



# Nitrogen-doped biochar fiber with graphitization from *Boehmeria nivea* for promoted peroxymonosulfate activation and non-radical degradation pathways with enhancing electron transfer

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## ABSTRACT

Advanced oxidation has great promise in the degradation of organic pollutants, but the high preparation requirements, adjustment difficulty, high cost, potential hazard, and low repeatability of catalysts limit the practical applications of this technology. In this study, a metal-free biochar-based catalyst derived from biomass fiber was prepared assisted by graphitization and nitrogen incorporation (PGBF-N). The heterogeneous catalysis of peroxymonosulfate (PMS) was triggered by PGBF-N with degradation rate 7 times higher than that of pristine biochar. The high catalytic efficiency was attributed to the accelerated electron transfer originated from the high degree of graphitization and nitrogen functionalization of PGBF-N, in which the non-radical pathways containing carbon-bridge and singlet oxygen-mediated oxidation were elucidated as the predominant pathways for tetracycline degradation, instead of the dominant role of radical pathway in pristine biochar. Vacancies and defective edges formed on sp<sup>2</sup>-hybridized carbon framework as well as the nitrogen doping sites and ketonic group of PGBF-N were considered as possible active sites. The excellent degradation rate in actual water indicated that the PGBF-N/PMS system dominated by non-radical pathway exhibited a high anti-interference ability to surrounding organic or inorganic compounds. This study provides a facile protocol for converting biomass fiber into functional catalyst and enables underlying insight in mediating dominated degradation mechanism of heterogeneous catalysis by biochar fiber.

## 1. Introduction

Sulfate radical-based advanced oxidation processes (SR-AOPs) have been suggested as an effective approach to degrade persistent organic pollutants by scission of the peroxide O—O bond of peroxymonosulfate (PMS) or persulfate (PS) [1–3], with the longer half-life (30–40 μs) and higher redox potential ( $E^\circ = 2.5\text{--}3.1\text{ V}$ ) of  $\text{SO}_4^{\cdot-}$  than that of  $\cdot\text{OH}$ . Metal-free carbon materials exhibit great potential as green alternatives of catalysts for heterogeneous catalytic reactions in SR-AOPs [4–6], owing to the following merits: no-metal leaching, acid-base resistance, biocompatibility, restorability, and versatility [7–11]. Carbocatalyst, containing carbon basal plane with delocalized  $\pi$ -electrons, electron-rich functional group, and carbon in the form of  $\pi$ - $\pi^*$ , could hold the post of electron donors and regulators in the activation process [11,12]. Graphene oxide and its reduced derivatives were synthesized by

thermal annealing (rGO-CM), chemical reduction of hydrazine hydrate (rGO-HH), and hydrothermal reaction of ammonia solution (rGO-HT), respectively, and the best PMS activation was observed by rGO-HT which showed the highest content of ketonic group (C=O) [12]. Theoretical evidences revealed that the boundary defects like zigzag/armchair edges and vacancies can be considered as the active sites for O—O bond cleavage in PMS [12].

Besides the generation of free radicals to attack pollutants in SR-AOPs [13,14], non-radical activation pathways, including the singlet-oxygen-mediated oxidation [15–18] and carbocatalyst-bridged mechanism (carbonaceous material acting as a bridge for facilitating electron transfer from organic pollutants to the metastable PS/PMS without any reactive species production) [19–21], have been attracting increasing attention. Non-radical activation pathways show several remarkable advantages including: 1) enhancing anti-interference to

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organics and inorganics in the environmental background [15]; 2) avoiding radical self-quenching by propagation reaction [22]; and 3) fully utilizing the oxidized capacity of the oxidant. It is obvious that increasing the contribution of non-radical activation pathway in activating PS/PMS for pollutant degradation is one of the potential ways to further improve the performance of SR-AOP technology in practical application.

The initiation of the catalytic process requires a high concentration of electron cluster density. Electron accelerated transfer and heteroatom doping can induce the electron reconfiguration in unique electronic circumstance, which are treated as theoretically feasible approaches for the formation of activated state of PS/PMS and generation of reactive species. Incorporating heteroatom into carbon lattice could enhance the extent of charge delocalization thereby break the inertness of network structure of  $sp^2$ -hybridized carbon. Nitrogen doping is one of the most facile and promising approaches to strengthen the reactivity of catalyst, since the N with localized unpaired electrons is capable of 1) improving the electron density of the neighboring carbon atoms; 2) enhancing the  $\pi$ -electrons flow in  $sp^2$ -carbon by conjugation [23]; 3) generating more functional groups and defects; and 4) increasing the surface polarity of the carbon material for attractive interaction with the polar adsorbates. Chen et al. synthesized a series of graphene with different N bonding configurations controlled delicately by regulating thermal annealing temperature to illustrate the role of Lewis basic sites with lone-pair electrons and graphitic N with higher electronegativity for disrupting the inertness of graphitic ( $sp^2$ -bonding carbon) network [23].

Since the commonly used carbon precursors for carbocatalyst (e.g., fullerene, graphene (oxide), carbon nanotubes) preparation are relatively expensive, ecologically toxic, and difficult for scale-up, it is desirable to develop a promising metal-free carbon material by applying low-cost and widespread carbon precursors such as biomass wastes [24–26]. However, the complex components in pristine biochar, as well as the disordered structure of amorphous carbon, cannot effectively realize the directional transfer of electrons. A more regular carbon configuration ( $sp^2$ -hybridized carbon) with high degree of graphitization is of great importance, otherwise heteroatom doping only increases the disorder and uncontrollable structure of the resulting biochar. Carbon materials with high graphitization and favorable functional groups are open frameworks to be decorated, which show excellent electrochemical characteristics and porous structure, drawing huge deal of scientific interests in the field of energy storage [27–30] and environmental remediation [31–34]. For example, highly graphitic biochar self-assembled with  $g$ - $MoS_2$  nanosheets was synthesized by our group to exhibit an outstanding activity in photodegradation [35]. The increasing degradation rate could be ascribed to the larger accessible surface areas for avoiding nanosheet agglomeration and the superior electrical conductivity for promoting electron transport.

Biomass fiber, collected from Ramie (*Boehmeria nivea* (L.) Gaud.), has the advantage of wide distribution, relatively simple constituent (mostly cellulose) and internal special ultra-fine pore structure, and it can be used as carbon precursor to obtain fiber-like activated biochar with chemical stability, large surface area, flexibility, and excellent electrical performance [36–38]. In order to facilitate electron transfer of biochar-based catalyst for PMS activation, especially the non-radical activation, a graphitic biochar fiber (PGBF) with unique structural and electronic characteristics was first synthesized via an efficient and green template-free route with  $K_2FeO_4$ . On this basis, doping N element into PGBF (PGBF-N) was conducted to create an electron-abundant circumstance, modulated functional groups and defective sites for PMS activation. Biochar fiber with abundant free flowing  $\pi$ -electrons on graphitization structure works as an excellent electron-bridge to accelerate electron transfer, and the doped nitrogen with lone pair electron and higher electronegativity could further activate electron flow and electron reconfiguration with the adsorbed PMS molecule. Tetracycline (TC) posing amphoteric behavior [39–41], a frequently detected

antibiotic in water, was used as a representative to evaluate the effects of the as-prepared carbocatalyst in PMS system. The key purposes of this research are to 1) synthesize a series of metal-free biochar-based catalysts derived from biomass fiber by facile operation and characterize their structure and electrical properties; 2) explore the importance of graphitization and nitrogen doping on regulating dominant pathways; 3) analyze the active sites of the prepared biochar fiber in PMS activation for pollutant degradation; and 4) discuss the degradation mechanisms.

## 2. Materials and methods

### 2.1. Materials

Ramie was provided by a local Ramie Institute of Hunan Agricultural University in China. Tetracycline (TC: purity > 98.5 %), potassium ferrate ( $K_2FeO_4$ ), were purchased from Sigma-Aldrich, and were used without purification. Urea ( $CH_4N_2O$ ), Oxone® (as  $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ , Alfa Aesar) were provided by Shanghai Macklin Biochemical Co., Ltd. In addition, the solutions were prepared using deionized water (18.25 M $\Omega$  cm) that produced by an Ulupure (UPRII-10 T) laboratory water system.

### 2.2. Biochar-based catalyst synthesis

Raw silk reeled off from Ramie bark was treated as biomass fiber (Scheme 1). The obtained biochar was successively subjected to dipping with  $K_2FeO_4$  (0.1 M) at solid-to-liquid ratio of 1 g: 100 mL, grinding with urea at the mass ratio of 1: 2, calcining at temperatures of 900 °C and acid washing, which was named as PGBF-N. For comparison, the black solids obtained from above operation but without  $K_2FeO_4$  soaking, nitrogen doping or both were denoted as BF-N, PGBF or BF, respectively. The synthesis details and characterization methods were provided in Supporting Information (SI).

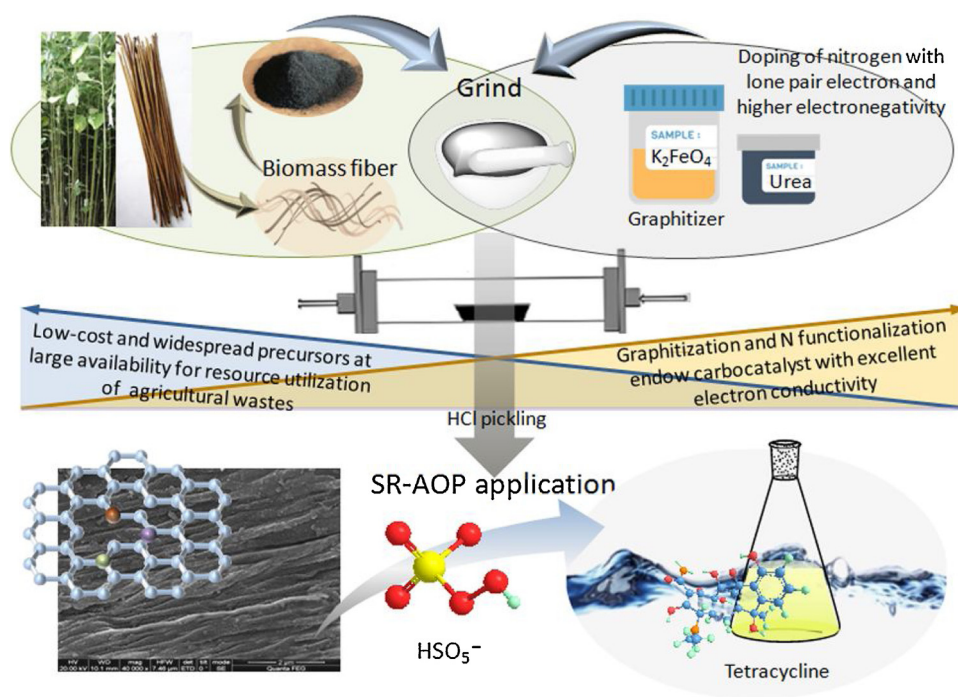
### 2.3. Catalytic degradation experiments

The catalytic degradation performance of samples was carried out in a 250 mL brown bottle in a thermostatic shaker with a shaking rate at 160 rpm. In a typical process, 10 mg of carbocatalyst was suspended in a 100 mL of TC solution ( $C_0 = 20$  mg/L) for 30 min to establish the adsorption-desorption equilibrium (pre-experiment was carried out for 24 h and confirmed that the equilibrium state of adsorption-desorption was reached at 15 min). Then a certain amount of PMS (final solution containing 1 mM) was added into the above solution to trigger the degradation reaction. The solution samples were withdrawn, filtered using 0.45  $\mu$ m PVDF disposable filters and injected into a vial loading with methanol at each time interval, followed by analysis with UV spectrophotometer ( $\lambda_{max} = 357$  nm) and high-performance liquid chromatograph (HPLC, Agilent, Waldbronn, Germany) at detecting  $\lambda$  of 355 nm.

## 3. Results and discussion

### 3.1. Characterization of biochar-based catalysts

SEM images of PGBF-N with different magnifications are shown in Fig. 1 to display the morphologies and microstructures. In the overall view of the low-resolution SEM image, the final material exhibited rod-like microstructure with an average diameter of around 50  $\mu$ m, which was found to be consisted of plentiful twisted strips with diameters of about 250 nm (Fig. 1c). The intertwined like-fibrous framework, inherited from the natural morphology of biomass fiber of Ramie, should allow for effective electron transfer and mass diffusion during catalysis. The relatively rough surface with some small bumps on beam was derived from minerals in biomass after pyrolysis, in line with the

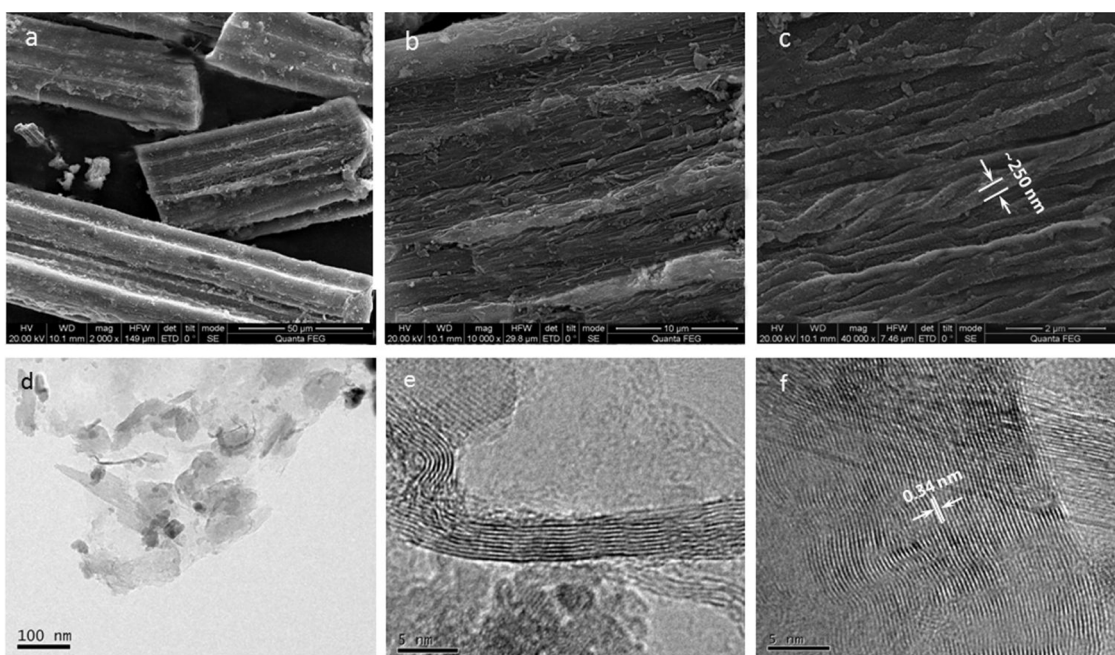


**Scheme 1.** Schematic illustration of the synthesis of PGBF-N as biochar-based catalyst for TC degradation.

observation reported in XRD. For comparison, SEM images of other carbocatalysts are also given in Fig. S1, all materials retained the inherent morphology of biomass fiber of slender column. There was little difference in morphology between BF and BF-N with a rough surface. More smooth and porous structure was formed on PGBF after modification, which was owing to the activation of KOH (hydrolyzed by K<sub>2</sub>FeO<sub>4</sub>) to produce gas (CO and CO<sub>2</sub>) for pore-creating. The distinct lattice fringes with interlayer spacing of  $\sim 0.34$  nm were observed in the high-resolution TEM (HRTEM) image of PGBF-N (Fig. 1e and f), which matched well with that of the (002) plane of graphite [27]. Compared with the disordered lattice on HRTEM image of pristine biochar (Fig. S2), the regular lattice arrangement further demonstrated

the high degree of graphitization of PGBF-N.

A broad peak was observed in wide-angle X-ray diffraction pattern of BF (Fig. 2a), showing the amorphous feature and no peaks that were indicative of crystalline phases in carbon structure of pristine biochar. Upon modification with K<sub>2</sub>FeO<sub>4</sub> followed by thermal treatment, two obvious diffraction peaks at 26.3° and 44.1° which were corresponding to the representative d-spacing (002) and in-plane (100) structure could be observed, revealing the present of crystalline planes of graphite carbon [21]. On the basis of the comparison among the XRD patterns, it could be concluded that catalytic activation of K<sub>2</sub>FeO<sub>4</sub> in preparation was likely to inspire the improvement of graphitization degree (PGBF), as well as slight effect on crystallinity of samples by nitrogen doping in



**Fig. 1.** SEM images (a, b and c) and high-resolution TEM images (d, e, and f) of PGBF-N.



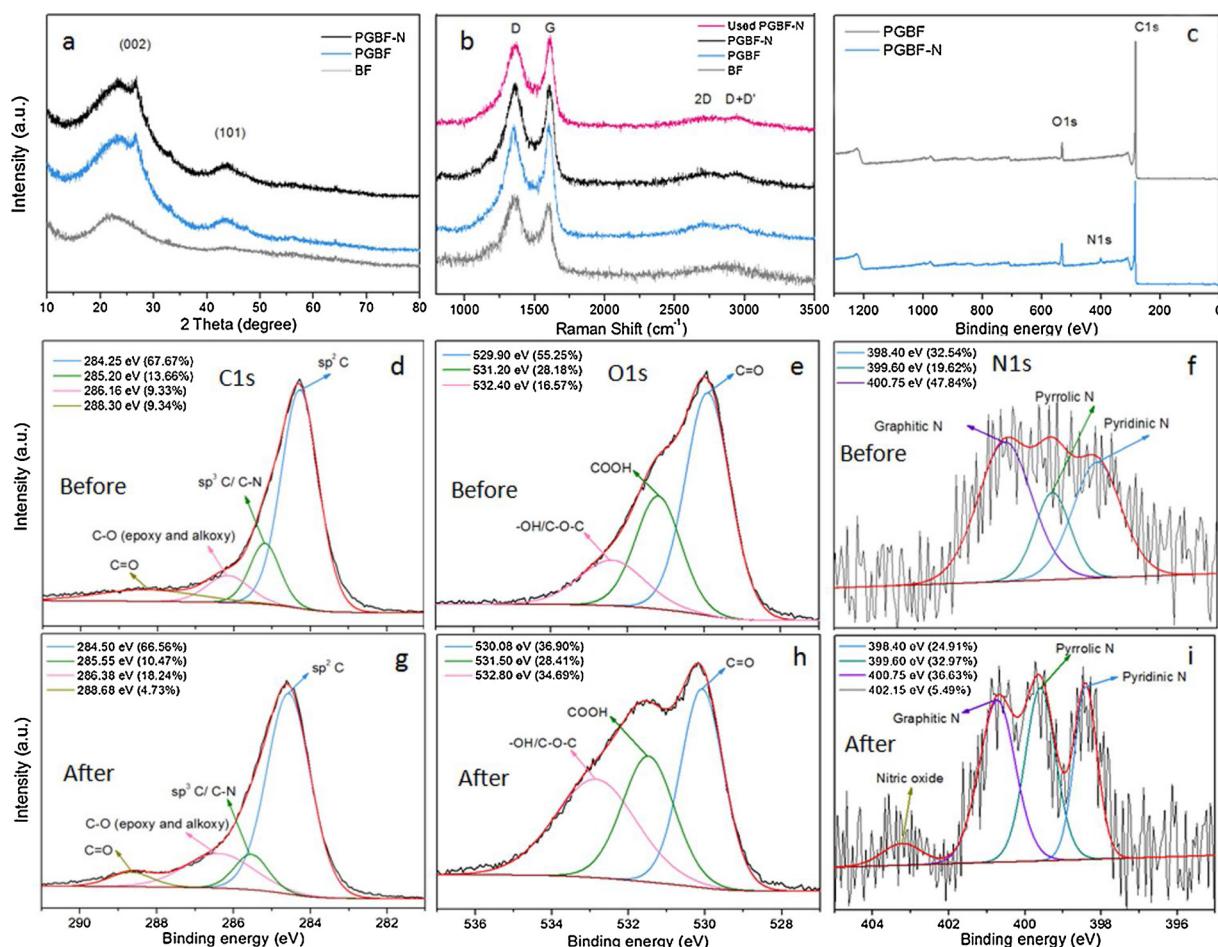


Fig. 2. XRD patterns of BF, PGBF, and PGBF-N (a); Raman spectra of BF, PGBF, PGBF-N, and used PGBF-N (b); XPS survey spectra of PGBF, PGBF-N (c); High resolution XPS spectrum of C 1s (d and g), O 1s (e and h); and N 1s (f and i) of PGBF-N before and after reaction.

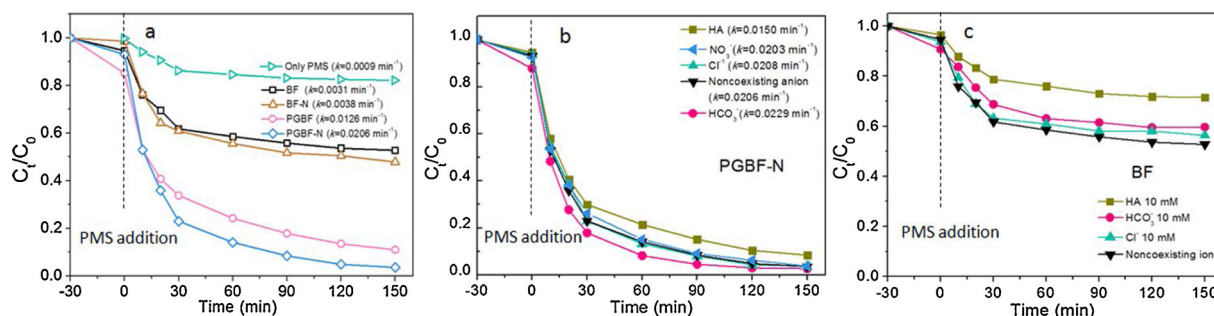
PGBF-N. Several unexpected peaks at  $\sim 33^\circ$  and  $\sim 64^\circ$  are ascribed to the crystalline minerals of calcite (PDF-# 05-0586) and quartz (PDF-# 46-1045) that converted from impurities in biomass.

Figure S4 shows the adsorption-desorption isotherm measured at 77 K to examine the textural characteristics of the synthesized biochar-based catalysts. An IV-type isothermal curve as well as a large H4-type hysteric loop of desorption branch could be observed, which indicated the characteristic of mesoporous and stack structure of the slit pore. Mesoporous formation is designed to the sectional decomposition and conversion of amorphous carbon to denser graphitic carbon by the thermal annealing process [11,42], in which the modulation and transformation of  $sp^3$  C cause skeleton collapse and defective edge restructure. The pore size distribution, originated from desorption branch and calculated by the BJH model, demonstrated an average pore size of 3.953 nm in PGBF-N, with the total pore volume up to 0.096  $\text{cm}^3/\text{g}$ . The BET specific surface area (SSA) of PGBF-N was calculated to be about 81.243  $\text{m}^2/\text{g}$ , which might be appropriate balance between mass transfer and conductivity, since porosity and graphitization tend to be inversely proportional. Appropriate SSA and pore distribution are conducive to exposing more reaction sites for substrate contact and catalysis without destroying electron conduction.

The graphitic structure of carbon matrix was also demonstrated by Raman spectroscopy as shown in Fig. 2b. Typical D band ( $\sim 1350 \text{ cm}^{-1}$ ) related to the defect sites or disordered carbons, and G band ( $\sim 1585 \text{ cm}^{-1}$ ) associated with  $E_{2g}$  mode stretching vibration of the honeycomb-like  $sp^2$ -hybridized carbon network of graphite were observed. The intensity ratio of  $I_D/I_G$  for BF was calculated to be 1.092, indicating the disorientated carbon structure in pristine biochar. The

decreased  $I_D/I_G$  ratio to 0.982, as well as an intense 2D band (at about  $2700 \text{ cm}^{-1}$ ) assigned to the two-phonon double resonance was observed in PGBF which was modified with catalysis of  $\text{K}_2\text{FeO}_4$  in preparation, confirming the promotion of graphitization. For graphitization, amorphous Fe species were firstly reduced to metallic Fe [27] which played catalytic role for transformation of carbon configuration, as following: 1) dissolution-precipitation mechanism, in which the dispersed carbon in molten salts at high temperature transfer freely to the surface of iron particles and reconstructed as graphitic carbon on it [6]; and 2) carbide decomposition mechanism, in which the carbon atoms could be decomposed from the carbide intermediate,  $\text{Fe}_3\text{C}$  layers (metallic carbide), at higher temperature to form graphitic carbon layer [43]. Incorporation of nitrogen into hexagonal carbon induced downshift of the G peak and slight increase of  $I_D/I_G$  ratio in PGBF-N compared with PGBF, which might be attributed to the more defective sites density and edge plane exposures from N doping [11].

To further explore the surface chemical composition and the valence state of elements in biochar-based catalysts, X-ray photoelectron spectroscopy was performed and analyzed. Besides the fairly low O/C atomic ratio (8.09 %), extra nitrogen (2.12 at.%) was observed in the full survey of PGBF-N (Fig. 2c), indicating the successful incorporation of nitrogen element into carbon skeleton. The high-resolution spectra of the N1s region in Fig. 2f can be deconvoluted into main three components at binding energies of 398.40, 399.60 and 400.75 eV, corresponding to pyridinic N, pyrrolic N, and graphitic N, respectively. N-bonding configuration with high proportion of graphitic N is owing to the conversion from the pyridinic/pyrrolic N to graphitic N at annealing temperature since the substitutional heteroatoms within graphitic



**Fig. 3.** Removal of TC in the presence of different biochar-based catalysts in PMS system (a); Effect of coexisting organics and inorganics on the degradation of TC in PGBF-N/PMS system (b) and BF/PMS system (c). Conditions: [biochar fiber] = 0.1 g/L, [PMS] = 1 mM, [temperature] = 25 °C, [TC] = 20 mg/L.

lattice have greater thermostability than that doped in non-hexatomic ring [23].

The surface functional groups in carbocatalysts were also confirmed by FTIR spectroscopy (Fig. S5), in which several characteristic peaks of porous graphitic carbon were observed including 1637 cm<sup>-1</sup> assigned to the skeletal vibration of C=C bonds in aromatic ring, 1470 cm<sup>-1</sup> ascribed to ketonic C=O stretching vibration, 1385 cm<sup>-1</sup> attributed to the stretching vibration of the C-C benzenoid ring, and 1072 cm<sup>-1</sup> designed to C-O (alkoxy) stretching vibration. Upon treatment with nitrogen doping, the new stretch at 2262 and 1271 cm<sup>-1</sup> can be originated from the conjugated triple bond of carbon-nitrogen and coupling of the C-N, respectively. These results are consistent with the observation from the high resolution XPS spectrum of C1s and O1s (Fig. 2).

### 3.2. Catalytic performances of biochar-based catalysts

Catalytic activities of the as-prepared biochar-based catalysts were evaluated by activating PMS for TC degradation. Fig. 3a shows a slight TC removal by only PMS degradation as well as insignificant adsorption by PGBF-N alone, indicating that most of the TC decrease comes from degradation through PMS activated by biochar-based catalyst. The degradation rate constant,  $k_{\text{obs}}$ , is assessed to gain more insight on the quantitative characterization of TC degradation by fitting with  $\ln(C_0/C) = k_{\text{obs}} t$  ( $C_0$ : the initial TC concentration, and  $C$ : the TC concentration at contact time  $t$ ), and corresponding results are shown in Table 1. Unmodified BF, without graphitization and nitrogen hybridization, exhibited a certain catalytic efficiency of 48.3 %, which was owing to the activation by versatile functional groups and persistent free radicals (PFRs) formed in biochar [44]. PMS activation was enhanced by biochar-based catalyst that undergone graphitization, as high as 89.1 % TC removal obtained in treatment of PGBF. Graphitic-based materials with uniformly honeycomb-like carbon framework (sp<sup>2</sup>-hybridized C) possess abundant  $\pi$ -electrons, whose chemical inertness could be disrupted by introducing vacancies and defects for delocalized-electron flow and transfer to trigger catalysis. However, the biochar composition is tanglesome with amorphous carbon domination. Even with a large number of edge defects reflected by  $I_D/I_G$ , pristine biochar cannot cause the directional flow of electrons, implying that only the vacancies and defects constructed on boundaries of well-organized carbon matrix showed desired catalytic properties. PGBF was observed by a lower  $I_D/I_G$  ratio along with graphitization, indicating the more excellent

electron conduction ability to activate PMS than BF. On this basis, the incorporation of nitrogen atoms with lone pair electrons and high electronegativity can not only enhance electron density, but also induce electron rearrangement by conjugation with sp<sup>2</sup>-hybridized C to accelerate electron delocalization. Although nitrogen doping reduced TC adsorption due to the decreased  $\pi$ - $\pi$  stacking interaction between graphitic basal plane in carbon material and contaminants [23], PGBF-N displayed outstanding degradation capacity with  $k_{\text{obs}}$  of 0.0206 min<sup>-1</sup> and removal efficiency of 96.5 %. However, only slight changes were observed between the treatment of BF-N and BF, indicating that the nitrogen doping on the disordered carbon was of little significance, which once again confirmed the critical role of graphitization in synthesis process for biochar-based catalyst on their activation of PMS. In addition, the excess functional groups (e.g. C-OH, amorphous C, and pyridine N) on the BF-N could be regarded as PMS and radical scavengers [11], thus resulting in less available PMS and reactive species for efficient TC degradation.

Additionally, the possible intermediates of TC were identified by HPLC-MS for deeper understanding of the degradation process, and several products (the MS spectra shown on Fig. S6) and probable two TC degradation pathways were proposed and elaborated in Scheme 2. P1 ( $m/z = 431$ ) and P2 ( $m/z = 417$ ) were generated from the demethylation of the dimethylamino group in TC. Subsequently, P2 was fragmented into P3 (by deamidation), P4 (by ring opening and dealcoholization), and P5 (by deacetylation) step by step. Pathway II mainly included dehydration, hydroxylation, and fragmentation through attack by reactive species. The generation of P6 was attributed to the dehydration and conversion of amide group to aldehyde group on P1, while P7 was produced by dehydration and hydroxylation on P2. Subsequently, P8 was obtained by deacetalization of P6 and dealcoholization of P7. P8 was decomposed into P9 via cleavage of the carboatomic ring, followed by the decarboxylation of P9 to form P10. These intermediate products were then further fragmented and produced carbon dioxide and water, which was consistent with the observation from the maximum TOC removal of 61.86 % by PGBF-N (Fig. S7).

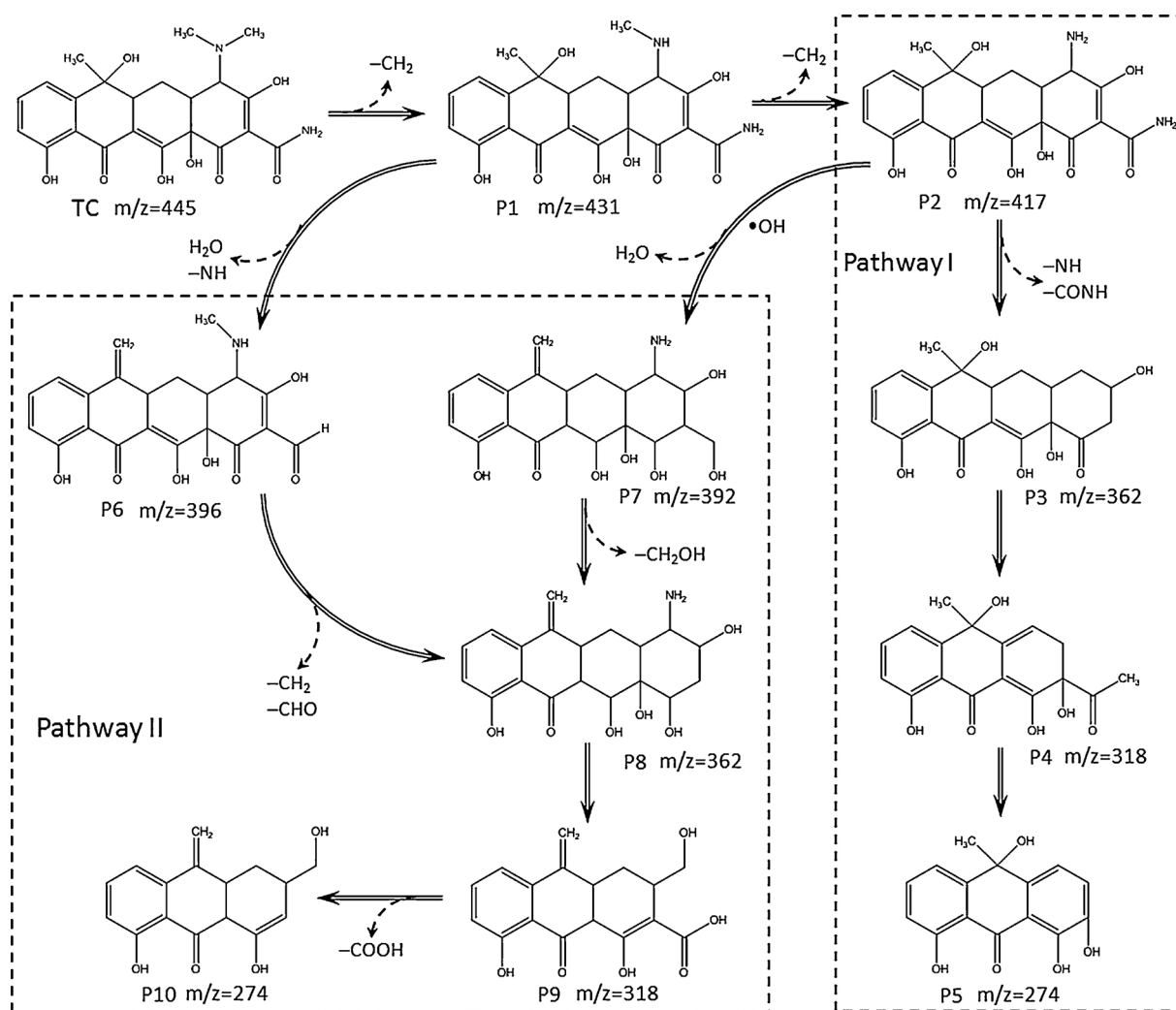
### 3.3. Catalytic mechanisms

Methanol (MeOH) and *tert*-butyl-alcohol (TBA) were employed as scavengers for both sulfate and hydroxyl radicals, and hydroxyl radicals, respectively. Fig. 4c shows an insignificant quenching ability on PGBF-N/PMS system even with high-ratio radical scavengers.

**Table 1**

The pollutant degradation rate constants in different scavengers by PMS/different biochar-based catalysts.

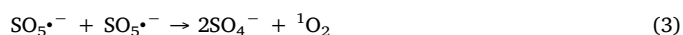
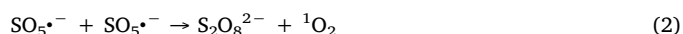
Carbocatalyst		MeOH	TBA	Phenol	BN	L-histidine	NaN <sub>3</sub>	None
	n[scavenger: PMS]	1000	1000	100	100	10	10	–
PGBF-N	$k_{\text{obs}}$ , min <sup>-1</sup>	0.0176	0.0161	0.0052	0.0066	0.0078	0.0064	0.0206
PGBF	$k_{\text{obs}}$ , min <sup>-1</sup>	0.0098	0.0105	0.0042	0.0051	0.0075	–	0.0126
BF	$k_{\text{obs}}$ , min <sup>-1</sup>	0.0025	0.0026	0.0007	0.0010	0.0024	–	0.0031



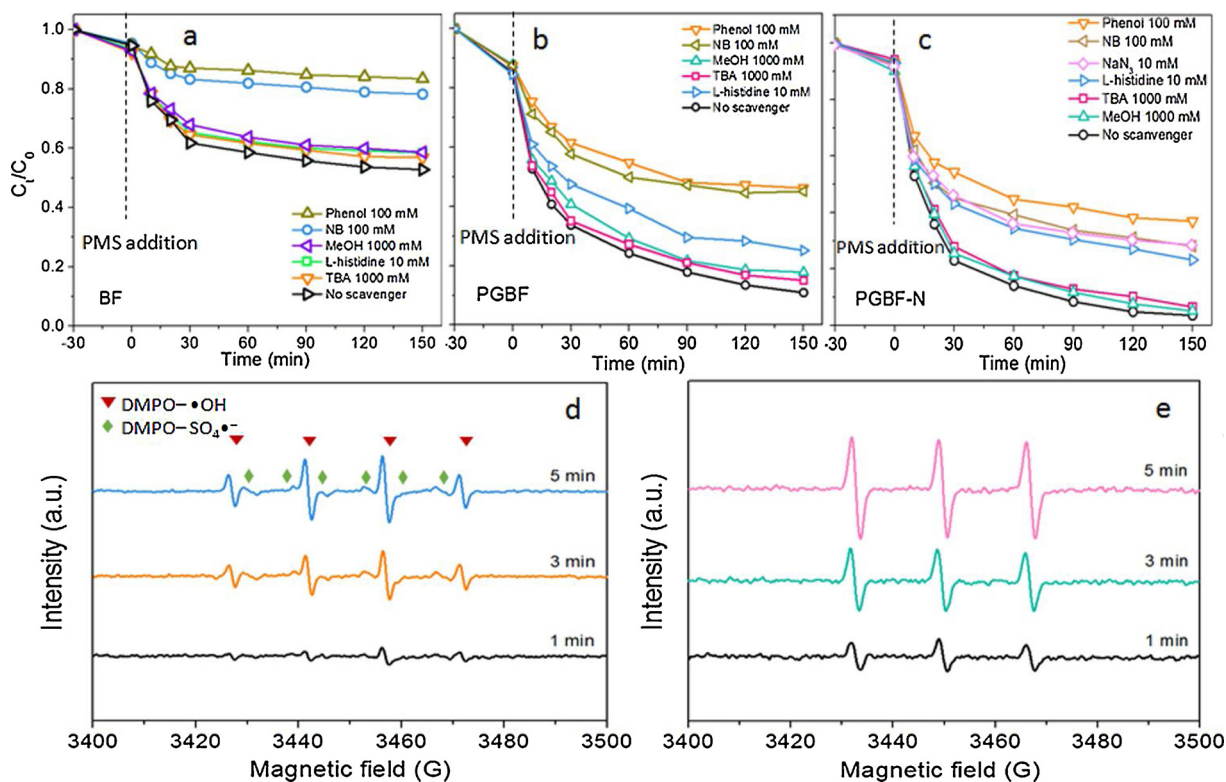
**Scheme 2.** Possible intermediates and proposed transformation degradation pathways of TC in PGBF-N/PMS system.

Unexpectedly, TBA exhibited a slightly higher inhibiting impact on TC degradation than methanol, due to the hydrophobic interaction on catalyst surface impeding further surface reactions [16]. It can be inferred that free radicals (without long lifetime and long-distance migration) are generated and performed oxidation degradation on the catalyst surface. Based on this result, the more hydrophobic scavengers, phenol ( $k_{\text{SO}_4^{\bullet-} + \text{phenol}} = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{HO}^{\bullet} + \text{phenol}} = 6.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and nitrobenzene (NB,  $k_{\text{HO}^{\bullet} + \text{NB}} (3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) > k_{\text{SO}_4^{\bullet-} + \text{NB}} (< 10^6 \text{ M}^{-1} \text{ s}^{-1})$ ), were selected to terminate the surface free radical reaction. The evident decreases of TC removal percentage could be found in the present of phenol and NB of 100 mM, with the  $k_{\text{obs}}$  declining from  $0.0206 \text{ min}^{-1}$  to  $0.0052 \text{ min}^{-1}$  and  $0.0066 \text{ min}^{-1}$  (Table 1), respectively, nevertheless the removal of TC still proceeded even when radicals were captured. These results illustrated that both  $\text{SO}_4^{\bullet-}$  and  $\text{HO}^{\bullet}$  were generated and participated in the reaction for certain degree of degradation, which also implied the more predominant role of non-radical pathway in TC degradation. The singlet oxygen ( $^1\text{O}_2$ ), as a potential reactive oxygen species in non-radical pathway, was confirmed by quenching experiments with sodium azide ( $\text{NaN}_3$ ) and L-histidine at 10 mM. Results in Fig. 4c showed that both  $\text{NaN}_3$  and L-histidine led to inhibition of TC degradation, as the calculated reaction  $k_{\text{obs}}$  decreased to  $0.0064$  and  $0.0078 \text{ min}^{-1}$ , respectively. The existence of  $^1\text{O}_2$  was preliminarily proved, and  $^1\text{O}_2$  accounted for a certain degree of TC decomposition. On the other hand, almost complete inhibiting effect was observed in the BF with phenol (Fig. 4a), indicating the absolute dominant role of the free radical pathway in

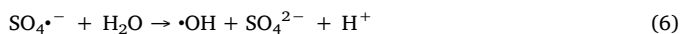
group of pristine biochar. On the contrary, the calculated degradation rates in Table 1 demonstrated that PGBF (Fig. 4b) undergone graphitization had potential in carbon-bridge mediated oxidation, which was reflected by a large degradation of TC under various scavengers. While considering the consumption of PMS molecules by L-histidine, it might be concluded that reactive species  $^1\text{O}_2$  played a limited role in PGBF/PMS system, although TC degradation was inhibited with rate drop from  $0.0126$  to  $0.0075 \text{ min}^{-1}$ . As to the graphitization and nitrogen doping in PGBF-N, graphitic nitrogen bound onto the  $\text{sp}^2$ -hybridized carbon was strongly electronegative thereby attracted electrons from adjacent carbon networks, inducing the neighboring carbon atoms to be positively charged, which was conducive to mediating the formation of  $^1\text{O}_2$  by nucleophilic reaction of PMS molecules. The nucleophilic PMS molecules released electrons toward positively charged carbon atoms and partial electrophilic groups to form anion  $\text{SO}_5^{\bullet-}$  radicals (Eq. 1).  $^1\text{O}_2$  was generated by the self-reaction of  $\text{SO}_5^{\bullet-}$  which possessed high reaction rate and low activation energy [16]. The phenomenon of radical quenching test suggested that modification with graphitization and nitrogen functionalization might induce the predominant pathway of pollutant degradation to achieve transition from radical pathway to non-radical pathway.







**Fig. 4.** Quenching experiments of BF (a), PGBF (b), and PGBF-N (c) in PMS system under different scavengers; and EPR spectrum of species adducts trapped by DMPO (d) and TEMP (e) in PMS/PGBF-N system. Conditions: [biochar fiber] = 0.1 g/L, [PMS] = 1 mM, [temperature] = 25 °C, [TC] = 20 mg/L.

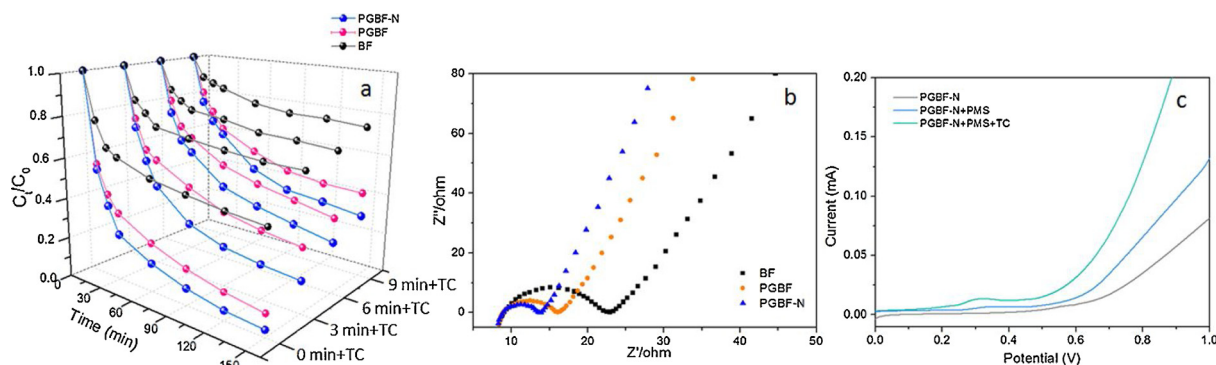


However, due to the stronger attraction between scavenger and catalyst surface through hydrophobic force, the substance covering could further affect the interaction between PMS or TC and catalyst surface and exaggerate the quenching effect, revealing it is not rigorous to get the conclusion only by radical quenching experiment. Electron paramagnetic resonance (EPR) was applied as a powerful tool to further probe the generation and revolution processes of main reactive species on PGBF-N/PMS system, in which DMPO and TEMP were treated as spin trapping agents to trap the generated species for subsequent detection. As shown in Fig. 4d, the EPR results provided evidence of the presence of DMPO-SO<sub>4</sub>•<sup>-</sup> and DMPO-•OH adducts in characteristic signals, and revealed that both radicals were generated immediately in the first few minutes, then a gradual revolution from SO<sub>4</sub>•<sup>-</sup> to •OH with time accounted for the higher intensity of DMPO-•OH signal. When TEMP was used as the spin trapping agent, an obvious typical three-peak signal ( $a_N = 17.0$  G) with equal intensity, assigned to TEMPO, was observed with an increasing trend of the signal intensities as the reaction proceeded, suggesting that <sup>1</sup>O<sub>2</sub> might be the dominant reactive species responsible for TC degradation.

To gain more insight on the non-radical pathway for TC degradation, the distinction between reactive species-dominated oxidation and carbon-bridged mediated oxidation could be drawn by delayed adding contaminants at different time intervals after mixing the carbocatalyst and PMS. The reactive species with considerably short lifetime are produced on the catalyst surface once the PMS molecules are close and attached onto the surface. If the interaction between the biochar-based catalyst and PMS is more prone to species production, a longer time

interval for delayed adding contaminants will lead to a remarkable decrease in degradation efficiency due to the constant consumption of oxidizing species. It was worthwhile mentioning that the removal rate of TC decreased a little as the increased time interval for delayed adding contaminants, since it still remained at a high removal level of 70 % at 9 min intervals (Fig. 5a, Table 2), indicating the rather high contribution of TC degradation came from the bridged-role of biochar-based catalyst for electron transfer, that is, the non-radical pathway dominated by carbon-bridge oxidation was identified as the most contributory degradation pathway. The PMS molecules pre-adsorbed on the sp<sup>2</sup>-hybridized structure of the biochar-based catalyst were activated to a metastable state since the O–O bond was weakened by electron arrangement with carbon framework. Once the electron-rich pollutants were added, the redox reaction occurred directly between pollutant molecule as an electron donor and the metastable PMS as electron acceptor with the help of PGBF-N. On the basis of the results, it can be concluded that the PGBF-N could be treated as an electron mediator to promote the electron transfer from pollutants to the PMS molecules for achieving pollutant oxidation. The same operation was carried out by catalyst of PGBF, and larger inhibition of TC removal was observed with smaller value of  $k_{obs}$ , indicating that the electron-bridged effect of PGBF was not as good as that of PGBF-N. These results implied that incorporation of nitrogen with highly electronegative into sp<sup>2</sup>-hybridized C might inspire more metastable PMS by electron readjustment to weaken O–O bond for pollutant degradation through electron-bridged oxidation, which also could be attributed to the increase in surface polarity and conductivity of the carbon material by nitrogen incorporation, making the surface more susceptible to interaction with polar substances. Compared with the significant inhibiting effect of adding pollutants at different time intervals in treatment of BF, it illustrated the important role of sp<sup>2</sup>-hybridized carbon proportion, namely the graphitization degree, on the carbon-bridged oxidation of TC.

To shed light on the electron-transfer process from pollutants to



**Fig. 5.** The removal efficiency of TC under different regular time intervals for pollutant adding after carbocatalysts and PMS mixing (a); EIS measurement of biochar-based catalysts loaded on GCEs with frequency range from  $10^{-1}$  to  $10^5$  Hz ( $[\text{Na}_2\text{SO}_4] = 0.5$  M); Linear-sweep voltammograms under different conditions (1 mM PS or both 1 mM PS and 20 mg/L TC) at a scan rate of  $5 \text{ mV s}^{-1}$  from 0.1 to 1.0 V (c).

**Table 2**

The pollutant degradation rate constants at different time intervals for adding pollutants.

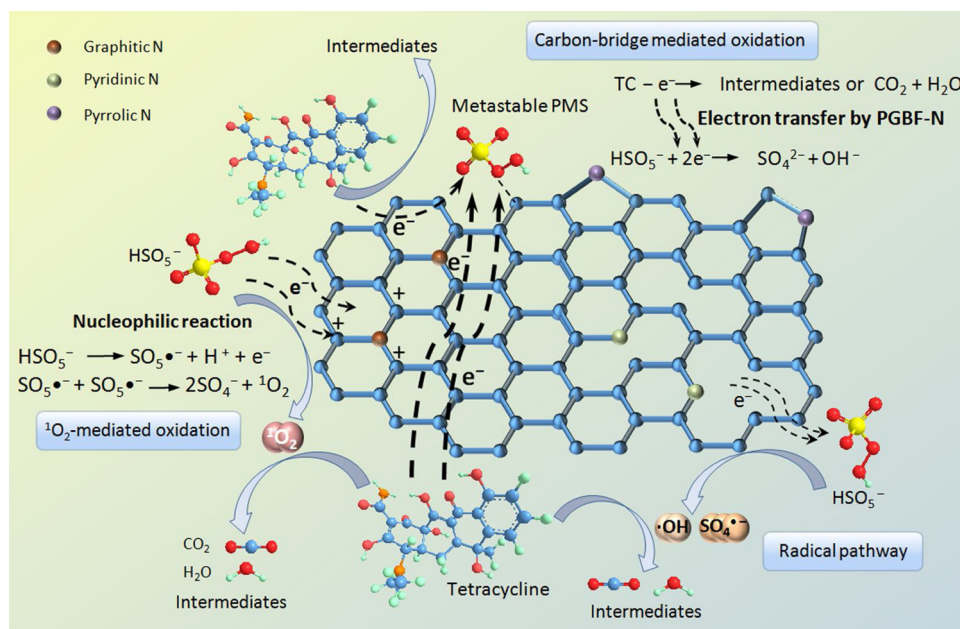
Time interval		Different biochar-based catalysts		
		PGBF-N	PGBF	BF-N
0 min	$k_{\text{obs}} (\text{min}^{-1})$	0.0207	0.0130	0.0039
3 min	$k_{\text{obs}} (\text{min}^{-1})$	0.0113	0.0069	0.0025
6 min	$k_{\text{obs}} (\text{min}^{-1})$	0.0083	0.0059	0.0019
9 min	$k_{\text{obs}} (\text{min}^{-1})$	0.0075	0.0053	0.0017

metastable PMS-carbon complexes, the conduction of biochar-based catalyst was elucidated by electrochemical measurements. The impedance of carbocatalyst is one of the important factors affecting the electron transfer, which could be provided from Nyquist plots in EIS measurement based on the diameter of the semicircle [21,35]. The smallest semicircle diameter is detected by PGBF-N shown in Fig. 5b, revealing the most excellent electronic conductivity of PGBF-N compared with that of BF and PGBF. In addition, the LSV plot (Fig. 5c) obtained in PGBF-N was observed by an increased current in terms of solution with 1 mM PMS, implying the interaction and electron rearrangement between PMS with biochar-based catalyst. It was

worthwhile mentioning that the subsequent injection of TC led to another current enhancement, demonstrating the rapid electron transfer on the established ternary system of PMS/PGBF-N/TC, in which current flow formed on PGBF-N as bridge to facilitate electron transfer from TC molecules to metastable PMS. Mechanisms of PMS activation by PGBF-N for degradation behavior of TC molecules described above are presented in detail by Scheme 3. Besides the PMS molecules gaining electrons to generate free radicals, the positive charge on the adjacent carbon of graphite nitrogen induces the PMS molecules to lose electrons to produce  $^1\text{O}_2$  through nucleophilic reactions. Direct electron transfer pathway also exists, because the promoted graphitization with increased  $\text{sp}^2$ -hybridized carbon shows more superior electric conductivity than  $\text{sp}^3$ -hybridized ones. The metastable PMS molecules that attracted on the biochar surface take electrons from TC molecules through the electron bridge role of PGBF-N to achieve the purpose of TC decomposition.

### 3.4. Active site of PGBF-N in catalysis

The essence of catalytic activation of PMS ( $\text{HO-SO}_4$ ) involves in the weakening and breaking of the superoxide  $\text{O-O}$  bond and realizing the electron transfer between catalyst and PMS molecules. In order to centralize electron density and destruct the chemical inertness of  $\text{sp}^2$ -



**Scheme 3.** Proposed mechanism of PMS activation by PGBF-N for degradation behavior of TC molecules.



hybridized carbon network for electron flow, several active sites, including vacancies and defects (zigzag/armchair edges) with delocalized  $\pi$ -electrons, versatile functional groups with lone pair electrons, and  $sp^2$ -hybridized C atom activated by conjugation with heteroatoms, were discussed for PMS activation. Electron-rich oxygen groups terminated at the defective edges were reported to be more reactive than (001) plane of graphene to achieve PMS activation [45,46]. The high-resolution spectrum of O1s presented in Fig. 2 (e, and h) was received to show the details of versatile oxygen functional groups on PGBF-N before and after heterogeneous catalysis. There were three fitted peaks in O1s spectrum centering at  $\sim 530.0$ ,  $\sim 531.3$  and  $\sim 532.6$  eV, which were referred to the binding of C=O (ketonic group), COOH (carboxyl), and H-O/O-C-O (epoxy and alkoxy), respectively. The simultaneous and opposing changes of content proportion between ketonic C=O and O-C-O could be found in both C1s and O1s scans after catalysis, implying the conversion from ketonic C=O to C-OH/O-C-O moieties in the catalytic process, which was in good consistent with the FTIR result (Fig. S5). Taking the phenomena in stability test into account, it can be inferred that the ketonic C=O as the Lewis basic sites with lone-pair electrons was more likely to effectively increase the electron density of the neighboring carbon ring and initiate the redox reaction.

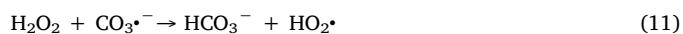
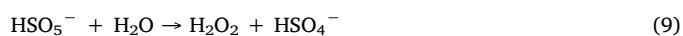
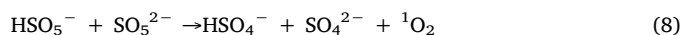
Concerning to the heteroatom doping site, total N content of PGBF-N shows a negligible reduction after catalytic reaction, while an evident reconstruction of N bonding configuration analyzed by XPS can be obtained in the used carbocatalyst (Fig. 2 f, and i). It should be noted that N1s high-resolution spectrum displayed the decrease of graphitic N (from 47.84 % to 36.63 %) and pyridinic N (from 32.54 % to 24.91 %), along with the synchronized increase of pyrrolic N (from 19.62 % to 32.97 %), indicating the graphitic N and pyridinic N might be treated as potential active site for PMS activation and TC degradation. Because graphitic N has the greatest potential to accelerate the transfer of electrons from adjacent carbon atoms and effectively destroy the inertness of conjugated graphitic carbon network [11,22], the increase in positive charge of carbon atoms caused by graphitic N is conducive to weakening O-O bonds to form surfaced metastable PMS by electron rearrangement or generate reactive substances ( $^1O_2$ ) through nucleophilic addition reaction of PMS toward positively charged carbon.

In addition to the versatile oxygen functional groups and heteroatom doping, the imperfect hexagonal units with vacancies, zigzag/armchair edges incorporated on  $sp^2$ -carbon lattice were also well demonstrated to be served as active sites in heterogeneous catalysis [12,23,47]. The defective edge at the boundary of  $sp^2$ -hybridize C framework, originated from crack of the perfect honeycomb unit, has a closer Femi level to the bulk structure and unique electronic state of dangling  $\sigma$  bonds with unconfined  $\pi$ -electrons, thereby showing excellent catalytic properties. Notably, there is no significantly improved removal rate of TC between treatment of BF and BF-N, suggesting that it is meaningless by nitrogen doping on pristine biochar. For biochar systems with a fairly complex composition, the formation of  $sp^2$ -hybridize carbon is critical, because the defects formed in hexagonal graphitic carbon network are conducive to electron transfer. The doping of heteroatoms on the disorientated system can just increase the intricacy but cannot effectively orient the electrons for achieving redox reaction.

### 3.5. Catalyst recyclability and its application on real water samples

To further explore the practical application, the effects of several common matrix species on catalytic performance of biochar fiber were investigated systematically. Previous research including the results of BF in this study (Fig. 3c) revealed the inhibitory effect of some common inorganic species, which was attributed to the reaction with sulfate and hydroxyl radicals to generate weaker radical species [48]. While results shown in Fig. 3b demonstrated little inhibiting effect of usual anions (e.g.  $Cl^-$ ,  $NO_3^-$ ) on TC degradation within 10 mM, indicating TC degradation by PGBF-N was dominated by non-radical pathway which

could avoid radical quenching reaction and suffer less interference from background substances in water. One unanticipated finding was that the addition of  $HCO_3^-$  at 10 mM in present study promoted PMS decomposition and TC degradation, which was different from those papers reported that  $HCO_3^-$  served as a scavenger to reduce the degradation efficiency [35]. This might be attributed to the buffering action of  $HCO_3^-$  kept the solution alkaline throughout the reaction, where an alkaline environment would benefit dissociation of  $HSO_5^-$  into  $SO_5^{2-}$  and provide more opportunities for inducing  $^1O_2$  evolution in non-radical pathway through Eq. 8 [49], coinciding with the pH test that alkaline environment enhanced the removal rate of TC (Fig. S9). Qiu et al. (2019) also reported a synergistic effect of bicarbonate/MNCs/PMS, in which the generated carbonate radicals inspired the formation of  $HO_2^\bullet$ , thereby promoting the  $^1O_2$  generation through a series of chain reactions (Eqs. 9–13) [50]. Different results of ion interference from various studies may be ascribed to different predominant reactive species and molecular structures of pollutants.



In order to deeply investigate the practical application of biochar-based catalysts in actual natural water, tap water, river water and pharmaceutical wastewater containing various organic and inorganic compounds in different contents (characteristics shown in Table S1) were employed as medium of TC solution in comparison with deionized water. Results of TC degradation efficiency in Fig. 6a showed similar trend obtained from tap water and deionized water. Based on differences in water characteristics, the higher levels of organic matter make negligible negative effect on TC degradation, which implied the weak competitiveness of natural organic matters on reactive activity with  $^1O_2$ , and weak electron-donating ability of organic matters for triggering carbon-bridged oxidation, taking into account the insignificant content of inorganic compounds. As to the treatments in the medium of river water and pharmaceutical water, higher adsorption capacity of PGBF-N for TC was observed due to the adhesion and encapsulation by suspended particles and colloids. However, a large amount of reducing substances, reflected by the high COD value (Table S1), make competition for consumption of PMS and reactive substances, accounting for the decline of degradation rate in pharmaceutical water.

The recycling experiments were performed on four-cycles to evaluate the reusability and stability of the biochar-based catalysts in PMS system for TC removal. Results presented in Fig. 6b demonstrated a significant decline in removal efficiency by PGBF-N/PMS with approximately 60 % in the fourth cycle experiment, which could be resulted from the surface passivation (containing irreversible conversion of the active site and cannibalistic surface oxidation reaction), and surface coverage by organics [4,16]. It was worthwhile mentioning that, on the whole, the proposed PGBF-N showed a relatively good degradation and recycling performance compared with other carbon materials (Table. S2), which was due to the fact that the non-radical pathway, especially the carbon-bridged oxidation, dominated in the PGBF-N/PMS system, in which the biochar fiber acted as an electron mediator (electron transfer from PMS to contaminants) with minimizing surface passivation.

## 4. Conclusions

In conclusion, biomass fiber was utilized to synthesize biochar-based catalysts through modified process with graphitization and

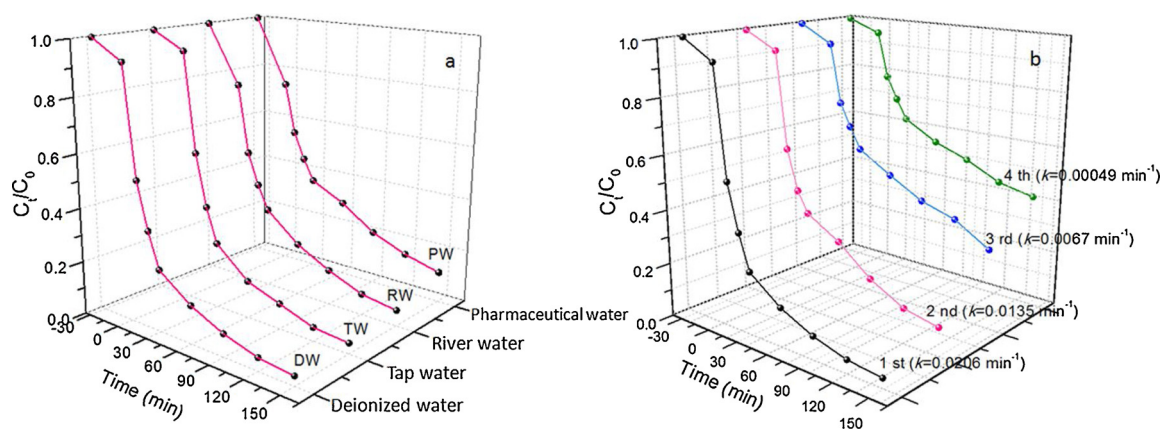


Fig. 6. Degradation for TC removal in different water samples (a) and Cycling performance (b) by PGBF-N/PMS system. Conditions: [PGBF-N] = 0.1 g/L, [PMS] = 1 mM, [temperature] = 25 °C, [TC] = 20 mg/L.

nitrogen incorporation. The prepared PGBF-N has great application potential with high catalytic degradation efficiency toward targeted pollutants dominated by non-radical pathways with enhancing electron transfer. Graphitization and nitrogen doping are proven to have the ability to increase the contribution of non-radical pathways which suffer less interference from background environment in real wastewater containing complex components. Based on the catalyst characterization results before and after the reaction, it is proposed that the electron-rich ketonic functional group, graphitic N and defect sites on carbon network are possible active sites to promote the TC degradation. These findings still open opportunities for design of metal-free catalyst on basis of the mechanistic concept that graphitization and nitrogen functionalization allow degradation mechanisms trend to non-radical pathways to overcome the negative effects of free radical.

#### CRedit authorship contribution statement

**Shujing Ye:** Conceptualization, Methodology, Data curation, Writing - original draft. **Guangming Zeng:** Supervision, Project administration, Funding acquisition. **Xiaofei Tan:** Supervision, Project administration, Funding acquisition. **Haipeng Wu:** Resources, Supervision, Funding acquisition. **Jie Liang:** Investigation, Visualization. **Biao Song:** Data curation, Investigation, Writing - review & editing. **Ning Tang:** Writing - review & editing, Visualization. **Peng Zhang:** Data curation, Writing - review & editing. **Yuanyuan Yang:** Investigation, Visualization. **Qiang Chen:** Investigation, Visualization. **Xiaopei Li:** Writing - review & editing.

#### Declaration of Competing Interest

There is no actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within five years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

online version, at doi:<https://doi.org/10.1016/j.apcatb.2020.118850>.

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