A Mini Review: The Activation of Biocarbon Materials and their Complexes to Persulfate

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ABSTRACT

Recently, the Persulfate (PS) based oxidation process (AOP) has received wide attention due to its excellent performance. However, PS activation as the crucial point for AOP has become a hot research topic in recent years. Due to environmentally friendly characteristics (wide sources and low economic expenditure), biomass carbon (BC) and its composites have gradually attracted significant attention in activating PS. Therefore, the present work systematically summarizes the recent research progress of BC and its composite material used for PS activation. The current preparation technologies of BC and its composite materials are demonstrated, with a focus on their application in the practical treatment of organic wastewater.

Abbreviations: PS: Persulfate; BC: Biomass Carbon; AOP: Advanced Oxidation Process; PDS: Perdisulate; NZVI: Nano-Scale Zero-Valent Iron; PFR: Persistent Radicals; FMO: Frontier Molecular Orbital Theory; DD: Double Descriptor Method; ZVI: Zero-Valent Iron; SMX: Sulfonymethoxazole

Introduction

Nowadays, the continuous growth of the world population, the ever-increasing depletion of fossil fuel reserves [1], and the rapid pace of urbanization and mechanization, have led to the wanton discharge of a significant number of toxic organic and inorganic pollutants, thus, such urgent issue should be reasonably resolved, otherwise it will do great harm to us [2]. How to better deal with the wastewater containing refractory organic pollutants has aroused wide concern. Advanced Oxidation Process (AOP) [3-5] is a new technology for water treatment to effective removal of organic pollutants [6]. In general, many other organic pollutants that can be treated by this method will eventually be mineralized into small inorganic molecules, like CO_2 and H_2O, thus eventually achieving complete removal. So far, AOPs has developed into a method for fundamentally degrading pollutants [7-9]. In this method, the persulphate (PS) oxidation technology is widely used considering its excellent degradation performance, a more obvious oxidation reduction potential (2.6 V-3 V) and a broader pH processing range (4-9) [10]. Therefore, the persulfate-based advanced oxidation process in the future wastewater treatment has very broad application prospect [11].

In most cases, the major oxidant species in persulfate systems are the sulfate radical($\bullet SO_4^-$) and the hydroxyl radical ($\bullet OH$). Persulphates can be divided into two categories, namely, persulfate (PMS) and perdisulate (PDS). However, due to the unique structure, the O-O bond is difficult to break to form ($\bullet SO_4^-$), so it needs to undergo a certain process to activate the persulfate. The current activation methods mainly include thermal activity method, alkali activation, transition metal ion activation, and ultraviolet activation [12]. However, the thermal activity method usually requires a high energy consumption, and the alkali activation and the transition metal ions activation often arise new problems in the cost and subsequent processing period. It is reported that carbon materials can effectively achieve activation of PS, but the cost is too expensive. Fortunately, BC have more advantages over other carbon materials [13], such as extensive source and lower cost. And recent works has reported that biomass carbon made from 300-500℃ calcination has good results on PS activation. The annual biomass waste production from various sources is very huge. As a more environmentally friendly carbon material, biomass carbon shows considerable potential for PS activation and much effort has been devoted to it. Other articles also summarize the application of biomass as a catalyst in some advanced oxidation processes of persulfate activation [14]. However, the effect of biomass catalyst in the advanced oxidation of sulfate radical remains to be systematically arranged. Hence, in this mini review, the recent mechanisms and application of biocarbon materials in activated persulfate are summarized and new insights into the future applications in activated PS are simultaneously provided. The present work also provides a direction for the better use of BC in the future.

Modification Method of BCs

BC possesses strong adsorption ability due to its high surface area and has a fairly high degradation rate owing to the presence of high porosity and large oxygen-containing functional groups [15]. Despite of the good performance, the annual utilization rate of BC is less than 10% in China. Its catalytic properties can be improved by activation and doping, which can increase the specific surface area and create mesoporous structure, thereby increasing active sites and oxygen functional groups, promoting π-electron transfer, and also regulating the electron density in biochar [16]. Transitional metal ion activation of PS has proved to be an effective method, but the use of this method is abandoned because it is difficult to recover and has the risk of secondary pollution towards the environment. However, the load of transition metal ions with BC has successfully solved this problem. Da Ouyang, et al. [17]. pyrolysis of pine needles under oxygen-limited conditions, obtaining BC, at different temperatures and dispersed in 50 ml 3.0

mM $NH_3 \cdot H_2O$ while adding 20 mL ultrapure water dissolved 1.39 g $FeSO_4 \cdot 7H_2O$ and 1.01 g $Fe(NO_3)3 \cdot 9H_2O$. After 45Hz 100W treatment 1h, the solution was separated, and the obtained biomass carbon was washed with ultrapure water until the washing liquid was neutral. The degradation experiment of PS on 1,4-dioxane was also conducted. Its highest degradation efficiency of 1,4-dioxane was 98.6%. Yan et al. [18]. pyrolyzed rice husk at 350℃ for 6 hours under the condition of limited oxygen, and dispersed it into 0.054 mol/L $FeSO_4 \cdot 7H_2O$ solution with pH=5, 250 ml. NZVI/BC loaded with nano-scale zero-valent iron (NZVI) was prepared by dripping 250 ml of 0.108 mol l-1 $NaBH_4$ solution, and then PS was applied to trichloroethylene. The data showed that when the mass ratio of NZVI/BC was 1:5, the degradation rate was 99.4%.

In addition to doping the transition metal ions, the physicochemical properties of biochar can be enhanced by acid or alkali treatment [19]. Acid activation method refers to the modification by soaking the biomass in or dispersed in a certain concentration of acid solution [20,21], including phosphoric acid, nitric acid, etc. Currently, phosphate acid activated biomass carbon technology has been widely use. The alkaline modification is performed by soaking or suspending the BC at different alkaline concentrations from room temperature to 100℃. The soaking and mixing time may last several hours or days (mostly 6-24 hours), depending on the raw materials used for modification, and the most commonly used bases are potassium hydroxide, sodium hydroxide, etc. But after the activation, it also costs a lot of consumables for washing. Atomic doping [22-24] is also a common method to modify the catalytic capacity of biomass carbon. For example, Wang, et al. [25], grinded melamine to the corn cob at various mass ratios, then poured the mixed precursor into the lid crucible, heated at 3℃ per min in the Marvel furnace to 550℃ and held for 4 hours. The obtained species were named CNBC1, CNBC2, CNBC3, CNBC4 and CNBC5, according to the mass ratio of corncore to melamine to activate PMS to degrade bisphenol A. The results showed that the efficiency of activated PMS processing BPA varied according to the mass ratio of BC and melamine, and it exhibited a BPA removal efficiency of 97.23% with mass ration of 1%. It should be noted that the removal performance, can be further enhanced with the suage of light. Figure 1a and Figure 1b are the contrast TEM diagrams before and after the doping modification, wherein it can be observed that both are sheet structures, meanwhile a smaller and looser distributed layered structure can be also observed in modified samples. Figure 1c is an EDS spectrum of CNBC, showing that CNBC contains large amounts of C, N and a small amount of O. LI, et al. [15]. successfully doped N in urea and Fe in iron salt into the BC by water thermal carbonization (HTC). The results showed that the best removal rate reached 98.2%.
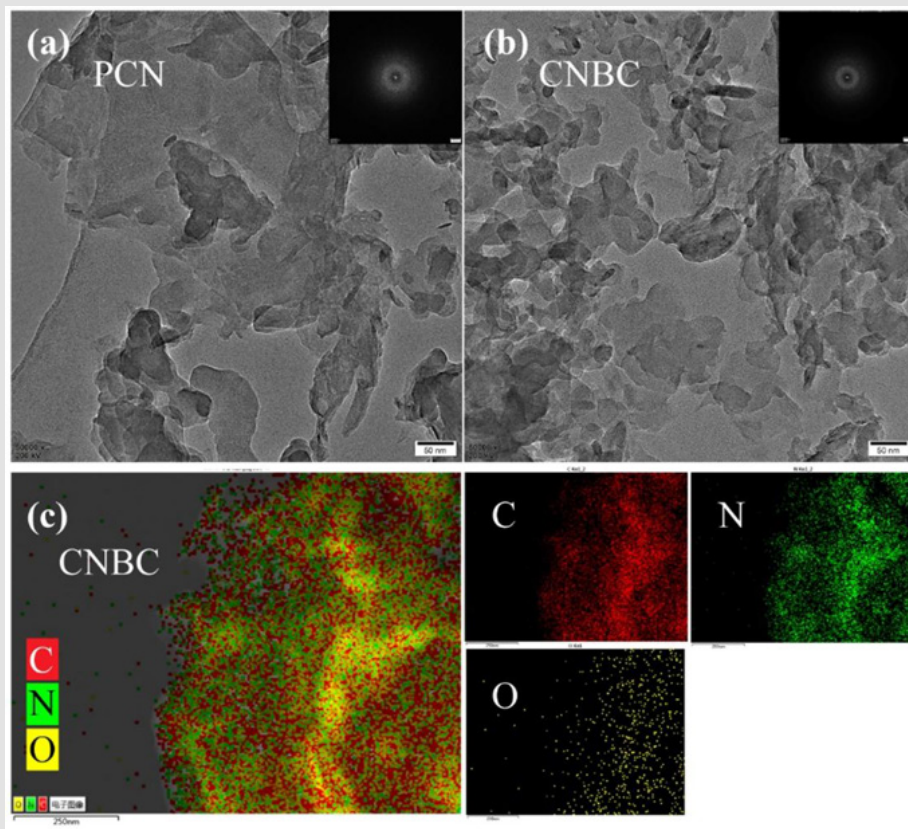
Figure 1: TEM images of

a)   (a-b) PCN

b)   (c) the EDS diagram of the CNBC. Reprinted with permission from [25], Elsevier.

PSM Principle of Activation of BC

Activate PS Principle

The major element composition of biomass carbon is C, followed by H and O. Normally, biocarbon has 45% ~ 65% C, H 1%~5% and O 10%~40% [26]. After the high temperature carbonization, H gradually emerged, which caused the content of C to rise, and eventually led to the increased aromaticity of BCs. The excellent performance of biomass carbon materials is closely associated with its rich surface functional groups [27]. The main surface functional groups are carboxyl, phenolic hydroxyl, hydroxyl, group, lactone, carboxylic anhydride and cyclic peroxide group, respectively [12,26]. Among them, the BC has good redox properties and surface charges, which all originated from the carboxyl groups and phenolic hydroxygroups on its surface [28]. The presence of carboxyl, hydroxyl groups and can absorb organic pollutants [29]. This results in that the pollutants can also be firmly adsorbed to the BCs by forming hydrogen bonds to the surface polar functional groups. So, how does the biochar activate the PS? After the reaction

of biochar, the ratio of -OH and -COOH decreased and -OH and -COOH can act as active sites in PS activation systems, where defect formation and increased graphitization generally strengthened the capacity of electron transfer [30]. However, there is no established theory, but four theoretical views exist: (1) its surface oxygen functional group can activate PS via defects caused by pyrolysis of ROS [15, 31]; (2) The defects and graphitized structure of biochar produced by pyrolysis can activate PS [32-34];(3) biocarbon can provide electrons and transfer electrons to PS to activate persistent radicals (PFR) in PS [35-37];(4) biochar may activate PS [38, 39].

Principles of Catalytic Degradation

Commonly, the present catalytic mechanism is divided into two parts: free radical pathway and non-radical pathway [40]. The O-O bond in PS activated by BC breaks to form ($\bullet SO_4$-), and the generated ($\bullet SO_4$-) will further react with H_2O to generate ($\bullet OH$) and SO_4^{2-}, which then mineralize and degrade the pollutants. The non-radical degradation pathway achieves mainly through electron transfer, and the generation of $^1O_2$ [41]. During non-radical

oxidation, it occurs mainly on the catalyst surface. Due to the low oxidation performance of non-free radicals, the non-free radicals able to oxidize the pollutants in the early stage of the reaction, with the reaction progressing forward, the free radicals made the pollutants oxidized into completely mineralized into CO_2 and H_2O. However, in most cases, the whole reaction process is collaboration the result of the above two pathways [42,43].

Application of BCs in Activating PS

The Activation of PS by Original BC

Herein, we mainly introduce the activation effect of BC with plants and sludge as the precursor on PS, and recent research progress on the performance of different catalysts is summarized in Table 1 below.

Table 1: Application of the primitive biocarbon catalyst in activating the PS for contaminants removal.

Precursor	Reaction system	Pollutants	Reaction conditions	Remove rate
Pine needle biochar coal	Pine Needle Biocarbon + PMS	1,4-Dioxane	1,4-Dioxane = 20.0 μM, PMS=8.0 mM, BC= 1.0 g / L, pH = 6.5, and T = 25℃, 240 min	85.2% [44]
Saw-end biochar	Saw End Biocarbon + PMS	Acid Orange 7 (AO7)	PMS= 9mmol/L, and SBC=1.5 g / L; pH=6, T=25℃, 180min	96% [45]
Litchi branch	Lye branch + PMS	BPA	BC=2.0g L /1, PMS=15 mM, pH=3, T=25℃, 120min	98.55% [46]
Waste malt root	Waste malt root derived biocarbon + PS	SMX	SMX = 250 μg/L, PS = 250 mg/L, BC= 90 mg/L.	94% [47]
Rice husk	Rice shell +PMS	BPA	PMS=10mM, pH=6, T=25℃, BPA=20mg/l	96.3% [48]
SDBC	SDBC+PDS	STA	STZ=20 mg/L, PDS = 10 mM, BC = 0.5 g/L, 90min	> 99% [49]
SDBC	SDBC + PS + US	BPA	BPA=20 mg/L, PS = 3 mM, BC = 2 g/L,US = 60 W; pH = 3, 80min	98% [50]

The Activation of PS by BC Doped with Transition Metal Ion

The Activation of PS by BC Doped with Iron Salt /ZVI: It has been reported that BC fail to reuse and possess poor stability, and therefore the degradation efficiency gradually decreases with continuous utilization. In order to solve such issues, doping transition metal ions has been adopted to activate PS of the degradation of contaminants. Among them, iron ions have become the research hotspot to activate PS on BC due to their non-toxic and low cost [51]. Jiang et al. [52]. chose sawdust as the precursor in a flask of the $FeCl_3·6H_2O$ solution and then oscillated the mixture at 200 rpm for 300 minutes in a thermostatic oscillator. Subsequently, the water in the mixture was removed by evaporation, and the obtained residue was dried overnight at 80℃. BC-Fe was made and used to activate PS for the degradation of BPA. The results confirmed that Fe-BC-700 could completely remove 20 mg/L BPA in 5 minutes with 0.2 g/L PMS and 0.15 g/L catalysts within 5 minutes. Its activation and degradation mechanism is shown in Figure 2: (1) Fe^0 can activate PMS to generate ($\bullet SO_4^-$) and Fe_2^+, and the generated Fe^{2+} further catalyzes PMS to generate ($\bullet SO_4^-$) (2) Fe^{3+} can react with PMS to generate ($\bullet SO5^-$) and Fe2+ (3) As a relatively weak transient substance, ($\bullet SO_5^-$) can further self-react to form ps.

Similarly, Wang, et al. [53]. used wheat straw as the precursor to prepare BC under oxygen restriction conditions at 500℃, with the addition of BC, PS, trivalent iron to sulfamethoxazole. The study combined Frontier Molecular Orbital Theory (FMO) theory and Double descriptor method (DD) method to give four possible degradation mechanisms as shown in Figure 3. The research results showed that when BC=0.75g/L, PS=0.75g/L, T=25℃, pH=5, the removal rate of sulfamethoxazole by BC-Fe activated PS was 93.3%. However, several works found that Fe^{2+} was very easily leaching in the BC/PS process, generating a new pollutant for the water environment. Therefore, the stability of BC doped with transition metal ions still needs to be highly improved. Recently, zero-valent iron (ZVI) has received increasing attention in activated PS studies with high reaction performance, due to its high activation efficiency and multi-phase catalytic function [54,55]. ZVI can be activated by acidification, oxidation to Fe^{2+}, by generating ($\bullet SO_4^-$) or by direct electron transfer with PS. However, due to their high surface energy and magnetic interaction, ZVI particles tend to aggregate into micron class particles, leading to reduced reactivity [56]. Therefore, in recent years, research on how to load ZVI to BC and apply it to activate PS for the treatment of organic sewage has attracted significant attentions. Table 2 shows the recent application of ZVI/BC in wastewater treatment in PS.
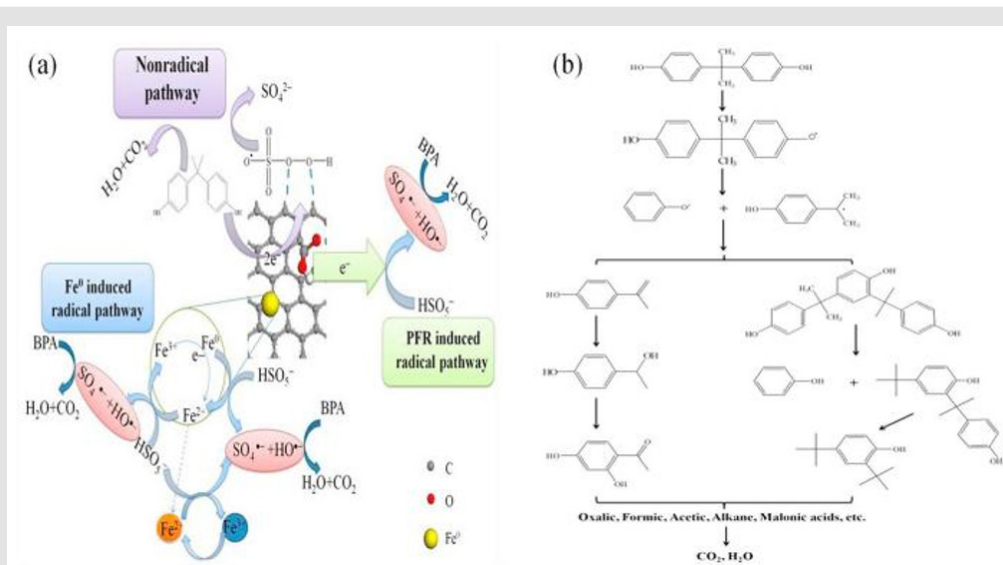
Figure 2: (a) Fe-BC-700 activates the proposed mechanism for the PMS. (b) Potential degradation pathway of BPA in the Fe-BC-700 / PMS system. Reprinted with permission from[52], Elsevier.
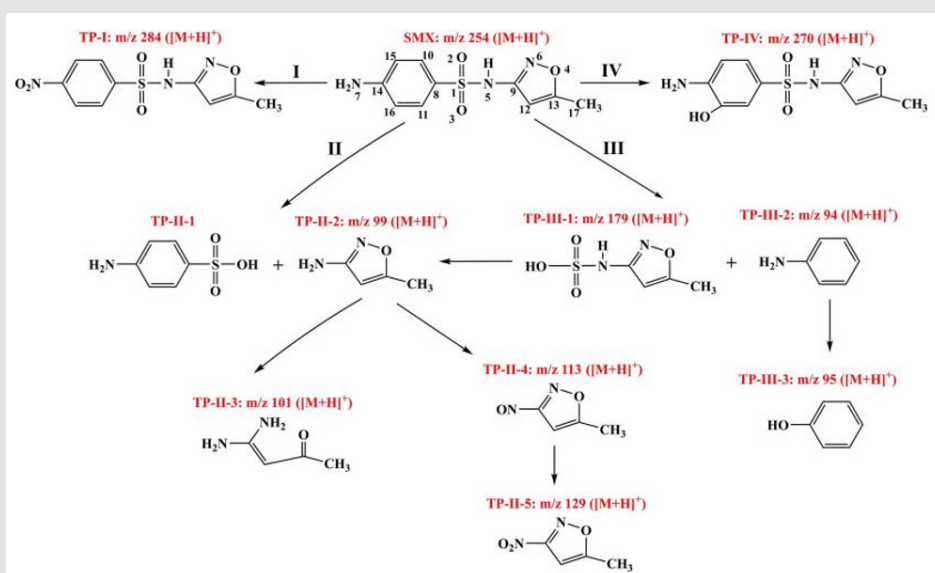

Figure 3: The possible degradation pathway of SMX by BC/Fe (III) / PS. Reprinted with permission from[53], Elsevier.

Table 2: Application of ZVI/BC in PS for the treatment of sewage.

Precursor	Reaction system	Pollutants	Reaction conditions	Remove rate
Wooden chips	NZVI/PGBC/PS	17-β-estradiol (E2)	NZVI/PGBC =100 mg/L; PS =400 mg/L; T=25℃, 45min.	>99% [57]
Soybean straw	NZVI-BC /PS	Atrazine	Soybean straw and Fe2O3 (mass ratio = 7: 1); pyrolysis at 800℃	93.8% [58]
Green tea	NZVI-BC /PDS	P-nitrophenol	NZVI-BC =0.8 g /L; n(PDS) / n(PNP) =100: 1;	96% [59]
Corn stalks	ZVI-BC/PS	Cyprofloxacin	pH=4.5; ZVI/BC=0.5 g/L; PS=10 mmol/L.	97.55% [60]
Bamboo	ZVI-BC /PDS	Sulfonadazine (SDZ)	ZVI/BC =0.05 mol/L; PDS=2 mM; pH=3; T=318 K.	>99% [61]
Rice husk	NZVI-BC/PS	Nonylphenol (NP)	NZVI/BC3=0.4 g/L; PS=5 mM; NP =20 mg/L,120min.	96.2% [62]

Other Doping of Transition Metal Ions: Apart from applications of metal salt and ZVI, doping applications have also been reported for other metal materials. For example, Co^{2+} has been widely used to activate PS, but problems such as toxicity pose potential risks to the environment. Recent studies have shown that the leaching rate of Co is low and thus has become a hot spot on the

catalysis. Yang et al. [63]. successfully synthesized Co-BC by loading Co to BC through a pyrolysis process, and applied it for the activation of PS for the degradations of amaranth and acetaminophen. The results showed that the degradation efficiency could reach 90% when CoIB= 50 mg/L, PMS = 400 mg/L, ACE = 5 mg/L, pH=6. Chen, et al. [64]. prepared the BC, which showed that the total removal rate of 5 heavy metals and 15 antibiotics was 57.4% and 42.3% in the presence of Cu, respectively. Although the transition metal ions perform well in the catalytic process, there is still a risk of leaching, and how to solve this risk completely remains to be studied in the near future. To sum up, in the activation of biocarbon material doped with transition metal ions to PS, as well as in the redox potential applied by transition metal ions on PS, the functional groups on the surface of biocarbon materials also play a pivotal role in transmitting electrons [12]. Therefore, in the subsequent work, we should clarify the role and path of BC in the transition metal ion activation process of PS, so that we can properly regulate the appearance and nature of BC to promote the degradation efficiency.

The Doping of Miscellaneous Atoms

Atomic doping can avoid the risk of leaching problems, and at the same time has an excellent ability to transport electrons. The majority of reported works are related to S, N doping. PMS degradation of BPA was activated using wood chips doped with N, as a precursor by Xu, et al. [65]. The results showed that under conditions of BPA = 10 mg/L, PMS = 2.0 mM, N-BC = 0.5 g/L, pH = 6.28 and T = 25℃, BPA was almost completely removed after 5min reaction. In another similar work, Xie, et al. [42]. prepared N-BC using molten salt-induced nitrogen-doped biomass nanosheets and studied the activation of PMS degradation of BPA. The data demonstrated that when BPA = 20 mg/L, PMS = 0.4 g/L, N-BC = 0.4 g/L, pH = 7 and T = 25℃, almost all BPA can be removed after 6 min reaction. An unbalanced electron density can be formed in the BC matrix by doping N, which provides a large number of transferable π electrons to the reaction, thus improving the catalytic efficiency of PMS activation for the degradation of organic matter [66]. In general, we argue that the graphite phase transition of carbon and nitrogen plays an important role in improving the reaction activity [67]. There are three forms of valence bonds for N in BC: pyridine N, pyrroN and graphite N, respectively. However, there is a big controversy about which kind of valence bond plays the major role, and this remains to be resolved in the future. Apart from N doping, other atomic doping was also applied to activate PS, but less reported information is available compared to N doping [68]. Xu, et al. [69]. successfully synthesized N, S-BC by one-step pyrolysis by using nanocellulose and thiourea to activate PMS for the degradation of sulfonymethoxazole (SMX) with a maximum degradation rate of 97.84%.

Application of Acid / Alkali Activated BC to Activate PS

Acid/alkali activation not only enables BC to display a negative and positive charge, respectively, but also simultaneously improves the hydrophilic and hydrophobic properties of BC. Acid activation can change the content of oxygen-containing functional groups on the BC surface. For instance, Li, et al. [70]. activated BC by hydrofluoric acid, increasing the carboxyl and phenol hydroxyl content by 23% and 50%, respectively. Unlike acid activation, alkali activation can result in a greater area and more porous structure of BC, because alkaline substances such as KOH and NaOH would etch the surface of carbon at high temperature, and then make the pore structure richly. This not only facilitates the transfer of electrons but also improves the pore volume of the BC and promotes the adsorption of pollutants on the BC. In the future, research can reasonably treat acid or alkali according to the mechanism of PS activation by BC, and then endow it ideal properties and structure to facilitate practical application.

Conclusion

In summary, this paper systematically outlines the application of various BCs in activation of persulfate, and expounds their synthesis process and physic chemical properties. In order to improve the degradation performance on organic pollutants, several modified methods, such as doping the transition metal ions and ZVI, acid and alkali activation, heteroatomic doping of the biomass, are adopted according to the actual needs. Furthermore, the action mechanism of BC in the PMS activation process and the AOP action mechanism of BC-PMS are subjected to in-depth investigation. The presence of oxygen-containing functional groups on the surface of BC, especially C=O, will activate PS. In addition, the collapse of biocarbon in pyrolysis and the improvement of graphitization also accounts for the activation of PS. Activated PS mineralized pollutants mainly through radical and non-radical reactions. Free radical reaction is mainly through the reaction of ($\bullet SO_4^-$) and water to generate ($\bullet OH$) to mineralize organic pollutants. While this reaction occurs, non-radical reactions are also ongoing. Non-radicals occur mainly on the BC surface by participating in the reaction through electron transfer and producing monolar oxygen. Although breakthrough progress has been made in activating PS to treat pollutants in the water medium, there are still some challenges faced with BC in the application of AOP. For example, how to use this advantage to treat pollutants in other systems such as soil, and how to prevent the leaching of transition metal ions. Moreover, the mechanism of electronic shuttle in PS activation by BC is still uncertain, which requires subsequently continuous research effort to address.

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