

# Activation of persulfate by biochar-based catalysts for elimination of refractory organic pollutants: a review

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**Abstract.** With the advancement of industrialization and urbanization, refractory organic pollutants (ROPs) have been detected in various types of water environments, leading to increasingly serious environmental problems. Currently, persulfate (PS)-based advanced oxidation processes (PS-AOPs) have received great attention due to their advantages such as short treatment time and high degradation efficiency. Biochar (BC), which comes from a wide range of sources and has significant catalytic activity, has been widely reported in PS activation studies in recent years. In this review, the main reaction pathways and the corresponding reaction mechanisms of ROPs degradation by PS-AOPs were firstly introduced. Then, the influencing factors and regulating means of BC performance in PS activation systems are systematically described, and different modification methods and principles are detailed. Finally, the author analyzes the current difficulties faced and puts forward an outlook on the future research direction. This paper aims to provide a reference for the development of controllable PS activation technology.

**Keywords:** Advanced oxidation processes; persulfate; biochar; activation.

## 1. Introduction

With the rapid development of industrial technology, a variety of difficult-to-degrade organic pollutants (ROPs, such as antibiotics, dyes, pesticides, etc.) are constantly being discharged into various water environments. These ROPs are characterized by strong persistence and difficult to be degraded by microorganisms, which seriously affects the environmental quality of water bodies and human health, and the traditional water treatment technology is difficult to control them in the standard range. In this context, the efficient removal of organic pollutants from water bodies has become a research hotspot. Thanks to the advantages of strong oxidizing ability and small secondary pollution, advanced oxidation processes (AOPs) have received wide attention in treating ROPs[1]. Among them, the persulfate (PS)-based AOPs system can generate sulfate radicals ( $\text{SO}_4^{\bullet-}$ , 2.5-3.1 V) as the main active species, which have higher redox potentials, wider pH ranges, and higher persistence than hydroxyl radicals ( $\text{OH}^{\bullet}$ , 1.9-2.7 V), and show a broader application prospect in the treatment of organic pollution.

In PS systems, the active species usually originate from the cleavage and transformation of O-O bonds [2]-[3], and the higher bond energy puts certain requirements on the activation technology, in which the bond energy of the O-O bond of permonosulfate (PMS) is 140-213 kJ/mol, and that of peroxydisulfate (PDS) is 140 kJ/mol. Common activation methods of PS include thermal activation, alkali activation, radiation activation, transition metal-based catalyst activation, and carbon material activation[4]-[5]. Biochar (BC) is a type of porous carbon material produced by pyrolysis of biomass at high temperatures in a certain atmosphere[6], which shows great potential for PS activation[7]. In addition, BC has various advantages such as highly porous structure, large specific surface area, wide source of raw materials[8] and rich functional groups[9] (containing -OH, -COOH, etc.), etc. Changes in raw material types, modifications or composites can change the physicochemical properties of biochar, thus affecting its catalytic activity. First, this review will classify the different activation mechanisms of PS and explain the mechanism of BC activation of PS. Then, this paper will describe the modulation of BC performance in PS activation from three aspects. Finally, the

author will briefly summarize the challenges of the current research, aiming to provide a reference for advancing the controllable PS activation technology.

## 2. Mechanism of activation of persulfate by biochar

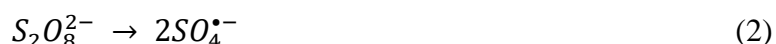
Unlike the traditional catalytic activation based on free radical mechanism, the mechanism of PS activation by BC is more complex. In addition to free radical mechanisms ( $\text{SO}_4^{\bullet-}$ ,  $\text{OH}^\bullet$  and  $\text{O}_2^{\bullet-}$ ), non-radical mechanisms (singlet oxygen and electron transfer) are also considered to be important pathways for BC to promote the production of active species from PS.

### 2.1. Free radical pathway

In the degradation of organic pollutants by PS advanced oxidation based on BC activation, the free radical mechanism usually involves three kinds of reactive radicals[10]:  $\text{OH}^\bullet$ ,  $\text{SO}_4^{\bullet-}$  and  $\text{O}_2^{\bullet-}$ . The free radicals have unpaired lone electrons, and thus most of them have the tendency to react with organic pollutants and can form stable molecules in the end, and generally show the characteristics of higher reactivity and shorter half-life. In the degradation process, the dominant reactive radicals are often different due to the different pollutant types and BC properties.

#### 2.1.1. OH or $\text{SO}_4^{\bullet-}$ dominant

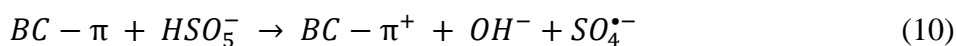
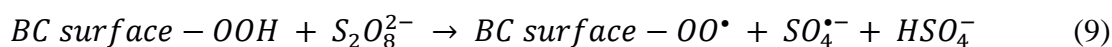
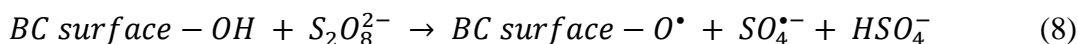
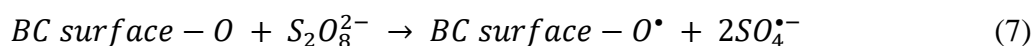
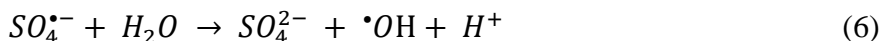
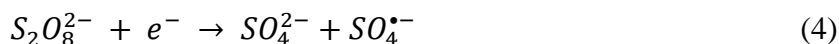
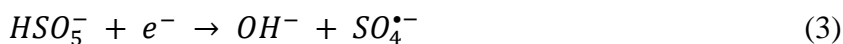
$\text{OH}^\bullet$  is a free radical formed by the loss of an electron by  $\text{OH}^-$ , which has a strong ability to gain electrons (oxidizing ability), oxidation potential of 1.9-2.7 V, short half-life ( $2 \times 10^{-8}$  s), low selectivity, and can react with a variety of organic pollutants and mineralize them.  $\text{SO}_4^{\bullet-}$  has a high degree of reactivity and oxidizing ability, with an oxidation potential of 2.5-3.1 V, and a half-life of  $3 \times 10^{-5}$  s, which facilitates its full contact with pollutants, but it has a certain degree of selectivity, as shown in reaction (1), but its generation mode is mainly from the PDS, but it has a certain degree of selectivity.  $4 \times 10^{-5}$  s [11], which is conducive to its full contact with pollutants, and its mineralization of organic pollutants mechanism as shown in reaction (1), but it has a certain degree of selectivity, and the generation mode is mainly derived from the decomposition of PDS (reaction (2)).



In PS activation, BC can be used as an effective catalyst to provide active sites, such as persistent free radicals (PFRs) [12] generated during the pyrolytic preparation of BC, oxygen-containing functional groups (-OH, C=O, -COOH, etc.) [13], and off-domain  $\pi$ -electrons, structural defects, and  $\text{sp}^2$  heterocarbon networks [14] in BC can be used as a feature to introduce more functional groups and pore structures to increase its specific surface area and adsorption capacity, thus promoting the generation of OH or SO and participating in the reaction. This can promote the generation of  $\text{OH}^\bullet$  or  $\text{SO}_4^{\bullet-}$  and participate in the reaction.

PFRs exist on the surface or inside of BC and can provide electrons to PMS/PDS[15], which activates to produce  $\text{SO}_4^{\bullet-}$  to promote the degradation of organic pollutants (Eqs. (3) and (4)), and the  $\text{SO}_4^{\bullet-}$  produced by this reaction may further react with  $\text{OH}^-$  or  $\text{H}_2\text{O}$  to produce  $\text{OH}^\bullet$  (Eqs. (5) and (6)); Fang et al.[16] pointed out that the number and type of PFRs in the active site is the BC-activated PS, Zhang et al.[17] found that the degradation of antibiotics such as tetracycline was closely related to PFRs on the BC surface in the activation of PS, and that PFRs could act as active sites to catalyze the production of  $\text{OH}^\bullet$  and  $\text{SO}_4^{\bullet-}$  by  $\text{PS}_4^{\bullet-}$ ; Ghauch et al.[18]'s study showed that oxygen-containing functional groups could promote the activation of PS (among which -COOH was the most obvious), and that oxygen-containing functional groups on the surface of BC could prompt the PS to produce more active species (Eqs. (7)-(9)); active sites with off-domain  $\pi$  electrons (e.g., vacancies) on BC can act as electron donors to cleave the O-O bond in PMS to generate  $\text{SO}_4^{\bullet-}$  and form a cycle (Eqs. (10)-(11)); PMS is more easily activated by BC due to the asymmetric molecular structure as

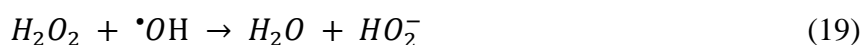
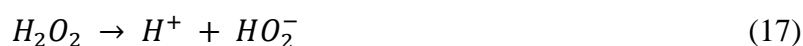
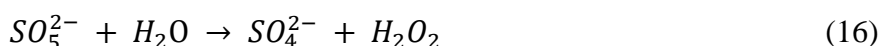
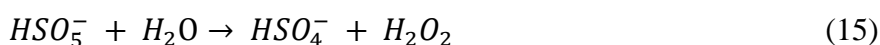
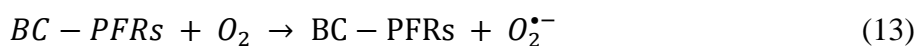
compared to PDS, and some of the defective structures in BC have a higher electron density, which can activate PMS by electron transfer to produce  $SO_4^{\bullet-}$ . The study by Wang et al.[19] confirms the promotion of this process by structural defects; BC has a  $sp^2$  carbon hybridization network, which promotes the production of  $\bullet OH$  and  $SO_4^{\bullet-}$  by providing free-flowing  $\pi$ -electrons. In addition, BC itself can act as a reducing agent to react with  $SO_4^{\bullet-}$  to restore it to  $SO_4^{2-}$ , releasing  $\bullet OH$ .



In the actual activation process,  $\bullet OH$  or  $SO_4^{\bullet-}$  pathways often coexist. In addition to the selectivity of the pollutant and the performance of the biochar, pH is one of the most important factors in determining the dominant radical species. Zhu et al.[20] activated PDS for the degradation of Acid Orange 7 using wood biochar and showed that the reaction could proceed rapidly over a wide range of pH (3-10), and Feng et al.[21] 's study showed that  $SO_4^{\bullet-}$  was more dominant under acidic conditions.

### 2.1.2. $O_2^{\bullet-}$ dominant

In the PS system for the treatment of organic pollutants in water, superoxide radicals ( $O_2^{\bullet-}$ ) are mainly formed by the electron gain from dissolved oxygen in the water column (equation (12)), whereas in the BC/PS system, the active sites on the BC, such as the PFRs, can produce a similar effect (equation (13))[22]-[23]. In addition, the activation of PMS by BC in a series of reactions to produce  $O_2^{\bullet-}$  is also an important route to oxidize organic pollutants (Eqs. (14)-(20)).  $O_2^{\bullet-}$  has a weaker oxidizing capacity compared to  $\bullet OH$  and  $SO_4^{\bullet-}$ , and is less likely to dominate the oxidation of organic pollutants directly, but is often used in secondary reactions to generate other reactive species, such as as an intermediate for generating monoclinic oxygen ( $O^1_2$ )[24] (Eqs. (21)-((23)). 23)). It is noteworthy that  $O_2^{\bullet-}$  can show strong selectivity in the removal of certain organic pollutants, and the experiments of Wang et al.[25] confirmed that  $O_2^{\bullet-}$  plays an important role in the PS-activated degradation of BPA.



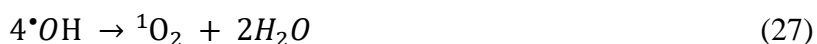
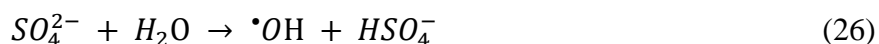
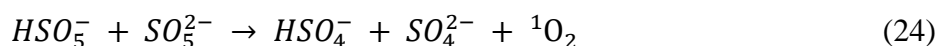


## 2.2. Non-radical pathway

Non-radical mechanisms include singlet oxygen and electron transfer mechanisms, which typically have a lower oxidizing capacity than free radical mechanisms, but have a wider pH range (including acidic, neutral and basic conditions). In addition, the non-radical mechanism makes full use of the oxidative properties of PS and is highly reactive to specific pollutants[26], and can also be used for the initial oxidation of organic pollutants before applying the radical system to further mineralize the intermediates to CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>[27]-[28]. Due to its high oxidation potential and selectivity, the non-radical mechanism is resistant to interference from a variety of inorganic ions (NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, halogens, etc.) and background organics[29], which is beneficial for BC in natural water bodies. It facilitates the application of BC in natural water bodies and reduces the production of intermediates (e.g. halogenated products).

### 2.2.1. Singlet oxygen pathways

Singlet oxygen (<sup>1</sup>O<sub>2</sub>) is a non-radical reactive species, which can be generated from the reaction of the intermediate O<sub>2</sub><sup>•-</sup> (Reaction Eqs. (21)-(23)) or from the self-decomposition of PMS/PDS (PMS: Reaction Eq. (24); PDS: Reaction Eqs. (25)-(27)), and also from the graphitized structure of the biochar[30], the doped atoms[31], the oxygen vacancies[32]-[33], the metal ions[34], and the surface groups (carbonyl, hydroxyl, etc.) [35]-[36]etc. can also be used as active sites for the formation of O<sup>1</sup><sub>2</sub>. O<sup>1</sup><sub>2</sub> has a weaker oxidizing ability than free radicals for most organic pollutants, and the reaction rate is also lower, but due to the π-electron vacancies in the 2p orbitals of O<sup>1</sup><sub>2</sub>, it has a strong reactivity for electron-rich organic pollutants (e.g., phenolics and most of the organics containing unsaturated bonds), which are prone to electrophilic additions. Sun et al.[37] have found that in their research O<sup>1</sup><sub>2</sub> shows a better performance towards electron-rich organic pollutants in the weakly acidic and neutral conditions. showed high degradation rates for electron-rich organic pollutants under weakly acidic and neutral conditions.



### 2.2.2. Surface electron transfer pathway

The low electrochemical impedance and good conductivity of BC materials can induce a direct electron transfer process. In the process of surface electron transfer, the pollutants adsorbed by BC can act as electron donors, the substable PS as electron acceptors, and BC as an electron conductor to catalyze the process[38], which promotes the transfer of electrons to oxidize the organic pollutants. Since the graphitized structure and pores are important media for transporting charges, they can effectively influence the electron transfer process[39]-[41]. If BC is modified to reduce the surface resistivity, the electron transfer efficiency can be further improved[42]. In addition to direct electron transfer, BC can produce some active substances as electron mediators to activate PS, and this process is closely related to electron holes, the porous structure of biochar, and surface electron transfer complexes[38]. In addition, the graphitized porous structure of biochar not only provides activation sites for electron holes, but also allows a strong electron acceptance effect with aromatic organic pollutants through the conjugated π-electron system, and the surface electron-transfer complexes have a low electrochemical impedance, which can provide electrons and direct electron transfer.[43]

### 3. Performance modulation of biochar materials

Because BC is widely available, inexpensive and in line with the needs of sustainable development, it has received extensive attention from researchers. In the BC/PS system, the activation effect of PS is significantly affected by BC, which has the characteristic of easy-to-regulate performance, so there are many reports on improving the activation effect of PS by regulating the performance of BC.

#### 3.1. Effect of different raw materials and preparation conditions on the activation effect

##### 3.1.1. Influence of biomass feedstock on activation effect

BC is divided into three categories according to the source of raw materials [44]: plant-derived BC (PBC), animal-derived BC (ABC) and sludge-derived BC (SBC). The biochar from different sources are basically the same in the types of major constituent elements, but the proportion of each element varies greatly, and each element constitutes the active sites on the BC surface (oxygen-containing functional groups, PFRs, defective structures, etc.), so that there are some differences in the effect and mechanism of activation of PS by BC from different sources.

PBCs are often characterized by a high content of mineral elements, for example, Si element is one of the important elements in plant growth, which is beneficial for promoting photosynthesis and thus easily accumulates in plants. Han et al. [45] found that amorphous silica in BC can interact with C atoms, which enhances the stability of the structure of BC and prevents it from being oxidized. Common biomass feedstocks for PBCs include peanut shells and coconut shells, etc. Hung et al. [46] prepared metal-free coconut shell biochar for the activation of PMS for the degradation of sulfonamide antibiotics by thermochemical conversion at 700 °C, and the removal of contaminants was up to 80% under optimal conditions (30 min). In addition to Si, other mineral elements also contributed significantly to the activation of the BC/PS system. Zeng et al. [47] prepared BC from peanut shells (3.2% ash content), and it was found that the endogenous mineral elements of the plant (e.g., K, Ca, and Fe) facilitated the formation of the internal structure and surface functional groups in the charring process of the biomass. [48] enhanced the adsorptive capacity and catalytic properties of the BC.

Due to the abundance of proteins in animals, ABCs usually have a high N content, and the presence of reactive nitrogen functional groups improves the electron transfer capacity [49]. Wang et al. [50] prepared BC from panda feces as a raw material pyrolytically for the degradation of sulfadimethoxine pyrimethamine by activated PMS, and found that non-radicals were predominant in the panda feces BC/PMS system, as measured by cyclic voltammetry and linear scanning voltammetry. Notably, the system was also found to be resistant to the environment of certain inorganic ions and humic acids.

The composition of SBC is more complex, with a higher ash content compared to PBC and ABC, and contains more Si and heavy metal elements [51] (Cr, Cu, Cd, etc.) in the ash. In addition, SBC may introduce natural reactive N doping or metal loading due to the addition of coagulants (polyacrylamide, polymerized aluminum chloride, polymerized ferric sulfate, etc.) in the wastewater treatment process [52]. Therefore, the complexity of sludge composition makes the effect and mechanism of SBC activation of PS difficult to predict. Wu et al. [53] confirmed in their study that the physicochemical properties of the wastewater determine the content of organic and metal substances in the sludge, and further determine the structure of the SBC. In this study, two sludges with different organic compositions and metals were selected to be explored, and it was found that the higher the organic N content of the feedstock, the higher the DEGREE of polymerization and N-heterocyclics content of the SBC, and the stronger signals of PFRs could be detected. In addition, this study also found that heavy metals such as Fe in sludge existed as complexes and ions in BC, which could also directly activate PS.

Therefore, the type, material composition and structural characteristics of the feedstock should be fully considered in the selection of biomass feedstock, and the nature of the feedstock directly determines the activation performance and mechanism of BC on PS.

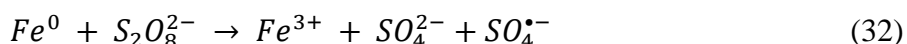
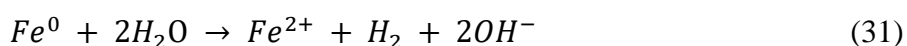
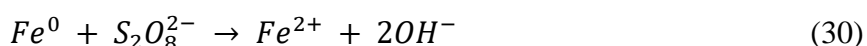
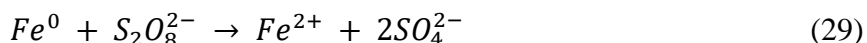
### 3.1.2. Influence of BC preparation conditions on activation effect

BC is generally prepared by pyrolysis under low or no oxygen conditions. Since the raw materials may be rich in cellulose and lignin, the internal pyrolysis of these substances is intensified at high temperatures [54], resulting in the breakage of inter- and intramolecular chemical bonds and the release of small molecules, such as CH<sub>4</sub> and CO<sub>2</sub>, and the escape of the resulting gases and volatile components leading to the formation of pore structures in BC. As the pyrolysis temperature increases, the generation of pore structures accelerates, resulting in an increase in the specific surface area of BC. Therefore, usually in a certain temperature range, the increase of the pyrolysis temperature of BC will lead to the increase of the specific surface area of BC, which in turn promotes the effect of BC activation of PS. Zhao et al.[55] prepared loofah sponge-based BC at three different temperatures, namely, 400°C, 600°C, and 800°C, and ultimately found that the best activation effect was achieved by the BC prepared at 800°C, with a degradation rate of pollutants reached 96% (30 min). In addition, the increase of pyrolysis temperature leads to the enhancement of the aromaticity of BC, which implies that the BC/PS system may produce a strong electron donating-accepting effect through the π-electron conjugation system when interacting with aromatic pollutants.[56]

### 3.2. BC composite with transition metal matrix materials

Pristine BC can modulate the performance by various methods, but its degradation efficiency is still relatively limited for certain pollutants. The presence of single electrons in the electronic orbitals of transition metals makes it easy to gain or lose electrons, but it is easy to be limited in transferring electrons, so the BC can be composited with transition metal-based materials to promote the rate of electron transfer to improve the effect of activated PS.

Iron-based materials are most common in transition metal-based materials/PS activation systems, where nano zero-valent iron (nZVI) has been shown to activate PS generation to remove ROPs such as phenol [57]-[58] , and its activation of PDS to produce Fe<sup>2+</sup> and SO<sub>4</sub><sup>•-</sup> is shown in the mechanism of reaction equations (28)-(32).



nZVI has a large specific surface area and strong reactivity[59] , however, the nZVI particles have a high surface energy and are prone to agglomeration under their own magnetic interactions[60] , which in turn leads to a decrease in their effective surface area. In addition, nZVI is prone to rapid oxidative inactivation when exposed to air[61] . In contrast, loading nZVI onto BC with porous properties can introduce surface functional groups and achieve better dispersion[62] . Hussain et al.[63] prepared nZVI by reduction of Fe<sup>2+</sup> using sodium borohydride under nitrogen atmosphere and synthesized nZVI/BC composites with rice husk derived BC for the degradation of nonylphenol by activated PDS. Characterization results showed that the porous surface of BC had a good effect in preventing the aggregation of nZVI. Guo et al.[64] synthesized nZVI/BC composites for the activation of PDS for the degradation of pyrene, and it was shown that pyrene could be degraded to less toxic intermediates and then mineralized in the process.

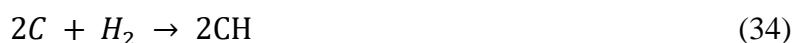
It is worth noting that, in addition to iron-based materials, other transition metal-based materials (e.g., copper-based, cobalt-based, etc.) have also received a certain degree of attention in research. Li et al.[65] synthesized CoFe<sub>2</sub>O<sub>4</sub> /BC composites, and in the study of their activation of PMS to degrade bisphenol A, it was found that BC not only provided a good support for the dispersion of CoFe<sub>2</sub>O<sub>4</sub> , but also promoted the surface Co-OH-complex formation. Zhang et al.[66] prepared mushroom-derived BC/CuFe<sub>2</sub>O<sub>4</sub> composites for the activation of degradation of tetracycline. It was found that

BC not only reduces the agglomeration of magnetic  $\text{CuFe}_2\text{O}_4$  particles, but also the graphitic carbon in BC acts as an electron donor for PDS, increases the electron transfer rate, and promotes the activation of the non-radical pathway of PDS and the production of more reactive species for the degradation of pollutants.

### 3.3. Modification of BC

#### 3.3.1. Physical treatment modification

Physical treatment modification methods include steam modification, gas blowing modification and heat treatment modification. The principles of steam modification and gas blowing are similar in that they can improve the framework and pore structure of BC[67]. Steam modification promotes the decomposition of volatile components on the BC surface [68] (Reaction Eqs. (33)-(34)), which leads to the expansion of pores, whereas gas blowing usually uses  $\text{CO}_2$ , because it promotes the formation of new pores and enlarges the specific surface area of BC [69]. Currently, steam modification and gas blowing are less commonly used in BC/PS systems, and thermal modification is frequently used because of its ease of association with other techniques. There are many thermal modification methods, mainly including hydrothermal modification, additional thermal treatment and thermal annealing, etc., and the modification processes and principles involved are also different. Fan et al. [70] degraded tetracycline using hydrothermally modified Cu/Zn-BC activated PS, and the effect of BC loaded with Cu on the specific surface area of BC was reduced after hydrothermal modification, and the characterization results showed that the hydrothermal modification improved the surface morphology of BC. Kim and Ko [71] BC was modified by additional thermal treatment at three different temperatures, and it was found that its activated PS degradation of acetaminophen became progressively better with the increase of the calcination temperature, and the specific surface area and total pore volume of BC as well as the free radical content in the reaction system were also significantly enhanced, and furthermore, it was found that the additional thermal treatment of the surface was favorable to the conversion of poorly crystalline organic phase of BC into rigid organic phase such as graphite. organic phase to rigid crystalline carbon structures such as graphite[72]. Miao et al. [73] used graphite biochar (GBC) modified by thermal annealing to activate PDS, and compared with pristine GBC, the thermal annealing modification increased the intrinsic defects of GBC and facilitated the non-radical pathway dominated by surface electron transfer.



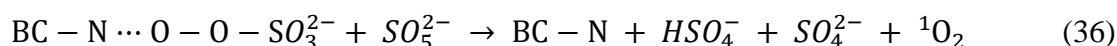
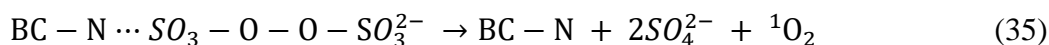
#### 3.3.2. Chemical treatment modification

Chemical treatment is most common for acid and base modification at the pre-treatment or post-treatment stage, and both the type and concentration of acid/base are important factors affecting the effectiveness of BC modification. Common acid modification reagents include hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), etc.[74]-[76] Acid modification of BC has the effect of removing impurities such as ash, increasing the specific surface area, and introducing oxygen-containing functional groups, etc. Yu et al.[77] found that the acid treatment could remove some of the soluble substances and cellulose in BC, and significantly increase the specific surface area of BC, and Ma et al.[78] used HCl to modify anaerobic biogas residue BC, and the results showed that the content of oxygen-containing functional groups was significantly increased, providing a large number of active sites for the reaction. In the same way as acid modification, alkali modification can also increase the specific surface area of BC[79], Zhang et al.[80] modified SBC using KOH (700 °C, 1 h), and the specific surface area of the BC obtained increased nearly 10-fold ( $81.35 \text{ m}^2/\text{g} \rightarrow 907.95 \text{ m}^2/\text{g}$ ). More importantly, alkali modification can also introduce hydroxyl groups on the BC surface and reduce the polarity, Wang et al.[81] found that ultrasound-enhanced alkali modification of BC can introduce a large number of oxygen-containing functional groups.

### 3.3.3. Nitrogen doping modification

Hetero-element doping is an effective means to improve the activation effect of BC on PS, which can be modified by doping with one or even more of the elements such as N, S, P, B, etc., of which nitrogen doping modification is the most common, and its activation effect is considered to be the best among the single-element doping modifications[82]. Nitrogen doping is divided into endogenous doping and exogenous doping, endogenous doping utilizes the N in the biomass feedstock, and the activity of the generated BC (N-BC) is often limited by the low N content of the biomass feedstock, and different biomass feedstocks have a large variability of the activation effect[83], for the lack of endogenous N in the BC can be used to use nitrogen-containing compounds such as urea and other nitrogen-containing compounds as an exogenous material for the nitrogen dopant modification.

N-BC can introduce active sites such as pyrrole N, pyridine N and graphite N or N-containing functional groups. Pyrrole N can adsorb contaminants via hydrogen bonding[84], and graphite N can convert PMS/PDS into substrates and generate  $^1\text{O}_2$  via self-decomposition to degrade contaminants[85] (Reaction Eqs. (35)-(36)). Annamalai and Won Sik Shin[86] used ball-milled N-BC to activate PS degradation of trimethoprim, the identification of active species showed that  $^1\text{O}_2$  was the most dominant species leading to the degradation of the pollutant compared to  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$ . In addition to the formation of active species, N-BC can also promote the surface electron transfer-oriented non-radical pathway. The electronegativity of elemental N (3.04) is larger than that of elemental C (2.55), so N doping can reduce the electrochemical impedance of the surface electron transfer complexes by modulating the spin density and the charge distribution [87], and thus effectively enhance the activation of BC, which can be better realized by co-doping N and S which can be better realized by the co-doping of N and S[88]. In addition, Guo et al. suggested that pyrrole N and pyridine N are favorable for the formation of electron-rich regions, and thus they can be used as Lewis basic sites to improve the affinity for electrophilic pollutants (e.g., phenolic compounds) [89].



## 4. Conclusion and outlook

BC-mediated PS activation is considered a promising treatment technique for ROPs, but still faces many challenges in research and practice:

(1) Activation pathway identification and regulation: Currently, the origin and contribution of mixed pathways involving radicals and non-radicals are understudied and controversial. In addition, it is not yet possible to precisely regulate the different pathways in the reaction system.

(2) Toxicity assessment and risk control: On the one hand, the degradation products of ROPs may still be highly toxic. On the other hand, non-homogeneous activation also increases the risk of secondary pollution, such as the use of BC/metal matrix composites accompanied by metal leaching. Therefore, it is more important to focus on the environmental impact in future studies, or to reduce the risk of secondary contamination by means of material improvement, etc.

(3) Real water body treatment: Real water bodies contain substrates such as soluble organic matter (DOM),  $\text{NO}_2^-$  and  $\text{HCO}_3^-$ , which may consume the active species produced by PS and affect the treatment effect. Therefore, future studies should give more consideration to pollution removal under real water bodies.

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