**Refined regulation and nitrogen doping of biochar derived from ramie fiber by deep eutectic solvents (DESs) for catalytic persulfate activation toward non-radical organics degradation and disinfection**

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**Abstract**

Sulfate radical-based advanced oxidation process (SR-AOPs) has great promise in water treatment, there is thereby a pressing need yet still a significant challenge to rationally design an efficient and green catalyst for heterogeneous catalytic reactions. In this study, deep eutectic solvents (DESs) were prepared and employed to simultaneously achieve structural engineering of fibrils separation and surface modifying of nitrogen doping on biochar derived from filaments biomass (NRBF) of Ramie (*Boehmeria nivea* (L.) Gaud). The more regular structure and pure carbon with reasonable configuration, and the N doped in hexatomic ring of NRBF were great impetus to improve the catalytic performance for peroxydisulfate (PDS) activation, with 4.5 times higher degradation rate of tetracycline than pristine biochar. The in-depth mechanistic study of PDS activation confirmed that dominated pathway was in transition from original reactive species (1O2) in pristine biochar system to a direct electron-shuttle pathway in NRBF system. Moreover, the non-radical dominated NRBF/PDS system showed good potential for bacteria (*Escherichia coli*) inactivation in disinfection application. Therefore, this work provides the underlying insights to guide the design of a functional and green biochar converting from Ramie filaments by an environmentally friendly facile protocol to achieve multiple purposes of wastewater decontamination and disinfection.

**Keywords**: Biochar; Ramie fibrils; Catalytic degradation; Bacteria inactivation; DESs

1. **Introduction**

Advanced oxidation process have been extensively studied as an alternative approach with high efficiency and easy operation for water treatment [1, 2], including decontamination and disinfection [3-5]. Persulfate based AOPs could be achieved by stimulation of external energy or heterogeneous catalytic processes [6, 7],demonstrating excellent application prospect due to the high oxidation potential and stability of persulfate. Besides the valence changes by transition metals as catalysts [8], carbon-based catalysts exhibit great potential to activate persulfate by lengthening and cleaving the peroxide O–O bond of peroxydisulfate (PDS) through the active sites of carbon basal plane with delocalized π-electrons, and electron-rich functional groups [9-12]. It would be fascinating to incorporate carbonaceous materials into wastewater as metal-free catalysts for heterogeneous degradation of organic pollutants, with merits of non-metal leaching, acid/base tolerance and versatility [13, 14]. Regular-structured carbons, such as carbon nanotubes, (reduced) graphene (oxide), and nanodiamonds, had been proven to be effective in a variety of catalytic processes, which is attributed to the unique electron mobility, low-dimensional structure and high conductivity [9, 15, 16].Incorporation of heteroatom into carbon framework could enhance charge delocalization and induce inertness destruction of sp2-hybridized carbon plane to create more versatile catalytic centers [11, 17, 18]. However, the large-scale practical applications of regular-structured carbon materials for water treatment are restricted by the high cost of fabrication and non-negligible biological toxicity of particles.

Biochar, produced from pyrolysis of wide-array of biomass wastes, has attracted extensive attention in heterogeneous catalysis, as an facile-preparation, low-cost, and environmentally friendly (“green”) carbonaceous material [19-21]. Biochar with tunable porous structure and favorable functional groups is open framework to be decorated for more active regions to donate or mediate electron. Biochar based catalysts showed good PDS activation for pollutant degradation through the reactive species generation and carbon-bridge role [18, 22, 23]. However, its present application is still not satisfactory because of the request for additional loading of active metallic components [24]. The complex composition and disordered structure of biochar could impede electron transfer and consume radicals, which limits the further exploration of biochar function [25] Disorders of biochar prompts us to simplify it by tuning the structure and surface properties, aiming to minimize the limitations on catalytic performance of biochar.

However, the traditional modification of biochar usually involves complicated fabrication processes with toxic and expensive reagents, besides, the intrinsic structure of biomass might be obviously destroyed during dissolution processes [26].Deep eutectic solvents (DESs), as green and tailorable eutectic solvents with biocompatibility and reusability, are composed of two or more ionic compounds with a certain proportion of hydrogen bond donors and receptors [27]. DESs possess the properties of both ionic liquid and organic solvent, showing tunable design for specific applications, such as pre-treatment of lignocellulosic biomass for digestive hydrolysis and fractionation (isolation and extraction of lignin) [28, 29]. Tan et al. (2018) [30] employed protein denaturant DES (formed from urea/guanidine hydrochloride) to achieve the controllable exfoliation of natural silk fibers into nano-scale fibrils (without crystallinity change) through the partial dissolution and intercalation. Due to the reservation of fibrillar structure of natural silks, the prepared nano-scale fibrils showed outstanding electrical characteristic and thermal stability [30].

Both structure engineering and surface modification are fascinating approaches to create more active centers and accelerate electron transfer of carbocatalyst for enhancing PDS activation [17]. The preparation of most carbocatalyst with catalytic potential often requires the use of toxic and harmful reagents, such as acids and alkalis, to improve the surface properties and pore structure of biochar for exposure of active sites. It not only causes waste of resources, but also needs subsequent processing of solution to avoid the damage of the ecological environment. It is urgent to develop a green approach to prepare cost-effective biochar with appropriate structure and surface properties. In order to synchronously improve the structure and surface properties of biochar for catalytic application, *Ramie* filaments was used as precursor and modified by DESs to obtain an N-doped refined biochar (NRBF) possessing relatively unique structure and electronic characteristic. Considering the tested DESs was prepared by choline chloride (ChCl) and urea as hydrogen bond acceptor and donor, respectively, the modification of DESs could synchronously realize the purposes of both fibrils separation (structural engineering) and nitrogen introduction (surface modifying with heteroatom doping). Nitrogen with lone-pair electron and higher electronegativity improves the local electron density and prompts electron rearrangement. Besides, the more regular structure on NRBF might allow the electron flowing smoother for electron reconfiguration in PDS system. It is expected that an environmentally friendly strategy was proposed to recycle and convert *Ramie* biomass into a functional carbocatalyst to achieve multiple effects of wastewater purification and disinfection through PDS activation process.

1. **Materials and methods**
   1. **Materials**

Filaments biomass, collected from Ramie (*Boehmeria nivea* (L.) Gaud.) with wide distribution, has advantages of relatively pure constituent and internal special fiber structure, and it can be used as carbon precursor with chemical stability, flexibility, and conductivity [25]. *Boehmeria nivea* (L.) Gaud was obtained from Ramie Institute of Hunan Agricultural University in China. Choline chloride (ChCl, purity >98.0%), and urea (CH4N2O, purity >99.0%) were purchased from Sigma-Aldrich, and used without purification. Tetracycline (TC: purity >98.5%), sodium peroxydisulfate (Na2S2O8, PDS, purity >98.0%) were provided by Shanghai Macklin Biochemical Co., Ltd. Deionized water (18.25 MΩ•cm), produced by Ulupure (UPRII-10 T) laboratory water system, was used as medium of the solution without additional instruction.

* 1. **Synthesis of biochar-based catalysts**

The used DES was prepared by mixing choline chloride and urea at the molar ratio of 1: 2 in a round-bottom flask. The mixture was stirred and assisted with oil bath at 60°C until a homogeneous liquid without any solid particles form, and cooled down for further use. Filaments biomass, reeled off from Ramie bark, was treated as precursor, and it was degummed in a boiling solution of 0.5 wt% Na2CO3. After being washed and dried, the pre-treated biomass was transferred into a quartz boat and calcined in tube furnace operating at 900°C with heating rate of 5°C/min and continuous flow of N2 gas to prepare pristine biochar (PB). For modification, the above PB was soaked into DESs with a solid-to-liquid ratio of 1:100 (g: mL) in Teflon-lined autoclave, and continuously heated at temperature of 120°C lasting 12 hours after dispersing evenly. Undergone filtration and vacuum drying at 60°C overnight, the separated ultrafine solids were calcined at same condition in tube furnace, and the resulted was called as NRBF. For comparison, nitrogen-doped biochar (NPB) was prepared at the same pyrolyzed operations by grinding PB with urea at the mass ratio of 1:2. The illustration of catalyst synthesis and mechanism is shown in Scheme 1. More details and characterization methods were given in Supporting Information (SI).

* 1. **Catalytic performance experiments**

2.3.1 Tetracycline degradation

The catalytic degradation of TC by biochar samples/PDS system was carried out in conical flask in a thermostatic shaker at a shaking rate of 150 rpm. Unless otherwise stated, 10 mg of carbocatalyst was suspended in a 100 mL of TC solution (C0=20 mg/L), and the first 30 minutes are needed to achieve the adsorption-desorption equilibrium, followed by addition of PDS (final solution containing 1 mM) to trigger the degradation reaction with PDS activation. Periodically, 1 mL solution samples were withdrawn, undergone filtration by 0.45 μm PVDF disposable filters, and then injected into a vial loading with 10 μL 1M sodium thiosulfate as terminating agent. The residual TC concentration was quantified by high performance liquid chromatograph (HPLC, Agilent 1260 Infinity, USA) at detecting λ of 360 nm.

2.3.2 *Escherichia coli* disinfection

The disinfection performance of NRBF/PDS system was evaluated using a test object of *Escherichia coli* (*E. coli*) whose population is often used as a hygienic standard for drinking water. After the experimental vessels were autoclave sterilized, a certain amount of bacteria was added to the sterile solution, and the prepared NRBF was then dispersed in the above solution. PDS (the final concentration of the solution was 1 mM) was subsequently added to trigger the sterilization process under oscillation at room temperature. The mixture was taken out after 30, 60, and 120 minutes of reaction, and diluted with 0.8% NaCl sterile water to an appropriate multiple. Plate counting method with Eosin-Methylene Blue Agar was used to measure the number of colonies. The morphological changes of *E. coli* across the oxidation process by NRBF/PDS system were characterized and analyzed through biological scanning electron microscopy (Hitachi SU-8010).

**3. Results and discussion**

**3.1 Characterization of biochar-based catalysts**

As presented in Fig. 1, the transformation of morphology and microstructure on biochar undergone modification of DESs was characterized by SEM with different magnifications. Both particles of biochar-based catalysts adopt a rodlike morphology which was consisted of plentiful strips, inherited from the natural morphology of Ramie fiber. A high magnification SEM image (Fig. 1a and b) of PB reveals that the interlinked filaments aggregated and coalesced mutually to form a surface status with grooves in one direction on the original biochar. After the DESs processing, the connected substances and surface cementing substances of filaments were damaged, allowing the refined fibrils with diameter of about 200 nm to be separated from each other. The successful separating fibrils from fiber biomass was ascribed to the intercalation effect and swelling phenomena by DESs, since the DESs have ability for permeating into the fiber filaments and loosen the linking force between fibrils by weakening the hydrogen bonds [30], decreasing their hydrophobic interaction, and destroying the linked substances, and it is therefore the refined fibrils would be separated from the whole biomass fibers.

To further explore the textural characteristic and porous structural property of the biochar-based catalysts before and after modification, N2 adsorption-desorption isotherm and the pore size distribution were analyzed (Fig. 1c and f). Both biochar exhibited I/II-type isothermal curves with the abrupt adsorption inflection at low relative pressures, suggesting the characteristic of micro-pores [31]. And there were H4-type hysteretic loops of desorption branch in isotherm, assigned to the narrow fissure pores, originating from the interstices between the filamentous structures. As presented in Table 1, the calculated BET specific surface area (SBET), as well as the contribution of micropore area, was higher in NRBF than that in PB. Moreover, the pore size distribution, calculated by the DFT model, exhibited the smaller pore diameter and higher proportion of micropores on NRBF. It demonstrated that DESs could penetrate smoothly into the space of the filamentous structure, thereby increasing the gap distance between each fibrils or even achieving the separation of the filament structure through swelling effect and part dissolution of the linked substances, which might create abundant micro-pores of fissure.

The analysis of X-ray photoelectron spectroscopy was performed in order to explore the element composition as well as their valence state of the prepared biochar-based catalysts. The full survey in Fig. 2g shows that many impurity elements which appeared in PB, especially the Ca, and Mg (Fig. S1a), were disappeared in NRBF, while a small tip assigned to element nitrogen (2.33 at.%) was only occurred in NRBF, suggesting the carbon skeleton was successfully doped with nitrogen through the solvent intercalation treatment of DESs. Moreover, a sharp increase in carbon content was obtained after modification, with the O/C atomic ratio decreased from 21.04% on PB to 4.56% on NRBF. This is also supported by the observation from Fourier Transform Infrared Spectroscopy (FTIR) representing the surface functional groups on biochar (Fig. 3a). Except the higher intensity of a peak assigned to the vibration of aromatic compounds (~1580 cm-1) on NRBF, peak at 1440 cm−1 attributed to the saturated carbonyl acid terminated by hydroxyl with hydrogen bond of NRBF was decreased than that of PB. Besides, peak at 1040 cm−1 designed to C–O–C stretching vibration in ether group was broader and slightly decreased in NRBF spectrum, suggesting the peak intensity was reduced compared with PB. All results showed that refining separation by DESs could improve carbon purity and simplify the complicated components of biochar in order to reduce the hindrance during electron migration.

The high resolution spectrum of C1s region in Fig. 2 was analyzed to show details of the carbon configuration, in which there were several fitted peaks locating at ~284.8 eV ascribed to the graphitic structure (sp2 C, C=C), ~285.5 eV referred to sp3-hybridized carbon (C–C), ~286.3 eV attributed to the C–O in phenolic or etheric groups, ~287.2 eV belonged to the C=O in carbonyl groups, and ~289.8 eV corresponded to the carboxy groups (–COOH). In addition, a novel peak around 292 eV originated from the π-π\* shake up emerged, due to the relatively high pyrolysis temperature, inferring the occurrence of partial graphitization [23]. Compared with the original biochar, the sp2 to sp3 carbon area ratio of NRBF (12.81) is much larger than BF (6.25) as shown in Table 2, which was another evidence of more partially graphitic structure on NRBF [32]. The corresponding spectra of N1s region of NRBF can be deconvoluted into main three components: pyridinic N at 389.5 eV, pyrrolic N at 399.5 eV, and graphitic N at 400.4 eV. A relatively high content of graphitic N (49.49%) was obtained, owing to the greater thermostability by substitutional heteroatoms within graphitic lattice than that doped in non-hexatomic ring. Graphitic N was proven to exhibit high catalytic activity, because the shortest bond length of C–N on graphite N shows the greatest potential for affecting electron cloud density [11].

The carbon configuration of samples was also demonstrated by Raman spectroscopy (Fig. 3b), in which the typical peaks were observed. The D band (~1350 cm−1) corresponding to the K-point phonons of A1g symmetry of ring breathing vibration mode is regarded as the signal of the 6-fold aromatic rings by disorder or the edge of graphite carbon, and G band (~1585 cm−1) belonging to the zone-centre phonon of E2g symmetry stretching vibration is considered as the signal of honeycomb-like sp2-hybridized carbon network in graphite. Typically, there are three steps involved in the transition process from tetrahedral amorphous (ta-C) to a complete graphitic one (g-C): 1) turning from ta-C to the form of amorphous carbon (a-C); 2) converting from a-C to the micro-crystalline graphite (ng-C) with plenty aromatic clusters; and 3) transforming from ng-C to graphitic carbon by growth along one axis [23, 33]. In the stage 2, research confirmed that the increased amount of aromatic rings would improve the intensity of D peak, thereby proportionally enhancing the I(D)/I(G) value [33, 34], which might account for the larger I(D) to I(G) ratio of NRBF(1.13) than that of BF (1.03). On the basis of the slightly right-shifted G peak, it could be identified that the migration of electron cloud on corresponding sp2-hybridized C could be achieved through the changes of C–N bond strength and length between atoms. The greater ratio value of I(D)/I(G) on NRBF might imply the more number and clusters of aromatic compounds than PB, instead of reflecting the content ratio of sp3-to sp2-hybridized carbon component.

**3.2 Catalytic performance for pollutant degradation by biochar-based catalysts**

TC, a kind of frequently detected antibiotic, was chosen as the target pollutant to evaluate the catalytic performance of carbocatalysts in PDS activation. Concerning the adsorption equilibrium in first 30 min, NRBF showed a fast but relatively small adsorption of TC. It exhibited the TC molecules were attracted rapidly onto the surface, following by being degraded to restore available adsorption sites of catalyst for continuous TC removal. As shown in Fig. 4a, PB exhibited a certain catalytic ability for TC degradation, resulted from activated PDS by versatile functional groups, or persistent free radicals formed at high temperature [35]. The catalytic efficiency was quantitatively characterized by degradation rate constant (*kobs*) fitting with ln(C0/C)= *kobs* t. Compared with the *kobs* value of PB, there was little enhancement in that of NBF, but NRBF made great improvement with the *kobs*risen from 0.0051 min-1 (by PB) to 0.0221 min-1. The results demonstrated the little significance of nitrogen doping on catalytic performance of biochar when it has tanglesome carbon structure and complicated components with unnecessary function groups, especially the surface terminated by hydrogen bond [25]. The disordered structure not only failed to realize the oriented flow of electrons, but also possessed more boundary adverse functional groups that consume oxidizing species. The separation of refined fibrils on NRBF by DESs was proven to be promising for improving carbon purity and reducing terminal adverse functional groups. Besides, the monotonous and regular structure of the separated fibrils enabled the electrons flow directionally. Research from Han et.al [32] also confirmed the separated cellulose-hemicellulose/lignin by chemical treatment could be transformed into a partially graphitic structure, and the resulted biochar showed better electrical characteristic than biochar converted from original lignocellulose. Incorporation of nitrogen into organized carbon matrix (aromatic structure) enhanced the π-electrons flow through the combined function of creating more defects constructed on boundaries and improving the electron density, thereby promoting the catalytic degradation of TC by NRBF. In terms of PB, the disordered structure is not conducive to the directional transfer of electrons. Partial electrons move laterally between the C generated from fibrils and the C generated from linked substances in PB. The highest adsorption capacity yet mild catalytic degradation rate of PB might be caused by that both adsorption and catalysis depended on the similar active sites of oxygen-containing functional groups. Moreover, the excess adverse functional groups (e.g. C–OH, and pyrrolic N) of PB could be regarded as oxidant scavengers, leading to less available oxidizing substances for TC degradation [12]. Considering the limited oxygen-containing functional groups but the highest degradation rate of NRBF, it manifested that the catalytic performance of NRBF may be more dependent on electron shuttle by bridge role, which was different from the PB that was relied on functional groups dangled on catalyst surface.

The implications of diverse background substances are of great importance for the efficiency of oxidation system in practical application. The PDS activated by NRBF could maintain high removal efficiency for TC degradation in a wide pH range from 3 to 9, and the increased alkalinity slightly promoted the removal of TC (Fig. S2). It might be explained by the accelerated hydrolysis of S2O82− (Eq. 6) under alkaline condition for the subsequent chain reaction and PDS decomposition. The anti-interference ability of the NRBF/PDS system was investigated toward several common matrix species which were proved to be inhibitory effect on oxidation by radical depletion and matter competition in previous studies [36]. Results on Fig. 4b showed inorganic anions (Cl–, NO3–, and HCO3–) at concentration of 10 mM exhibited mild inhibiting effects on TC removal, preliminarily revealing the TC degradation by NRBF/PDS was not dominated by the radical pathway. One unanticipated finding was that the addition of HPO42– as coexisting species promoted the adsorbed amount and degradation rate of TC molecules by NRBF catalyst. Besides the buffering action of HPO42– kept the solution alkaline, HPO42– also might serve as a chelating agent and was beneficial for TC and PDS molecules reaching onto the NRBF surface, allowing a rapid electron transfer from pollutants to carbon-PDS\* complex across NRBF. Although the TC degradation was slightly inhibited by humic acid (HA) at high concentration via competitive consumption of oxidants, the TC removal efficiency remained at 92.05% with HA of 30 mg/L (Fig. S3). To further explore the influences of complicated conditions, the medium of TC solution was replaced by actual natural water, such as tap water (TW), river water (RW) and pharmaceutical discharge wastewater (discharge water from pharmaceutical plant, PDW) which contained various organic and inorganic compounds at different concentration (Fig. 5a). It is unexpected that the higher catalytic performance of NRBF/PDS was obtained in river water compared with the control test in deionized water. It may be explained by the quinone groups of natural organic matter widely existed in river water [37, 38], which had been proved to activate PDS or promote radical chain reaction to participate in the degradation process of TC (Equation 1–2) [39]. The high COD value in pharmaceutical discharge water, represented a large number of reducing substances which might consumes PDS and reactive species, was mainly responsible for the decline of TC degradation.

*Quinones + H2O → 2 Semiquinone• − + 2 H+* (1)

*Semiquinone• − + S2O82− → SO4• − + Quinones* (2)

**3.3 Mechanisms of PDS activation by NRBF**

The essence of PDS activation is related to the weakening and cracking of the superoxide O–O bond in PDS molecules (O3S–O–O–SO3), realizing the electron transfer between carbocatalyst and PDS molecules. The reactive species-mediated pathway involves the process that PDS molecules obtain electrons from catalyst thereby are decomposed to reactive species, while the non-species pathway involves the process that metastable PDS\* attached on carbocatalyst directly gain electrons from TC via two-electron conduction (Equation 3~5). The inhomogeneous distribution of electron density and the smoothness of electric flow are important characteristics of carbocatalyst for PDS activation. It was reasonably mentioned that active sties on carbocatalyst with unique electronic state, such as vacancies and defect edges on carbon plane, and versatile functional groups with lone pair electrons, were more conducive to interact with PDS by electron rearrangement to form the metastable carbon-PDS\* complex with activated state. Comparison of the high-resolution spectrum of C1s on NRBF before and after PDS activation (Fig. 2b and c) showed that the peaks of π-π\* vibration completely disappeared on used NRBF, indicating the defects on aromatic cluster with asymmetric electron configuration were regarded as active center. Details in the area ratios of the fitting peaks for each element before and after oxidation were estimated and shown in the Table 2 and S2. Synchronous and opposite changes in content proportion were observed on ketonic C=O and C–O from both C1s and O1s scans, as well as the great decline of C=O/C–O. Based on the conversion from ketonic C=O to C–O moieties, it can be inferred that the C=O acting as Lewis basic sites with unpaired electrons could be able to increase the electron density of the hanged carbon and promoted its reactivity. A distinct reconstruction of N bonding configuration was also obtained after catalytic reaction with regard to the heteroatom doping site. The high-resolution spectrum of N1s displayed that the content of graphitic N and pyridinic N was decreased from 49.49% to 20.56%, and 41.36% to 14.87%, respectively, along with simultaneous increase in content of pyrrolic N from 9.15% to 64.57% after PDS activation (Table S3). It could be concluded that heteroatom doping on hexagonal units could be treated as potential active site, and was more likely to inspire electron flow between catalyst and PDS molecules. More aromatic clusters, higher C=O/C–O ratios, and conjugation of heteroatoms with unpaired electrons in NRBF contributed to the excellent catalytic performance of NRBF/PDS system. The increase of O proportion between NRBF and used NRBF was attributed to the surface passivation by the catalytic oxidizing environment and the oxidation by the generated reactive species. Due to the irreversible conversion of active site, especially the graphitic N, as well as the cannibalistic surface oxidation [14], TC removal efficiency by NRBF/PDS system decreased after four-cycles (Fig. 5b), with lack of reactive sites for triggering electron transfer. Considering the poor recycling of transition metals with metal-leaching risk[40] and other carbon materials [10, 41], the prepared NRBF maintained relatively good reusability performance with 61.3% removal efficiency at fourth use, which might be explained by the dominated role of NRBF-bridged electron shuttle mechanism mitigating and minimizing the surface passivation.

*S2O8−\* + TC → (NRBF-catalyst) → 2 SO42− + products* (3)

*TC −2 e− → (NRBF-catalyst) → products* (oxidation half reaction of Eq. 3) (4)

*S2O8−\* +2 e−→ (NRBF-catalyst) → 2 SO42−* (reduction half reaction of Eq. 3) (5)

Identification of reactive species involved the generated reactive species with discrepant oxidation and anti-interference abilities on carbocatalyst/PDS system was conducted and presented in Fig. 6. Classical scavengers, methanol (MeOH) and *tert*-butyl-alcohol (TBA), showed little effects on TC degradation even at a molar ratio of 1000:1 (scavenger/PDS). Taking their hydrophilic properties and the extremely short lifetime of free radicals into account, the free radicals produced on the catalyst surface might cannot be in effective contact with hydrophilic scavengers [23]. Dimethyl sulfoxide (DMSO) were selected to terminate the reaction of surface-bounded radicals, but the degradation curve was hardly affected at 10 mM DMSO, demonstrating the feeble contribution of SO4•− and•OH on TC degradation. It demonstrated that there were other reactive species involved in non-radical pathway. Thus, benzoquinone (BQ) and sodium azide (NaN3) were employed as scavengers for O2•− and 1O2, respectively, and exhibited moderate suppressed effect with the calculated reaction *kobs* reduced to 0.0064 and 0.0078 min−1, respectively (Table 3). The existence and function of 1O2 on oxidation were proved, and it also inferred that the superoxide ions can either participated in oxidation or generated 1O2 through reaction with H2O molecules (Equation 9~11) [6, 17].

*S2O82− + 2 H2O→ HO2− + 2 SO42− + 3 H+* (6)

*S2O82− + HO2− → SO4•− + SO42− + O2•− + H+* (7)

*3 S2O82− + 4 OH−→ 2 O2•− + 6 SO42− + 4 H+* (8)

*O2•− + H2O → HOO• + OH−* (9)

*O2•− + HOO• → HOO−+ 1O2* (10)

*HOO• + HOO• → H2O2 + 1O2* (11)

Electron paramagnetic resonance (EPR), a powerful tool to demonstrate the existence and evolution of reactive oxidizing species, was conducted assisted with spin trapping agents of DMPO and TEMP in NRBF/PDS system. The results in Fig. 6b showed the relatively weak signals of DMPO-SO4•− and DMPO-•OH adducts with glitches, indicating that the amount of produced •OH and SO4•− is small or even negligible in oxidation process. However, the characteristic signals of DMPO-O2•− could be detected in DMPO system. Meanwhile, it could be clearly observed by a high-intensity typical three-peak signal with equal intensity (aN=17.0 G), assigned to the classical spectrum of TEMPO belonged to 1O2 species. Results concluded that 1O2 was the main reactive species accounting for pollutant degradation, which was in good consistent with the quenching tests.

Diverse organic probes were applied to investigate the degradation of various organic pollutants with distinctive characteristics on NRBF/PDS system. Phenol can be degraded by both SO4•− and•OH with high second order rate of *kSO4•−+phenol* =8.8×109 M−1 s−1, *kHO•+phenol* =6.6×109 M−1 s−1, which is usually used as a hydrophobic scavenger of radicals near the surface [11]. Combined with the above experimental results shown that almost no free radical generated, more than 80% of phenol degradation, presented in Fig. 6c, was originated from non-radical pathways. Furfuryl alcohol (FFA), employed as effective scavenger to determine the contribution of 1O2 (*k*1O2*+FFA* =1.2 ×108 M−1 s−1) [18], was observed by modest removal efficiencies of 61.5% with less degradation rate than phenol removal. These results illustrated that 1O2 was generated and participated in the reaction, but 1O2-mediated oxidation was not elucidated as the dominated pathway on NRBF activated PDS. In addition, bisphenol A (BPA) had been proven to be barely oxidized by 1O2 [42], while BPA as an organic probe showed a certain degree of degradation efficiency by NRBF/PDS system. Above findings led us to conclude that the electron-shuttle mechanism mediated by carbocatalyst without reactive species occurred on the ternary system of pollutant/NRBF/PDS. Moreover, the electron-rich 2,4-dichlorophenol (2,4-DCP) which is easier to act as an electron donator demonstrated a much higher degradation rate than phenol, indicating that bridged role of NRBF for electron-shuttle showed great potential on oxidation.

To gain more insight on the distinction between reactive species-mediated oxidation and electron-shuttle mechanism, tests of extending the delayed time to add pollutant after mixing the carbocatalyst and PDS were proceeded. Considering the short lifetime and transport distance of the reactive species, they were generated on catalyst surface once the PDS molecules contacted with catalyst and disappeared immediately through self-consumption. A longer delayed time interval for adding pollutant might lead to a sharp drop in pollutant degradation because of the constant consumption of oxidizing substances, if the oxidation system is more prone to species production. It is noteworthy that extending the delayed time of adding pollutant made a little impact on the TC degradation by NRBF/PDS system (Fig. 7a). There were similar degradation rate at time interval of 0, 3, and 6 min, and maintained the high pollutant removal level of 92.7% at 9 minute intervals, shown on Table S4, indicating the greatest contribution on TC degradation come from the carbon bridge mediated electron-shuttle mechanism. Even when the reactive species were almost completely consumed, the redox reaction for pollutant degradation also occurred between the adsorbed TC (as an electron donor) and the metastable carbon-PDS\* complex (as electron acceptor) directly via electron shuttle with the help of NRBF. The same condition was performed on PB and the corresponding results were shown in Fig. S4, both degradation efficiency and rate decreased legibly with the delayed time of adding TC extending. Taking the quenching tests on PB group into account, it could be concluded that 1O2-mediated oxidation was served as main degradation pathway in PB/PDS system. After the modification of DESs to obtain a higher purity carbon and more regular structure on NRBF for more excellent electronic conductivity, the dominated PDS activation mechanism by biochar catalyst transitioned from reactive species mediated oxidation to electron-shuttle mediated pathway.

To gain a better understanding of the electron-shuttling process on NRBF, Linear-sweep voltammograms (LSV) analysis was conducted to evaluate the half oxidation-reduction by simulated reaction environment of TC/NRBF/PDS system. As shown in Fig. 7b, a slight increase in current was observed by adding PDS into electrolyte, because of the interaction between PDS molecules and NRBF surface. Due to the strong electronegativity of the doped atom, graphitic nitrogen bound onto the carbon network tended to attract electrons from adjacent carbon, which induced the adjacent carbon atoms to be positively charged. The nucleophilic PDS molecules were adsorbed on sp2-hybridized structure of NRBF and shared partial electron with the positively charged carbon atoms to form a metastable state of carbon-PDS\* complex through electron arrangement along with O–O bond weaken. Subsequently injecting TC with abundant electrons, the increased significantly current and oxidation peaks were detected in the LSV plot. The obtained results revealed that a rapid current flow was established on ternary system of TC/NRBF/PDS, in which the target organics, PDS, and NRBF served as electron donor, acceptor, and mediator for electron-shuttling, respectively, to promote electron transfer from TC molecules to the metastable carbon-PDS\* complex.

Whether it is the formation of reactive species on the carbocatalyst surface or the electron shuttling from pollutants to carbon-PDS\* complex with the bridged-role of carbocatalysts, the electron conductivity of the catalyst was critical and identified by electrochemical measurements. The Nyquist plots originated from electrochemical impedance spectroscopy (EIS) were carried out and shown in Fig. 7c. The electron transfer capability of biochar-based catalysts was described according to the diameter of semicircle [17]. All diameters of the EIS semicircle were obviously smaller than the bare glassy carbon electrode (GCE) (Fig. S5), and the order of the impedance of biochar was NRBF<NPB<PB, which was in good consistent with their results of catalytic performance. It can be concluded that incorporation of nitrogen with high electronegativity and unpaired electrons is likely to improve the electron density and facilitate the π-electrons flow. Moreover, compared with a more disordered structure, doping N atoms on a relatively purely ordered structure can play a better role on electron triggering and transfer. More number of ordered aromatic clusters as well as the N doped in hexatomic ring, reflected by the greater ratio of I(D)/I(G), endowed NRBF with the most superior electric conductivity.

In addition, the possible degradation process of TC by NRBF/PDS system was deduced according to the oxidation intermediates identified by HPLC-MS. Several TC products were detected on the MS spectra (Fig. S6), and the probable molecular structure of products and three TC degradation pathways were elaborated in Scheme 3. Multiple hydroxylation and dehydration by the attack of oxidizing species, and N-demethylation process were the mainly reactions in Pathway I. In pathway II, TC molecules were proceeded the dehydration, N-demethylation, deamidation, hydroxylation, ring opening, and dealcoholization in sequence [25]. And Pathway III was successive fragmentation process included the loss of N-methyl, amino and amide groups, acetyl group, and phenolic hydroxyl group [43]. Ultimately, intermediate products were further converted into inorganic mineral by cleavage of carbon ring and fragmentation.

1. **Catalytic performance for bacterial inactivation by NRBF/PDS system**

The disinfection ability of NRBF/PDS system was also explored to expand the application of the resultant biochar in groundwater and drinking water treatment. The *E. coli* was chosen as indicator, and the corresponding results on the amount change of viable cells during inactivation were displayed in Fig. 8. Compared with the blank treatment, only a negligible reduction of active *E. coli* cells was received under 120 min of incubation by PDS or NRBF alone. Previous studies had shown that the negative effects of biochar on bacterial activity are generally derived from: (1) the hazards of the PAHs produced and retained in carbon pores during pyrolysis, as well as the residual heavy metals from biomass components; and (2) the biotoxicity threats of persistent free radicals (PFRs) interacted with the hydrogen peroxide and oxygen molecules in aqueous solution for peroxidation [18, 44]. However, the low impurities, regular morphology and high pyrolysis temperature allowed NRBF to be a friendly habitat of bacteria. It suggested that the individual existence of NRBF with hypotoxicity will not cause a major negative ecological impact to organisms. On the contrary, the combination of NRBF with PDS exhibited the quite large inactivation efficiencies, as about 5.19-log decline on *E. coli* cells. Identical conclusions were obtained in observation from bio-SEM with the changes of cellular morphology (Fig. 8). Most *E. coli* cells in only NRBF group showed a well-preserved rod-like morphology with smooth surface, which was similar with the normal shape in blank treatment. After catalytic oxidation of NRBF/PDS system, deformed and shrunken cell morphology was observed, indicating that the cell membrane of *E. coli* was destroyed. Different from the free radical-induced lipid peroxidation caused by transition metal catalyzed system on previous studies [45, 46], the non-radical pathway, dominated in NRBF/PDS oxidation system, may account for the membrane damage. Oxidation occurred between the electron-rich components (e.g. polysaccharide, protein, and lipid substance) on cell membrane with the metastable PDS-carbon complex by electron shuttle, and the further cell deformation was caused by the increased permeability along with cell swelling, rupture, leaking cellular components. Compared with photocatalytic disinfection, the advantage and characteristic of this SR-AOPs system is the controllability of inactivation process by adjusting the oxidant dose. Due to the harmless of NRBF, the inactivation can be terminated once the oxidant was consumed without the solid-liquid separation operation of catalyst, which was different from the inevitable disinfection of photocatalyst when exposed to light.

**5. Conclusions**

Herein, NRBF was manufactured from *Boehmeria nivea* (L.) via thermal pyrolysis and modification by green and tailored DESs. Both separation of fiber structure and introduction of nitrogen on biochar were synchronous realized by DESs modification for the first time to improve the catalytic performance. An environmentally friendly and high-performance biochar was obtained for PDS activation in pollutant degradation and bacteria inactivation. The high catalytic efficiency of NRBF was attributed to the efficient electron transfer originated from the more regular structure, and more cluster number of aromatic compounds with N doping. Different from the dominant role of reactive species in oxidation of PB/PDS system, non-radical process of NRBF-bridge mediated electron shuttle was regarded as dominated pathway of PDS activation by NRBF, which suffered less interference from background conditions. Regions of concentrated electron density, such as electron-rich ketonic group, defect and N doping on hexatomic network were possible active sites to promote PDS activation. The NRBF/PDS non-radical system was proved to be able to achieve bacterial inactivation by destructing the cell membrane. The inactivation process is proposed for the first time to be controlled by adjusting the oxidant dosage, owing to the harmlessness of NRBF alone. These findings open opportunities for developing an effective metal-free catalyst in wastewater purification, on basis of the mechanistic concept that structural engineering and nitrogen modification by DESs on biochar.

**Conflicts of interest**

There are no conflicts of interest to declare.

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**Table 1 Details in porosity characterizations of biochar-based catalysts**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Biochar sample** | **SBET a (m²/g)** | **Smes b (m²/g)** | **Smic c (m²/g)** | **Vtotal d (cm³/g)** | **Vmic e (cm³/g)** | **Average pore size** **(nm)** |
| **PB** | 479 | 140 | 339 | 0.379 | 0.235 | 3.12 |
| **NRBF** | 565 | 42 | 523 | 0.285 | 0.237 | 2.05 |

aSBET: the specific surface area analyzed by BET method.

b Smes: the mesoporous area got by the t-plot method external surface area.

c Smic: the microporous area calculated by t-Plot method, and Smic = SBET – Smes.

d Vtotal: the total volume.

e Vmic: the microporous volume obtained by t-Plot method.

**Table 2** **Carbon content and configuration of biochar-based catalysts by XPS**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Biochar sample** | **C proportion (at.)** | **C=C (%)** | **C–C (%)** | **C–O (%)** | **C=O (%)** | **COOH (%)** | **π-π\* shake (%)** | **C=C/C**–**C** | **C=O/C**–**O** |
| **PB** | 81.87 | 59.45 | 9.51 | 9.08 | 5.02 | 12.93 | 0.301 | 6.25 | 0.55 |
| **NRBF** | 93.41 | 64.59 | 5.04 | 8.22 | 9.61 | 6.53 | 6.01 | 12.81 | 1.17 |
| **Used NRBF** | 84.89 | 65.02 | 11.04 | 10.27 | 5.72 | 7.95 | 0.00 | 5.91 | 0.56 |

**Table 3** **The pollutant degradation rate constants in different scavengers by PDS/different biochar-based catalysts.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Biochar** |  | **MeOH** | **TBA** | **DMSO** | **BQ** | **NaN3** | **None** |
|  | n[scavenger: PDS] | 1000 | 1000 | 10 | 10 | 10 | - |
| NRBF | *kobs*, min-1 | 0.0201 | 0.0198 | 0.0185 | 0.0049 | 0.0041 | 0.0221 |
| PB | *kobs*, min-1 | 0.0053 | 0.0057 | 0.0050 | 0.0029 | 0.0013 | 0.0051 |

**Figure captions**

**Scheme 1** Schematic illustration of biochar-based catalyst of the NRBF modified with DESs.

**Fig. 1** SEM images (a, and b), N2 adsorption-desorption isotherm (c) and pore-size distribution curve (inset) of PB; SEM images (d, and e), N2 adsorption-desorption isotherm (f) and pore-size distribution curve (inset) of NRBF.

**Fig. 2** High resolution XPS spectrum of C 1s (a, b and c), O 1s (d, e and f) of PB, NRBF, and used NRBF; XPS survey spectra of NRBF (g); and N 1s scan (h and i) of NRBF, and used NRBF.

**Fig. 3** FTIR (a) and Raman (b) spectra of PB, and NRBF.

**Fig. 4** (a) Removal of TC in the presence of different biochar-based catalysts in PDS system; and (b) Effect of coexisting inorganics on the degradation of TC in NRBF/PDS system. Conditions: [biochar fiber]=0.1 g/L, [PDS]=1 mM, [temperature]=25°C, [TC]=20 mg/L.

**Fig. 5** (a) TC removal in different water samples in NRBF/PDS system; and (b) Cycling performance of NRBF for PDS activation. Conditions: [PGBF-N]=0.1 g/L, [PMS]=1 mM, [temperature]=25°C, [TC]=20 mg/L.

**Fig. 6** (a)Quenching experiments of NRBF under different scavengers; (b) EPR spectrum of species adducts in NRBF/PDS system at reaction of 5 min; and (c) Degradation of various organics by NRBF catalyzed PDS activation. Conditions: [NRBF]=0.1 g/L, [PDS]=1 mM, [temperature]=25°C, [TC]=20 mg/L.

**Scheme 2** Proposed mechanism of PDS activation by biochar-based catalyst before and after DESs modification for degradation behavior of TC molecules.

**Fig. 7** (a) TC degradation under different delayed time intervals for pollutant adding after mixing the NRBF and PDS; (b) LSV plot of NRBF under different conditions (1 mM PDS or both 1 mM PDS and 20 mg/L TC) at a scan rate of 5 mV s−1 from –1.0 to 2.0 V; and (c) EIS measurement of different biochar-based catalysts loaded on GCEs (frequency range: 10-1~105 Hz, [Na2SO4] =0.2 M).

**Scheme 3** Possible intermediates and proposed transformation degradation pathways of TC in NRBF/PDS system.

**Fig. 8** Images of inactivation of *E. coli* on plate under different reaction conditions at 120 min: (a) blank group (number ×104); (b) NRBF alone (number ×104); (c) NRBF/PDS system (number ×100); the number of *E. coli* colonies by Plate counting method on different treatments (d); SEM images of *E. coli* cells on blank (e), treatment of NRBF alone (f) and NRBF/PDS system (g, and h) after inactivation of 120 min.

**Scheme 1**



**Fig. 1**



**Fig. 2**



**Fig. 3**

****

**Fig. 4**



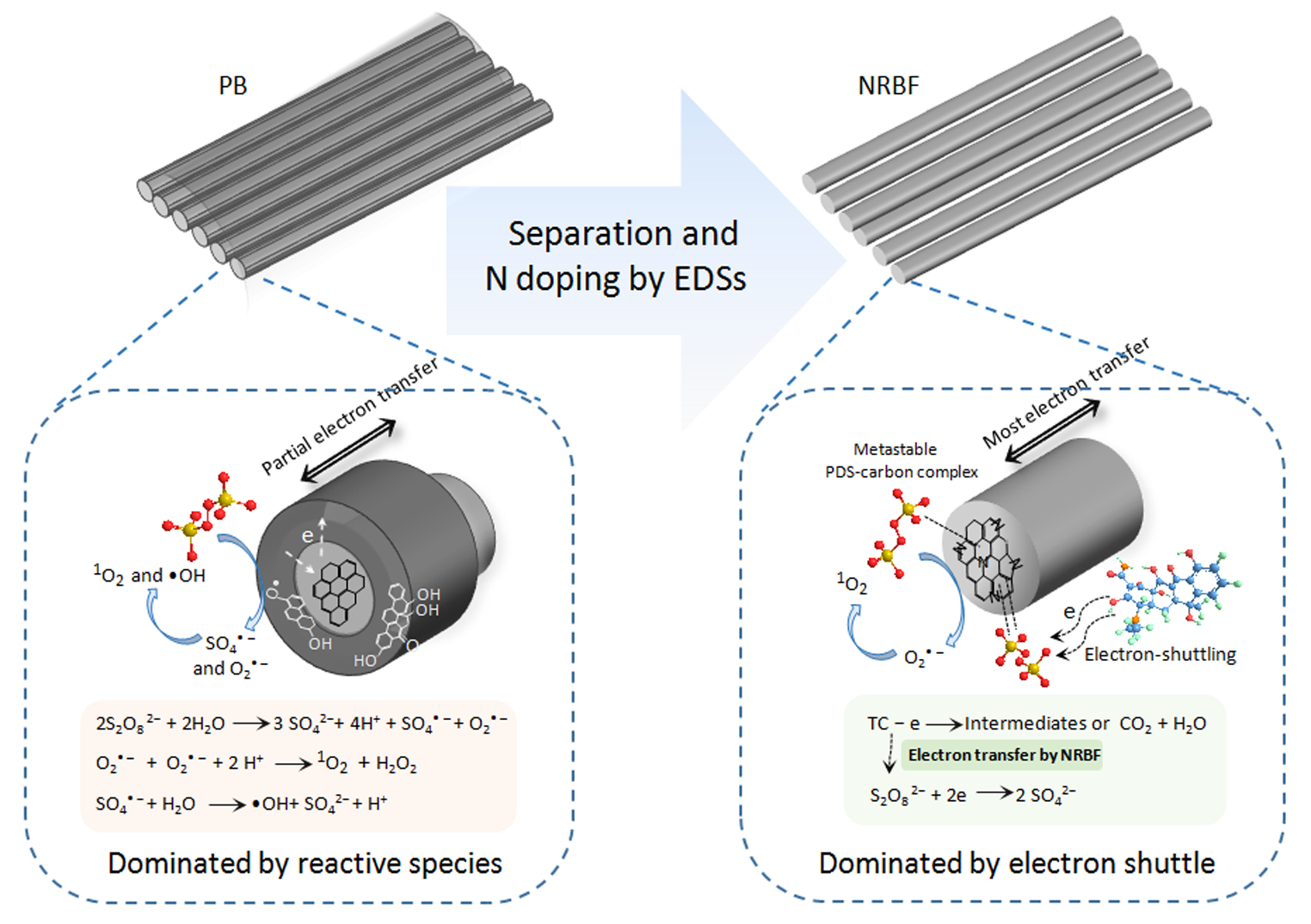
**Fig. 5**



**Fig. 6**



**Scheme 2**



**Fig. 7**



**Scheme 3**



**Fig. 8**



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2. [↑](#footnote-ref-2)