived from various precursors, such as agricultural and industrial wastes, have been reported to efficiently remove organic pollutants, including tetracycline (Dou et al. 2022), ciprofloxacin (Choong et al. 2023b), bensulfuron methyl (Yang et al. 2023), and acid orange 7 (Pan et al. 2024). The improvement in catalytic activity is usually put down to the presence of defects and surface functional groups introduced by heteroatom doping, such as C=O, pyridinic N, and graphitic N moieties, which facilitate singlet oxygen ($^1\text{O}_2$) generation and promote electron transfer (Zhou et al. 2025). Increasing evidence suggests a trend in which N and B co-doped biochar shifts from a radical-dominated oxidation pathway ($\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$) to a nonradical process ($^1\text{O}_2$ and electron transfer), improving selectivity and enhancing resistance to interference in complex matrices (Dou et al. 2022; Pan et al. 2024; Yang et al. 2023). However, discrepancies remain regarding the identification of the key active sites and mechanisms under different N:B ratios (Wang et al. 2024). Nevertheless, previous studies have mainly demonstrated that N/B co-doping can enhance catalytic activity or promote a shift toward nonradical oxidation, while the composition-dependent mechanism remains insufficiently resolved. In particular, it is still unclear how the N:B ratio regulates the balance between adsorption and catalysis, which structural features dominate PMS activation under different N:B regimes, and how these changes influence $^1\text{O}_2$ generation.

In addition to these mechanistic uncertainties, current preparation strategies also present practical limitations. The multi-step pyrolysis method employed for N and B co-doped biochar was primarily inspired by a strategy that enhanced the catalytic activity of graphene oxide by two-step thermal annealing, while avoiding B–N bonds formation (Chen et al. 2019; Choong et al. 2023b). However, these multi-step synthesis increases preparation costs and may collapse pore structures, reducing accessible active sites and catalytic stability (Rong et al. 2025).

To address these issues, this study synthesized a series of nitrogen and boron co-doped biochar from sawdust using a one-step calcination method with different mass ratios of urea (N source) and boric acid (B source). The effects of N:B ratios on PMS activation and sulfamethoxazole (SMX) degradation were systematically investigated.

Particular attention was given to linking catalytic performance with pore structure, surface functional groups, defect density, and reaction kinetics. This work aims to establish composition-dependent structure–activity relationships, clarify the N:B ratio-dependent shift in PMS activation mechanisms, and identify the key active sites responsible for enhanced SMX degradation under different N:B regimes.

2 Materials and methods

2.1 Catalyst synthesis and characterization

The biochar was prepared following the reported method with minor changes (Zhang et al. 2022). First, sawdust, urea, and boric acid at a certain weight ratio were mixed with a table-top programmable planetary ball mill (MSK-SFM-1S, HF-Kejing) for 4 h. The sawdust constituted 50% of the mixture, while the mass ratio of urea to boric acid for the remaining 50% was set at 4, 2, 1, 0.5, and 0.25. The resulting mixtures were transferred into a 100-mL ceramic crucible, which was then placed into a muffle furnace for calcination at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. The temperature was maintained at $700\text{ }^\circ\text{C}$ for 2 h to complete the carbonization process. After cooling, the obtained materials were rinsed with deionized water and subsequently dried at $60\text{ }^\circ\text{C}$ for 24 h. The final samples were designated as BC, N-BC, B-BC, N:B-4, N:B-2, N:B-1, N:B-0.5, and N:B-0.25, respectively.

Chemicals and reagents used in this work are introduced in Text S1. The morphology, pore structure, surface chemistry, and defect characteristics of the catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 adsorption–desorption, X-ray photoelectron spectroscopy (XPS), X-Ray diffraction (XRD), Raman spectroscopy, and Synchrotron radiation soft X-ray absorption spectroscopy (sXAS), with the detailed characterization methods provided in Text S2.

2.2 Batch experiments

The degradation of SMX using N and B co-doped biochar via PMS activation was performed in a 50-mL beaker. The experiment was carried out at room temperature ($25 \pm 2\text{ }^\circ\text{C}$) with continuous magnetic stirring of 600 rpm (Dalong MS-H-ProA, China). Initially, 20 mL of an aqueous solution containing SMX ($10\text{ }\mu\text{M}$) and PMS (0.5 mM) was prepared in a 50-mL beaker at its natural pH of 3.4 ± 0.1 without adjustment. Next, biochar was added as catalyst at 0.5 g L^{-1} to activate PMS and initiate the degradation reaction.

Adsorption experiments were conducted at $25\text{ }^\circ\text{C}$ using biochar catalysts only without adding PMS to determine the contribution of background adsorption to SMX removal.

Samples were filtered and analyzed using liquid chromatography with ultraviolet detection; PMS was determined iodometrically.

The experimental details regarding the effects of typical water constituents, initial pH, and different water matrices on SMX degradation are shown in Text S3.

2.3 Analysis of reactive species formation

Reactive oxygen species (ROS) were identified using quenching experiments and electron paramagnetic resonance (EPR) spectroscopy. Tert-butanol (TBA), methanol (MeOH), furfuryl alcohol (FFA), p-benzoquinone (p-BQ), and potassium dichromate ($K_2Cr_2O_7$) were used as scavengers for $\cdot OH$, $SO_4^{\cdot-}$, 1O_2 , $O_2^{\cdot-}$, and electron transfer, respectively. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were used as spin-trapping agents in EPR measurements. Detailed procedures and calculations of ROS contributions are provided in Text S4.

2.4 Electrochemical analysis

Electrochemical measurements were performed in a three-electrode system with biochar-modified electrodes as working electrodes. The electrochemical double-layer capacitance was estimated from cyclic voltammetry (CV) curves recorded within ± 0.05 V around open-circuit potential (OCP) at scan rates of 30–60 mV s^{-1} , and OCP changes were monitored to evaluate interfacial electron transfer behavior during PMS activation (Gao et al. 2024; Xing et al. 2021). Detailed procedures and calculations are shown in Text S5.

2.5 Theoretical calculation

Details of theoretical calculations (Su et al. 2024) are shown in Text S6.

2.6 Statistical analysis

The results are represented as mean values $\pm$ standard deviation (SD), based on duplicate or triplicate experiments. One-way analysis of variance (ANOVA) and a post hoc *t*-test were used to evaluate statistical significance among different groups, with a significant difference defined as $p < 0.05$.

3 Results and discussions

3.1 Characterization of biochar

The flake-like nanostructures of BC, N-BC, B-BC, and N:B-0.25 are presented by SEM measurements in Fig. 1a–d, respectively. Notably, the material maintains its flake-like nanostructure even after modification with N and B. Further TEM observations confirm that N:B-0.25 features a flake-like nanostructure (Fig. 1e), which is in good agreement with the results acquired from

SEM measurements. Moreover, high-resolution TEM (HR-TEM) characterization of selected regions reveals distinct lattice fringes at the edge with an interplanar spacing of 3.35 Å, corresponding to the (002) crystal plane of the graphite structure (Fig. 1f). Collectively, these results demonstrate that the N and B co-doped biochar mainly retains a graphite-phase structure.

XRD results in Fig. 1g show that all samples exhibit broad humps at $\sim 26^\circ$ and $\sim 43^\circ$, assignable to the (002) and (100) reflections of carbon, indicating predominantly amorphous/low-graphitized biochar. Doping causes negligible peak shifts and no new crystalline phases, suggesting that the carbon framework is well retained, while subtle changes in the (002)/(100) features imply modulation of defects and structural ordering. Weak sharp peaks matching SiO_2 (PDF#79-1906) likely originate from trace silicate phases present in the sawdust precursor. Raman spectroscopy was further employed to investigate the lattice disorder under different N:B ratios (Fig. 1h). D band (1350 cm^{-1}) corresponds to the degree of disorder, while the G band (1585 cm^{-1}) is associated with the E_{2g} vibrational mode of sp^2 hybridized carbon. I_D/I_G ratio often indicates the degree of defects and graphitization in biochar (Dung et al. 2024). Compared to BC ($I_D/I_G=0.96$), single N-doped biochar introduces abundant intrinsic carbon defects ($I_D/I_G=1.33$) (Li et al. 2024). B doping disrupted the sp^2 carbon network, moderately increasing defects ($I_D/I_G=1.06$) (Annamalai and Shin 2023). N and B co-doped biochar generally exhibited higher I_D/I_G ratios (1.40–1.50) compared to biochar that was single doped with N or B, indicating greater defect sites (Pan et al. 2024). These defects enhance charge delocalization and provide additional adsorption and catalytic sites. Figure S1a demonstrates a strong linear correlation ($R_{16}^2=0.88$) between the N:B ratio and the I_D/I_G ratio except for N:B-4, indicating synergistic defect formation.

Figure S2a compares the XPS spectra that reveal the elemental compositions and surface functional groups in biochar with varying N:B ratios. A distinct N 1s peak (400.1 eV) confirmed successful N incorporation in the co-doped biochar. However, B 1s (191.1 eV) in B-doped biochar was extremely low and undetectable. This agrees with N_2 sorption results, as B primarily modifies pore structure rather than being readily incorporated into the carbon lattice (Güneş, 2024). Table S1 shows single doping with N reduced the C content compared to BC. In contrast, B-doping alone had a negligible impact. Co-doping further decreased C content while markedly increasing O and N contents, reflecting the synergistic effect of N and B co-doping. High-resolution XPS spectra were analyzed to identify active sites (Fig. S3). Figure S2b illustrates the variation of surface functional groups (at.%) with different N:B ratios. Most functional groups

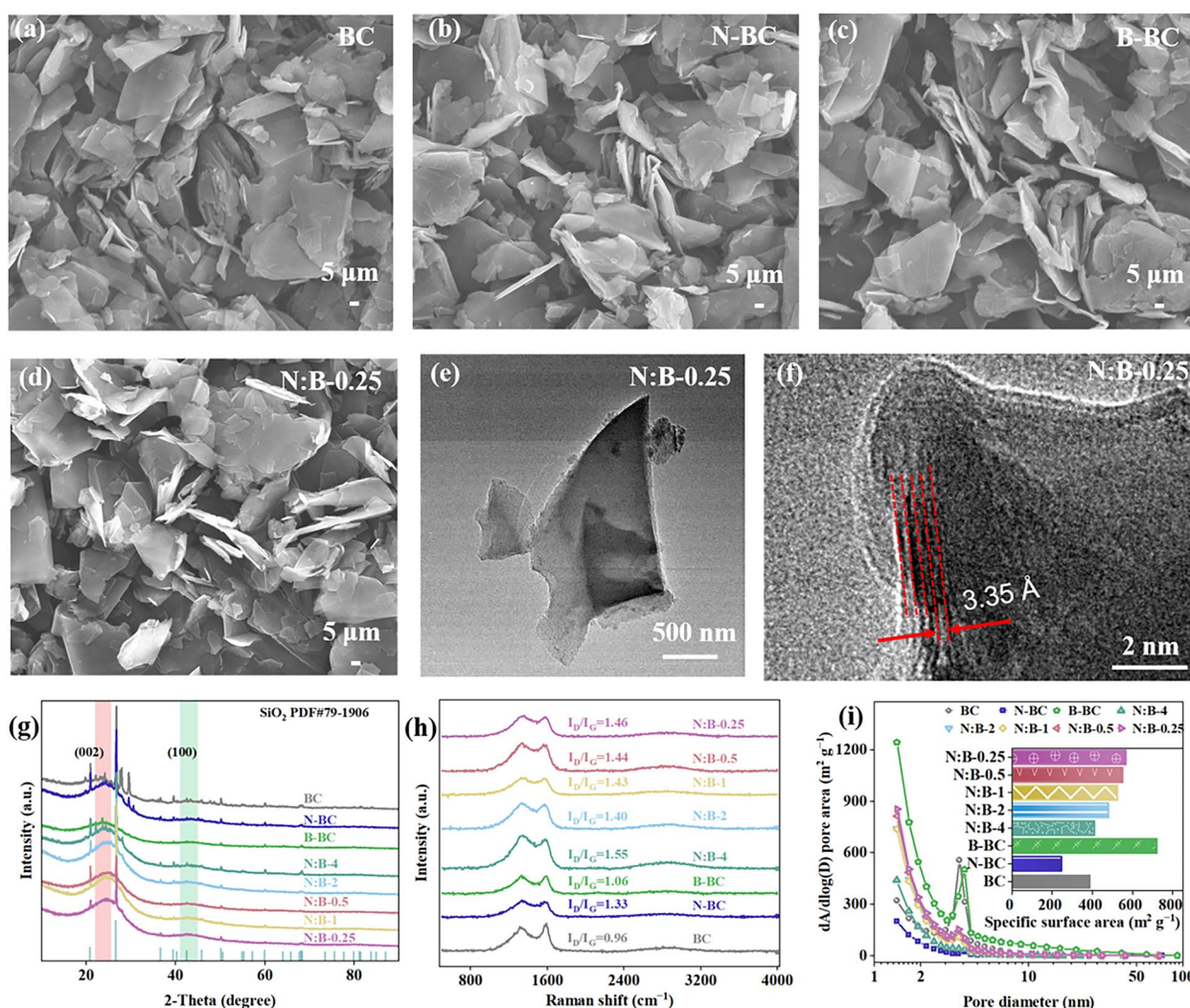


Fig. 1 SEM images of **a** BC, **b** N-BC, **c** B-BC, and **d** N:B-0.25; **e** TEM and **f** HR-TEM images of N:B-0.25; **g** XRD patterns; **h** Raman spectrum; **i** pore size distribution and specific surface areas for different biochar samples

showed no strong linear correlation with N:B ratio across 4–0.25, except for C=O (Table S2). Within N:B=4–1, weak linear correlations ($R^2 > 0.50$) were observed for C–C/C=C, C–OH, C=O, and C–O–C. At lower ratios (1–0.25), stronger linear correlations ($R^2 > 0.50$) emerged for oxygen- and nitrogen-containing groups, including pyridinic-, pyrrolic-, and graphitic-N, indicating enhanced synergistic effects (Fig. S4a).

Figure S5a presents that all the biochar displayed a Type IV curve with an H_4 hysteresis loop. This confirms that the predominant pore structure was mesopores. This mesoporous structure is due to the volatilization of urea during pyrolysis (Dou et al. 2022). Both N and B atoms, which are similar in size to carbon, diffuse into the carbon matrix, facilitating a synergistic pore-development

effect (Wang et al. 2024). Compared to BC, B doping significantly increased the porosity, as evidenced by the increased N_2 adsorption at relative pressures below 0.1 (Zhang et al. 2022). Figure 1i further confirms that B-BC also had more macropores. In contrast, the SSA of N-BC decreased to 244 m² g⁻¹, probably due to partial collapse of mesoporous channels caused by excessive N incorporation (Singh et al. 2024). However, co-doping enhances the SSA of the biochar. Furthermore, the pore volume (PV) of co-doped biochar except for N:B-4 increased with decreasing N:B ratio, while their average pore diameters (2.21–2.43 nm) were smaller than those of pristine and singly doped biochar (Table S3), confirming a synergistic pore-regulating effect. Such hierarchical pore structures provide abundant adsorption sites and

enhance mass transfer, favoring PMS activation and SMX degradation (Shao et al. 2025). The modification of pore structure by N and B doping is partly attributed to altered lignin decomposition during pyrolysis. B promotes radical formation, accelerating lignin breakdown and gas release, which favors micropore development and SSA enhancement (Zhang et al. 2022). BC was dominated by mesopores (73.5%) with limited micropores. After heteroatom doping, N-BC and B-BC exhibited a more balanced mesopore–micropore distribution, indicating promoted micropore formation (Fig. S5b). Co-doping tailored the pore architecture, where micropores supply adsorption sites and mesopores/macropores enhance mass transfer, jointly promoting catalytic performance (Dung et al. 2024).

Figure S6a–f shows the CV curves of the six biochar samples that were prepared as electrodes in electrochemical tests. The electrochemical double-layer capacity (C_{dl}) in Fig. S6g was calculated based on the scan rate and the current values (I_a and I_c), summarized in Table S4. For example, the ESCA values of N:B-0.25 and N:B-4 were 1.29 mF cm^{-2} and 0.66 mF cm^{-2} , respectively, which are greater than the value of a graphite plate. N:B-0.25 exhibited a normalized capacitance 1.97 times higher than that of N:B-4, suggesting a significantly higher density of active catalytic sites and thus a greater overall efficiency of the PMS oxidation process.

3.2 Catalytic activity assessment of biochar of different N:B ratios

To evaluate the catalytic performance of biochar co-doped with varying N:B ratios, both adsorption and PMS-mediated degradation of SMX were systematically investigated (Fig. 2). Figure 2a displays without PMS, BC and N-BC removed approximately 62% and 8% of SMX, respectively, indicating that N doping alone suppressed adsorption, likely by reducing hydrophobicity and π – π interactions. In contrast, B-BC showed almost total removal of SMX within 4 min, indicating enhanced adsorption affinity. Among the co-doped samples, N:B-0.25 showed a faster SMX decline than BC, implying a synergistic but composition-dependent interaction between N and B dopants. With PMS addition (Fig. 2b), most biochar showed markedly enhanced SMX removal compared with PMS alone, confirming that catalysts were essential for PMS activation. Notably, B-BC showed the highest SMX removal, which was mainly associated with its strong adsorption capacity (Fig. S7a). N and B co-doped biochar displayed much higher catalytic efficiencies than pristine or single N-doped biochar. Among the co-doped samples, N:B-0.25 showed balanced adsorption-assisted PMS activation. This suggests that tuning

the N:B precursor ratio can improve active-site chemistry and PMS activation efficiency.

Pseudo-first-order rate constants (k) further quantified the performance trends (Fig. 2c). Adsorption rate constants were generally below 0.10 min^{-1} , while catalytic rate increased up to 0.47 min^{-1} . PMS addition increased SMX removal rates by 114% for BC and by 248–529% for co-doped biochar. The greatest enhancements occurred at N:B ratios between 0.25 and 1. B-BC showed only modest improvement ($\approx 30.9\%$), indicating limited PMS activation. This suggests B alone is insufficient to generate effective electron-transfer or ROS-active sites.

Correlation analysis in Fig. 2d demonstrates distinct adsorption and catalytic processes. Adsorption rate constants exhibited a clear association with N:B ratio ($R^2=0.87$), indicating that surface chemical composition and porosity primarily control adsorption. In contrast, the catalytic rate constants followed a nonlinear inverse relationship with the N:B ratio, with lower N:B ratios showing faster PMS activation and higher SMX degradation rates. Together with the adsorption kinetics and PMS decomposition kinetics, this trend suggests a gradual change in the relative contributions of adsorption and PMS activation: at higher N:B ratios (4–1), PMS activation is dominated by adsorption-assisted pathways, while at lower ratios (1–0.25), enhanced PMS decomposition indicates a greater contribution from catalytic activation.

PMS decomposition was further examined to clarify the catalytic mechanism (Fig. S7b–c). Co-doped biochar rapidly decomposed PMS, confirming strong activation ability. PMS decomposition followed a similar trend to SMX degradation (Fig. 2b); dual heteroatom doping greatly enhances PMS activation, thus promoting the generation of ROS. The kinetic constants derived from pseudo-first-order model fitting (Fig. S7d) revealed that the PMS decomposition rate ($k=0.41$ – 0.47 min^{-1} for N:B-0.25 to 1) closely matched the catalytic degradation rates of SMX. This tight correlation further supports that SMX degradation is primarily governed by the efficiency of PMS activation rather than direct adsorption. At low N:B ratios (≤ 1), the coexistence of electron-deficient B sites and electron-rich N functionalities facilitated electron transfer to PMS, thereby promoting rapid PMS activation. In contrast, excessive N doping at higher N:B ratios weakened PMS activation, resulting in slower decomposition kinetics. Overall, balanced N–B co-doping governs PMS activation efficiency and drives the shift from adsorption- to catalysis-controlled kinetics.

3.3 Reactive species generation of biochar of different N:B ratios

Quenching experiments were performed to elucidate the ROS involved in PMS activation (Fig. 2e). The

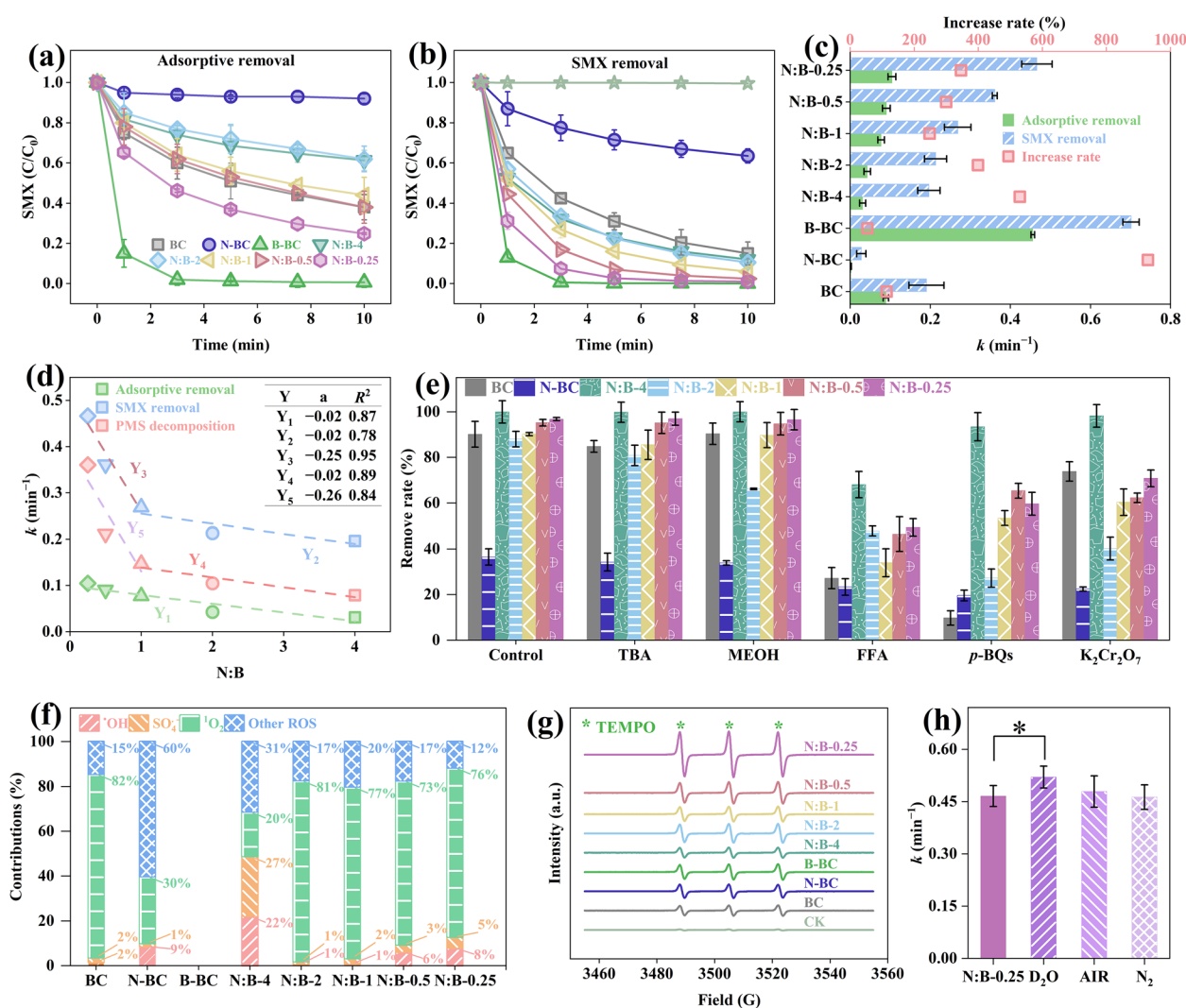


Fig. 2 **a** SMX adsorptive removal in pure adsorption systems; **b** SMX removal in catalytic systems with PMS; **c** Pseudo-first-order rate constants (k) and corresponding increase rate; **d** Correlation between N:B ratio and k for SMX adsorptive removal, PMS decomposition, and SMX removal; **e** ROS quenching in different media ([TBA] = [MeOH] = [FFA] = 100 mM; [p-BQ] = [$K_2Cr_2O_7$] = 10 mM); **f** Quantitative contributions of $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and $^1\text{O}_2$ for different biochar samples; **g** EPR spectra of TEMP- $^1\text{O}_2$ adducts; **h** k for SMX remove in N:B-0.25/PMS systems under D_2O , air, and N_2 atmospheres

presence of excess TBA reduced SMX removal by 0.01–8.17%, and the excess MeOH caused only marginal reduction of SMX removal (0.01–1.31%, except for N:B-4), indicating that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were not the dominant reactive species. In contrast, the introduction of FFA markedly suppressed SMX degradation (removal decreased by 36.13–69.82%), underscoring the crucial role of $^1\text{O}_2$. The addition of $K_2Cr_2O_7$ also suppressed SMX removal (18.13–54.34%), indicating that electron transfer from the catalyst is a key step in the activation process. Similarly, quenching $\text{O}_2^{\cdot-}$ with p-BQ reduced SEM removal by 31.32–89.16%, suggesting that superoxide radicals also contributed significantly.

Quantitative analysis of ROS contributions revealed that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ contributed only 1–8% and 1–5%, respectively, whereas $^1\text{O}_2$ dominated the process, accounting for 73–82% of SMX degradation (Fig. 2f). These results clearly demonstrate that $^1\text{O}_2$ was the predominant species driving PMS activation and SMX degradation in pristine BC and N and B co-doped biochar (except for N:B-4), with other ROS providing supplementary contributions. In the N:B-4/PMS system, $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ accounted for 22% and 27%, respectively, while in nonradical pathways, $^1\text{O}_2$ accounted for 20%.

Given its superior activity, N:B-0.25 was selected for EPR analysis, where no DMPO- $\cdot\text{OH}$ and

DMPO- $\text{SO}_4^{\bullet-}$ signals were detected (Fig. S8a). Instead, a heptet signal attributed to 5,5-dimethylpyrroline-N-oxide (DMPOX) was observed, commonly associated with rapid conversion of unstable DMPO- $\text{SO}_4^{\bullet-}$ adducts or oxidation by $^1\text{O}_2$ (Dou et al. 2022). Clear triplet signals of TEMP- $^1\text{O}_2$ were detected, with N:B-0.25 showing the strongest intensity, confirming $^1\text{O}_2$ generation (Fig. 2g). Replacement of H_2O with D_2O , which prolongs the lifetime of $^1\text{O}_2$ by ~15-fold (Qi et al. 2025), led to a significant increase in the degradation rate constant, further substantiating the key role of $^1\text{O}_2$ (Fig. 2h). Only the signal of DMPOX was detected, while the characteristic signal of the DMPO- $\text{O}_2^{\bullet-}$ adduct was absent (Fig. S8b). Furthermore, additional tests under N_2 - and air-saturated conditions showed no significant difference in SMX degradation, suggesting that dissolved oxygen had a negligible contribution to $\text{O}_2^{\bullet-}$ formation. Collectively, the quenching, EPR, and D_2O isotope experiments consistently demonstrate that $^1\text{O}_2$ is the principal oxidant, while $\text{O}_2^{\bullet-}$ acts only as a transient intermediate, with electron transfer between PMS and the catalyst surface playing a key initiating role.

OCP measurements evaluated interfacial electron transfer behavior after PMS and SMX addition (Fig. S9). The potential increase followed the order SM-CK $\approx$ N:B-4 > N:B-2 > N:B-1 > N:B-0.5 $\approx$ N:B-0.25 after PMS addition, while SMX addition caused negligible changes, indicating indirect oxidation via reactive intermediates. Low N:B ratios (≤ 1) showed stable potential increases, suggesting balanced electron-donating and electron-deficient sites that enable sustained electron transfer and favor nonradical $^1\text{O}_2$ generation, in agreement with kinetic and EPR results.

3.4 Mechanisms of N:B ratio on the SMX degradation

The enhanced SMX degradation performance of N and B co-doped biochar arises from the synergistic modulation of their surface electronic structure, pore morphology, and defect chemistry. Nitrogen doping introduces electron-rich sites that facilitate charge transfer to PMS, while boron doping contributes electron-deficient centers that promote PMS adsorption and activation. At moderate to low N:B ratios (≤ 1), these dual effects generate abundant active sites that serve as efficient catalytic centers for PMS activation and $^1\text{O}_2$ generation. The non-linear dependence of reaction rate constants on the N:B ratio (Fig. 2d) indicates a mechanistic shift from adsorption-dominated to electron-transfer-dominated oxidation. To further elucidate how N:B co-doping governs these processes, the following subsections investigate three intrinsic factors: (1) the evolution of pore structure, which influences mass transfer and site accessibility; (2) the modification of surface functional groups, which

determines the type and density of reactive sites; and (3) the development of defect structures, which regulates charge distribution and electron mobility in the catalytic system.

3.4.1 Changes of pore structures and correlation with adsorption/degradation kinetics

Figure 3a indicates the N:B ratio exhibited a strong negative linear correlation with SSA ($R_6^2=0.99$) and PV ($R_7^2=0.94$). In contrast, the PD showed no significant correlation with the N:B ratio ($R_{s1}^2=0.18$, Fig. 3b). These results indicate that SSA and PV are the primary affected material properties when changing the N:B ratios in biochar synthesis. These two properties were further associated with the adsorption and degradation reaction kinetics, as shown in Fig. 3c,d. For example, the adsorption rate constants were strongly correlated with SSA ($R_8^2=0.92$), suggesting that a larger SSA provided more accessible adsorption sites. Similarly, when SSA increased from 408.80 to 523.51 $\text{m}^2 \text{g}^{-1}$, the degradation rate constants followed a similar trend as adsorption rate constants. This suggests that SMX removal was mainly influenced by adsorption-related properties within this SSA range. At higher SSA values, the rate constants for PMS activation and SMX degradation increased more rapidly than the adsorption rate constants, implying that pore development may further improve PMS accessibility and expose additional catalytic sites (Fig. 3c). Similarly, PV showed an apparent positive association with the rate constants (Fig. 3d), suggesting that enlarged pore volume may facilitate SMX diffusion and PMS transport within the porous framework. (Fig. 3d). Overall, the correlation analysis suggests that SSA and PV are important textural factors affecting both SMX adsorption and PMS activation, likely by improving site accessibility and mass transfer within the porous structure (Wang et al. 2024).

3.4.2 Effects of surface functional groups and defects on the SMX degradation

Since the overall fitting between surface functional groups and rate constants was weak (Table S2), segmented linear fitting was further applied, and the results are shown in Fig. S4b. (i) At lower N:B ratios (1–0.25), C–C/C=C, whereas C–OH at higher ratios (4–1) were more active. Both C–C/C=C and C–OH acted as electron donors for the generation of $\text{SO}_4^{\bullet-}/^{\bullet}\text{OH}$ (Dai et al. 2024); C–C/C=C predominates at lower N:B ratios (1–0.25), while C–OH is more active at higher N:B ratios (4–1). (ii) C=O and C–O–C contents were strongly correlated with adsorption rates at higher N:B ratios (4–1), suggesting their primary role in modulating adsorption-driven SMX removal. Within this range, the C=O content reached its maximum at N:B-1. Notably, as C=O

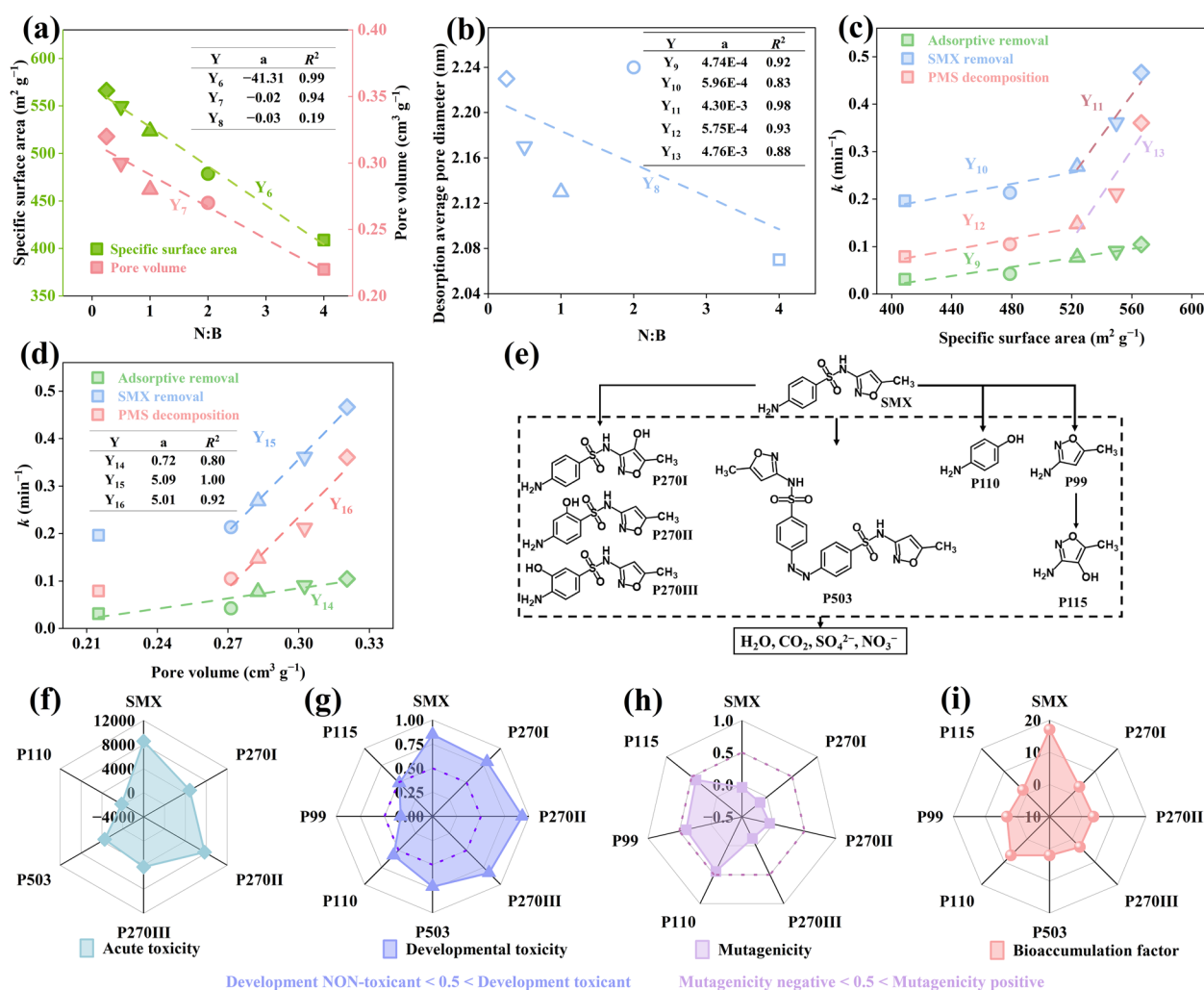


Fig. 3 **a** Correlation between N:B ratio and SSA and PV; **b** Average pore diameter at different N:B ratios; **c** Descriptive relationships between SSA and rate constants for SMX adsorptive removal, PMS decomposition, and SMX removal; **d** Descriptive relationships between PV and rate constants for SMX adsorptive removal, PMS decomposition, and SMX removal; **e** Proposed decomposition pathways of SMX in the N:B-0.25/PMS system; **f** Acute toxicity; **g** Developmental toxicity; **h** Mutagenicity; **i** Bioaccumulation factor of SMX and its by-products in the N:B-0.25/PMS system, predicted using the Toxicity Estimation Software Tool (T.E.S.T.)

increased, the enhancement in catalytic rate constants was much greater than that of adsorption (over 6.24-fold), suggesting that ketonic C=O not only participates in adsorption but also acts as a crucial active site for ¹O₂ generation during PMS activation (Chen et al. 2023). (iii) graphitic N exhibited a linear correlation with adsorption constants at lower N:B ratios (1–0.25), while its impact on PMS activation was disproportionately amplified (>6-fold), confirming graphitic N facilitated the formation of electron-rich domains and strengthened interactions with PMS, thereby driving ¹O₂ generation (Yang et al. 2022).

A positive correlation between I_D/I_G and SSA or PV was observed (Fig. S1b), suggesting that co-doping

simultaneously promotes porosity and defect density. Figure S1c shows the relationship between I_D/I_G and reaction kinetics: the adsorption rate constants increased proportionally with the I_D/I_G ratio ($R_{17}^2=0.93$) or the defect density. Moreover, the I_D/I_G ratio demonstrated a strong positive correlation with the catalytic degradation rate constant ($R_{18}^2=0.81$). At higher SSA (>523 m² g⁻¹), defect sites are likely to play a more pronounced role in governing PMS decomposition due to the enhanced ¹O₂ generation (Meng et al. 2023). For example, Fig. S9 confirms the enhanced electrons transfer between potential defects on N:B-0.25 biochar and PMS, promoting the generation of peroxymonosulfate radicals (SO₅^{•-}), which are further oxidized to produce ¹O₂ (Feng et al. 2023;

Wang et al. 2022). Conversely, excessive N:B ratios (e.g., N:B-4) led to overdeveloped defects, which disrupted the π -conjugated network, impaired electrical conductivity, and reduced catalytic performance, shifting SMX removal to be primarily limited by adsorption rather than catalysis (Yao et al. 2024). This aligns with the ROS contribution analysis, where $^1\text{O}_2$ accounted for only 20% in the N:B-4/PMS system.

3.4.3 Proposed degradation pathways of SMX in the N:B-0.25/PMS system

Figure 3e shows the degradation process of SMX in this system. HPLC-QTOF-MS analysis confirmed some intermediate product generation such as $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_4\text{S}$, $\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_6\text{S}_2$, $\text{C}_6\text{H}_7\text{NO}$, $\text{C}_4\text{H}_6\text{N}_2\text{O}$, and $\text{C}_4\text{H}_6\text{N}_2\text{O}_2$ (Table S5). This suggests that electrophilic substitution on the aromatic ring yielded the ortho-hydroxylated derivative P270, a degradation process facilitated by the synergistic effect of the electron-donating amine group ($-\text{NH}_2$) and the electron-withdrawing sulfonamide group ($-\text{SO}_2-\text{NH}-$). In addition, P270 could also originate from selective oxidation by $^1\text{O}_2$, either via aniline radical formation or through endoperoxide intermediates, highlighting hydroxylation of the benzene ring as a crucial step in SMX transformation. Meanwhile, radical-induced intermolecular coupling of two SMX molecules generated a polymerization product P503 ($m/z=503$), indicating that transient radicals can trigger condensation prior to subsequent oxidative fragmentation. The polymerization product P503 ($m/z=503$) may be associated with secondary coupling of SMX-derived intermediates. Previous studies have reported that $^1\text{O}_2$ can selectively attack the $-\text{NH}_2$ group connected to the aromatic ring of SMX and promote the formation of dimer products (Sun et al. 2021).

Another degradation route involved cleavage of the S-C bond, leading to small-molecule products like P110 and P99. P99 was further oxidized through deep hydroxylation and unsaturated bond rupture to produce P115 ($m/z=115$), suggesting that desulfonation, hydroxylation, and bond scission are key processes driving SMX decomposition toward complete mineralization into CO_2 , H_2O , NO_3^- , and SO_4^{2-} .

SMX and its degradation products were assessed for toxicity using the Toxicity Estimation (T.E.S.T.) software (Table S6). Figure 3f shows that, except for P270II, the acute toxicity of most degradation products is lower than SMX, indicating a reduction in acute toxicity. Figure 3g reveals that P110, P99, and P115 exhibit lower developmental toxicity than SMX, while other products maintain similar or slightly higher toxicity. In terms of mutagenicity (Fig. 3h), all products, including SMX, are classified as “mutagenicity negative”, with values under 0.5. Figure 3i

demonstrates that the bioaccumulation potential of degradation products is generally reduced compared to SMX, suggesting a lower capacity for accumulation in organisms. These results collectively indicate that, while a few products may still pose developmental or acute toxicity risks, the overall toxicity of SMX is reduced after oxidation. The N:B-0.25/PMS system, as an effective degradation solution, significantly alleviates the toxicity of SMX and its products.

3.4.4 Theoretical calculations and PMS activation mechanism

Figure 4a displays the carbon K-edge X-ray absorption spectroscopy spectra of BC and B-BC samples. Compared with pristine BC, B-BC displays markedly diminished π and σ antibonding orbital intensities, a hallmark confirming that B doping efficiently triggers carbon defect formation in the BC matrix. Guided by these experimental observations, structural models were further constructed for DFT simulations. Specifically, BC was modeled as a pristine carbon structure (Fig. 4b), B-BC was represented by a defective carbon structure with carbon vacancies (Fig. 4c), and N:B-0.25 was constructed by introducing graphitic N into the defective carbon framework (Fig. 4d).

PMS features three predominant oxygen sites, which are designated as O1 (Fig. 4e), O2 (Fig. 4i), and O3 (Fig. 4m) for the sake of clarity. DFT calculations were performed to elucidate the adsorption characteristics of BC, B-BC, and N:B-0.25 at these three distinct oxygen sites of PMS (Fig. 4f–h, j–l, and n–p). Our computational findings reveal that, among the three oxygen sites, O1 (Fig. 4f–h) serves as a reaction-relevant adsorption configuration: it enables stable adsorption while retaining high structural stability, and PMS adsorbed through this site readily undergoes deprotonation to form $\text{SO}_5^{\cdot-}$. Notably, with respect to the O3 site, the N:B-0.25 delivers the most favorable adsorption energy (-2.060 eV) compared to BC and B-BC (Fig. 4n–p), indicating its stronger affinity toward PMS.

The favorable adsorption of PMS on the catalyst surface may provide the prerequisite for subsequent surface-mediated activation pathways involving defect-related carbon sites and graphitic N-associated sites. Accordingly, B doping in N:B-0.25 serves as an effective inducer of defect formation, and N presumably plays a crucial role in fine-tuning the electronic configuration of carbon species located at these defect sites. As evidenced by Bader charge analysis and charge density difference calculations (Fig. 4q,r), N:B-0.25 brings about a concurrent decrease in the steric hindrance effect and electron density of the carbon atoms at defect sites, relative to those in B-modified defective carbon without N

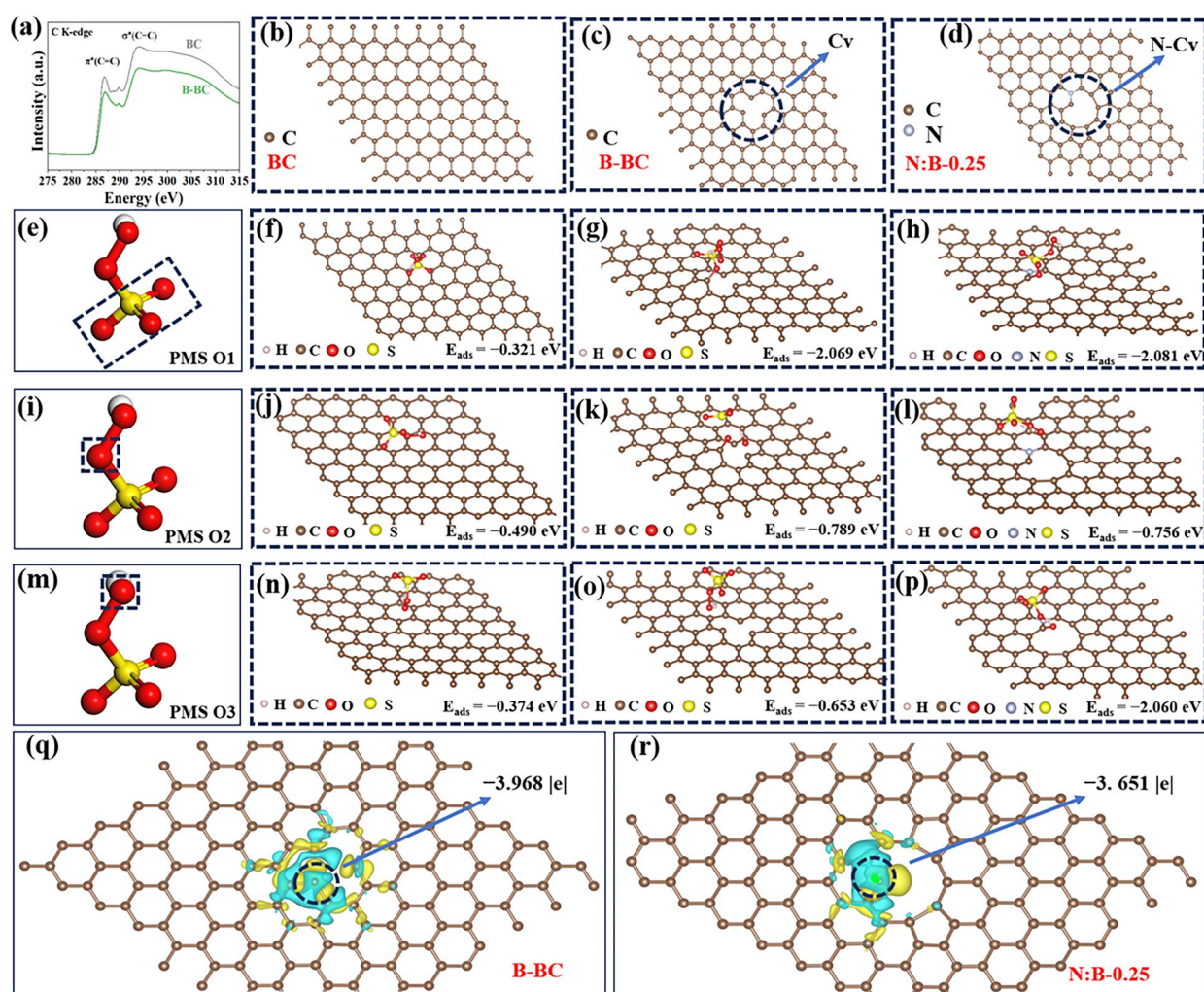


Fig. 4 a Carbon K-edge sXAS of BC and B-BC; Structural models of b BC, c B-BC, and d N:B-0.25; e O1 site of PMS; adsorption configurations of PMS at the O1 site on f BC, g B-BC, and h N:B-0.25; i O2 site of PMS; adsorption configurations of the O2 adsorption site on j BC, k B-BC, and l N:B-0.25; m O3 site of PMS; adsorption configurations of the O3 adsorption site on n BC, o B-BC, and p N:B-0.25; Bader charge analysis and charge density difference calculations of q B-BC and r N:B-0.25

doping. Such a change consequently improves the PMS adsorption capability.

Collectively, the experimental and theoretical results indicate that 1O_2 formation in the N:B-0.25/PMS system is likely governed by multiple PMS activation routes within coupled surface-mediated pathways. Quenching experiments, TEMP-EPR spectra, and D_2O enhancement confirm the dominant role of 1O_2 , whereas OCP responses indicate the involvement of interfacial electron transfer during PMS activation. In this process, persulfate-related anion radicals, especially $SO_5^{\bullet-}$, may be generated on defect-rich sites and further undergo self-reaction to produce 1O_2 . In

parallel, PMS may undergo surface-mediated electron transfer, leading to its self-decomposition and subsequent 1O_2 generation (Fang et al. 2023; Qi et al. 2025). Specifically, defect sites may facilitate PMS activation by promoting O–H bond dissociation and $SO_5^{\bullet-}$ formation, followed by $SO_5^{\bullet-}$ self-reaction to produce 1O_2 (Liu et al. 2024). Meanwhile, graphitic N is considered a highly active N configuration because its electron-withdrawing effect induces electron-deficient carbon sites adjacent to N atoms, thereby facilitating PMS adsorption/activation and promoting $SO_5^{\bullet-}$ -mediated 1O_2 generation (Tang et al. 2024). By comparison, C=O-related pathways, including direct PMS interaction and nucleophilic addition/epoxy-like intermediate

formation, may become more relevant to $^1\text{O}_2$ generation (Chen et al. 2023) at higher N:B ratios (>1).

Overall, Sections 3.4.1 to 3.4.4 reveal that N:B co-doping enhances PMS activation through the coupled regulation of pore accessibility, surface functional groups, and defect density. These synergistic effects explain the optimized catalytic performance of N:B-0.25 and the adsorption- to catalysis-dominated trend with varying N:B ratios. Accordingly, a plausible overall mechanism for PMS activation and SMX degradation over N,B co-doped biochar is proposed in Fig. 5.

3.5 Assessment of SMX degradation in complex water matrices using the N:B-0.25/PMS system

Natural water matrices typically contain inorganic anions (10 mM) and natural organic matter, which can affect or even inhibit PMS activation and SMX degradation (Wang et al. 2024). A series of degradation experiments were undertaken in the context of treating realistic water to assess the robustness of the N:B-0.25/PMS system. These investigations were carried out in the presence of various salts, humic acid, and different pH levels. Figure 6a shows that SO_4^{2-} , Cl^- , and H_2PO_4^- exerted only slight effects—consistent with their ability to scavenge $^{\bullet}\text{OH}$ and $\text{SO}_4^{\bullet-}$ (Table S7)—whereas $\text{CO}_3^{2-}/\text{HCO}_3^-$ markedly suppressed SMX removal by deactivating PMS and promoting the formation of the less reactive $\text{CO}_3^{\bullet-}$. SMX degradation was most efficient under acidic–neutral conditions (pH 3–7) and declined in alkaline media (Fig. 6b), yet the N:B-0.25/PMS system maintained $>91.8\%$ efficiency across pH 3–9, demonstrating strong pH tolerance (details in Text S7). Figure 6c shows that a higher concentration from 5 mg L^{-1} progressively reduced SMX removal efficiency, because of two possible reasons: (1) competition for adsorption sites on the biochar surface, thereby limiting their ability to form reactive surface complexes, and (2) scavenging non-selective radicals (e.g., $^{\bullet}\text{OH}$ or $\text{SO}_4^{\bullet-}$),

which further suppresses oxidative pathways (Zhang et al. 2013). Reusability tests were further conducted to assess catalytic stability. Figure 6d shows that the degradation efficiency gradually declined with each reuse cycle. This decrease was probably caused by degradation intermediates accumulating on the catalyst surface and blocking active sites, thereby hindering PMS activation. A continuous-flow reactor was constructed by immobilizing biochar onto cotton (Fig. 6e). At a flow rate of 3 mL min^{-1} , the N:B-0.25/PMS system achieved $\sim 99.6\%$ SMX removal after 200 min of continuous operation. This result demonstrates that the catalyst maintained high activity under continuous flow conditions, further confirming its potential for practical wastewater treatment. Figure S10 demonstrates the SMX degradation performances in various water matrices. Compared with DI water, where SMX was rapidly degraded within 10 min, the degradation rates in other water matrices (e.g., drinking water, river water, and secondary effluent) were much slower, which is caused by the joint effects of competitive adsorption and radical quenching by background constituents. Nevertheless, the N:B-0.25/PMS system still maintained appreciable removal efficiencies ($>70\%$ within 20 min) in all real water samples.

4 Conclusions

This study demonstrates that biochar derived from waste sawdust can be effectively engineered through N and B co-doping to enhance peroxymonosulfate activation. Lowering the N:B ratio from 4 to 0.25 increased the SMX degradation rate constant by 2.35 times. At higher N:B ratios (4–1), SMX removal was mainly governed by adsorption-related properties, with catalytic activity closely associated with surface area and pore structure. In contrast, at lower N:B ratios (1–0.25), catalytic rates increased markedly, indicating a transition to catalysis-dominated degradation. Structural analyses

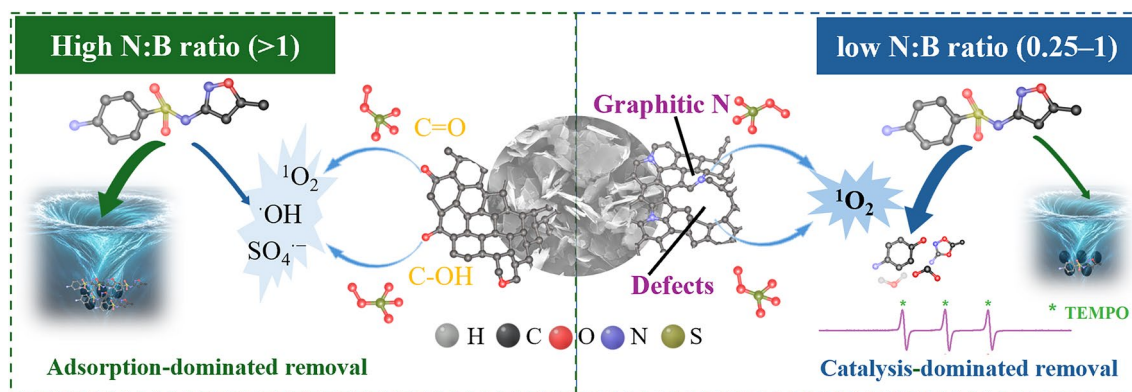


Fig. 5 Proposed mechanisms of SMX removal in the N/B co-doped biochar/PMS system

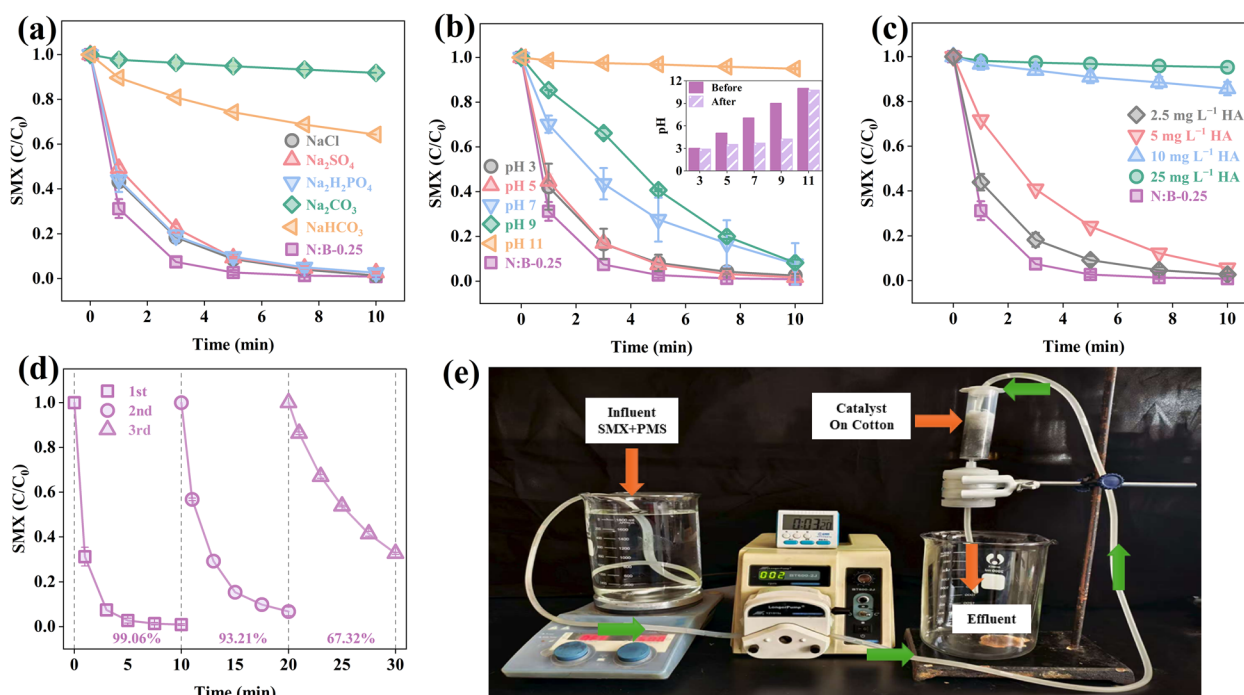


Fig. 6 Effects of **a** different anions; **b** initial solution pH; **c** HA on the degradation of SMX in the N:B-0.25/PMS system; **d** reusability experiments in the N:B-0.25/PMS system. Conditions: [biochar] = 0.5 g L⁻¹, [PMS]₀ = 0.5 mM, [anion: 10 mM CO₃²⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, Cl⁻, and H₂PO₄⁻]₀ = 10 mM, [HA]₀ = 2.5, 5, 10, 25 mg L⁻¹, pH = 3.69 and [SMX] = 10 mM

revealed that decreasing the N:B ratio increased defect density and graphitic N content, which facilitated electron transfer and promoted ¹O₂ generation. Consistently, DFT calculations revealed that defect-rich N,B co-doped sites strengthen PMS adsorption and favor deprotonation toward SO₅^{•-} formation, thereby promoting the nonradical ¹O₂ pathway. Overall, these findings highlight the critical role of compositional tuning in regulating adsorption–catalysis balance and provide a practical strategy for designing efficient biochar-based catalysts from agricultural wastes for water purification.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s42773-026-00647-3>.

Supplementary material 1.

Acknowledgements

We gratefully acknowledge Professor Wen Liu and Dr. Ruohan Zhang for generously providing access to the instruments used in this study. Support for synchrotron analysis from the National Synchrotron Radiation Laboratory (NSRL) in Hefei is gratefully acknowledged. Support for DFT calculations from the High-Performance Computing Platform of Peking University is also gratefully acknowledged. This study was funded by National Key Research

and Development Program (2023YFC3207701), the Agricultural Science and Technology Innovation Program of China (CAAS-CFSGCLCA-IEDA-202302).

Author contributions

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Funding

This study was funded by the National Key Research and Development Program (2023YFC3207701), the National Natural Science Foundation (425307019), the National Support Plans for the Top of the Notch Youth Talents, the Agricultural Science and Technology Innovation Program of China (CAAS-CFSGCLCA-IEDA-202302), and the Central Public-interest Scientific Institution Basal Research Fund (No. Y2025YC30).

Data availability

Data will be made available on reasonable request.

Declarations

Competing interests

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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Received: 1 April 2026 Revised: 2 June 2026 Accepted: 1 July 2026

Published online: 30 September 2026

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