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# Carbonaceous Catalyst Activated Persulfate for Degradation of Antibiotic Pollutants in Water

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**Keywords:** carbon materials; persulfate; antibiotics; mechanism.

**Abstract.** In recent years, the frequent use of antibiotics has led to the continuous release of antibiotics into the water environment, which not only poses a potential threat to public health, but also contributes to the generation and spread of antibiotic resistance. In addition, due to the high environmental persistence and low biodegradability of antibiotics, it is difficult to be effectively degraded by traditional water treatment processes. Therefore, it is urgent to develop clean and efficient treatment technologies. Advanced oxidation processes (AOPs), which can effectively remove refractory organic pollutants from water, has become a promising water treatment technology. In this regard, persulfate(PS)-based AOPs(PS-AOPs) has attracted extensive attention of researchers. In this system, PS can be activated by energy and catalysts to produce highly oxidizing active species, and achieve efficient degradation of antibiotics. Due to its rich surface functional groups, high specific surface area and high adsorption properties, researches on the activation of PS by carbonaceous materials have been reported continuously. In this paper, the research progress of carbon nanotubes, graphene, biological carbon, active carbon and hetero-atom doped carbon materials as catalysts to activate PS and degrade antibiotics is reviewed. In addition, the structure and properties of different carbon materials and the activation mechanism of free radical and non-free radical mediated by carbon materials were introduced, and the effects of PS dosage, catalyst dosage, temperature and pH on the degradation of antibiotics were discussed. Finally, this paper points out the important development direction in the future, that is, the development of environmental protection, high efficiency, low cost carbon materials and further research on the actual wastewater treatment performance.

## Introduction

In practice, antibiotics are widely used in medical and health care, aquaculture, livestock disease treatment and other fields,[1-3] making outstanding contributions to human health and animal disease prevention and control. However, after antibiotics are ingested in humans or animals, only a relatively small amount is absorbed and utilized, while the unused portion is excreted through urine and faeces and into various environmental media.[4, 5] The accumulation of antibiotics will bring a series of hidden dangers to the ecosystem and natural environment. Moreover, antibiotics are persistent and difficult to degrade, which will not only make water pollution more serious, but also cause a series of intractable environmental problems (such as the emergence of drug resistance). More seriously, the presence of antibiotics in water will facilitate the proliferation of resistant bacteria, posing a threat to human health and the effectiveness of antibiotic drugs.[6] Therefore, it is necessary to take measures to efficiently remove antibiotics from water.

At present, there are many ways to remove antibiotics, such as adsorption, biological treatment, flocculation and AOPs. The adsorption method can only transfer antibiotics between liquid and solid phase without actual degradation.[5] Because antibiotics have bacteriostatic or bactericidal effects, the removal of antibiotics by biological treatment is not ideal.[7] Although the traditional flocculation method can effectively remove suspended particulate matter and natural organic matter (NOMs), the traditional method has poor effect on the removal of trace antibiotics.[8] AOPs overcomes the shortcomings of the above methods and mainly activates peroxides through energy and catalysts to generate active species with strong oxidability, including hydroxyl radical (•OH) and sulfate radical($SO_4\bullet-$), so as to achieve efficient degradation of antibiotics in water.[9, 10] AOPs based on hydrogen peroxide ($H_2O_2$), especially Fenton technology, have been widely used in water treatment. However, Fenton system requires high operating conditions (highly acidic environment) and its cycle stability is also poor. In addition, the continuous replenishment of reactive reagents such as $H_2O_2$ and ferric salt leads to the generation of a large amount of iron sludge, which increases the cost of subsequent treatment.[11-14] Compared with $H_2O_2$ system, AOPs based on PS has become a more promising water treatment technology, mainly due to: (1) PS is solid at room temperature, which is convenient for transportation and storage; (2) $SO_4\bullet-$ produced by PS activation has higher redox potential (2.5−3.1V) and longer half-life period (30−40μm) than •OH; (3) $SO_4\bullet-$ has better selectivity than •OH and is more inclined to attack electron rich organic pollutants; (4) $SO_4\bullet-$ can play an oxidation role in a wide pH range (2.0-8.0) [15-18]

PS can be activated by energy (ultrasonic, ultraviolet, electrical and thermal energy, etc.) or catalysts (transition metal base materials and carbon materials, etc.) [19, 20] Although heat energy can effectively activate PS, continuous energy input significantly increases the treatment cost, which is not suitable for large-scale water treatment projects. In the ultrasonic activation system, the efficiency of ultrasonic activation is low because of the relatively small range of ultrasonic action and uneven energy distribution. The efficiency of UV activated PS is high, but the ability of UV /PS system to treat actual wastewater is limited because the penetration of UV light in water is greatly affected by water quality. The electrochemical activation reaction mainly occurred on the electrode surface, and the energy consumption and processing time increased due to the limitation of mass transfer. In contrast, catalyst-based PS activation is considered to be a promising AOPs. In recent years, carbon materials have been frequently used to activate PS due to its rich surface functional groups, high specific surface area and high adsorption performance. [2-4, 21] For example, Chen et al studied the degradation of tetracycline (TC), oxytetracycline (OTC) and doxycycline (DTC) by activated persulfate (PDS) with carbon black (CB), and the removal rates of these antibiotics were 52%, 60% and 87%, respectively, within 40min; [22] Peng et al. found that activated PMS could completely degrade sulfamethoxazole (SMX) in 20min when they studied $Co_2P$/ biochar composite activated by persulfate (PMS). [23]

In recent years, the study of structure-activity relationship of catalysts in PS-AOPs system activated by carbon materials has attracted much attention. In addition, different structures of carbon materials may play a key role in the activation mechanism. Therefore, the review of past studies is helpful to better understand the nature of activated PS by carbon materials. In this paper, the structure and properties of different carbon materials and their free radical/non-free radical activation pathways were systematically described, and the effects of various environmental factors on the degradation of antibiotics by carbon materials/PS system were discussed, in order to provide scientific basis for the development of this technology in the field of degradation of antibiotics.

## Application of Different Carbon Materials in PS Activation

**Carbon Nanotubes.** Carbon nanotubes (CNTs) is a typical one-dimensional nano material, which is usually a hollow tube composed of single-layer or multi-layer graphite sheets, which is often used as an efficient adsorbent due to large surface area and abundant pore structure.[24-26] In addition, the lateral wall electron transfer rate of CNTs is high and the mass transfer resistance is low, which is conducive to electron transfer. The oxygen-containing functional groups on the surface of CNTs can promote the electron transfer of organic pollutants to PS, thus improving the activation performance. [27, 28] Surface defects of CNTs can also be important active sites for adsorption and catalysis of PS, improving the catalytic activity of CNTs. [29]

CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). When the target pollutant has a high degree of desaturation, it can provide more delocalized π electrons and generate π-π conjugation with the delocalized π electrons of SWCNTs, increasing their adsorption performance. The delocalized π electrons of SWCNTs can also be transferred to the PMS, facilitating the cleavage of O−O bonds to form •OH and $SO_4\bullet-$, thus accelerating the degradation of pollutants. [30] For example, Duan et al. found that lone pair electrons on N could effectively enhance the π-π bond on the surface of SWCNTs, improve the catalytic activity of SWCNTs, and increase the degradation rate of phenol in the study of n-doped phenol oxidation of SWCNTs. [31] Yu et al. also found a coiled carbon framework with highly delocalized π electron systems on the outer surface of SWCNTs, which favored electron enrichment or vacancy defects and increased electron transfer rates during PDS activation. [24] MWCNTs, which are made of many graphene sheets rolled into a cylindrical shape, have high stability, high mechanical strength and excellent electrical conductivity, and can be used as catalyst carriers. [26, 32, 33] Feng et al. found that polyhydroquinone coated magnetite/multi-walled carbon nanotubes (Fe3O4/MWCNTs/PHQ) could effectively activate PDS and degrade flumequine (FLU), in which MWCNTs could not only serve as an excellent carrier of electron transfer, but also directly activate PDS to produce active species. [34] Nie et al. found that the application of MWCNTs as the cathode could effectively activate PDS and remove 77% of acyclovir within 240min.[35]

**Graphene.** Graphene is a new kind of two-dimensional nanomaterial, arranged in hexagonal lattice, which can be separated from the surface of graphite. Its surface contains rich functional groups including hydroxyl (−OH), carbonyl (C=O) and epoxy (−CH(O)CH−). [36, 37] Graphene has the potential to be used as a catalyst or carrier because of its excellent electrical conductivity, chemical stability and high adsorption properties. [38, 39] However, the surface of the original graphene is hydrophobic and tends to agglomerate, and the zero band gap and high chemical potential in its structure make it exhibit catalytic inertia. Studies have been carried out to improve the catalytic activity of graphene by reducing the oxygen content of graphene, grinding or heat treatment, adjusting the structure and surface properties of graphene.[39-42] At the same time, the change of the oxidation degree of graphene can also strengthen its catalytic activity, such as the preparation of reduced graphene oxide (RGO) and graphene oxide (GO). The activation efficiency of the edge of the carbon atom is not limited by the π shape of the carbon atom sp2, which mainly depends on the edge of the carbon atom; In addition, organic pollutant molecules with conjugated structure can produce π-π stacking interaction with RGO, so as to improve the surface activity of RGO and accelerate the degradation process of organic matter through the special functional groups of organic matter. [38, 43] GO has a large number of functional groups (−OH, carboxyl (−COOH), −CH(O)CH−, etc.) on its surface, which increases its hydrophobicity, enables it to interact strongly with organic pollutants in aqueous solution, and promotes the removal of organic pollutants. [44]

**Biochar.** Biochar (BC) is a low-cost, accessible and green carbon material, which can be made from various biomass raw materials [37], such as straw [45], sludge [13], algae [46] and wood [47]. The preparation method of BC is relatively simple and it can be obtained through various thermochemical processes [13, 23, 46]. The catalytic activity of the prepared BC can be further improved by certain means. [20, 48] Modification of BC form is a common measure and can be achieved by heat treatment or acid-base treatment. Heat treatment can adjust the carbon content, pH value and Zeta potential of BC. Moreover, higher pyrolysis temperature is beneficial to increase the surface area and porosity of BC. For example, Zou et al. investigated the relationship between different pyrolysis temperatures and BC structure and catalytic performance using Spirulina platensis as a precursor. With the increase of pyrolysis temperature, the crystallinity, the amount of sp2 hybrid carbon, pore size and conductivity of the material increased, and the catalytic activity also increased gradually. [46] Acid treatment can significantly reduce the mesoporous surface area and total volume of BC, and introduce oxygen-containing groups on the surface of BC. These oxygen-containing groups can be used as active sites for activating PS and increase the catalytic activity of BC. [49] Alkali treatment can introduce −OH on the surface of BC, and reduce the polarity by forming a positive surface charge, so as to improve its catalytic activity. [20]

**Activated carbon.** Activated carbon, (AC), with high specific surface area, good porosity and abundant surface functional groups, is the ideal choice as PS activator. [11, 12, 50, 51] AC comes from a wide range of sources and can be prepared from a variety of biomass waste, coal-based, plastic-based and asphalt-based precursors. [37] AC has many functional structures, including sp2 hybrid carbon, delocalized π electron, oxygen-containing functional groups and so on. [37] For example, Guo et al. found that in-situ S-doped AC(SDAC) can increase the number of sp2 hybrid carbon and defect sites, and increase the content of C=O, thus improving the catalytic activity of SDAC to PDS. [52] According to the aggregation form, AC can be further divided into powdered activated carbon (PAC) and granular activated carbon (GAC). [53] PAC's powdery structure gives it a higher specific surface area and better adsorption performance, but it is less reusable and difficult to recycle.[37] In this regard, GACS are generally well reusable [11]. Forouzesh et al. reported synergistic effects of oxidation and adsorption on the removal of metronidazole (MTZ) in GAC/PDS systems. [54]

**Heteroatom doped carbon materials.** In recent years, heteroatomic doping, as an important means to enhance the properties of carbon materials, has attracted more and more attention. Elements commonly used for doping mainly include non-metallic elements N, S, and P and metal elements Cr, Co, Fe and so on. [50, 55, 56] It is found that hetero-atom doped carbon materials can: 1) improve the defect degree of carbon materials [55], 2) increase catalytic activity through conjugation and activation of sp2 carbon grids [57], 3) accelerate electron transfer between pollutant and PS [58], 4) enhance surface hydrophilicity. [59] Zhong et al. found that the activation efficiency of BC to PDS could be improved by doping BC with N atoms, thus increasing the removal rate of TC. [58] The doping of N atom can also reduce the C=C content of BC surface, improve the graphitized structure of BC surface, and introduce more active centers. [58] Huang et al. prepared S-doped AC sample (SAC) with a planetary ball mill at 450rmp for 24h. In a certain range, the C–S–C content on SAC surface was positively correlated with the amount of S doping. High C–S–C content could provide more active sites for PMS, thus improving the catalytic performance of SAC. [60] Generally, the catalytic activity increases with the increase of heteroatom doping, but excessive doping may bring adverse effects. [37] Liu et al. found that the removal rate of 4-nitrophenol (PNP) was improved after PS was activated by ordered mesoporous carbon (S-OMC) doped with appropriate amount of sulfur. When S is excessive, the removal rate of PNP begins to decline, which is due to the serious collapse of the pore structure of carbon material, which reduces the effective exposure of active sites. [61]

In metal element doping, Fe, Ni, Cu and Co are also widely used in PS activation. [2, 62-64] Co doped carbon materials can enhance the dispersion of metal sites, improve the catalytic activity and cyclic stability of carbon materials, and attract much attention in the activation of PS. For example, Han et al. found that when Co doping pomelo peel carbon carbon (Co−PPCC) activated PMS and degraded TC, as the dose of Co−PPCC increased, the contact frequency of TC molecule and active site of Co−PPCC increased, which promoted the generation of SO4•− and thus improved the removal rate of TC. [65] Li et al used Fe(NO3)3•H2O, Co(NO3)2•6H2O and urea as N precursors to doped three-dimensional graphene-loaded CoFe2O4(CoFe2O4/N-3DG) to activate PMS for degradation of benzotriazole (BTA). [66] Using thiourea and ferric chloride hexahydrate as the precursor system, Wang et al. obtained Fe-S co-doped graphite phase carbon nitride (FeOy/(S-g-C3N4), which could effectively change the charge density and distribution on the surface of g-C3N4 and improve the activation efficiency of PMS. [67]

## Progress in Activation of Carbon Materials

In the activated PS system of carbon materials, the activation modes of PS include non-free radical and free radical path. The radical pathway usually involves SO4•−, •OH, and superoxide anion (O2•−). In PS activation systems, •OH is usually derived from the transformation of SO4•− (Eqs. 1 and 2) [68], which can effectively remove antibiotics mainly through hydrogen capture reaction or addition reaction on aromatic ring. [22, 40, 61] However, due to its low selectivity, NOMs and halogen ions widely existing in actual water bodies are easy to compete with target pollutants and consume •OH, which not only leads to lower utilization rate of oxidants, but also may produce toxic halogen by-products. SO4•− has a higher REDOX potential than •OH and is more selective, tending to attack electron-rich sites. Many studies have shown that SO4•− is suitable and mineralized at pH 2−10, and is the main active species under acidic and neutral conditions. Although the activity of SO4•− is low in alkaline environment, it can react with OH− to transform into •OH, and continue to degrade antibiotics efficiently (Eq. 3). [22, 43] O2•− has low oxidation capacity, which however can react with water or H+ to produce singlet oxygen (1O2) with higher oxidation capacity (Eqs. 4 and 5), accelerating the degradation of pollutants. [10, 22, 69] Non-radical pathways mainly include 1O2 and direct electron transfer. [13] In general, 1O2 can be generated by two intermediates, SO5•− and O2•− (Eqs. 5 and 6), or by decomposition of a composite of carbon material and PS [70]. Compared with SO4•−, •OH and O2•−, 1O2 has higher selectivity and moderate oxidation capacity, and tends to attack antibiotics containing benzene ring. [70] The direct electron transfer process can occur in carbon materials with low electrochemical impedance and good electrical conductivity, which can not only transfer electrons directly, but also produce some active substances as dielectric to activate PS. In addition, the modification of carbon material can reduce its surface resistivity, improve its surface defect structure and improve electron transfer efficiency. [37, 61] The effect and mechanism of oxidative degradation of antibiotics by activated PS of different carbon materials are shown in Table 1.

$$SO_4^{\bullet-} + OH^- \rightarrow {}^{\bullet}OH + SO_4^{2-} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \tag{2}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \tag{3}$$

$$2O_2^{\bullet-} + 2H^+ \rightarrow {}^1O_2 + H_2O_2 \tag{4}$$

$$2O_2^{\bullet-} + 2H_2O \xrightarrow{C=O} {}^1O_2 + H_2O_2 + 2OH^- \tag{5}$$

$$2SO_5^{\bullet-} \rightarrow {}^1O_2 + 2SO_4^{\bullet-} \tag{6}$$

**Table 1.** Effect of different carbon materials activated PS oxidative degradation of antibiotics.

| Carbon materials | Substrate | Carbon material dose (g/L) | Type and dose of oxidant | pH | Reaction rate constant (min−1) | Free radical/non-free radical paths | Literature |
|---|---|---|---|---|---|---|---|
| **GAC** | MTZ | 5 | PDS, 58mM | 3.9 | 0.0006 | SO4•− | [11] |
| **AC** | SMX | 0.1 | PDS, 0.5mM | 7.2 | 0.12 | SO4•−, | [12] |
| **GAC** | SMX | − | PDS, 5mM | − | − | •OH, SO4•− | [1] |
| **BC** | SMX | 0.1 | PDS, 0.5mM | 7.2 | 0.048 | SO4•− | [12] |
| **BC** | SMX | 0.09 | PDS, 0.25g/L | − | 0.03 | •OH ,SO4•− | [71] |
| **BC** | SMX | 0.1 | PDS, 0.5g/L | 5.6 | 0.0239 | •OH, SO4•−, 1O2, Direct electron transfer | [72] |
| **Ni@NPG** | sulfachloropyridazine (SCP) | 0.2 | PMS, 2g/L | − | 0.4577−0.4623 | •OH, SO4•−, 1O2, O2•− | [73] |
| **EGB** | SMX | 0.05 | PDS, 4mM | 3.2−9.2 | 0.0201 | •OH, SO4•−, 1O2, O2•− | [74] |
| **MWCNTs** | Acyclovir | − | PDS, 11.1mM | 2−10 | − | Direct electron transfer | [75] |
| **CNTs** | ATC | 0.1 | PDS, 0.21mM | 3−7 | 0.153 | Direct electron transfer | [76] |

Note: − Indicates unknown.

## Factors Affecting the Degradation of Antibiotics by Activated Persulfate from Carbon Materials

**PS Dosing Quantity.** The dosage of PS is an important factor affecting the degradation effect of antibiotics. A large number of research results show that when other conditions remain unchanged, the increase of PS concentration in a certain concentration range can improve the yield of active species and then improve the degradation efficiency of antibiotics. [17, 43, 55, 57] For example, Kang et al. found that increasing the concentration of PDS produced more •OH and SO4•− and accelerated the removal of SCP. [77] Huang et al. found that as the concentration of PDS increases, the amount of SO4•− and 1O2 increases, and the degradation rate of TC increases [78]. However, when the PS concentration is excessive, increasing the PS concentration will not further improve the degradation efficiency, and even weaken the degradation ability of the system. [13, 43, 57, 79] This could be for several reasons: 1) Excessive PS will directly consume ROS [13]. For example, when the concentration of PS in the system is too high, PS ions react with SO4•− to generate S2O8•−(Eq. 7) with lower activity. 2) Although excessive PS can increase the ROS production rate, the self-quenching reaction of ROS can also be accelerated, thus reducing the degradation rate of antibiotics. [43, 57, 79] Through chemical experiment and cost analysis, the optimum PS dosage can be determined.

$$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \quad (7)$$

**Catalyst Dosage.** The amount of catalyst is another important factor affecting the degradation effect of antibiotics. The increase of catalyst dosage can usually provide more active centers, increase the PS activation efficiency, and then generate more reactive oxygen species, and accelerate the removal rate of antibiotics. [43, 80] For example, Magioglou et al. found that as the concentration of BC increased, the system produced more •OH, SO4•−, thus improving the removal efficiency of SMX [48]. Yin et al. also found that when the concentration of sludge-derived biochar (SDBC) increased from 0.5g/L to 3g/L, the 1O2 yield of the system increased and the degradation rate of SMX increased from 50.4% to 98.3% [13]. The removal rate of antibiotics is usually positively correlated with the dosage of catalyst, but excessive catalyst may also weaken the degradation performance of the system. For example, Kakavandia et al. found that when the dosage of AC exceeded 0.4g/L, the degradation rate and degradation rate of TC decreased, which may be because the main active species under ultrasonic irradiation is 1O2. However, the high dose of AC catalyst inhibited the production of 1O2 [81].

**Catalyst Dosage.** From the perspective of kinetics and thermodynamics, the synergistic effect between temperature and carbon material is helpful to improve the degradation rate and efficiency of antibiotics. [17, 37, 52, 80] For example, Yu et al. reported that when the temperature increased from 10℃ to 50℃, the removal rate of sulfadiazine (SDZ) increased from 25.6% to 99.9% [17], for the following reasons: 1) The increase of temperature will increase the proportion of active groups, and then increase the collision probability between antibiotics and active groups [17, 82]; 2) With the increase of temperature, the surface area and volume of micropores increase, which is conducive to enhancing the chemisorption of carbon materials to antibiotics and PS [37, 52]; 3) High annealing temperature can transform sp3 bond into sp2 bond through graphitization, thus increasing electron transfer rate between antibiotics and PS. [37, 82] However, too high temperature will reduce the efficiency of carbon material to degrade antibiotics by affecting the functional groups, graphite structure and porous structure of carbon materials. For example, Kang et al reported that when studying the adsorption capacity and catalytic oxidation capacity of Ni@NCNTs to sulfachlorpyrazine (SCP) at different temperatures, SEM images show that high annealing temperature will lead to deactivation of carbon nanotubes, decrease of 1O2, decrease of SCP removal efficiency, and produce a large number of by-products in the oxidation process [57]. Guo et al. found that excessive temperature would lead to the collapse of carbon skeleton, which would increase the pore size of carbon material, thus increasing the total pore volume (Vp). However, high temperature will lead to a decrease in the number of oxygen-containing functional groups, resulting in a decrease in the catalytic efficiency of PS [52]。

**pH.** The pH value of solution affects the dissociation morphology of antibiotics, surface charge of carbon materials and reactive oxygen species. First, the degree of antibiotic dissociation is closely related to the pH of the solution. For example, SDZ dissociation constant pKa1 is 1.5. When pH < pKa1, SDZ mainly exists in the form of neutral (SDZ0) and anion (SDZ−) in solution. While when pH >pKa1, SDZ exists in the form of cation (SDZ+) [83]. Secondly, when the pH of the solution is higher than the isoelectric point of carbon material and antibiotics, the surfaces of both are negatively charged, resulting in electrostatic repulsion, which is not conducive to adsorption. [17, 37, 43, 48, 55, 58] In addition, Fe doped carbon materials are also prone to iron hydroxide precipitation under alkaline conditions, reducing the degradation efficiency of antibiotics. [55, 84,] Third, the pH of the solution changes the composition of free radical species. Under acidic conditions, the composition is mainly SO4•−, and H+ may interact with SO4•− and •OH [37, 43]; Under neutral alkaline conditions, SO4•− and •OH can coexist [37]. Under strong alkaline conditions, SO4•− tends to be converted to •OH, which will further react with OH− to form water [85, 86]. Jiang et al. activated PDS with mesoporous carbon-loaded nano-iron (Fe0/MC), and both SO4•− and •OH were abundant when pH=5. [85] In addition, Yao et al. found that the adsorption capacity of AC to p-chloroaniline (PCA) significantly decreased at pH 3, which inhibited the direct electron transfer of PCA to AC/PDS, thus reducing the removal rate of PCA. [51]

## Conclusion and Outlook

In recent years, carbon-based materials have been widely used as PS activator to treat antibiotic wastewater due to their low cost, high efficiency and environmental protection. In this paper, the research progress on the degradation of antibiotic pollutants by activated PS with carbon materials is reviewed, including the structure and properties of different carbon materials, activation progress, reaction mechanism, effect and influencing factors of different carbon materials. Although some achievements have been made in AOPs based on activated PS by carbon materials, there are still problems to be solved: On the one hand, due to the adsorption of degradation products and masking of active sites, the problem of poor cyclic stability of carbon materials is widespread. The development of environmentally friendly, efficient and low-cost carbon materials is still one of the key tasks. On the other hand, the current research is mainly focused on the laboratory phase, where experiments are usually carried out using simulated wastewater of a single composition. The concentration of antibiotics in actual wastewater is not fixed, and the composition is complex, which can easily affect the catalytic reaction. Therefore, more attention should be paid to the effect of coexisting components in actual water on antibiotic degradation in future studies.

## References

[1] Song H, Yan L, Jiang J, Ma J, Pang S, Zhai X, Zhang W and Li D 2018 Chemical Engineering Journal 344 12-20.

[2] Zhong Q, Lin Q, Huang R, Fu H, Zhang X, Luo H and Xiao R 2020 Chemical Engineering Journal.380 122608.

[3] Peng J, Wu E, Wang N, Quan X, Sun M and Hu Q 2019 Journal of Molecular Liquids 274 632-8.

[4] Song H, Li Q, Ye Y, Pan F, Zhang D and Xia D 2021 Separation and Purification Technology 272 118971.

[5] Feng L, Li X, Chen X, Huang Y, Peng K, Huang Y, Yan Y and Chen Y 2020 Science of the Total Environment 708 135071.

[6] Wei Z, Liu J and Shangguan W 2020 Chinese Journal of Catalysis 41(10) 1440-50.

[7] Chen G, Yu Y, Liang L, Duan X, Li R, Lu X, Yan B, Li N and Wang S 2021 Journal of Hazardous Materials 408 124461.

[8] Du H, Yang Z, Tian Z, Huang M, Yang W, Zhang L and Li A 2018 Chemical Engineering Journal 333 310-9.

[9] Zhi D, Lin Y, Jiang L, Zhou Y, Huang A, Yang J and Luo L 2020 Journal of Environmental Management 260 110125.

[10] Li H, Liu Y, Jiang F, Bai X, Li H, Lang D, Wang L and Pan B 2022 Science of The Total Environment 806 150968.

[11] Forouzesh M, Ebadi A and Aghaeinejad-Meybodi A 2019 Separation and purification technology 210 145-51.

[12] Liang J, Xu X, Zaman WQ, Hu X, Zhao L, Qiu H and Cao X 2019 Chemical Engineering Journal 375 121908.

[13] Yin R, Guo W, Wang H, Du J, Wu Q, Chang J-S and Ren N 2019 Chemical Engineering Journal 357 589- 99.

[14] Niu B, Wang N, Chen Y, Yu M, Hou Z, Li Z and Zheng Y 2021 Separation and Purification Technology 257 117893.

[15] Wang J and Wang S 2018 Chemical Engineering Journal 334 1502-17.

[16] Ahmadi S, Igwegbe CA and Rahdar S 2019 International Journal of Industrial Chemistry 10(3) 249-60.

[17] Yu M, Sun C, Wang L, Zang K, Li M, Zhou L and Zheng Y 2021 Chemical Engineering Journal 416 129122.

[18] Li Z, Guo C, Lyu J, Hu Z and Ge M 2019 Journal of hazardous materials 373 85-96.

[19] Song H, Yan L, Wang Y, Jiang J, Ma J, Li C Wang G, Gu J and Liu P 2020 Chemical Engineering Journal 391 123560.

[20] Wang C, Huang R, Sun R, Yang J and Sillanpää M 2021 Journal of Environmental Chemical Engineering 9(5) 106267.

[21] Qin F et al. 2020 Journal of Hazardous Materials 398 122816.

[22] Chen Y, Yin R, Zeng L, Guo W and Zhu M 2021 Journal of Hazardous Materials 412 125256.

[23] Peng Y, Tong W, Xie Y, Hu W, Li Y, Zhang Y and Wang Y 2021 Environmental Pollution 268 115930.

[24] Yu J et al. 2020 Progress in Materials Science 111 100654.

[25] Tan CW, Tan KH, Ong YT, Mohamed AR, Zein SHS and Tan SH 2012 Environmental Chemistry Letters, 10(3) 265-73.

[26] Roushani M, Rahmati Z and Dizajdizi BZ 2019 Journal of Electroanalytical Chemistry 847 113192.

[27] Zhang S, Rong F, Huang S, Zhao S, Wang M, He L, Zhang Z and Du M 2022 Separation and Purification Technology 120530.

[28] Cheng X, Guo H, Zhang Y, Korshin GV and Yang B 2019 Water research 157 406-14.

[29] Wu L et al. 2022 Journal of Hazardous Materials 128536.

[30] Dai Z, Li D, Ao Z, Wang S and An T 2021 Journal of Hazardous Materials 405 124684.

[31] Duan X, Sun H, Wang Y, Kang J and Wang S 2015 Acs Catalysis 5(2) 553-9.

[32] Zhang X, Feng M, Qu R, Liu H, Wang L and Wang Z 2016 Chemical engineering journal 301 1-11.

[33] Duan X, Ao Z, Zhou L, Sun H, Wang G and Wang S 2016 Applied Catalysis B: Environmental 188 98-105.

[34] Feng M, Qu R, Zhang X, Sun P, Sui Y, Wang L and Wang Z 2015 Water Research 85 1-10.

[35] Nie C, Ao Z, Duan X, Wang C, Wang S and An T 2018 Chemosphere 206 432-8.

[36] Chen X, Oh W-D and Lim T-T 2018 Chemical Engineering Journal 354 941-76.

[37] Gao Y, Wang Q, Ji G and Li A 2022 Chemical Engineering Journal 429 132387.

[38] Wang S and Wang J 2020 Chemosphere 239 124812.

[39] Pervez M, He W, Zarra T, Naddeo V and Zhao Y 2020 Water 12(3) 733.

[40] Xiao P-f, An L and Wu D-d 2020 New Carbon Materials 35(6) 667-83.

[41] Kang Y-G, Vu HC, Chang Y-Y and Chang Y-S 2020 Chemical Engineering Journal 387 124012.

[42] Cruz-Alcalde A, López-Vinent N, Ribeiro RS, Giménez J, Sans C and Silva AM 2022 Chemical Engineering Journal 427 130994.

[43] Dang VC, Tran DT, Phan AT and Pham NK 2021 Journal of Physics and Chemistry of Solids 153 110005.

[44] Cui M, Li Y, Sun Y, Wang H, Li M, Li L and Xu W 2021 Journal of Polymers and the Environment 29(7) 2227-35.

[45] Wang B, Li Y-n and Wang L 2019 Chemosphere 237 124454.

[46] Zou Y, Li W, Yang L, Xiao F, An G, Wang Y and Wang D 2019 Chemical Engineering Journal 370 1286-97.

[47] Huang D, Zhang Q, Zhang C, Wang R, Deng R, Luo H, Li T, Li J, Chen S and Liu C 2020 Chemical Engineering Journal 391 123532.

[48] Magioglou E, Frontistis Z, Vakros J, Manariotis ID and Mantzavinos D 2019 Catalysts 9(5) 419.

[49] Gasim MF, Lim J-W, Low S-C, Lin K-YA and Oh W-D 2022 Chemosphere 287 132458.

[50] Zhang Y, Zhang B-T, Teng Y and Zhao J 2020 Environmental Technology & Innovation 19 100956.

[51] Yao C, Zhang Y, Du M, Du X and Huang S 2019 Chemical Engineering Journal 362 262-8.

[52] Guo Y, Zeng Z, Zhu Y, Huang Z, Cui Y and Yang J 2018 Applied Catalysis B: Environmental 220 635-44.

[53] Ghanbari F and Moradi M 2017 Chemical Engineering Journal 310 41-62.

[54] Forouzesh M, Ebadi A, Aghaeinejad-Meybodi A and Khoshbouy R 2019 Chemical Engineering Journal, 374 965-74.

[55] Xi M, Cui K, Cui M, Ding Y, Guo Z, Chen Y, Li C and Li X 2021 Chemical Engineering Journal 420 ,129902.

[56] Sun W, Pang K, Ye F, Pu M, Zhou C, Huang H, Zhang Q and Niu J 2021 Separation and Purification ,Technology 279 119723.

[57] Kang J, Duan X, Wang C, Sun H, Tan X, Tade MO and Wang S 2018 Chemical Engineering Journal 332 ,398-408.

[58] Zhong Q, Lin Q, He W, Fu H, Huang Z, Wang Y and Wu L 2021 Separation and Purification Technology, 276 119354.

[59] Vieira O, Ribeiro RS, Pedrosa M, Ribeiro ARL and Silva AM 2020 Chemical Engineering Journal 402 ,126117.

[60] Huang M, Wang X, Liu C, Fang G, Gao J, Wang Y and Zhou D 2021 Journal of Environmental Chemical Engineering 9(6) 106536.

[61] Liu S et al. 2020 Chemical Engineering Journal 384 123304.

[62] Li X, Jia Y, Zhou M, Su X and Sun J 2020 Journal of Hazardous Materials 397 122764.

[63] Duan P, Chen D and Hu X 2021 Chemosphere 269 128740.

[64] Xie J, Chen L, Luo X, Huang L, Li S and Gong X 2022 Separation and Purification Technology 281 ,119887.

[65] Han S, Xiao P, An L and Wu D 2022 Environmental Science and Pollution Research 29(15) 21656-69.

[66] Li X, Zhang D, Liu Z, Lyu C, Niu S, Dong Z and Lyu C 2020 Chemical Engineering Journal 400 125897.

[67] Wang S, Liu Y and Wang J 2020 Chemical Engineering Journal 382 122836.

[68] Huang W, Xiao S, Zhong H, Yan M and Yang X 2021 Chemical Engineering Journal 418 129297.

[69] Zou J, Yu J, Tang L, Ren X, Pang Y, Zhang H, Xie Q, Liu Y, Liu H and Luo T 2020 Chemosphere 261 ,127747.

[70] Luo H, Fu H, Yin H and Lin Q 2021 Journal of Hazardous Materials 128044.

[71] Kemmou L, Frontistis Z, Vakros J, Manariotis ID and Mantzavinos D 2018 Catalysis Today 313 128-33.

[72] Avramiotis E, Frontistis Z, Manariotis ID, Vakros J and Mantzavinos D 2021 Catalysts 11(7) 850.

[73] Kang J, Zhang H, Duan X, Sun H, Tan X and Wang S 2019 Journal of Cleaner Production 218 202-11.

[74] Qi Y, Ge B, Zhang Y, Jiang B, Wang C, Akram M and Xu X 2020 Journal of Hazardous Materials 399 123039.

[75] Nie C, Dai Z, Meng H, Duan X, Qin Y, Zhou Y, Ao Z, Wang S and An T 2019 Water research 166 115043.

[76] Kim D-G and Ko S-O 2020 Environmental Research 188 109767.

[77] Kang J, Duan X, Zhou L, Sun H, Tadé MO and Wang S 2016 Chemical Engineering Journal 288 399-405.

[78] Huang H, Guo T, Wang K, Li Y and Zhang G 2021 Science of The Total Environment 758 143957.

[79] Wang S, Xu L and Wang J 2022 Chemical Engineering Journal 428 131066.

[80] Sun C, Chen T, Huang Q, Zhan M, Li X and Yan J 2020 Chemical Engineering Journal 380 122519.

[81] Kakavandi B, Bahari N, Kalantary RR and Fard ED 2019 Ultrasonics Sonochemistry 55 75-85.

[82] Yang W, Jiang Z, Hu X, Li X, Wang H and Xiao R 2019 Chemosphere 220 514-22.

[83] Cai T, Liu Y, Wang L, Dong W, Chen H, Zeng W, Xia X and Zeng G 2019 Chemical Engineering Journal 375 122070.

[84] Shang Y, Chen C, Zhang P, Yue Q, Li Y, Gao B and Xu X 2019 Chemical Engineering Journal 375 122004.

[85] Jiang X, Guo Y, Zhang L, Jiang W and Xie R 2018 Chemical Engineering Journal 341 392-401.

[86] Rahmani AR, Salari M, Shabanloo A, Shabanloo N, Bajalan S and Vaziri Y 2020 Journal of Environmental, Chemical Engineering 8(5) 104202.