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Review

A review on the catalytic ozonation of pollutants in wastewater by heteroelements-doped biochar: Internal and external doping strategies

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ABSTRACT

Biochar has been widely developed for the remediation of water pollution, and how to improve the performance of biochar has attracted widespread attention. Heteroelements doping makes biochar have more active centers and durability in catalytic ozonation, which has great development prospects and has attracted the interest of researchers. This study reviews the application of heteroelements dope biochar in catalytic ozonation for wastewater treatment. First, the types of doping elements are discussed, and different doping methods and preparation methods are introduced in detail, among which external doping is widely used, and internal doping is cost-effective and easy to operate. Secondly, the application and mechanism of catalytic ozonation for the degradation of different pollutants are discussed. In addition, the economic costs of different doping methods are compared, and the challenges faced by heteroelements-doped biochar in catalytic ozonation in the future are proposed. This study provides a theoretical basis for the synthesis of low-cost and high-efficiency biochar catalysts for catalytic ozonation in real industrial wastewater treatment.

1. Introduction

Industrial wastewater treatment has always been one of the essential works in environmental governance. With the continuous development, product upgradation and technological innovation for industrial wastewater has become more diversified, making it difficult to degrade pollutants, such as dyes, antibiotics, heavy metals, and petroleum hydrocarbons [1]. Advanced oxidation technologies (AOPs) have proven to be one of the most effective means of treating industrial wastewater [2], among which ozone (O_3) oxidation technology is vastly adopted. Compared with other wastewater-treatment technologies, O_3 has the advantages of low cost and high reoxidation potential. Additionally, the risk of secondary pollution is low [3]. To reduce the activation energy of the reaction and energy consumption, it is essential to prepare a highly efficient catalyst to improve the pollutant oxidation efficiency [4].

Biochar (BC) is a carbon material prepared via biomass pyrolysis under anaerobic conditions. It is similar to activated carbon, graphene, and other carbon materials in nature and has a vast range of sources. Agricultural and forestry crops and activated sludge can be used as raw materials for BC preparation. Additionally, the conversion of waste biomass to BC effectively relieves the pressure of urban waste treatment. For example, fruit peels and shells, kitchen waste, livestock feces [5], and some invasive alien species, such as water hyacinth, can be used as raw materials for BC production [6]. In the early stages of research, the primary focus was direct pyrolysis of biomass to produce BC.

However, the catalytic capacity of BC prepared by direct pyrolysis is limited by its physical and chemical properties, porosity, and pore structure. Additionally, the specific surface area limits, adsorption capacity, and the types and quantities of functional groups are small, thereby affecting the catalytic capacity. Therefore, recent studies have proposed several modifications to BC. Diverse modification methods have been used to regulate BC catalytic capacities. Currently, the most used modification approach is hybrid element doping, which can be divided into metal and non-metal doping. The addition of metals can change the electron cloud density on BC surface, increase the types of functional groups, and introduce new active sites. The formation of stable metal centers on BC improves its ability to degrade pollutants [7]. Muhammad et al. used (Fe) BC to degrade methylene blue at a 95 % removal rate within 60 min, doubling O_3 oxidation degradation efficiency alone. For carbon materials, after non-metallic doping, owing to the electronegativity difference between themselves and carbon atoms, the electron distribution is readjusted on the surface, forming a local microelectric field, accelerating the electron transfer speed, and thus enhancing the catalytic ability [8]. Cheng et al. used nitrogen-doped biochar (N-BC) to catalytic O_3 oxidation, and the degradation rate increased by 50 % compared to that of BC to catalytic O_3 [9]. Although

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doping with heteroelements enhances the physicochemical properties of biochar, how to utilize different doping methods to obtain cost-effective and high-performing heteroelements-doped biochar is a matter of concern.

At present, there are two most commonly used doping methods, namely external doping and internal doping. External doping refers to the process of introducing heteroelements or metal atoms onto the surface of biochar after its preparation is complete, using dopants through physical or chemical methods. These elements interact with the surface of the biochar, forming new active sites. Internal doping primarily utilizes the elements inherent in the raw materials to form interactions within the material at high temperatures, incorporating the elements in this way. Therefore, selecting the appropriate doping method is particularly important for obtaining the desired biochar.

Introducing metals and heteroelements into biochar is a promising that modification strategy for catalytic ozonation. However, to date, the research progress on the catalysis of ozone by biochars doped with different elements is not well understood, and there is a lack of research on the advantages and disadvantages of different doping methods as well as their preparation techniques. Therefore, this study reviews the doping types of BC composite materials, describes the preparation method of synthesis BC and the mechanism of catalytic O_3, and discussed the economic costs of different doping methods, with reference significance for future theoretical research and practical applications.

2. Ozonation in wastewater treatment

O_3 oxidation technology has been widely studied in wastewater treatment, especially in the pretreatment and advanced treatment of sewage plants, where it has shown significant effects on the removal of organic pollutants. Among the 21 organic pollutants screened, 15 were detected at levels below 20 mg/L, which is considered low. O_3 molecules release oxygen atoms to produce strong oxidants that are toxic to many wastewater microorganisms [10]. O_3 disinfection or ozonation also has the advantage of inactivating pathogenic protozoa and other pathogens that form harmful cysts. In recent years, it has been widely used to treat urban drinking water in Canada and the United States (National Water Research Institute 2000). O_3 is produced by irradiating oxygen with ultraviolet light or, in some cases, through discharge. The generation of O_3 is done in situ and is released in the form of bubbles in the water being treated, which helps in its advantage of producing few dangerous by-products, and the removal of odors and tastes (Munter, 2001). Ozonation of pollutants can occur either through direct reactions with molecular O_3 or indirectly with hydroxyl radicals produced from the decomposition of O_3 [11].

O_3 oxidation is a process that utilizes O_3 molecules to oxidize organic matter, which can be divided into two methods: direct oxidation and indirect oxidation. Direct oxidation refers to the reaction where O_3 molecules directly oxidize pollutants. This method is selective and primarily targets organic compounds containing double bonds, being more effective for unsaturated hydrocarbons and aromatic compounds. In direct oxidation, there is a selective reaction between O_3 molecules and pollutants, and the reduction of TOC content is not significant. The main effect is the transformation of large organic molecules into smaller ones, with the overall degree of oxidation being low. These fragmented small molecules typically have a high degree of biodegradability. Indirect oxidation involves the initial decomposition of O_3 in water to produce strongly oxidative free radicals (mainly ·OH), which then react with organic matter. This method is non-selective and can rapidly oxidize or even mineralize organic compounds in water, quickly reducing the TOC content. It is effective for a wide range of refractory organic pollutants.

3. The mechanism of catalytic O_3 by biochar

BC is a carbon material produced by the high-temperature pyrolysis of biomass, as depicted in Fig. 1. Commonly used biomass includes

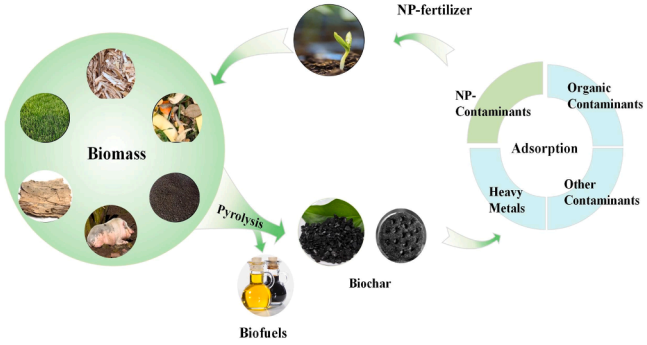

Fig. 1. The biomass preparation procedure (see Xiaofei Tan et al. 2015, Chemosphere) [12].

sludge, agricultural and forestry waste, animal bones, and food residues. Owing to the vast range of raw materials (mostly waste as raw materials) and the processing of waste to produce high-value-added products, in line with the current concept of sustainable development, simple production processes, and low costs, BC has been vastly emphasized and applied in the past decade. The properties of BC and activated carbon are similar, but the functional groups in BC are richer than those in activated carbon. These groups promoted catalytic ozonolysis to produce high ROS levels under certain conditions, thereby enhancing the ability of O_3 oxidation to remove organic matter. The major active sites in BC that participate in catalytic O_3 include O-containing functional groups, heteroatomic functional groups, and carbon chain defect structures. Catalytic BC O_3 can be divided into three methods of catalytic O_3: direct, indirect, and surface-triggered. (1) The electron-rich region of BC reacts with water to produce OH; thus, triggering O_3 decomposition to produce ·OH, BC surface O-containing functional groups (carbonyl, quinone, etc.), and defect sites as Lewis base sites can be combined with water molecules in solution via electron donor-acceptor interactions to produce OH^- and O_3 under the action of OH^- to produce ·OH and oxidize organic matter (R) to produce CO_2 and water.

$$BC + H_2O \rightarrow BC - H_3O^+ + OH^- \quad (1\text{-}1)$$

$$O_3 + OH- \rightarrow \cdot OH \quad (1\text{-}2)$$

$$OH + R \rightarrow CO_2 + H_2O \quad (1\text{-}3)$$

(2) The carbonyl and quinone groups on BC surface directly react with O_3, catalyze O_3 decomposition to produce ·OH during oxidation, and then oxidize organic matter (R) to eventually produce CO_2 and HO_2.

$$BC + O_3 \rightarrow \bullet OH \quad (1\text{-}4)$$

$$OH + R \rightarrow CO_2 + HO_2 \quad (1\text{-}5)$$

(3) O_3 is adsorbed on BC surface, and the surface-active sites react with O_3 to generate ROS. Simultaneously, some pollutants are adsorbed on BC surface, and ROS oxidizes the pollutants to decompose them.

$$BC + O_3 \rightarrow BC - O \quad (1\text{-}6)$$

$$BC + R \rightarrow BC - R \quad (1\text{-}7)$$

$$BC - R + BC - O \rightarrow CO_2 + H_2O \quad (1\text{-}8)$$

In recent years, an increasing number of studies have been conducted on the use of BC to catalyze O_3 degradation of pollutants in water. Zhang et al. prepared BC from sewage sludge and used it to catalyze O_3 removal from phenol in water. The removal rate reached 97 % within 30 min. Experiments have demonstrated that the highly efficient catalytic properties of BC for O_3 are predominantly due to the large number of carbonyl groups on its surface [13]. Moussavi et al. reported that BC prepared from pistachio shells can catalyze reactive red dye ozonation and degradation. Their research demonstrated that 71 % of the TOC in

the solution could be removed within 60 min. Characterization verified that hydroxyl and phenolic

hydroxyl groups on the BC surface were the major reaction sites [14]. Chen et al. used BC prepared by the direct pyrolysis of petroleum sludge to catalyze O_3 degradation of petrochemical wastewater, compared with O_3 alone. The TOC removal rate doubled (from 26.9 % to 53.5 %) and pollutants containing oxygen (Ox), nitrogen (NO_x), and sulfur (O_xS) were reduced by 33.4, 58.2, and 12.5 %, respectively [15]. Li et al. prepared peanut shell BC at 600 ℃ for ketoprofen catalytic ozonation in water. The enhanced catalytic ozonation ability of peanut-shell BC was attributed to an increase in active sites, enhancement of chemical bond energy, and production of delocalized electrons. A large amount of $^1O_2$ was produced in a short time, and ketoprofen removal rate reached 99 % in 5 min via the non-free radical pathway [16]. Zhang et al. used sludge pyrolysis in coking wastewater to prepare BC for catalytic ozonation of phenol in an aqueous solution. Post carbonization at 700 and 900 ℃, the catalytic ozonation efficiency of phenol can reach 95 %. The sludge BC surface contains several carbonyl groups, which stimulates O_3 to produce more $O_2^-$and $^1O_2$ and plays a decisive role in the degradation system [13].

In general, The active sites on biochar primarily consist of oxygen-containing functional groups, defects, and persistent free radicals (PFRs). The quantity of these active sites may be insufficient to provide efficient catalytic activity, especially when dealing with large amounts or refractory pollutants. The number and type of surface functional groups on biochar significantly affect its catalytic performance. Studies have shown that biochars prepared at different pyrolysis temperatures exhibit similar trends in surface functional groups, with a general decrease in the total amount of surface functional groups, a reduction in the content of acidic functional groups, and an increase in the content of basic functional groups. This limits the catalytic efficiency and application range of biochar under different pH conditions. However, a lower pyrolysis temperature can lead to a lower degree of carbonization, which also weakens the catalytic performance of biochar. Therefore, the performance of biochar cannot be regulated through pyrolysis conditions alone. It is often essential to modify BC to increase its specific surface area and enrich its pore structure. This provided more active sites for improving the catalytic capacity. Diverse modification methods have been investigated to improve the catalytic performance of BC based on its own properties. Metal and non-metal heteroatom doping is the most common and effective method for improving the performance of BC [17].

4. Doping types and preparation methods of biochar

4.1. Metal doping and nonmetal doping

4.1.1. Metal-doped biochar

Metal was doped demonstrate high catalytic ability in catalytic systems, and BC is often used as a carrier of catalytic materials in AOPs, which is not only inexpensive but also vastly used due to its simple modification method. Post metal modification of BC, the shortcomings of metal catalyst AOPs systems are not only improved, but also compared with BC alone. It also increases the number of active sites and stimulates to produce more ·OH [18].

Currently, the Fe-BC system is the most vastly studied in the field of catalytic O_3. Fe-BC has magnetic advantages, which solve the problem of catalyst' solid–liquid separation in water treatment systems [19]. Fe doping can enhance the specific surface area and porosity, thereby providing more active sites and improving the efficiency of mass transfer. It also helps to increase the degree of defects in carbon materials; these defects and functional groups can act as active sites to participate in catalytic reactions, enhancing the catalytic performance of BC. Fe doping can improve the electron transfer efficiency of BC, which is particularly important for catalytic redox reactions. The addition of Fe can act as an electron donor or acceptor, accelerating the electron transfer process. Moreover,BC with Fe doping involves not only radical pathways but also non-radical pathways in the catalytic process, such as the generation of singlet oxygen. This synergistic effect can enhance the degradation efficiency of pollutants. Additionally, manganese oxide, cobalt oxide, and other internal O-containing functional groups obtain stable metal centers on BC surface, which is not only conducive to the improvement of adsorption performance, but also enriches the types of functional groups (e.g., hydroxyl, quinone, and carboxyl). It also changes the electronegativity and dispersity of BC surface [8,19–21].

4.1.2. Non-metallic doped biochar catalyzes O_3

$$Biochar_{surface}-OH+O_3 \rightarrow Biocharsurface-O^{\cdot}+HO_3^{\bullet} \quad (1\text{-}14)$$

$$Biochar_{surface}-OOH+O_3 \rightarrow Biocharsurface-OO^{\cdot}+HO_3^{\bullet}+O_2^{\bullet} \quad (1\text{-}15)$$

N-doping is one of the most extensive ways, wherein non-metallic heteroatom-doped BC catalyzes O_3. The chemical properties of N are similar to those of carbon. N-doping of BC can replace the carbon atom in BC, and the outermost electron in the N atom can provide electrons for sp^2 hybrid carbon. In N-BC, N atoms are predominantly present in five forms: graphite N, pyridine N, pyrrole N, amino groups, and N oxide [22] (Fig. 2). Amino- and N-oxides exist on the BC surface in the form of functional groups, thereby increasing the number of Lewis base sites. Because BC itself has a base site, the addition of N functional groups helps improve its catalytic ability. At high temperatures, the breaking and reformation of chemical bonds become easier. The chemical bonds between the nitrogen atoms of pyridinic and pyrrolic nitrogen and the carbon atoms may break, and then the nitrogen atoms may recombine with carbon atoms to form graphitic nitrogen. High-temperature treatment can promote the recrystallization of carbon materials, which may lead to the rearrangement of carbon atoms, providing new binding sites for nitrogen atoms to form graphitic nitrogen. Nitrogen atoms may also migrate on the surface or within the carbon materials, seeking more stable binding sites. This migration could lead to the transformation of pyridinic and pyrrolic nitrogen into graphitic nitrogen. The graphitic N formed post N doping increased the BC conductivity to a certain extent. Pyridinic N and pyrrolic N have unhybridized lone-pair electrons and strong electron-donating abilities, which can effectively provide active sites to improve the catalytic performance of N-BC [23]. In S-doped BC, S atoms predominantly exist in two forms: thiophene S (C-S-C, peaks at 163.9 and 165.1 eV) and oxide S (C-SO_x-C, x = 2, 3, 4; peaks at 168.3 and 169.5 eV). Due to the low stability of oxidized S, S content changes with temperature and is gradually converted to thiophene S, wherein the C-S-C bond is considered an important active site for catalytic O_3 [24]. Compared to S and N, P has the lowest electronegativity, but its covalent radius is larger than those of N and S. Therefore, P doping can increase the specific surface area of BC and produce micropores [25]. The use of exogenous P doping, generally using H_3PO_4 and $(NH)_4PO)_3$, can

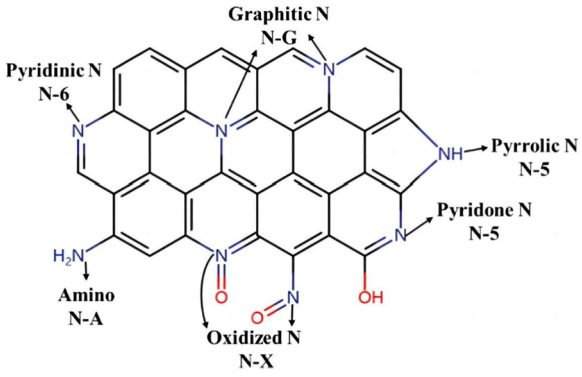

Fig. 2. N-containing functional groups in N-BC (see Gao 2022, Fuel Processing Technology); Nitrogen review [22].

increase the number of acidic groups on BC surface [26]. N, S, and P doping significantly improves the performance of BC; however, its poor durability is an obvious disadvantage. B, which improves the durability of BC, also has low electronegativity and is similar in size to carbon atoms. The C-B-σ bond and the BCO species acting as positively charged B dopants can more easily regulate the electron distribution and adjust the physicochemical properties of sp^2 hybrid carbons, thus providing more defect sites. Additionally, the additional O on the carbon surface caused by B doping can effectively improve chemical stability [27]. A recent report indicated that B-doped BC is expected to provide a new pathway for becoming a highly stable and eco-friendly metal-free carbon catalyst [28,29]. Cheng et al. used N-BC to catalyze O_3 degradation of ATZ at 700 ℃. N-BC accelerated ROS formation on O_3 surface, and the electron-rich O-containing functional groups and sp^2 hybrid system of conjugated heteroelements played important roles as active sites in the degradation process [30].

4.2. Doping methods of biochar

4.2.1. External doping and internal doping

The external doping method involves the use of additives containing metal or non-metallic ions to co-pyrolyse the biomass, whereas the internal doping method uses biomass-containing metals and miscellaneous elements for direct pyrolysis. The externally doped BC method is vastly adopted. Raw biomass materials were pretreated. BC is then formed through pyrolysis, impregnated with external additives, and stirred and dried [31], secondary pyrolysis with additives is also conducted [32]. Internal doping does not require additional additives, and direct pyrolysis of biomass-containing miscellaneous elements was selected. This is known as internal doping. Therefore, internal doping depends on the composition of the elements contained in the biomass. Currently, little is known about waste biomass containing miscellaneous elements, such as Fe- and N-rich sludge [33,34], and plants containing more protein and kitchen waste. In the catalysis field, internally doped organisms have gradually attracted attention in AOPs systems.

4.2.1.1. Externally doped biochar methods. When metal and non-metallic hybrid elements are externally doped into BC, the raw biomass materials can be pretreated before BC pyrolysis and then charred at high temperatures. As depicted in Fig. 3, Cheng et al. used a 0.5 g cigarette tip to soak in a 20 mL urea solution for 20 min, heated it at 10 ∘C/min to 600, 750, and 900 ∘C, and pyrolysed it for 2 h to produce N-BC. The N content of N-BC ranged from 4.04 % to 11.69 % [35]. Xu et al. first used $FeCl_3$ to impregnate sawdust, mixed it with dicyandiamide, heated it, and pyrolysed Fe-N-BC for 1 h under O-free conditions. The synergistic effect between Fe and N played an active role in the catalytic degradation reaction [36]. Another pretreatment method involves heteroatom doping in special gas atmospheres, such as NH_3 and

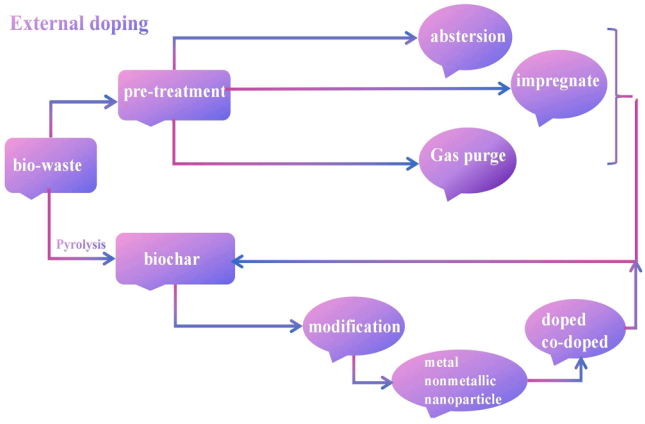

Fig. 3. External doping methods for biochar.

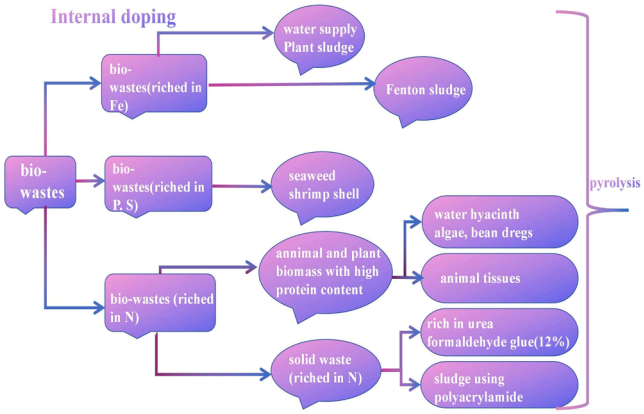

Fig. 4. Internal doping methods for biochar.

H_2S. Zhang et al. reported that in BC preparation using cotton as the raw material, the N content increased from 1.09 % to 3.48 % in an atmosphere of CO_2 and NH_3 because the C-O functional group on BC surface reacted with NH_3 by absorbing H_2O to form an amino compound [37]. Zheng et al. prepared Ga_2S_3 modified BC (Ga/S-BC) composites by impregnating bagasse in a GaS_2 solution and heating it in an H_2S gas stream (30 mL/min), where S doping was more stable [38].

Another doping method is the co-pyrolysis of miscellaneous elements with biomass or the re-pyrolysis of BC after adding additives to form further modifications. Liu et al. mixed water hyacinth and $ZnCl_2$ with different mass ratios evenly and prepared N-BC with more developed pore structure by co-pyrolysis at 600–800 ℃ for 2 h [39]. Shang et al. formed BC by pyrolysing corn straw at 120 ℃. The mixture was then mixed with melamine and $MgCl_2{\cdot}6\ H_2O$ and maintained at 600 ℃ for 2 h to produce MgO-N-BC. The Mg and N functional groups in the composite were formed by melamine and $MgCl_2{\cdot}6\ H_2O$ additives decomposition during heating [40]. Hou et al. previously reported that bamboo shoot shells were used as raw materials; $ZnCl_2$ and KCl were mixed in a 200 ∘C hydrothermal carbonization to synthesize BC, and then melamine was doped as an additive to pyrolyse the composite BC to form BC at 800 ∘C, with increased nitrogen content and enhanced adsorption properties [41].

Other doping methods include the processing of metals and non-metals into the form of nanoparticles-doped BC (i.e., loading the nanomaterials on the surface of BC to prepare BC nanocomposite materials), which can greatly improve the performance of BC. Combining the characteristics of these 2 materials, they have excellent physical and chemical properties, high catalytic activity and stability, and recyclability. The introduction of inorganic nanostructures, such as metal NPs, is an effective way to improve the properties of BC. Ling et al. synthesized (MgO@N-biochar) nano-biochar composites using MgO NPs and N double doping to increase the surface-active site and specific surface area in order to facilitate the removal of TC [42]. Similarly, nano-ferric zero-valent (nZVI) has shown excellent catalytic performance in wastewater treatment, especially when BC is used as a carrier, which can improve the catalytic activity and stability of nZVI. Yan et al. reported that the BC pyrolysis of rice husk raw materials was used as the carrier of nZVI BC composite material, which showed high catalytic activity in degrading triclosan. Using BC as the carrier effectively prevented the agglomeration of nZVI and accelerated the production of ·OH, with a degradation efficiency of more than 98 % [43]. Researchers have reported that BC modified by CNTs can improve physical and chemical properties and enhance the removal of pollutants. Inyang et al. used mixed multi-wall CNT-coated BC with pecan and bagasse as raw materials before slow pyrolysis and then characterized the BC before and after adding CNTs. A large number of functional groups and defect sites were distributed on the surface of the composite, and the specific surface area, pore volume, and thermal stability were increased. The removal

efficiency of MB improved [44].

4.2.1.2. Internal biochar doping method. The method of internal doping of BC is aimed at biomass containing metal or non-metallic hybrid elements, which are obtained by direct heat treatment. The heat treatment method was the same as the preparation method for BC and predominantly included pyrolysis, hydrothermal carbonization, and microwave pyrolysis (Table S1). Because the biomass-containing metal heteroelements are relatively special, only iron mud (FS) is produced by the Fenton process and water plant sludge using Fe-containing flocculants. FS is an inevitable by-product of the Fenton oxidation of pollutants, and its composition is predominantly Fe hydroxide and natural biomass, which can be regarded as the reuse of Fe sources. Polyferric sulfate is often incorporated to water treatment plants and sewage sludge during the water quality regulation process as a flocculant that contains more Fe ions in the sludge. It is also a potential Fe source. Non-metallic internal doping is currently the major focus of N-BC research. The N content of nitrogen-rich biomass has been previously described. It can be inferred that biomass with an N content higher than 3 % can be defined as nitrogen-rich biomass. For N-rich biomasses, it is appropriate to generate N-BC via direct pyrolysis [45]. N-rich biomass is majorly concentrated in plants with high protein content, such as water hyacinth, algae, and waste residues of soybean products. Additionally, some industrial wastes can be used as raw materials for N-BC, including fiber boards rich in urea aldehyde glue (approximately 12 %), particle boards, and industrial sludge that uses polyacrylamide as a flocculant in the sewage treatment process. Zhao et al. used water hyacinth as a nitrogen source and co-pyrolyzed it with sludge to incorporate nitrogen into the structure of sludge biochar. After the co-pyrolysis process, the sludge biochar demonstrated an increased variety of nitrogen functional groups, which in turn improved the efficiency of catalytic oxidation [46].

The pyrolysis method, as the most commonly used means of the biomass carbonization process, blows off chemical components or ash and degrades mineralization under inert gas (N_2, Ar, and He), the carbonization temperature is between 350 –1000 ℃, the heating rate is between 3 –25 ℃/min, and the heating time is maintained between 1 and 5 h. Yu et al. used magnetic sludge BC produced by pyrolysis of Fenton sludge, which predominantly contains ferric OH^-. The pyrolyzed magnetic BC demonstrated the presence of Fe^{3+}, Fe^{2+}, and Fe^0 in the XRD pattern and exhibited strong catalytic activity [33] (Fig. 5a). Xu et al. used fiberboard as the raw material to directly pyrolyse N-BC at 300, 500, and 800 ℃, wherein the internal nitrogen content of BC was approximately 3 wt% [45]. Wang et al. used kelp as a raw material to directly pyrolyse N-BC (e.g., KBB for KOH and KBA for H_2SO_4 washing) and found abundant N-containing functional groups in the XPS spectrum, which were beneficial for the catalytic reaction (Fig. 5b) [47].

The hydrothermal carbonization method is a mild low energy heat–treatment method. The biomass is placed in a high-temperature and high-pressure reactor in full contact with water vapor, through a series of reactions such as ion exchange, so that carbohydrates form BC. The hydrothermal reaction temperature generally does not exceed 250 ℃, the heating time should be within 24 h, the hydrothermal carbonization method is more suitable for biomass with high water content, it is more economical and saves energy, less ash is produced, and there is higher hydrophobicity. Zhang et al. collected Fe sludge from the Fenton process of printing and dyeing wastewater and added biomass to prepare a sludge-based magnet BC through hydrothermal carbonization. The Fe content is about 25.2 %. In the hydrothermal process, carbohydrates are mainly involved in Fe ion reduction and chelation to synthesize Fe_3O_4 [45].Vahdati-Khajeh et al. reported that N-BC was prepared by hydrothermal carbonization of egg extract and sucrose in a high-pressure reactor and that the yield of BC could reach up to 90 %, with a N-doping content of about 12 % [48] (Fig. 6).

Unlike traditional pyrolysis, the microwave heating method uses microwaves to induce the internal structure of biomass such that it can be heated from the inside out. This heating method is more uniform, faster, and easier to operate. Microwave pyrolysis products have a more

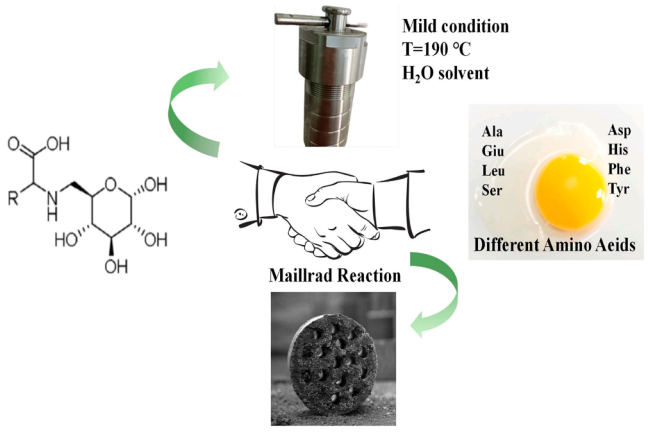

Fig. 6. Schematic mechanism of N-rich hydrochar synthesis from egg white biomass in the presence of sucrose (see Vahdati-Khajeh 2019, Surfaces and Interfaces).

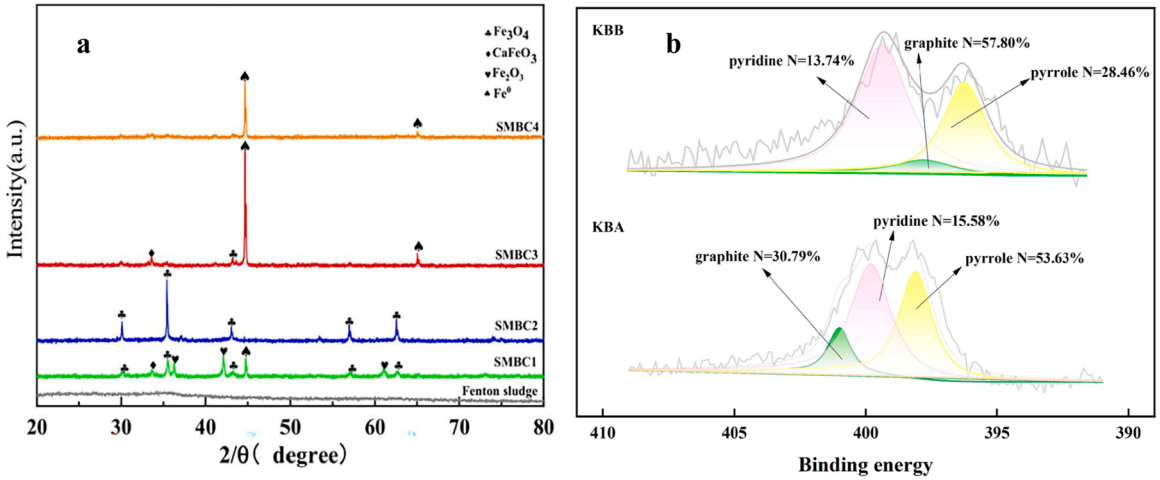

Fig. 5. (a) XRD patterns of raw Fenton sludge (see Ye 2022, Journal of Environmental Chemical Engineering) [46]; (b) N 1 s XPS patterns of Kelp N-BC (see Wang 2023, Science of the Total Environment) [47].

developed micropore structure than those produced by conventional pyrolysis technology. Yu et al. reported N-BC preparation by the microwave pyrolysis of industrial sludge treated with polyacrylamide as a flocculant. The nitrogen content was 4.61 wt%, and BC had a microporous structure [49]. Microwave heating can effectively reduce secondary pollution caused by sludge heating, such as heavy metal leaching.

4.2.2. Co-doping of metal and non-metal heteroelements

Both single-metal-doped and non-metal-doped BC have shortcomings, and the major research directions currently are the recyclability, stability, and economy of the catalysts. The introduction into metal-doped BC may be an effective way to improve its contaminant-removal ability, stability, and reusability. It has been reported that BC co-doped with metal and non-metal heteroelements has the advantages of metal catalysts, non-metal heteroatom catalysts, and carbon materials simultaneously. Electron transfer between metal oxides and oxidants on co-doped BC excites free radicals (·OH and $O_2^{\cdot-}$) generation, oxidative degradation of pollutants [35], and electron transfer between heteroelements and oxidants of co-doped BC. Additionally, the electron-transfer process between the contaminant and oxidant induces a nonradical pathway [50]. The modification of the surface functional groups by heteroelements and metallic elements promotes free electron transfer and facilitates electron transfer between the co-doped BC, oxidizer, and pollutant [51]. Additionally, heteroelements from non-metals (N, S, and P) provide lone electrons to metal oxides on co-doped BC to increase the number of active sites in the catalytic reaction [52]. Co-doped BC exhibits a good catalytic effect on dye degradation. Li et al. deoxidized acid orange (AO7) in an Fe-N BC system, and it was completely degraded within 90 min. The degradation efficiency was significantly higher than that of N-BC alone as a catalytic material [53]. External BC doping with a single metal is highly likely to lead to metal ion leaching during the catalytic process, resulting in secondary pollution. Although this risk factor can be effectively mitigated by co-doping with nonmetallic heteroelements, there is still the potential for metal leaching. A recent study found that although the degradation efficiency improved in the N-Cu/BC/tetracycline system, Cu leaching concentration was 3.915 ppm in the leaching experiment, which exceeded the maximum allowable emission concentration of Category II pollutants under environmental emission regulations [54]. Therefore, future studies should focus on ensuring the safety and stability of synthetic catalytic materials to guarantee catalytic efficiency.

4.2.3. Green material synthesis methods

Green synthetic materials have garnered widespread attention due to their environmentally friendly raw materials and absence of secondary pollution. This concept was initially developed by the U.S. Environmental Protection Agency and has since piqued the interest of numerous researchers [55,56]. The raw materials for green synthetic materials are sourced from biodegradable leaves, plants, and green tea extracts. Among these, Fe-N green synthetic materials are relatively common, and in recent years, research on the preparation of Fe^0-N co-doped BC through green synthesis methods has made progress. Sravanthi et al. used Pithecellobium dulce seeds (biomaterials), Calotropis dulce tea flower extracts (reductants and stabilizers), and chitosan to produce biomaterials-supported Fe 0 nanoparticles. Initially, $Fe(NO_3)_3$ and flower extracts were mixed in a 1:1 ratio and stirred continuously for 15 min to reduce Fe^{3+} ions, followed by drying. Compared to traditional Fe-N doping methods, such as modifying Fe_3O_4 nanoparticles with cyanamide and dicyandiamide, the use of green reductants in place of toxic reductants is advantageous.

5. Application of heteroatom-doped biochar to catalytic oxidation degradation of pollutants in water

The major reactions of species produced by heteroatom-doped BC-catalyzed O_3 oxidation (hydroxyl radical ·OH, superoxide $O_2^{\cdot-}$) include the free-radical and non-free-radical pathway (e.g., $^1O_2$) degradation of pollutants, and heteroatom-doped BC has demonstrated excellent performance in catalyzing the O_3 degradation of dyes, pharmaceutical wastewater, organic wastewater, and so on.

5.1. Dye wastewater

Dyes are vastly used in textiles, rubber production, enamel paint, plastics, cosmetics, and other industries. Dyes cause obvious colored pollution in water bodies. They overload the self-purification mechanism of water, reduce or prevent photosynthesis, and have carcinogenic effects on humans and animals. Common dyes used in industrial wastewater are methylene blue, acid orange, and reactive red. It has been vastly reported that heteroatom-doped BC catalyzes O_3 to degrade dyes. Babar et al. used Fe_xO_y-doped BC to catalyze O_3 to degrade methylene blue. The degradation efficiency of O_3 oxidation alone was only 76 %, whereas that of methylene blue by Fe-loaded BC was 95 %. The Fe-BC system stimulates O_3 to produce more ·OH, which significantly improves the catalytic capacity. When single ozonation process is used, intermediates are produced that cause O_3 decomposition resistance, resulting in inadequate pollutant removal. Fe_xO_y-BC added to the ozonation process increases aqueous[8]. Li et al. decreased AO7 hydrolysis in an Fe-N BC system. Fe^{3+}, Fe^{2+}, and N-functional groups (pyridine N, pyrrole N, graphite N, and N oxide) are the major active sites for O_3 activation by Fe-N BC. Electrochemical impedance spectroscopy (EIS) measurements were conducted on biochar (BC) and Fe-N-BC. Fe-N-BC showed a smaller semicircle and better conductivity, indicating lower charge-transfer resistance compared to BC, which implies faster electron transfer and a more significant current-potential response. Complete degradation is achieved within 90 min [53].

5.2. Antibiotic wastewater

Antibiotic wastewater is a high-concentration organic wastewater that is difficult to degrade due to its complex composition and presence of several types of organic matter. Recently, researchers investigated the degradation performance of antibiotic wastewater using a heteroelements-doped BC-catalyzed O_3 system. Tian et al. used the BC loaded with manganese to catalyze ATZ degradation by O_3 through use of BC as the sole catalyst at 2.5 mg/L O_3, and the degradation rate was only 48 %. Under the same conditions, for the BC loaded with Mn, the degradation rate reached 83 % [21]. Cobalt oxide is a modified material, wherein BC is used as a catalyst. Li et al. catalyzed BC supported by cobalt oxide to degrade bisphenol A by O_3, demonstrating a good degradation effect under the two pathways of free-radical and electron transfer, and the removal rate reached 95.8 % within 8 min [57]. These metal oxides provide BC with unique surface characteristics and increase its surface area. The number of active sites also increased [58]. Wang et al. used kelp as a raw material for the direct pyrolysis of N-BC to catalyze O_3 degradation of a refractory herbicide (IMZC). Kelp, an N-rich S biomass synthesis of N/S-BC, provides more active sites. Graphite N and thiophene S play a leading role in the catalytic process, promoting ·OH, $O_2^{\cdot-}$, $^1O_2$ production, and they have a positive impact on IMZC degradation [47]. Zhao et al. used industrial sludge with the invasive species water hyacinth by co-pyrolysis, doping nitrogen into the sludge biochar through the pyrolysis process for use in catalytic O_3. They achieved a 93 % degradation of high-concentration TC wastewater within 130 minutes. The addition of water hyacinth enriched the variety of nitrogen functional groups. However, upon co-pyrolysis, the high temperature and mutual interactions lead to the instability of pyridinic N and pyrrolic N, which then transform into graphitic N, thereby enhancing the catalytic ability. This is because graphitic nitrogen usually has higher thermodynamic stability than pyridinic nitrogen and pyrrolic nitrogen. At high temperatures, the system tends to form more stable structures; at the same time, high temperatures can allow carbon

atoms to rearrange, forming more stable sp^2 hybridized structures, which helps nitrogen atoms to transition from pyridinic or pyrrolic states to graphitic nitrogen states. In addition, high temperatures may promote dehydrogenation reactions, causing pyridinic nitrogen and pyrrolic nitrogen to lose hydrogen atoms, thereby transforming into graphitic nitrogen, thereby enhanced the efficiency of catalytic O_3 [59]. He et al. prepared colored BC using waste tea as the raw material and loaded it with MnO_x (MN-NWT) for heterogeneous catalytic O_3 oxidation, achieving excellent 2–3–5-trimethylpyazine degradation (TMP). The Lewis acid sites in the MN-NWT include polyvalent Mn sites, O vacancies, and surface hydroxyl groups. As the major active site for catalytic O_3, 95.3 % of TMP was degraded within 30 min, and the degradation efficiency of TMP reached approximately 88 % after repeated usability tests [60].

5.3. Other organic wastewater

It is difficult for some high-concentration organic wastewaters (e.g. COD and TOC) to meet the standards when treated using conventional biological methods, which will cause activated sludge death. Heteroatom-doped BC-catalyzed O_3 can effectively treat high-concentration wastewater and improve biodegradability of water quality. Pan et al. reported that the sludge produced during coking wastewater treatment process was pyrolysed to produce BC, and a bimetallic BC composite material doped with Fe and Co was prepared to enhance the O_3 oxidized coking wastewater. According to previous studies, in heterogeneous O_3 catalytic reactions, variable-valence metal ions and surface oxygen-containing groups are the active centers of the catalyst, and electron transfer is a key step in the catalytic process. Fe/Co biochar can effectively catalyze the decomposition of O_3 to generate ·OH, O_2^-, and $^1O_2$. The adsorption sites on the catalyst surface are conducive to the oxidation and decomposition of O_3 to produce free radicals, which are beneficial for the adsorption, enrichment, and degradation of pollutants in wastewater. Considering the standard reduction potentials E0 (Co (III)/Co(II)) = 1.81 V, E_0 (Fe(III)/Fe(II)) = 0.77 V, and E0 (O_3/O_2) = 2.07 V, O_3 can oxidize Fe(II)/Co(II) on the catalyst surface to Fe(III)/Co(III), while Fe(II) on the catalyst surface can reduce Co(III) to Co(II), thus forming Fe(III) or Co(II). The valence cycle of Fe(II)/Co(II) and Fe (III)/Co(III) metal ions formed promotes the decomposition of O_3 and organic matter [61]. In a study by Zhuang et al., using rice as the BC raw material, Fe-oxide-modified BC catalyzed the rapid production of O_3 dependent ·OH in a short period of time, with COD and chroma removal rates of 74 and 81 %, respectively. The effluent met the A-level discharge standard of the Pollutant Discharge Standard for Municipal Sewage Treatment Plants (GB18918–2002) [20]. Luo et al. found that post anaerobic–aerobic (A/O) treatment, there was still a high chroma and COD in the biological wastewater treatment of the farm; the biogas residue of the farm was used to prepare BC as a carrier, loaded with MnO_2 to prepare the catalyst (MnO_2/BC), and the decolorization rate reached 91.29 %. The removal rates of NH_3-N, total phosphorus, and coloration reached 81.7 %, 90.2 %, 93.4 %, and 99.1 %, respectively. The catalytic action of MnO_2 can reduce the activation energy required for the reaction, improve the reaction rate, and promote the production of ·OH via electron transfer between O_3 molecules [62].

6. Economic cost of doping biochar

When using biochar as adsorption or catalytic material, the economic cost has also become an important indicator that cannot be ignored. Since the raw materials of biochar mostly come from agricultural and forestry wastes and some solid wastes, but considering the use of doping to improve its physical and chemical properties, the manufacturing of biochar needs to carefully compare the doping technology of biochar to balance its practicability and cost. The research summarized the production cost of externally doped and internally doped biochar, as shown in Fig. 2. The differences mainly include the production cost of raw materials and the preparation conditions of doped biochar (power consumption of some equipment such as ovens and high-temperature furnaces, the use of inert gas purging and the addition and use of some dopants) [63]. The increase of pyrolysis temperature has the greatest impact on the production cost of biochar. Under the heating condition of 200 ℃ −1000 ℃, the cost of electric energy loss has increased 0.15 times, and the cost has increased by about 8 RMB. Under the condition of using the same pyrolysis temperature, the cost of deriving biochar from different raw materials of biochar (taking industrial sludge and agricultural and forestry wastes as examples) increases from 5.1 RMB/Kg to 9.2 RMB/Kg. For doped biochar, the dopants used in external doping ($MnFe_2O_4$, Fe_3O_4, $FeCl_3$ carbamide, melamine), The price is between 11.4 RMB/Kg and 43.5 RMB/Kg; However, internal doping of biochar only costs the price of raw materials and the energy consumption price required for pyrolysis [8,19,20,35,40]. In addition, we also investigated commercial activated carbon, graphene, carbon nanotubes and other carbon materials commonly used in industry, and their market prices are generally between 20.5 RMB/Kg and 165 RMB/Kg. Through rough comparison, the price of biochar after modification (whether externally doped or internally doped) is still much lower than the price of carbon materials commonly used in industry, Moreover, the pollutant removal capacity of doped biochar is comparable to that of industrial carbon materials. In addition, the pollutant removal capacity is generally much higher than that of other cheaper adsorbents, such as red mud and zeolum etc [64,65] (Table S2). The Various of biochar and carbon materials commonly used in industry mentioned by different researchers have different sources, preparation conditions and doping methods, and their prices vary greatly. We may not be able to provide an accurate reference for comparison. Therefore, we make a preliminary reference for the drug price details provided by sinopharm group Laibo trading company in chinese mainland, The exact prices listed here do not have any commercial preferences.

7. Current status and insufficiencies

External doping allows researchers to intentionally introduce specific metals or heteroelements into biochar to obtain composite materials with desired functions. This targeted doping capability is crucial for designing materials with specific catalytic activities. Through external doping, the content of the target doping elements can be controlled more precisely, which is key to adjusting the electronic structure and surface properties of materials to optimize their performance. Precise control of doping levels helps to achieve fine-tuning of material properties. Although external doping provides the ability to precisely control the content of doping elements and to introduce target doping elements in a directed manner, it also has some drawbacks, including: (1) Complex operation: The external doping process may involve multiple steps, including pre-treatment, thermal treatment, and possible subsequent treatments. These steps require precise control to ensure the effective introduction and uniform distribution of doping elements. This complexity can lead to increased operational difficulty and higher requirements for technology and equipment. (2) High cost of dopants: The use of external dopants, especially some rare earth elements or precious metals, can significantly increase the cost of material preparation. These dopants may be expensive and may not be sustainable or cost-effective in large-scale production. (3) Waste from the use of dopants: In the external doping process, only a portion of the dopants may be effectively utilized, while the rest may be lost or wasted during the process. This waste not only increases costs but also potentially burdens the environment. (4) Potential environmental pollution: The use of external dopants may pose risks of environmental pollution, especially when handling and disposing of these chemical substances. If dopants are not managed properly, they can contaminate water bodies, soil, and more. (5) Metal leaching toxicity issues: In water treatment applications, metal-doped biochar may release toxic metal ions, which pose threats to the environment and human health. Therefore, while external doping

offers many advantages, in practical applications, one must also consider its operational complexity, cost, waste, and environmental impact. Solutions need to be sought to achieve a more sustainable and environmentally friendly material preparation process.

Internal doping indeed has some distinct advantages over external doping: (1) Simple operation: Internal doping typically utilizes elements already present in the material, conducted through direct pyrolysis or co-pyrolysis, without the need for additional dopants, which simplifies the operational steps and process flow; (2) Low cost: Since there is no need to purchase and use additional dopants, internal doping can significantly reduce the cost of material preparation; (3) Thermodynamic stability: Internal doping can enhance the thermodynamic stability of materials, which is particularly important for applications of materials at high temperatures; (4) Improved electrical conductivity and catalytic performance: Internal doping, as an effective regulation strategy, can significantly enhance the electrical conductivity and electrocatalytic performance of materials.

On the other hand, internal doping, while having the advantages of simple operation and low cost, also has some drawbacks, mainly including: (1) Inability to control the content of target elements: Internal doping relies on the elements naturally present in the raw materials, conducted through pyrolysis or co-pyrolysis, thus it is not possible to precisely control the content of doping elements. This may lead to inconsistent performance in the final product, making it difficult to meet the needs of specific applications; (2) The raw materials themselves may contain impurities: The raw materials used for internal doping may contain unknown or uncontrollable impurities. Since impurities in the raw materials may introduce additional energy levels or change the surface properties of the materials, this could have a negative impact on catalytic reactions. In the process of catalytic oxidation of pollutants in water, these uncontrollable factors may reduce catalytic efficiency or selectivity; (3) Consistency and reproducibility issues of product performance: Since internal doping depends on the inherent components of the raw materials, this may lead to inconsistent performance in different batches of products, affecting the reproducibility and consistency of the products.

8. Conclusion and outlook

This paper describes the methods, mechanisms, and applications of BC catalysis for O_3. The physical and chemical properties of BC were adjusted bythrough doping with metal and non-metal heteroelements to significantly improve the catalytic performance. Different heterochar doping and preparation methods have been proposed. The properties of synthetic materials are more controlled, and internal doping is more environmentally friendly, simple, and avoids resource waste. The applications of catalytic O_3 degradation for water pollution and new progress in diverse fields of hetero-doped BC are summarized.

Research on heteroatom-doped BC has gradually matured (i.e., in the metal-doped BC method) and the electron-transfer ability between these different valence metal ions helps oxidizers decompose and produce ROS, thus improving oxidation efficiency. However, the high cost of the metal and its oxides is still a major issue, and it is difficult to popularize it as a catalyst for industrial sewage treatment on a large scale.

In the non-metallic-doped BC method, current research only focuses on the doping content and does not elucidate the mechanism by which doping interacts with biomass to produce functional groups during the pyrolysis process. A high doping ratio only increases the content of impurity elements in BC but neglects the selection and formation of specific functional groups. Therefore, it is essential to precisely regulate the types and quantities of functional groups.

Presently, the BC catalytic system is limited to a single type of pollutant, which is very different from the complex water environment used in actual wastewater treatment. Few studies have been conducted to determine whether the use of BC to catalyze O_3 can effectively degrade multiple pollutants. Therefore, the mechanisms and interactions of diverse degraded pollutants should be further studied. Additionally, bio-oil, biogas, and other byproducts are produced during the pyrolysis and doping processes; therefore, their recovery and utilization must be considered.

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Declaration of Competing Interest

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

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Appendix A. Supporting information

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