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Unveiling the synergistic effect of internal Fe single atoms and introduced Fe₃C in Enteromorpha derived biochar with enhanced peroxymonosulfate activation property towards nitenpyram removal

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Abstract

This work demonstrated that Enteromorpha biochar with introduced iron (SFB900-3) could activate peroxymonosulfate (PMS) efficiently for NTP remediation. It removed 83.9%–95.1% of NTP in 60 min under a wide pH range from 3.15 to 8.95. Density functional theory (DFT) calculations revealed the synergistic relationship between internal Fe single atoms and introduced Fe compounds—Fe₃C. The adsorption capacity of SFB900-3 for persulfate improved from −0.953 eV to −4.214 eV, and the Bader charge analysis showed that Fe atoms as active sites (0.658 e) enhanced the adsorption capacity more than carbon (0.050 e). Moreover, the energy barrier for PMS dissociation reduced from 0.072 eV to −5.372 eV due to the longer length of O–O bond under the synergistic effect of Fe single atom and Fe₃C which increased from 1.467 Å to 3.890 Å. The quenching experiment confirmed that ¹O₂ was the main active substance in NTP degradation and its contribution rate was 88.2%, which was further verified by EPR detection. The effect factor experiments proved that the SFB900-3/PMS system had stable and efficient activity for NTP removal, which remained at 73.6% removal rate after three rounds of tests. This work provided novel guidance for constructing efficient and stable biochar-based materials for organic pollutant remediation.

Highlights

- Improved PMS activation by synergy of single Fe atom and Fe₃C was proposed.
- Variations in electron distribution and energy barrier enhance PMS activation
- The prepared SFB900 exhibited excellent stability.
- The degradation pathways of nitenpyram were explained in detail.

Keywords Biochar, Fe-single-atom, Fe₃C, Nitenpyram, Degradation

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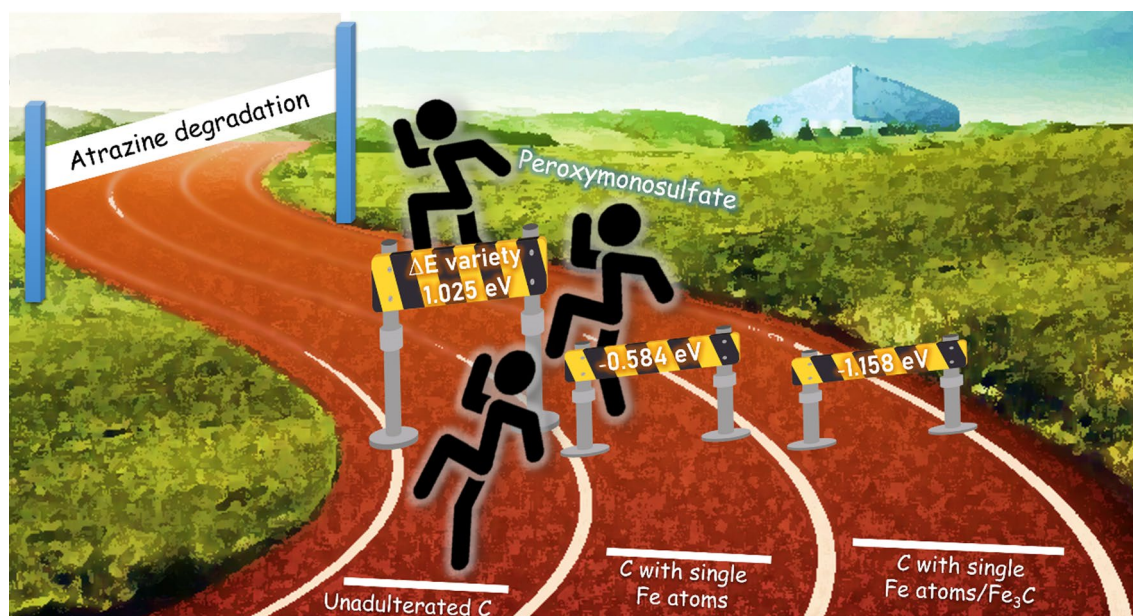
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Graphical Abstract



1 Introduction

Nitenpyram (NTP) is a neonicotinoid pesticide that has been promoted to replace highly toxic organophosphorus pesticides. In recent years, some reports have shown that NTP has frequently appeared in tea (Li et al. 2020b). Not only that, NTP has been detected in infants (2.8% of children had a hazard index between 0.1 and 1.0) and adolescents ($1.79 \mu\text{g g}^{-1}$ creatinine) (Wang et al. 2020b; Zhou et al. 2021b), and tap water and fresh vegetables are presumed to be potential sources. Although the researchers suggest it is not very harmful to human health, NTP is highly toxic to bees, an agriculturally important organism. Moreover, it is highly toxic to silkworms, which is significant in biology and possesses great economic benefits for agriculture (Yu et al. 2016; Zhu et al. 2020). Therefore, the residual harm of NTP in the water environment should not be underestimated.

Up to date, the NTP removal methods mainly include low-temperature plasma process, microbial process, and photocatalytic degradation (Li et al. 2013; Pang et al. 2020; Tang et al. 2020c), however, these methods possess many disadvantages such as high energy consumption, limited reaction conditions and low efficiency. In this case, the advanced oxidation process based on persulfate activation (PMS-AOPs) has

attracted the attention of researchers (Cai et al. 2022). PMS-AOPs can remove refractory organic pollutants with high efficiency and easy operation by the highly reactive oxygen species (ROS) like hydroxyl radical ($\cdot\text{OH}$, 1.8–2.7 V) and sulfate radical ($\text{SO}_4^{\cdot-}$, 2.5–3.1 V) (Wang et al. 2020a). During the process of PMS-AOPs on organic pollutants removal, the core issue is how to improve the activation efficiency of PMS. Therefore, various transition metal-based catalysts have been researched for the activation of PMS, especially iron, a common, reactive and inexpensive element (Han et al. 2020). However, there have been disadvantages of metal ion leaching and unsatisfactory catalytic performance in a long term (Pan et al. 2021). Hence how to improve the anchor and catalytic efficiency of iron is the current hot pot.

Fortunately, the emergence of single-atom catalysts (SACs) can solve the problem of the low activation efficiency of PMS. Compared with mononuclear metal compounds and metal nanoparticles (NPs), SACs own extraordinary catalytic activity, selectivity and stability, including oxidation and water–gas conversion (Li et al. 2021c). So far, abundant work of single-Fe-atoms on PMS activation for organic pollutants degradation have been reported (Wang et al. 2021; Yang et al. 2022; Zhang et al. 2022). However, the introduction of the single iron atom

into the material is difficult because of the extremely high surface energy of isolated atoms and the strong tendency for atoms to aggregate (Cui et al. 2021). The common strategy is to use N defects to anchor the dispersed Fe atoms and construct a catalyst containing transition iron–nitrogen coordination in a metal–nitrogen–carbon (Fe–N–C) framework, which is usually accompanied by the consumption of nitrogen precursors (Sun et al. 2020). Moreover, when using this method in biochar, the iron compounds will concomitantly generate with the introduction of Fe atoms, especially the iron carbide (Fe_3C) due to the high temperature pyrolysis and anoxic atmosphere. However, most studies focus on the activation of PMS by the interaction between single-atom catalysis or the transition metal compounds and biochar (Gao et al. 2021; Pang et al. 2021; Zhang et al. 2022). Some works are concerned with the interaction of Fe with N doping (Yao et al. 2022), or with the interaction of different sizes of iron, such as the comparison of nanoscale Fe with single-atom Fe (Li et al. 2021c). But those works neglect the synergistic activation of PMS by single-atom and compound. Especially in biochar, it is inevitable that some Fe-rich biomass produces internal Fe single atoms during high temperature pyrolysis (Peng et al. 2021). In this case, the introduced Fe compound will interact with the internal Fe single atoms. However, the synergistic mechanism of iron single atoms and iron compounds on enhanced PMS activation is still confusing and needs further investigation. In this case, in situ N-rich Enteromorpha (EP) was selected (Xiong et al. 2021b). The abundant inner N of EP possesses huge potential for N defect formation, thereby easily forming a Fe–N–C framework with the introduced iron during the pyrolysis process to achieve the anchoring of Fe single atoms (Peng et al. 2021). Besides, EP is one of the causes of red tides in the Yellow Sea, China (Qiu et al. 2020). Its impact on the local marine ecology and surrounding economy cannot be underestimated, so it has great significance to find a way for EP functionalization.

In this work, biochar loaded with single Fe atoms and the iron compound was prepared and used for efficient PMS activation for NTP removal. The batch experiment showed that the synergy of Fe single atoms and their compounds greatly enhanced the performance of NTP removal. The removal ratio was raised from 53.6% to 89.5%. This is attributed to the fact that the internal Fe single atom increases the adsorption energy of the catalyst to the PMS and the tendency of electron transfer to the PMS, which is conducive to the PMS decomposition. Then, the combination of Fe_3C further intensifies the process. Free radical and non-radical pathways were explained in detail. Finally, the experiment of effecting factors verified the ability of the material in practical

application. This work proposed an in-depth insight into the synergistic mechanism of iron single atoms and iron compounds and a feasible scheme for the functional transformation and efficient utilization of EP.

2 Material and methods

2.1 Materials and chemicals

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), including NTP (purity > 96.5%), iron acetylacetonate ($\text{Fe}(\text{acac})_3$), Fe_3C , $\gamma\text{-Fe}_2\text{O}_3$, peroxydisulfate (PMS), tert-butyl alcohol (TBA), methanol (MeOH), furfuryl alcohol (FFA), and p-benzoquinone (p-BQ). Unless otherwise stated, all experiments in this work used ultrapure water (Eco-S15Q, Hitech Instruments Co. Ltd., Shanghai, China).

2.2 Catalyst preparation

Two grams of EP powder was dispersed in 50 mL ethanol, and then $\text{Fe}(\text{acac})_3$ was added. The mixed precursor was ultrasonicated for fully uniform for 5 min. Then it was transferred to a constant temperature water bath and stirred vigorously at 40 °C until ethanol was completely evaporated. After that, the prepared precursor was placed in a tube furnace, and heated to 900 °C at a rate of 5 °C·min^{−1} with a nitrogen atmosphere for 3 h. After cooling, it was taken out and washed 3 times with ultrapure water and ethanol, respectively. Then it was dried in an oven at 60 °C for 24 h. In the order of the amount of $\text{Fe}(\text{acac})_3$ added (0.019 g, 0.038 g, 0.076 g and 0.152 g), the obtained biochar was named as SFB900-1, SFB900-2, SFB900-3 and SFB900-4. For comparison, the blank biochar without $\text{Fe}(\text{acac})_3$ was prepared and named SFB900-0.

2.3 Characterization and analytical methods

The morphologies of all as-prepared materials were characterized by transmission electron microscope (TEM) using a Tecnai F20 (FEI, USA). XPS patterns were obtained using a K-Alpha spectrometer (Thermo Fisher Scientific, USA) equipped with monochromatic Al K α X-rays at 1486.6 eV. The Fourier transform infrared (FT-IR) spectra of the nanocomposites were obtained with a Nicolet iS10 spectrometer (Thermo Nicolet, USA) as KBr (mass ratio of 1:200) pellets. The crystal structures of the nanocomposites were analyzed by X-ray diffraction (XRD) (Bruker, Germany) with Cu K α radiation ($\lambda = 1.54$ nm) over a 2θ range of 10° to 80° at a scanning rate of approximately 10°·min^{−1}. The Raman spectra were analyzed using Raman spectroscopy (Thermo Fischer DXR, USA). A300 EMXplus-10/12 EPR spectrometer (Bruker, Germany) was 0.1 mol

L–15,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as a capture agent.

2.4 Catalysis experiments

The NTP removal by SFB900 on PMS activation was in a 25 °C constant temperature stirrer (160 r min⁻¹). The porous structure is expected to give SFB900 a superior adsorption capacity, which is not negligible for the overall catalytic performance. Therefore, in the SFB900/PMS/NTP system, the test experiment was divided into two parts: adsorption and degradation. In the first 30 min, the SFB900 (0.2 g L⁻¹) can adsorb NTP (40 mg L⁻¹) to reach equilibrium. Then, with PMS (0.5 g L⁻¹) added, SFB900 can activate PMS to degrade NTP within 60 min. Without other states, all experiments were performed at the initial pH = 5.87 without adjustment. The samples were extracted at 0.5 mL and filtered with a 0.22 µm filter membrane at selected intervals. Then, the collected sample was detected by high performance liquid chromatography (HPLC, Agilent 1100, USA). All control experiments without PMS and/or catalysts were performed under the same reaction conditions. In order to verify the reuse performance of the prepared materials, the used materials were collected and dried after being washed with water and ethanol. The cycle experiment was repeated for 3 rounds. All experiments were performed in duplicate or triplicate, and the average value was taken for analysis.

2.5 Computational details

The first-principles calculations based on DFT were carried out on the Vienna Ab initio Simulation Package (VASP) code, using the Perdew-Burke-Ernzerh function for the exchange–correlation potential. The interaction between ions and electrons was described by projector augmented wave pseudopotential. The cutoff energy was 400 eV for the valence electrons. For structure optimization, a vacuum space of 15 Å along the z-direction was used to avoid the periodic image interaction between neighboring slabs, and a 4 × 4 × 1 k-point Γ -centered mesh was used for the calculation. The energy criterion was 10⁻⁵ eV/atom for each step, and all atoms were fully relaxed until the force on each atom was less than 0.03 eV Å⁻¹. In this work, a 1 × 1 × 1 supercell of Fe₃C (0 3 1) binding with the functionalized graphene plane with a rectangular boundary (10.08 Å × 9.60 Å × 20.00 Å) was used as the substrate for the adsorption of PMS. All presented models were drawn by VESTA.

3 Results and discussion

3.1 Characterization

The morphology and elemental mapping of two typical biochar SFB900-0 and SFB900-3 are shown in Fig. 1,

which are the stand of pristine biochar and the best performance modified biochar, respectively. As shown in Fig. 1a, some pure iron clusters (dark dots) were exhibited on SFB900-0. Figure 1b further points out the lattice of the Fe clusters, which is referred to the high percentage of in situ Fe elements in EP. Therefore, without introduced Fe, the SFB900-0 still has Fe single atoms existing in the form of Fe–N–C. This result is in line with previous research (Peng et al. 2021), due to the EP possessing abundant iron and nitrogen elements. After being modified with Fe(acac)₃, more iron compounds were produced on SFB900-3 (the bigger dark dots in Fig. 1c). Furthermore, Fig. 1d indicates the lattice of the pure Fe cluster, Fe₂O₃ and Fe₃C on SFB900-3. This finding suggests that more iron compounds and carbide species were generated with the introduction of Fe(acac)₃. So there were both Fe single atoms and iron compounds on SFB900-3. Then, the HAADF-STEM image and corresponding elements mapping profiles for C, N and Fe in SFB900-0 and SFB900-3 are presented in Fig. 1e, f, respectively. Both figures exhibit the uniform distribution of C, N, and Fe in SFB900-0 and SFB900-3. Besides, the C and N elements possess approximate density. The abundant in situ N provides the possibility for the N defects to further generate the Fe–N–C in both pristine biochar and modified biochar (Xiong et al. 2021c; Xu et al. 2020). As for iron elements, they are distributed uniformly in SFB900-0, which is also consistent with previous work (Peng et al. 2021). Naturally, the percentage of Fe in SFB900-3 is much higher than in SFB900-0, which indicates the successful introduction of Fe. Therefore, abundant N defects and Fe elements ensure the possibility of the coexistence of Fe single atoms and iron compounds.

The BET results, porosity characterizations and nitrogen adsorption–desorption isotherms of all as-prepared catalysts are shown in Table 1 and Additional file 1: Fig. S1. Notably, the specific surface area (SSA) of all samples was small. It is maybe due to the collapse of porous structures at high temperature (900 °C). Besides, the SSA of the as-prepared material was significantly negatively correlated with the amount of Fe(acac)₃, indicating that the generated Fe-products blocked the porous structure of the biochar. The SEM images of all as-prepared catalysts intuitively exhibited this result (Additional file 1: Fig. S2). SFB900-0 possessed a smooth surface with few pores and hence the SSA was small. With the increasing of Fe(acac)₃ amounts, the iron compounds on the catalyst surface gradually increased leading to the pores being blocked. The total pore volume of all as-prepared samples in Additional file 1: Fig. S1a has confirmed this hypothesis. The initial volume is small, and becomes progressively smaller as Fe(acac)₃ increases. Then, the pore size analysis showed

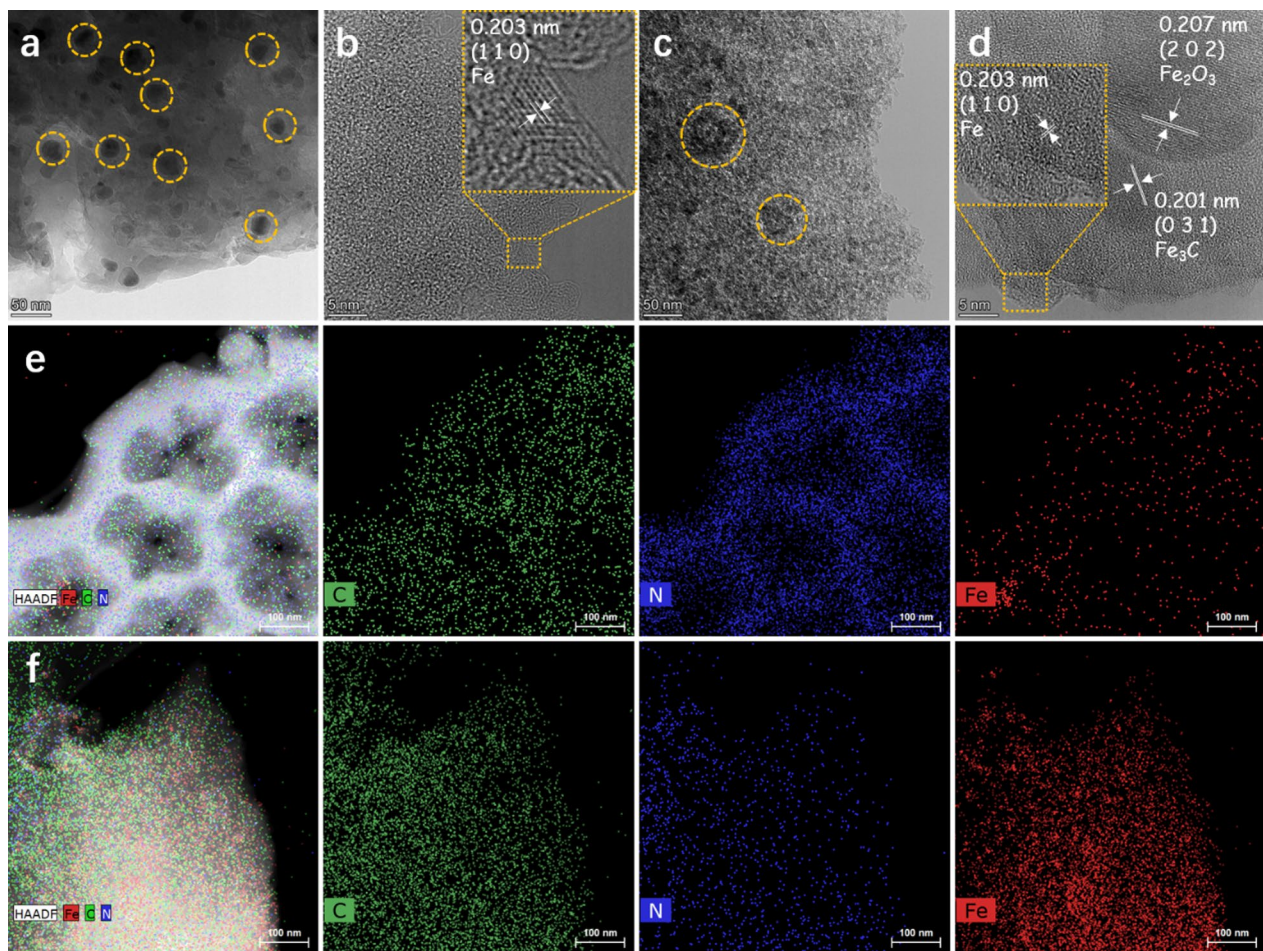


Fig. 1 TEM images of (a, b) SFB900-0 and (c, d) SFB900-3 samples at 50 nm and 5 nm. HAADF-STEM image and corresponding EDS mapping profiles for C, N and Fe in (e) SFB900-0 and (f) SFB900-3

Table 1 BET results and porosity characterizations of as-prepared materials

Materials	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{mic} ($\text{m}^2 \text{g}^{-1}$)	S_{mes}^* ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	V_{mic} ($\text{cm}^3 \text{g}^{-1}$)	Ave-pore radius (nm)
SFB900-0	27.1	14.6	12.5	0.022	0.006	3.16
SFB900-1	24.6	12.7	11.9	0.019	0.006	3.21
SFB900-2	18.5	11.4	7.1	0.015	0.005	2.85
SFB900-3	12.3	8.1	4.2	0.008	0.003	2.97
SFB900-4	10.7	6.6	4.1	0.007	0.003	3.08

* $S_{\text{mes}} = S_{\text{BET}} - S_{\text{mic}}$

that all samples had a similar porous structure with an average pore radius of 3.05 nm and a standard deviation of 0.15. This result can also obtain by pore size distribution images in Additional file 1: Fig. S1b–f. All these images exhibited a sharp peak at 2–4 nm, indicating the presence of abundant mesopores with smaller sizes inside those as-prepared catalysts. Moreover, the corresponding nitrogen adsorption–desorption curves

were consistent with type-IV isotherms, characteristic of mesoporous adsorption. This result is also consistent with the pore size analysis. Given the unsatisfactory porous structure in all samples, its excellent adsorption capacity for NTP may be related to the surface Fe-products.

XRD pattern in Fig. 2a further ensures the existence of iron compounds on SFB900-3. In fact, due to the

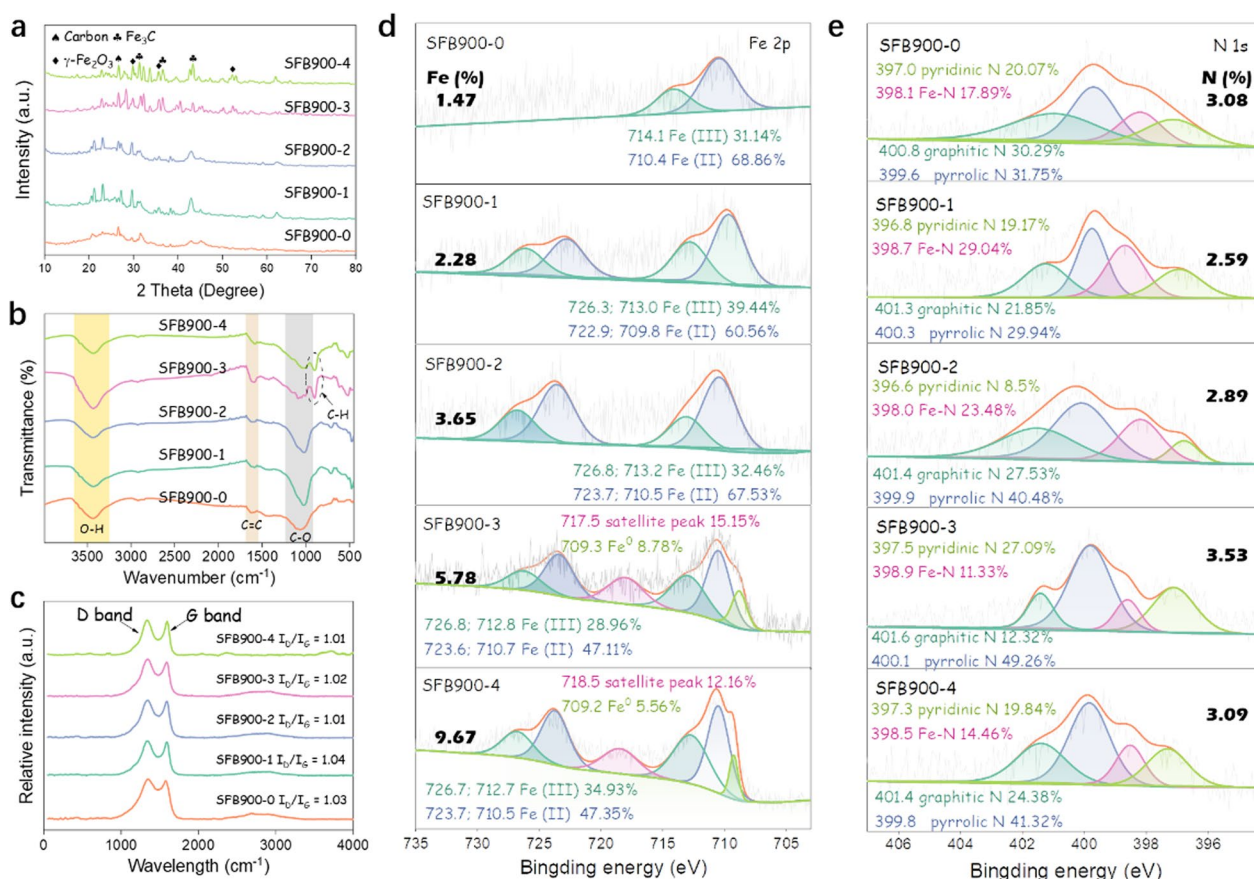


Fig. 2 (a) XRD pattern, (b) Raman spectrum and (c) FT-IR of all as-prepared materials. XPS high-resolution (d) Fe 2p and (e) N 1s of all as-prepared materials. (The next column refers to the total Fe or total N content)

introduction of Fe (SFB900-1), Fe_2O_3 and Fe_3C were generated in the material. As shown in Fig. 2a, all as-prepared samples had typical peaks of carbon at $2\theta = 27^\circ$, which indicates successful carbonization. Besides, except for SFB900-0, all samples exhibited typical peaks of Fe_2O_3 (JCPDS No. 39-1346) and Fe_3C (JCPDS No. 35-0772). Furthermore, it can be seen that the peaks of Fe_2O_3 and Fe_3C evolved sharper with the increase of introduced-Fe content. This result infers that the higher concentration of iron added during the preparation process, the better crystallinity of the Fe_2O_3 and Fe_3C in the as-prepared materials.

The D band and G band in the Raman spectrum reflect the disorder and defects in the carbon layer, and graphite structure in biochar, respectively (Fig. 2b). The D band and G band were observed in all as-prepared samples, indicating the presence of defects and graphite structures in them. The intensity ratio (I_D/I_G) was commonly used to evaluate the degree of defect for biochar (Xiong et al. 2021a). In this case, the I_D/I_G value of the five samples was almost no different. This finding indicates that the addition of $\text{Fe}(\text{acac})_3$ does not affect the defect state of EP

biochar and has little effect on the carbon skeleton structure. Namely, the introduction of iron does not affect the defect in pristine biochar. The defects in all samples presented few influences on their ability to activate persulfate for NTP removal. Additionally, the result of FT-IR exhibited a similar finding to Raman spectra, which eliminates the role of surface functional groups of those as-prepared catalysts in PMS activation. Figure 2c shows that all as-prepared samples possess similar surface functional groups, including the O–H bond and C=C bond (Shi et al. 2019; Wu et al. 2016). This result suggests that the introduction of iron had little influence on the surface functional groups in all samples. Although the peak of the C–O bond in SFB900-3 and SFB900-4 appeared split, which only indicates that the increase of introduced-Fe snatched the oxygen in biochar, so the part of the C–O bond split into the C–H bond (Li et al. 2019).

The XPS spectrum was provided to exhibit the chemical bonds of Fe 2p and N 1s in all as-prepared materials. In Fig. 2d, there are only two typical peaks in 714.1 eV and 710.4 eV in SFB900-0, which correspond to the Fe (III) and Fe (II), respectively (Lawrinenko et al. 2017; Yang

et al. 2019). With the increasing Fe content in SFB900, more peaks emerged in SFB900-1 and SFB900-2. This finding suggests that a variety of iron compound species are generated due to the externally introduced iron. Furthermore, there was even a typical Fe^0 peak and satellite peak in SFB900-3 and SFB900-4 because of the higher content of introduced Fe (Xiong et al. 2020a). The change in total Fe content in SFB900 intuitively showed this process. The total Fe content kept increasing attributed to the modification process, which also proved the iron was successfully loaded. On the contrary, the total N content did not change significantly in SFB900 (Fig. 2e). Because there was a shortage of introduction of external nitrogen. Besides, the weak volatility of total N content in materials may be attributed to the uneven distribution of in situ N.

As shown in Fig. 2e, all materials had four typical peaks in 400.8 eV, 399.6 eV, 398.1 eV and 397.0 eV with or without little fluctuation. Those four peaks are referred to the graphite N, pyrrolic N, Fe–N bond and pyridinic N, respectively. The appearance of the Fe–N bond proved the existence of Fe–N–C, as well as the existence of single Fe atoms (Li et al. 2016). Similarly, the volatility of Fe–N bond content may be the result of the irregular distribution of N defects. In fact, compared with other elements, the ratio of N content is very low (< 3.53%). So this volatility of Fe–N bond content is ignorable (0.40–0.75%). In other words, the content of iron compounds species played an important role in the synergy effect.

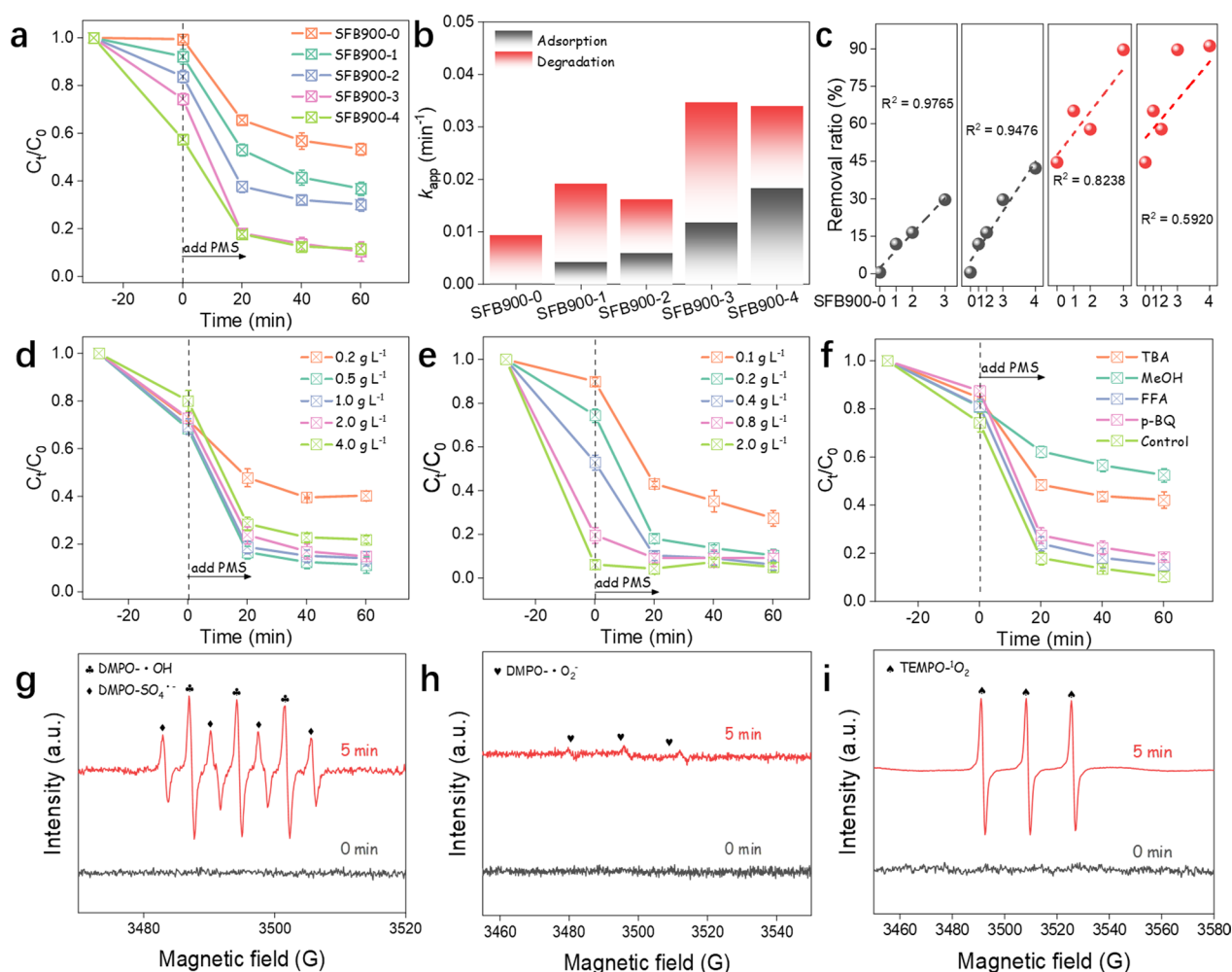


Fig. 3 a Adsorption and degradation performance of all as-prepared materials on NTP and (b) the related k_{app} . c Correlation analysis of iron content and adsorption/ degradation capacity of all as-prepared materials. The effect of (d) PMS dosage and (e) catalyst dosage on NTP removal. f Quenching experiment on NTP removal by prepared materials. EPR detection of (g) hydroxyl radical, sulfate radical, (h) superoxide radical and (i) singlet oxygen during the test of NTP removal. Conditions: [Biochar] = 0.2 g L⁻¹, [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25 °C, [initial pH] = 5.87, [TBA] = [MeOH] = 0.5 M, [FFA] = [p-BQ] = 0.1 M

3.2 Catalytic performance

NTP was selected as a target pollutant to evaluate the catalytic performance of all as-prepared materials for PMS activation. As shown in Fig. 3a, compared with non-modified SFB900-0, all iron-loaded materials showed a higher removal effect on NTP. In addition, the material with higher iron content possessed better catalytic ability. These results indicate that there is a certain synergistic effect between EP biochar and iron (Liu et al. 2021). According to the previous analysis, the defect and functional groups on catalysts present few differences. Besides, all as-prepared materials possessed similar content of a single Fe atom due to the approximative in situ N ratio. Therefore, this improvement may be attributed to the synergy of a single Fe atom captured by in situ N and abundant iron oxide species that were externally introduced. However, SFB900-4, the material with the highest iron content, had a similar removal ratio of NTP (90.1%) to SFB900-3 (89.5%). This result further confirms the synergy of the single iron atom and iron oxide species in modified catalysts and indicates that this synergy is related to the content of iron oxide species. Curiously, in the adsorption stage, the iron content in the materials showed a clear correlation with its adsorption capacity for NTP. This finding is consistent with BET analysis, the porous structure is poorer as the $\text{Fe}(\text{acac})_3$ increases, and hence the Fe products play a more important role. Furthermore, Fig. 3b exhibits the related apparent rate constant (k_{app}) of materials on NTP removal in the adsorption stages. The value of k_{app} increased with the higher iron content. However, the k_{app} of degradation rate showed a poor correlation with iron content. Moreover, Fig. 3c further reveals the relation of adsorption or degradation performance with iron content. In the adsorption step, the linear correlation coefficient (R^2) reached a very significant level ($n=3$, $R^2=0.9765>0.959$) and a significant level ($n=4$, $R^2=0.9476>0.878$) in different cases (Xiong et al. 2020b). This result indicates that the Fe-load greatly enhanced the adsorption capacity of SFB900 on NTP. In the degradation step, the linear correlation coefficient between the NTP degradation rate and loaded-Fe amount ($R^2=0.8238$) was much higher when the loaded-Fe amount was below (SFB900-3, 0.076 g). When the loaded-Fe amount further increased (SFB900-4, 0.152 g), the linear correlation coefficient value largely decreased ($R^2=0.5920$). Considering that the different SFB900 own a similar amount of internal single iron atom, while the higher introduced iron compounds (SFB900-4 compared to SFB900-3) cannot further improve the removal rate of NTP. This finding infers that the iron species possess a limited promotion effect on NTP removal by SFB900. Moreover, it indicates the potential synergistic effect of iron single atoms and iron species on NTP degradation.

To comprehensively consider the reaction efficiency and economic cost in practical applications, the dosage of PMS and material were studied. As shown in Fig. 3d, the SFB900-3/PMS system possessed the worst NTP removal rate (60.4%) when the PMS dosage was 0.2 g L^{-1} . While it raised to the highest when the PMS dosage reached 0.5 g L^{-1} . Besides, from the k_{app} shown in Additional file 1: Fig. S3, the rate is also the highest when the PMS dosage is 0.5 g L^{-1} . Thereafter, the removal efficiency of NTP was negatively correlated with the concentration of PMS. This is maybe caused by the excess PMS agglomeration that reduces the reaction efficiency of the SFB900-3/PMS system (Jiang et al. 2019; Tian et al. 2020). Therefore, a PMS concentration of 0.5 g L^{-1} had the highest efficiency and lowest economic cost. Then, the effect of SFB900-3 dosage on NTP removal is exhibited in Fig. 3e. The SFB900-3 had excellent adsorption capacity for NTP, so it could completely remove NTP by adsorption when its dosage reached 2.0 g L^{-1} . However, based on the result of the NTP removal rate within 90 min, the SFB900-3 dosage of 0.2 g L^{-1} possessed the best economic benefits. Because the NTP removal rate at this concentration was only ~6% lower than the highest efficiency. Moreover, despite the k_{app} of 0.2 g L^{-1} in the adsorption stage being poorer than the dosage of 2.0 g L^{-1} , it possessed the highest k_{app} in the degradation stage (Additional file 1: Fig. S4). The dosage between 0.2 g L^{-1} and 2.0 g L^{-1} exhibited a similar performance, and the NTP removal rate by SFB900-3 at 0.1 g L^{-1} was only 73%. Hence the optimum dosage of PMS and SFB900-3 was 0.5 g L^{-1} and 0.2 g L^{-1} , respectively. The subsequent experiments were carried out with these dosages.

3.3 Active species detection of NTP removal on SFB900-3

After revealing the intuitive reaction performance of the SFB900-3/NTP/PMS system, the quenching experiments are helpful to explore more in-depth reaction mechanisms in the process of NTP degradation (Tang et al. 2022a; Zheng et al. 2022). In this work, the tert-butanol (TBA), methanol (MeOH), furfuryl alcohol (FFA), and p-benzoquinone (p-BQ) were selected to quench $\cdot\text{OH}$, both $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, singlet oxygen ($^1\text{O}_2$), and superoxide radicals ($\cdot\text{O}_2^-$), respectively (Tang et al. 2022b). As shown in Fig. 3f, after the addition of TBA and MeOH, the NTP removal rate decreased to 74.3% and 67.8%, respectively. Because TBA reacts with $\cdot\text{OH}$ more preferent than $\text{SO}_4^{\cdot-}$ ($k_{\text{TBA}/\cdot\text{OH}}=(3.8-7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{TBA}/\text{SO}_4^{\cdot-}}=(4.0-9.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), but MeOH with $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ in a relatively comparable kinetic manner ($k_{\text{MeOH}/\cdot\text{OH}}=9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{MeOH}/\text{SO}_4^{\cdot-}}=3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (Fang et al. 2021). Therefore, the results in Fig. 3f indicate the few contributions of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$, but the contribution of $\text{SO}_4^{\cdot-}$ was higher

than that of $\cdot\text{OH}$. Hence the strong peaks of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ were detected in EPR (Fig. 3g). Notably, the NTP removal rate decreased to 17.6% and 14.5% after the addition of FFA and p-BQ, respectively. It was almost completely inhibited in the degradation stage, and the k_{app} of NTP removal after the addition of FFA and p-BQ was nearly zero (Additional file 1: Fig. S5). This result suggests the great contributions of $^1\text{O}_2$ and $\cdot\text{O}_2^-$. However, the EPR detection exhibited a weak peak of $\cdot\text{O}_2^-$ (Fig. 3h), which may be related to its rapid conversion to $^1\text{O}_2$ due to a fast reaction: $\cdot\text{O}_2^- + \cdot\text{OH} \rightarrow ^1\text{O}_2 + \text{OH}^-$ (Tang et al. 2022c). Therefore, $^1\text{O}_2$ may be the most significant active species in the SFB900-3/PMS/NTP system. Encouragingly, the EPR detection was consistent with this hypothesis via the strong peak of $^1\text{O}_2$ (Fig. 3i).

The main active species in the SFB900-3/PMS/NTP system have been revealed. Then, which iron compounds play a significant role in NTP removal needs to be carefully screened. This is helpful to further explore the synergistic effect of iron compounds and iron single atoms on the activation of PMS by SFB900-3. As shown in Fig. 4, the NTP removal rate on mixed SFB900-0 and various stable iron compounds was detected. As the

finding of Fig. 3a, pure SFB900-0 possessed poor adsorption ability on NTP removal, while the introduced Fe was beneficial for NTP adsorption. However, in Fig. 4a–c, all those mixed systems of SFB900-0/iron-compounds had bad adsorption ability on NTP removal, and the k_{app} in the adsorption stage was much lower than that of the SFB900-3 (Additional file 1: Fig. S6–S8). This result indicates that the free iron compounds can hardly influence the surface property of SFB900-0, and the improvement of adsorption capacity is mainly due to the strong positive charge brought by the iron that is immobilized on the surface of biochar (Feng et al. 2021). After the addition of PMS, the SFB900-0/ Fe_2O_3 system exhibited the worst NTP degradation rate at 52.1% (2 wt%), 58.6% (4 wt%) and 63.5% (8 wt%), respectively. The NTP removal rate was greatly decreased compared with the SFB900-3 result. The k_{app} in the degradation stage was greatly reduced, which was at most 3.29 times lower than that of the SFB900-3 (Additional file 1: Fig. S6). The results of the SFB900-0/ Fe_3C system were better, those materials with different amounts showed the fine NTP removal rate as 69.1% (2 wt%), 72.9% (4 wt%) and 77.6% (8 wt%), respectively. In addition, the k_{app} in the degradation stage

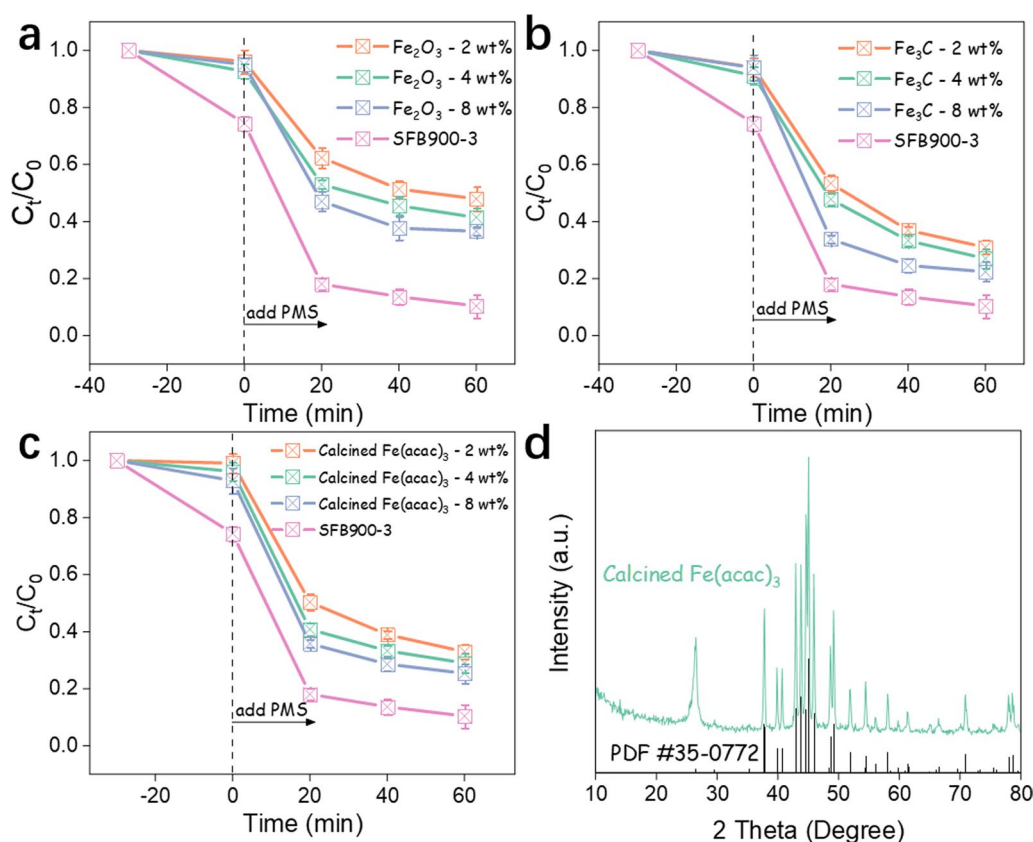


Fig. 4 SFB900-0/PMS system for NTP removal after supplemented with different amounts (a) Fe_2O_3 , (b) Fe_3C and (c) calcined $\text{Fe}(\text{acac})_3$. d XRD pattern of calcined $\text{Fe}(\text{acac})_3$. Conditions: [Biochar] = 0.2 g L^{-1} , [PMS] = 0.5 g L^{-1} , [NTP] = 40 mg L^{-1} , [temperature] = 25°C , [initial pH] = 5.87

was almost double the value of SFB900-0/ Fe_2O_3 (Additional file 1: Fig. S7). This finding indicates that the main role of the iron compounds for PMS activation is Fe_3C . Besides, the decreased NTP removal rate may be caused by the hardly interactive free Fe_3C and the single-Fe atom embedded in SFB900-0. Subsequently, considering that the preparation method of SFB900-3 in this work is related to the addition of $\text{Fe}(\text{acac})_3$. The pure calcined $\text{Fe}(\text{acac})_3$ was prepared under the same pyrolysis conditions. The NTP removal rate on the SFB900-0/calcined- $\text{Fe}(\text{acac})_3$ system was 67.1% (2 wt%), 71.0% (4 wt%) and 74.6% (8 wt%), respectively. Curiously, this result was similar to the value of the SFB900-0/ Fe_3C system. Even the k_{app} of those two systems were similar (Additional file 1: Figs. S7 and S8). This finding is reasonable when the XRD pattern revealed the crystal structure of calcined $\text{Fe}(\text{acac})_3$ (Fig. 4d). The calcined $\text{Fe}(\text{acac})_3$ has almost coincided with the standard PDF card of Fe_3C . It is speculated that $\text{Fe}(\text{acac})_3$ may deprive some of the oxygen in the biomass and partly produced Fe_2O_3 when pyrolyzed together with the EP powder, while it is

completely carbonized into Fe_3C in the hypoxic atmosphere under high temperatures. To sum up, there existed both Fe_2O_3 and Fe_3C in the SFB900-3, and the latter played a significant role in the PMS activation. Moreover, the NTP removal rate on the mixed SFB900-0/calcined $\text{Fe}(\text{acac})_3$ was poor than that of the SFB900-3, which indicates the potential synergy of iron single atoms and iron compounds, and mainly the Fe_3C .

3.4 Investigation of interfacial interaction and active sites with DFT calculation

To further explore the potential synergistic effect of single Fe atoms and Fe_3C , and reveal the possible active sites in the three systems, C/PMS, Fe-N-C/PMS and Fe-N-C/ Fe_3C /PMS, the adsorption of PMS on different systems were analyzed by DFT calculations. Meanwhile, to reveal the electron transfer at the PMS-substrate interface, charge density analysis and Bader charge analysis were performed, as shown in Fig. 5. The amount of electron transfer can be visualized by the three-dimensional charge density difference, as shown

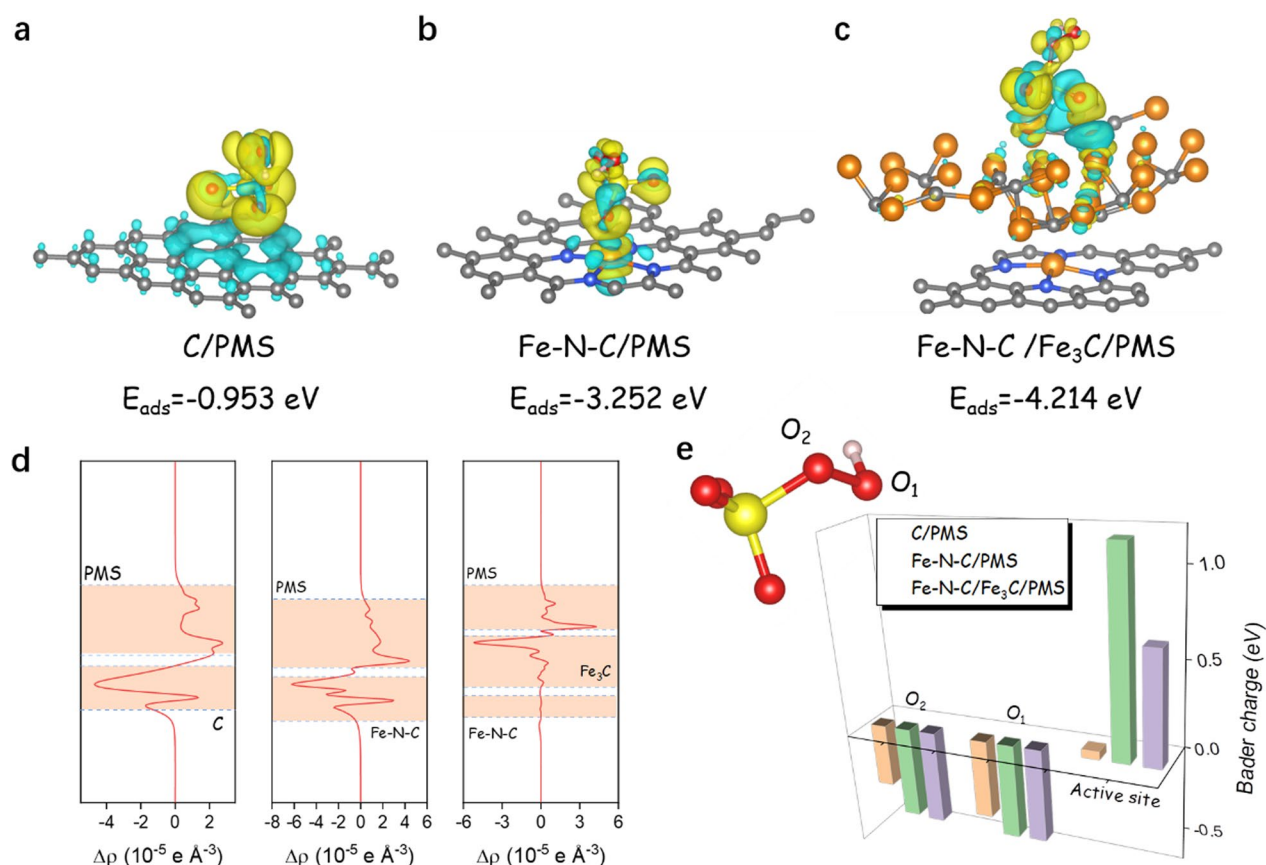


Fig. 5 Adsorption energies and the corresponding three-dimensional charge density difference calculated by DFT with different structures: **(a)** C/PMS, **(b)** Fe-N-C/PMS and **(c)** Fe-N-C/ Fe_3C /PMS. **d** Profile of the planar averaged charge density difference as a function of the position in the z direction. **e** Charge variation of O atoms and active sites in different structures by using the Bader method

in Fig. 5a–c. In all three configurations, there is a significant electron transfer between PMS and catalyst, indicating that PMS is through chemisorption on the substrate, and the interaction of Fe–N–C/Fe₃C/PMS is the strongest, followed by Fe–N–C/PMS. The difference in the average charge density of the corresponding plane perpendicular to the carbon layer direction further confirms the larger amount of charge transfer in Fe–N–C/Fe₃C/PMS (Fig. 5d). In addition, the electron depletion region is almost uniformly distributed in the C/PMS system, while it is concentrated around Fe atoms in Fe–N–C/PMS and Fe–N–C/Fe₃C/PMS, while the electron accumulation region appears in the PMS closest to the catalyst. On the O atom, this means that electrons are more easily transferred to the PMS (Li et al. 2020a; Liu et al. 2020).

Bader charges (Fig. 5e and Additional file 1: Table S1) further provide quantitative results of the charge transfer, where a clear charge redistribution can be observed. Both O atoms of the O–O bond in PMS accept electrons of three structures, in the order of Fe–N–C/Fe₃C > Fe–N–C > C. The C atoms or Fe atoms in the corresponding

adsorption sites or active sites tend to lose electrons, and the values of C, Fe–N–C and Fe–N–C/Fe₃C are 0.050 eV, 1.174 eV and 0.658 eV, respectively. The results are consistent with the findings of the charge density difference. These phenomena indicate that Fe atoms as active sites greatly enhance the adsorption capacity of the as-prepared material for PMS.

The dissociation process of PMS in the three systems, from the initial state to the final state, is shown in Fig. 6a–c. During this process, the l_{O-O} (O₁–O₂ length) in PMS was used to measure the ease of O–O bond breaking for each system (Additional file 1: Table S2). The reason for the O–O bond elongation is that the electron distribution on the PMS changes when interacting with the three different materials. In the three systems, the O–O bond length changes is in the order: Fe–N–C/Fe₃C/PMS (from 1.467 Å to 3.890 Å) > Fe–N–C/PMS (from 1.468 Å to 2.786 Å) > C/PMS (from 1.411 Å to 2.557 Å). The finding indicates that the Fe–N–C/Fe₃C system may be the most favorable for PMS activation. Furthermore, Fig. 6d indicates that the dissociation of PMS on the surface of C is an endothermic reaction, while it is an exothermic

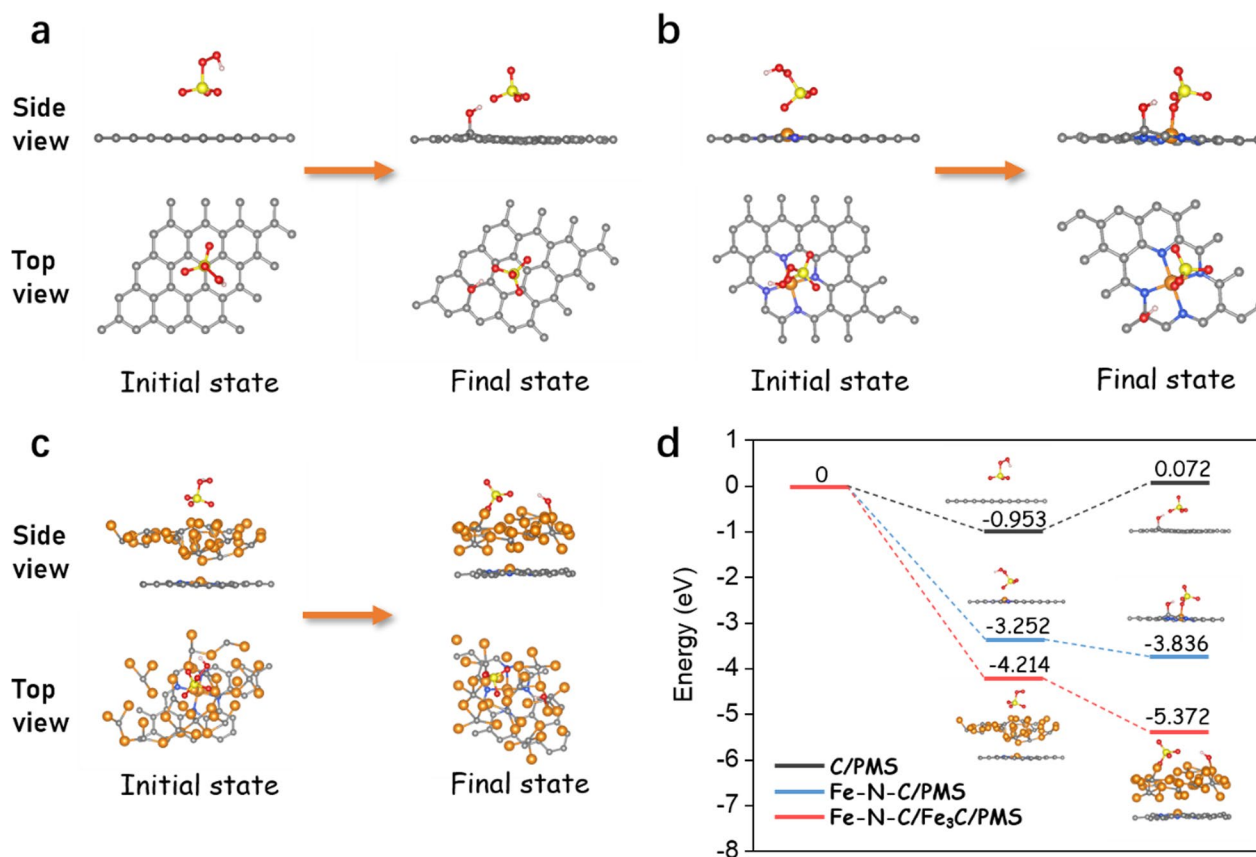
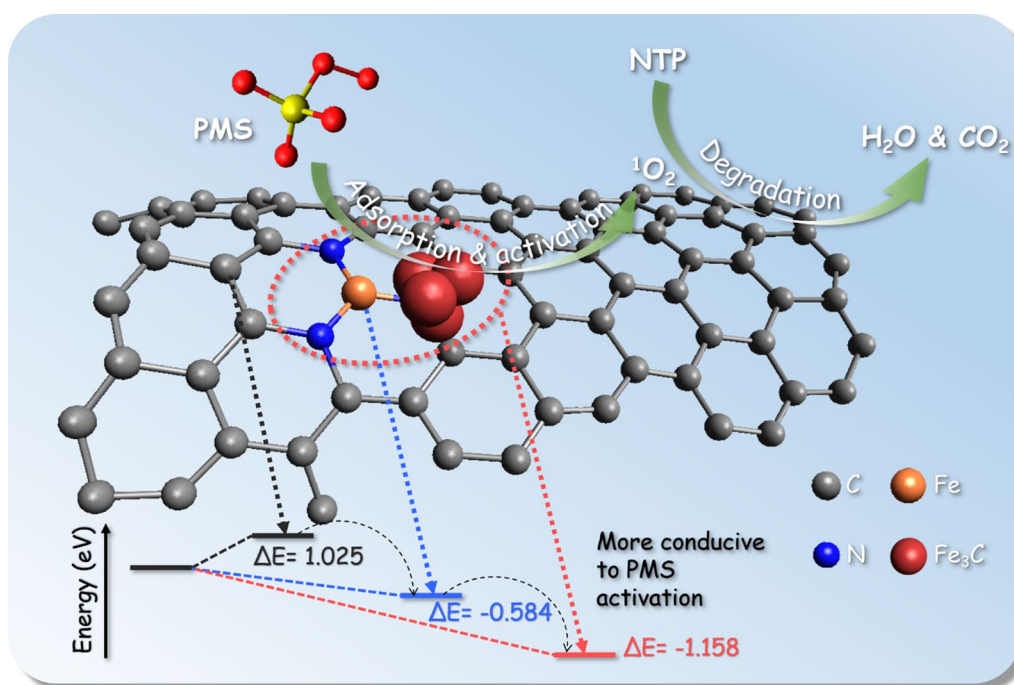


Fig. 6 Structure of PMS molecules adsorbed on (a) C, (b) Fe–N–C and (c) Fe–N–C/Fe₃C. d Schematic illustration and calculated potential energy profiles of PMS dissociation processes over the different systems



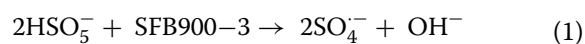
Scheme 1 Mechanism of the synergistic promotion of PMS activation by Fe single atoms and Fe₃C in SFB900-3

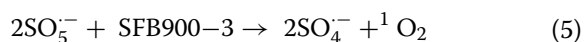
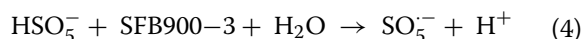
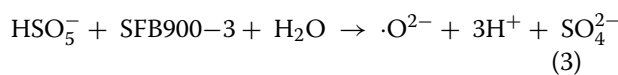
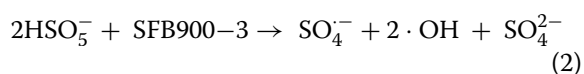
reaction on the surfaces of Fe–N–C and Fe–N–C/Fe₃C, with ΔE of 1.025 eV, -0.584 eV and -1.158 eV, respectively. This result indicates that the PMS dissociation step is favorable in thermodynamics in all systems (except the C/PMS system) (Meng et al. 2020). Besides, the change in the energy barrier indicates that the O–O bond breaking in PMS is fastest on the Fe–N–C/Fe₃C surface (Xue et al. 2021). Taken together, the DFT calculation results showed that the Fe–N–C/Fe₃C system possessed the optimal PMS activation performance, which sufficiently supported the synergistic promotion of PMS activation by Fe–N–C and Fe₃C.

3.5 Synergy of Fe single atoms with Fe₃C to the enhanced PMS activation

After comprehensively analyzing the results of ROS detective experiments and DFT calculations, the synergistic mechanism of iron single atoms and Fe₃C is shown in Scheme 1. At first, the introduction of Fe single atoms in pure carbon material (Fe–N–C) greatly enhances the adsorption capacity of the material for PMS (from -0.953 eV to -3.252 eV), because the original electron distribution is disturbed (Fig. 5a, b). The strong electron loss ability of the Fe atom makes the O–O bond in PMS gains more electrons. This process further leads to I_{O-O} increase in Fe–N–C-adsorbed PMS (Additional file 1: Table S2), which is beneficial to the cleavage of PMS. Second, with

the addition of Fe₃C, the change of O–O bond in PMS is further enlarged, and I_{O-O} reaches the maximum value. Meanwhile, Fe–N–C/Fe₃C exhibited the largest adsorption energy (-4.214 eV) for PMS. In this case, Bader charge analysis showed that the electron transfer ability of Fe atoms in Fe₃C is much smaller than that of Fe–N–C, while the electron transfer occurring on O₁ (from -0.568 e to -0.577 e), O₂ (from -0.581 e to -0.573 e) in both systems is similar. This indicates that Fe single atoms in Fe–N–C/Fe₃C play a synergistic role with Fe₃C on PMS adsorption, resulting in a further increase in adsorption energy. Finally, the analysis of the energy barrier pointed out that the activation process of PMS in the C/PMS system is unfavorable in thermodynamics. The Fe single atom turns the PMS cracking process favorable in thermodynamics (ΔE from 1.025 eV to -0.584 eV), which greatly improves the PMS activation performance of the material. The synergistic effect of Fe–N–C and Fe₃C further promoted the dissociation process of PMS, and the energy barrier was reduced from -0.584 eV to -1.158 eV. This result indicates that Fe–N–C/Fe₃C has the optimal PMS activation performance. Considering the whole reaction process, a total exothermic of 1.158 eV indicates that ¹O₂ could be easily generated in Fe–N–C/Fe₃C/PMS system, as shown in Eqs. (1)–(6).





Then, NTP is degraded into various intermediate products under the attack of ${}^1\text{O}_2$, and finally degraded into H_2O and CO_2 which is confirmed by TOC results (Additional file 1: Fig. S9).

3.6 Environmental factors and applications

To explore the stability and application capability of the SFB900-3/PMS/NTP system, several environmental factors were studied (Tang et al. 2022c). As shown in Fig. 7a, the NTP removal rate was negatively correlated with the pH value of the system in both the adsorption and degradation stages. As shown in Additional file 1: Fig. S10, the k_{app} decreases as the pH value increases. Under acidic conditions, the catalyst surface will enhance the

adsorption of PMS due to the increase of positive charges (Fig. 7b) (Wang et al. 2020c). As for the alkaline conditions, PMS will self-decompose to HSO_5^{2-} , which cannot generate $\text{SO}_4^{\cdot -}$. Therefore, the pH value of the reaction environment has less interference with the SFB900-3.

Inorganic anions such as HCO_3^- , Cl^- and NO_3^- are widely present in wild aquatic environments, and can react with reactive species ($\text{SO}_4^{\cdot -}$ and $\cdot \text{OH}$) and affect the catalytic reaction (Fig. 7c) (Li et al. 2021a; Yin et al. 2020). The results showed that the addition of these ions was not conducive to the degradation of NTP, because they would react with PMS to form less active substances ($\text{CO}_3^{\cdot -}$, $\cdot \text{Cl}$, $\cdot \text{Cl}^{2-}$, $\cdot \text{ClOH}^-$ and $\text{NO}_3^{\cdot}$) (Zhou et al. 2021a). Besides, they possess a similarly decreased k_{app} (Additional file 1: Fig. S11).

Further, the tap water (TW) and wild water (from Liuyang River (LW) and paddy water (PW), Changsha, China) were selected to confirm of ions influence. As the left part shown in Fig. 7d, compared with the result of the control team (ultrapure water), the NTP removal rate in TW, LW and PW decreased by 8.6%, 20.2% and 18.9%, respectively. The removal rate in PW was higher than that the LW. Based on the composition analysis of LW and PW (Table S3), it is speculated that the higher concentration of chloride ions in PW may lead to the formation of more active species during the SFB900/PMS reaction (Qiu

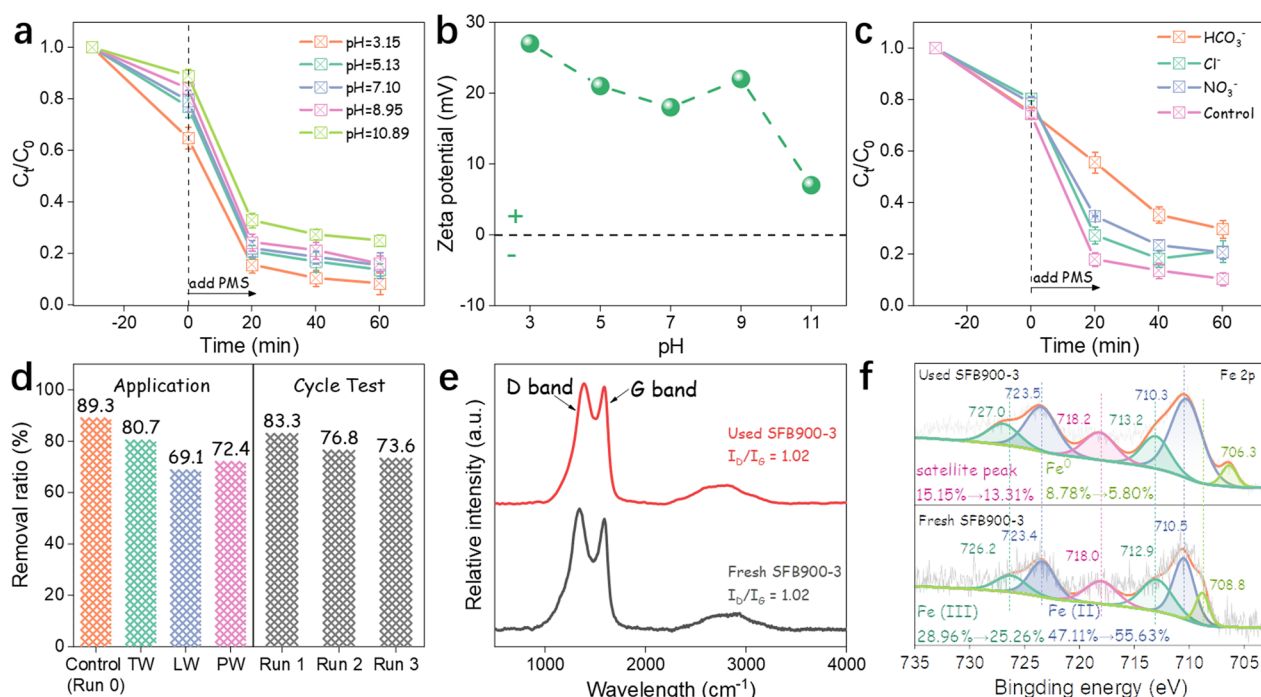


Fig. 7 **a** pH value effect on NTP removal by SFB900-3. **b** Zeta potential of SFB900-3 under different pH values. **c** Common coexistent ion influence on NTP removal by SFB900-3. **d** Application of SFB900-3 to remove NTP in different aquatic environments and its cycle test in the laboratory environment. The comparison of **(e)** Raman spectra and **(f)** XPS spectra of used and fresh SFB900-3. Conditions: [Biochar] = 0.2 g L⁻¹, [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25 °C, [initial pH] = 5.87, [ions] = 2 mM

et al. 2019). Nevertheless, the NTP removal rate in LW and PW still reached 69.1% and 72.4%, indicating that the SFB900-3/PMS system possesses application potential in wild aquatic remediation for NTP.

Moreover, the cycle utilization of the SFB900-3/PMS system for NTP removal was tested. The NTP removal rate was still 73.6% after three rounds. The decreased removal rate may be due to the inevitable partial loss of surface active sites on SFB900-3 during PMS activation (Li et al. 2021b; Ye et al. 2021). This result suggests the stability of SFB900-3 in the process of NTP remediation.

At last, the Raman and XPS spectra were selected for revealing the stability of SFB900-3's structure. As in Fig. 7e, the I_G/I_D value indicates that the carbon skeleton and structural defects in SFB900-3 exhibited few changes after PMS activation. Besides, Fig. 7f reveals the variation of Fe in fresh and used SFB900-3, indicating there existed the Fe(III)/Fe(II) cycle in SFB900-3 with some loss of Fe ions (Fu et al. 2019; Zhen et al. 2021). This finding maybe is the reason for the decrease in the NTP removal rate on used SFB900-3. In this case, the iron leaching concentration during the NTP removal on the SFB900-3/PMS system was detected by ICP-MS (Additional file 1: Fig. S12). The results showed that the maximum iron concentration was 0.109 mg L^{-1} within 60 min, which meets the national emission standard ($\leq 0.3 \text{ mg L}^{-1}$). Moreover, this finding confirmed the former hypothesis of the decreased NTP removal rate, and it also indicated that the SFB900-3 possessed the stable ability for PMS activation. In general, the SFB900-3/PMS system possesses the application potential in wild aquatic remediation.

3.7 Potential degradation pathways of NTP and toxicity analysis of its intermediates

High-performance liquid chromatography-mass spectrometry (HPLC/MS) was used to explore the intermediate products and the possible degradation pathways of NTP ($m/z=270.07$) by the SFB900-3/PMS system (Additional file 1: Fig. S14–S20). There are two different potential degradation routes of NTP on SFB900-3/PMS (Additional file 1: Fig. S13). In Route 1, the N-linked methyl groups are oxidized to carboxyl groups to generate P1 ($m/z=300.03$). Then, the C–C bond attached to the carboxyl group is broken under the continuous oxidation of the $^1\text{O}_2$, and the methyl group attached to the distal amino group is also removed. Those two reactions both cause P3 ($m/z=242.04$) generation. After that, the distal nitro group is removed to generate P6 ($m/z=199.05$). After that, a large group of branched chains connected by N is removed under the constant attack of $^1\text{O}_2$, and the P7 ($m/z=170.07$) is formed (Tang et al. 2020c; Zheng et al. 2022). At last, P8 ($m/z=113.01$) is gradually oxidized and broken under the continuous

attack of $^1\text{O}_2$, which makes it finally degraded to H_2O and CO_2 . In Route 2, $^1\text{O}_2$ attacks the edge methyl groups from the amino group to produce P2 ($m/z=256.09$). Then, the most distal nitro group is replaced by a hydroxyl group and occurs to generate P4 ($m/z=227.69$). Meanwhile, the novel hydroxyl group may dehydrogenate due to the strong oxidation ability of $^1\text{O}_2$ and generate the P5 ($m/z=227.05$) (Tang et al. 2020a, 2020b). Then, the follow-up is consistent with Route 1 again.

To further explore the fate of intermediate products in the process of NTP degradation, the abundance of NTP and its products was intuitively exhibited (Additional file 1: Fig. S13b, c). In Route 1, the NTP's abundance was decreased constantly with the catalytic process, while the trends of its intermediate products were chaotic. The evolution of the P1 ($m/z=300.03$) was striking. Its abundance increased soon in 0–20 min, then decreased quickly until it disappeared completely in 20–60 min. Besides, the abundance of P1 was the highest in all NTP's intermediate products in Route 1, which suggests that P1 was the main intermediate product. Notably, the intensity of P3 ($m/z=242.04$) appeared in 0 min, which can be explained by the spontaneous degradation of NTP. Moreover, the strong oxidation of $^1\text{O}_2$ greatly increases its decomposition rate. The abundance of P6 ($m/z=199.05$) increased briefly and disappeared rapidly. This finding implies that this product is a transient intermediate and transformed rapidly. The evolution of the remaining two intermediates P7 ($m/z=170.07$) and P8 ($m/z=113.01$) in Route 1 was similar. The abundance of those intermediate products showed a steady uptrend during the degradation process, which indicates that P7 and P8 were the most important products in the late stage of NTP degradation. Then, in Route 2 (Additional file 1: Fig. S13c), the P4 ($m/z=227.69$) was the main intermediate product in this NTP degradation pathway. Because its abundance was the highest in all NTP's intermediates, and its variation trend was similar to the P1 in Route 1. The finding suggests a potential degradation mode on NTP degradation in the SFB900-3/PMS system. The evolution of the P2 ($m/z=256.09$) and P5 ($m/z=227.05$) in Route 2 was similar. The abundance of those intermediate products showed few changes during the degradation process. This finding implies that these products are transient intermediates and transformed rapidly.

At last, the Toxicity Estimation Software Tool (T.E.S.T.) was introduced to further research the potential toxicity of NTP's intermediates (Tao et al. 2020). The data of *Daphnia* LC_{50} (48 h), Fathead minnow LC_{50} (96 h) and Oral rat LD_{50} in the Consensus method was used to estimate the acute toxicity of those intermediates. As Table 2 showed, the overall acute toxicity of these intermediates exhibited a trend that the value increased first and then

Table 2 Toxicological of NTP and its intermediates predicted by T.E.S.T

Sample	Acute toxicity (mg L ⁻¹)			Bio-concentration factor	Developmental toxicity	Mutagenicity result
	Fathead minnow LC ₅₀ (96h)	Daphnia LC ₅₀ (48h)	Oral rat LD ₅₀			
m/z = 270.07	N/A	4.20	2.30	N/A	Toxicant	Positive
m/z = 300.03	N/A	3.28	2.27	N/A	Toxicant	Positive
m/z = 256.09	N/A	4.36	2.23	N/A	Toxicant	Positive
m/z = 242.04	N/A	4.20	2.22	N/A	Toxicant	Positive
m/z = 227.69	3.20	4.47	N/A	0.76	Toxicant	N/A
m/z = 227.05	3.44	4.12	N/A	N/A	Toxicant	N/A
m/z = 199.05	2.64	3.57	2.38	0.52	Toxicant	Negative
m/z = 170.07	3.32	3.69	2.48	1.15	Toxicant	Positive
m/z = 113.01	2.47	3.35	2.43	1.17	Toxicant	Negative

Not applicable
Toxic(<10 mg L⁻¹)
Toxicant
Mutagenicity positive
Mutagenicity negative

decreased. This result indicates that the acute toxicity of NTP intermediates was reduced during the degradation process. Notably, the later appearance of NTP intermediates, the greater the bioconcentration factor. It is speculated that the early intermediates are normally unstable and they will constantly degrade thereby possessing less bioconcentration factor. Then, the developmental toxicity of all NTP intermediates was defined as a toxicant, which emphasized the importance of remediation with NTP contamination in the aquatic environment. To our delight, with the process of NTP degradation, the final NTP intermediate exhibited negative mutagenicity. All the above analyses indicate that the SFB900-3/PMS system is effective for NTP removal and has practical application potential.

4 Conclusion

In summary, the SFB900-3/PMS system with high and stable NTP degradation efficiency was presented. The excellent performance of the system for PMS activation originates from the synergistic effect of internal Fe single atoms and the introduced Fe compounds, which greatly improve the adsorption capacity of SFB900-3 for persulfate and reduce the activation energy. This result was verified by the DFT calculation. Hence, this system could remove 89.5% NTP in 60 min under neutral and acidic conditions. Then, the quenching experiment and EPR detection proved that the non-radical way (¹O₂) played an important role in the SFB900-3/PMS/NTP system.

Furthermore, the main degradation pathways of NTP were explained through LC/MS analysis. The toxicity of the intermediate product was simulated and analyzed to show that the catalytic system is effective in degrading NTP and has practical application potential. This work put forward the synergy of Fe single atoms and Fe₃C for efficient PMS activation and provided novel guidance for constructing efficient biochar on organic pollutant remediation.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s42773-023-00221-1>.

Additional file 1: Fig. S1 (a) Specific surface area and total pore volume of allas-prepared samples. Pore size distribution by non-linear density functional theory (NLDFT) (inserts are corresponding nitrogen adsorption and desorption isotherms) of (b) SFB900-0, (c) SFB900-1, (d) SFB900-2, (e) SFB900-3 and (f) SFB900-4. **Fig. S2** SEM images of (a) SFB900-0, (b) SFB900-1, (c) SFB900-2, (d) SFB900-3 and (e) SFB900-4 at 500 nm. **Fig. S3** The apparent rate constants (k_{app}) of NTP degradation in the SFB900/PMS system under different PMS concentration. Conditions: [Biochar] = 0.2 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S4** The apparent rate constants (k_{app}) of NTP degradation in the SFB900/PMS system under different catalyst dosage. Conditions: [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S5** The apparent rate constants (k_{app}) of NTP degradation in the SFB900/PMS system with different quencher, and the corresponding contribution rate. Conditions: [Biochar] = 0.2 g L⁻¹, [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S6** The apparent rate constants (k_{app}) of NTP degradation in the SFB900-0/PMS system with different proportions of Fe₂O₃. Conditions: [Biochar] = 0.2 g L⁻¹, [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S7** The apparent rate constants (k_{app}) of NTP degradation in the SFB900-0/

PMS system with different proportions of Fe₃C. Conditions: [Biochar] = 0.2 g L⁻¹, [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S8** The apparent rate constants (k_{app}) of NTP degradation in the SFB900-0/PMS system with different proportions of calcined Fe(acac)₃. Conditions: [Biochar] = 0.2 g L⁻¹, [PMS] = 0.5 g L⁻¹, [NTP] = 40 mg L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S9** The TOC removal rate of NTP on SFB900-3 without or with PMS within 60 mins. Conditions: [Biochar] = 0.2 g L⁻¹, [NTP] = 40 mg L⁻¹, [PMS] = 0.5 g L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S10** The apparent rate constants (k_{app}) of NTP degradation in the SFB900-0/PMS system under different pH value. Conditions: [Biochar] = 0.2 g L⁻¹, [NTP] = 40 mg L⁻¹, [PMS] = 0.5 g L⁻¹, [temperature] = 25°C. **Fig. S11** The apparent rate constants (k_{app}) of NTP degradation in the SFB900-0/PMS system with different proportions of calcined Fe(acac)₃. Conditions: [Biochar] = 0.2 g L⁻¹, [NTP] = 40 mg L⁻¹, [PMS] = 0.5 g L⁻¹, [temperature] = 25°C, [initial pH] = 5.87, [ions] = 2 mM. **Fig. S12** Iron leaching concentration of SFB900/PMS system during NTP degradation process. Conditions: [Biochar] = 0.2 g L⁻¹, [NTP] = 40 mg L⁻¹, [PMS] = 0.5 g L⁻¹, [temperature] = 25°C, [initial pH] = 5.87. **Fig. S13** (a) Possible pathways proposed for NTP degradation by the SFB900/PMS system. The Two potential degradation pathways of (b) Route 1 and (c) Route 2. **Fig. S14** LC/MS spectrogram of initial NTP solution with 40 mg L⁻¹. **Fig. S15** LC/MS spectrum of SFB900/PMS/NTP system after 10 min reaction. **Fig. S16** LC/MS spectrum of SFB900/PMS/NTP system after 20 min reaction. **Fig. S17** LC/MS spectrum of SFB900/PMS/NTP system after 30 min reaction. **Fig. S18** LC/MS spectrum of SFB900/PMS/NTP system after 40 min reaction. **Fig. S19** LC/MS spectrum of SFB900/PMS/NTP system after 50 min reaction. **Fig. S20** LC/MS spectrum of SFB900/PMS/NTP system after 60 min reaction. **Table S1**. Bader charge of different component in the structures. For the Bader charge in this table, the negative values indicate negative charge while positive values indicate positive charge. **Table S2**. Bond length, adsorption energy and energy barrier of PMS dissociation processes over the different systems. **Table S3**. Characteristics of the real water samples.

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Author's contributions

SX: Formal analysis, Investigation, Writing -Original Draft. HZ: Investigation. YD*: Conceptualization, Writing—Review and Editing, Funding acquisition, Supervision. RT: Investigation. JW: Validation. LL: Validation. ZZ: Validation. DG*: Writing—Review and Editing, Supervision. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this article.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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