A review on the use of persulfate activation in treating antibiotics-contaminated wastewater

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Abstract. With the progress of science and technology and social development, the misuse of antibiotics has led to water pollution that severely impacts the ecological environment and human health, and the effective treatment of antibiotics-contaminated wastewater has become an urgent problem. Recently, advanced oxidation processes based on persulfate have been widely concerned by scholars because of their good effect in degrading antibiotic pollutants. In this paper, the activation mechanism of persulfate degradation of antibiotic pollutants is firstly reviewed, and the two activation mechanisms of radical pathway and non-radical pathway are distinguished. Then, this paper summarizes the common activation techniques for persulfate treatment of wastewater contaminated with antibiotics, analyzes the principles and characteristics of different activation techniques, and focuses on the non-heterogeneous activation of persulfate in transition metal-based materials and carbon-based materials in terms of the generation of responsive species and the surface electron transfer. Finally, in view of the current needs and difficulties, the author puts forward some suggested research directions and challenges faced, intending to provide some theoretical guidance for the efficient treatment and effective control of antibiotics-contaminated wastewater in the future.

Keywords: Antibiotics, Advanced Oxidation Processes, Persulfate, Activation.

1. Introduction

Antibiotics are a class of medicine widely used in many fields, which can effectively treat diseases infected by specific pathogenic microorganisms. With the progress of science and technology, the use of antibiotics is gradually expanding, and its use is also increasing dramatically [1]. On the one hand, antibiotics have antibacterial properties, so the biological treatment process in the sewage treatment plant has a limited effect. On the other hand, they are not easily to be degraded naturally in the aquatic environment and their long-term residual will induce some pathogenic microorganisms to produce resistance genes, and even produce "superbugs", leading to further deterioration of water pollution. Therefore, the effective treatment of antibiotics-contaminated wastewater (ACW) has become a global environmental problem that needs to be solved urgently. Based on the above situation, Advanced Oxidation Process (AOP) has received much attention because of its ability to degrade antibiotics efficiently. AOPs can produce active species such as hydroxyl radicals (•OH,1.9-2.7V) to degrade antibiotics into a number of small molecules with low/non-toxicity, thus realizing the purification of ACW.

Persulfate (PS) is a commonly used oxidant in AOPs, and the breaking of the peroxygen bond (O—O) in PS can produce reactive species such as sulfate radicals ($SO_4^{\bullet -}$,2.5V-3.1V), it has a higher redox potential than •OH, and has the advantages of less secondary pollution and longer half-life, so it has a broader application prospect in the treatment of ACW. In this paper, we will review the research progress of antibiotic degradation by AOPs based on PS(PS—AOPs), including the activation mechanism of antibiotic degradation by PS and the common activation modes of antibiotic degradation in PS-AOPs system, and through the comprehensive analysis of the research on antibiotic degradation by PS, we aim to provide certain theoretical guidance for the management of ACW and environmental protection.

2. Activation mechanism of antibiotic degradation by persulfate

2.1. Free radical pathway

The PS-AOPs system can stimulate the activation of permonosulfate (PMS) and peroxydisulfate (PDS), creating a variety of free radicals such as •OH、$SO_4^{\bullet-}$ and superoxide radicals ($O_2^{\bullet-}$). These radicals possess robust oxidizing capabilities, effectively aiding in the breakdown of antibiotic pollutants (APs).

•OH is one of the most common oxidizing radicals in AOPs, and it also exists widely in PS-AOPs system, which is characterized by low selectivity, and can react with a variety of APs. The primary reaction mechanisms of •OH with APs consist mainly of direct electron transfer reaction, addition reaction, and hydrogen extraction reaction. Electron transfer reaction does not occupy a dominant position in the reaction of •OH with APs, but it can participate in the oxidation of some sulfur-containing APs. Velosa and Nascimento [2] pointed out in the study of degradation of sulfathiazole that •OH is expected to be the main degradation of sulfathiazole in a certain pH range. But the reaction mechanism of reactive substances remains primarily governed by hydrogen abstraction and addition reactions; for unsaturated APs containing C=C double bonds, •OH can form intermediates through addition reactions, and then be removed by the action of O_2 or other free radicals. Qin et al. [3] utilized a biochar(BC)-supported bimetallic oxide/PS system to degrade sulfamethazine in natural water, which indicated that the addition reaction was the main reaction mechanism for the degradation of sulfamethazine by •OH. In this study, the addition reaction is the main mechanism for the degradation of sulfamethazine by •OH; •OH can also be converted to organic radicals (R•) by extracting hydrogen atoms from APs through hydrogen abstraction reaction, and then reacted with free radicals or dissolved oxygen in the water body further.

Compared with •OH, $SO_4^{\bullet-}$ has a longer half-life (30-40 μs) and a higher redox potential, but this does not mean that $SO_4^{\bullet-}$ oxidizes a wider range of APs, on the contrary it has a stronger selectivity in the reaction with stronger selectivity. In the PS-AOPs system, •OH and $SO_4^{\bullet-}$ are often coexisted because some systems (e.g., UV/PMS system) can generate both radicals simultaneously, and there is also a possibility that $SO_4^{\bullet-}$ can be converted to •OH (Eqs. (1)-(2)), and it should be noted that the rate of •OH formation from $SO_4^{\bullet-}$ combined with H_2O is remarkably low, whereas the rate of •OH formation is significantly higher under alkaline conditions. Therefore, which radicals, •OH or $SO_4^{\bullet-}$, dominate in the PS-AOPs system is determined by the solution pH, and Zhang et al. [4] discovered that the alkaline environment helps the $SO_4^{\bullet-}$ generation in the UV/PMS system. In this system, the generation of $SO_4^{\bullet-}$ is facilitated by the alkaline environment, which also greatly minimizes the chances for by-products like haloketones to form.

$$SO_4^{\bullet-} + H_2O \rightarrow \bullet OH + SO_4^{2-} + H^+ \quad (1)$$

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

The reaction mechanism of $SO_4^{\bullet-}$ with APs is similar to that of •OH, which mainly includes three pathways of electron transfer, hydrogen abstraction, and addition-elimination, but $SO_4^{\bullet-}$ and •OH may have some differences in the specific reaction process and products. As shown in Figure 1, both •OH and $SO_4^{\bullet-}$ can oxidize APs containing —COOH functional groups, and for aromatic carboxylic acids (e.g., some penicillin antibiotics), $SO_4^{\bullet-}$ is easier to decarboxylate the contaminants through the electron transfer mechanism. For aromatic carboxylic acids (e.g. some penicillin antibiotics), $SO_4^{\bullet-}$ is more likely to decarboxylate and mineralize the pollutant to CO_2 by electron transfer, while •OH tends to undergo hydrogen abstraction and addition reaction; for aliphatic carboxylic acids, $SO_4^{\bullet-}$ generally extracts one electron from the of —COOH first to form RCO_2•, which further generates CO_2 and alkyl radicals (R•), while •OH mainly forms carbon-centered radicals by hydrogen abstraction and then generates a variety of products by oxygenation.

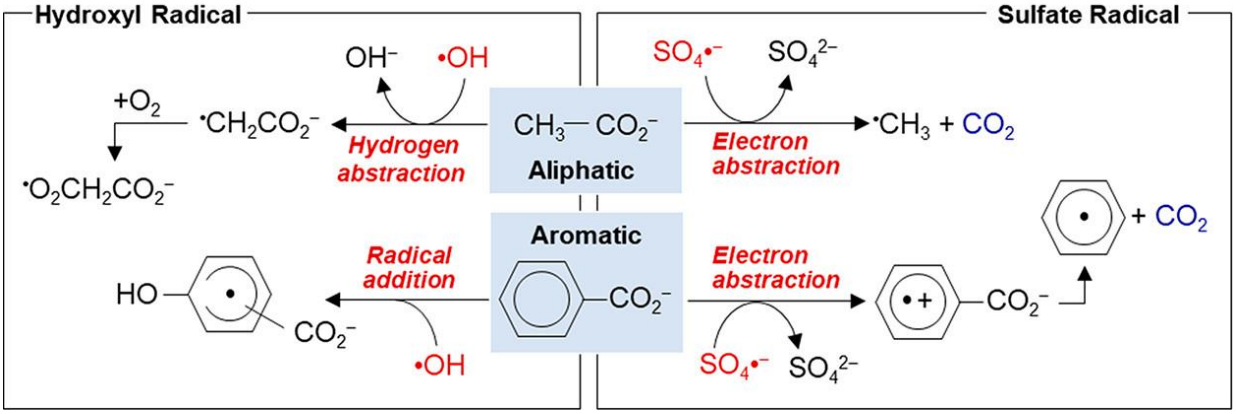


Figure 1. The activation mechanism of •OH and $SO_4^{\bullet -}$ (Lee et al. ,2020)[5]

Compared with •OH and $SO_4^{\bullet -}$, $O_2^{\bullet -}$ is much weaker oxidizing, can be formed by gaining electrons from dissolved oxygen in solution, and is difficult to be used as a direct interaction with APs, but it is an important intermediate for the generation of single linear oxygen ($^1O_2$) (Eqs. (3)-(4)). $O_2^{\bullet -}$ can show very strong selectivity towards some specific pollutants, which was confirmed in the study of Wang et al. [6]. Nevertheless, it should be pointed out that, $O_2^{\bullet -}$ acts more as an auxiliary role in the actual PS-AOPs system. Li et al. [7] confirmed that the defective structure of BC facilitates the activation of PDS, which produced a large amount of $O_2^{\bullet -}$converted to $^1O_2$, thus promoting the efficient degradation of ofloxacin.

$$O_2^{\bullet -} + \bullet OH \rightarrow {}^1O_2 + OH^- \quad (3)$$

$$O_2^{\bullet -} + 2H^+ \rightarrow {}^1O_2 + H_2O_2 \quad (4)$$

2.2. Non-radical pathway

2.2.1 Singlet oxygen

Singlet oxygen ($^1O_2$) is a high-energy excited state of molecular oxygen with vacant Π-electrons in its 2p orbital, so it is an electrophilic oxidant and has a certain oxidizing ability for APs rich in electron-donating groups. Electrophilic addition and electron transfer are the main mechanisms for $^1O_2$ to oxidize APs. For APs containing C=C double bonds, $^1O_2$ can convert them through addition reactions, and the specific addition mechanism mainly depends on the structure of the pollutant [8]. The common ways of addition between $^1O_2$ and olefinic APs mainly include ene reaction and [2+2] reaction two mechanisms: (1) ene reaction: the APs with allyl hydrogen react with $^1O_2$, and $^1O_2$ is the most effective way to oxidize APs. APs with allylic hydrogen reacts with $^1O_2$ to form the corresponding allylic hydroperoxide, during the reaction, the C=C double bond is transferred to the neighboring carbon, and the formed allylic hydroperoxide is further broken or rearranged to form the stable product; (2) [2+2] reaction: $^1O_2$ is added to one C=C double bond of the olefinic APs to form an unstable 1,2-dioxyethylene substance, which is then cleaved further into two carbonyl fragments.

The oxidizing ability of $^1O_2$ is significantly weaker than that of $SO_4^{\bullet -}$ and •OH, but its selectivity in oxidizing electron-rich organic pollutants is stronger, so its application in the field of ACW treatment is still being explored. Sun et al. [9] discovered that $^1O_2$ was instrumental in degrading sodium sulfadiazine in the rhodochrosite/PDS system under neutral conditions. This was particularly evident in the initial stage of pollutant degradation and facilitated the consecutive degradation of pollutants via the radical mechanism.

2.2.2 Surface electron transfer

Different from the direct electron transfer involved in the free radical mechanism in the previous paper, the surface electron transfer referred to in this paper is mostly found in the system of carbon-based materials (CBMs) activated PS. CBMs usually has low impedance and certain electrical conductivity, and therefore it can directly induce the electron transfer process. Activated carbon (AC) activated PS system, for example, in the surface electron transfer process, APs is adsorbed on the AC

and provides electrons and substable PS act as an electron acceptor, AC as an electron-conducting material to promote this process [10]. In addition, carbon materials can form surface electron transfer complexes with aromatic APs by conjugating Π electrons, which further reduces the material impedance, promotes surface electron transfer and provides electrons. Huo et al. [11] prepared N/S co-doped carbons for the activation of PS and this study demonstrated that the electron transfer contributes significantly to the degradation process of tetracycline.

3. Common activation methods for degrading antibiotics in PS—AOPs system

3.1. Thermal activation

Thermal activation is one of the commonly used means of PS activation, the process utilizes the thermal energy generated at high temperatures to sever the O—O bond of PS and thus produce reactive radicals, which promotes the free radical pathway significantly. The cleavage bond energy of PDS is relatively low and the can be cleaved at a certain temperature to generate $SO_4^{\bullet -}$ (Eq.(5)), while PMS requires higher temperature to cleave the O—O bond to •OH and $SO_4^{\bullet -}$ ((Eq. 6)). The temperature is an important factor affecting the thermal activation, the increase in temperature can not only increase the rate of $SO_4^{\bullet -}$ generation, but also promote the conversion of $SO_4^{\bullet -}$ to •OH. It is worth noting that the higher temperature does not mean the better pollutant removal effect, and when the concentration of $SO_4^{\bullet -}$ is too large, it may promote the consumption of $SO_4^{\bullet -}$ itself (Eqs. (7)-(8)). In addition, pH also significantly affects the effect of thermal activation, and the appropriate pH derived from the studies of different scholars often varies. Ji et al. [12] degraded sulfamethoxazole at 60°C and found that the degradation effect increased monotonically at pH in the range of 4.0-10. Fan et al. [13] pointed out that the most favorable pH for the degradation of sulfadimethoxazole at 50°C was 9. The reason for these differences may be the reaction characteristics of different APs and other conditions during the reaction.

$$S_2O_8^{2-} \xrightarrow{\Delta} 2SO_4^{\bullet -} \quad (5)$$

$$HSO_5^- \xrightarrow{\Delta} SO_4^{\bullet -} + \bullet OH \quad (6)$$

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

$$S_2O_8^{2-} + SO_4^{\bullet -} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \quad (8)$$

3.2. Radiation activation

Ultraviolet light (UV, 10-400 nm) can be stimulated to break the O—O bond in PS, which produces the corresponding active species to degrade APs. UV activation of PS can produce •OH and $SO_4^{\bullet -}$ with strong oxidizing ability and UV treatment is also a necessary part of wastewater treatment in the disinfection process, so the activation system of UV/PS has been widely used in the treatment of ACW. Generally speaking, the degradation of APs by UV mainly involves two pathways: (1) UV absorption by APs leads to the direct destruction of chemical bonds. Most APs are not sensitive to direct photolysis by UV, but in some cases this direct photolysis should not be neglected. (2) Under activation of UV, the chemical bonds of APs were degraded by the active species produced by PS, and the reaction mechanism was explained by Eqs. (9)-(14) [14]. Pirsaheb et al. [15] found that the maximum removal of ciprofloxacin and amoxicillin was 99.9% and 99.26% under optimal conditions., which demonstrated the considerable ability to remove APs by UV/PS. Wu et al. [16] confirmed that •OH and $SO_4^{\bullet -}$ were involved in the degradation of fosfomycin by the UV/PS system, of which •OH playing a significant role in the mineralization of Fosfomycin. In addition, the UV/PS system can not only remove APs, but has been shown to remove antibiotic resistance bacteria in ACW. [17].

$$\text{Photocatalysts} \rightarrow h^+ + e^- \quad (9)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (10)$$

$$h^+ + H_2O \rightarrow \bullet OH \quad (11)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet -} \quad (12)$$

$$S_2O_8^{2-} + O_2^{\bullet -} \rightarrow SO_4^{2-} + SO_4^{\bullet -} + O_2 \quad (13)$$

$$h^+/SO_4^{\bullet -}/\bullet OH + \text{antibiotics} \rightarrow \text{small molecule substance} + H_2O + CO_2 \quad (14)$$

3.3. Transition metal-based materials activation

In recent years, the non-homogeneous activation of transition metal-based materials (TMMs) has received extensive attention from scholars. The non-heterogeneous activation of PS in natural minerals such as iron-based, copper-based, manganese-based, cobalt-based and the corresponding synthesized materials. Since TMMs have crystal structures and active sites, the mechanism of their activation PS is more complicated, which mainly includes.

(1) Radical pathway (Eqs. (15)-(20)): high valence metal oxides (expressed as M^{n+}) and PDS/PMS will be reduced to relatively low valence metal oxides (expressed as $M^{(n-1)+}$), and at the same time generate $S_2O_8^{2-}$ or $SO_5^{—}$ and other corresponding oxidation products. or $SO_5^{—}$. Then, $M^{(n-1)+}$ can reduce $S_2O_8^{2-}$ or $HSO_5^{—}$ in solution to $SO_4^{\bullet -}$ and O_2, utilizing the reactive radicals generated in such redox cycling process [18] to degrade APs.

$$M^{n+} + S_2O_8^{2-} \rightarrow M^{(n-1)+} + S_2O_8^{\bullet -} \quad (15)$$

$$M^{n+} + S_2O_8^{2-} + H_2O \rightarrow M^{(n-1)+} + HSO_5^- \quad (16)$$

$$M^{n+} + HSO_5^- \rightarrow M^{(n-1)+} + SO_5^{\bullet -} + H^+ \quad (17)$$

$$M^{(n-1)+} + S_2O_8^{2-} \rightarrow M^{n+} + SO_4^{\bullet -} + SO_4^{2-} \quad (18)$$

$$M^{(n-1)+} + HSO_5^- \rightarrow M^{n+} + SO_4^{\bullet -} + H^+ \quad (19)$$

$$2SO_5^{\bullet -} \rightarrow 2SO_4^{\bullet -} + O_2 \quad (20)$$

(2) Non-radical pathway: Unlike similar materials, copper-based materials mainly activate PS through the non-radical pathway, Li et al. [19] found that cubic Cu_2O can interact with PMS to form surface complexes, which in turn generates the active species $^1O_2$.Wang et al. [20] further showed that $^1O_2$ is the primary substance in the PMS/CuO system, and at the same time demonstrated that $O_2^{\bullet -}$ is an important precursor of $^1O_2$. Additionally, Mn^+ can interact with H_2O to form a hydroxyl complex [M^{n+}—OH], which can be used as an active site to combine with $S_2O_8^{2-}$ to form a substable intermediate [M^{n+}—O···O—SO_3], which can continue to react with $S_2O_8^{2-}$ to form $O_2^{\bullet -}$, which in turn binds to the intermediate to form $^1O_2$.To achieve the modulation of the non-radical pathway, Jawad et al. [21] evaluated the effect of Multi-metallic catalysts to activate PMS and found that inserting MgO could generate highly oxidized metal centers, which facilitate the generation of [Cu^{n+}—O···O—SO_3] intermediates from PMS and thus promotes the generation of $^1O_2$. Unfortunately, this does not change the highly selective but relatively weakly oxidizing nature of $^1O_2$, and some scholars have argued that the contribution of $^1O_2$ is relatively small in most TMMs/PMS systems [22].

Obviously, the activation mechanism of PS involved in the TMMs/PS system is complex, and how to effectively regulate the two pathways to promote the generation of active species is a major difficulty. In addition, the leaching toxicity of cobalt-based and copper-based materials should be considered when using them in the practical management of ACW. Qiu et al. [23] modified CoS_2 by Fe_3O_4, which significantly reduced the leaching of cobalt ions while activating PMS to produce $^1O_2$, but many studies still lack the relevant risk assessment or means to reduce the risk, which also limits the potential of engineering applications of TMMs.

3.4. Carbon-based material activation

CBMs includes biochar (BC), activated carbon (AC), graphene, carbon nanotubes (CNTs), carbon black, etc. In recent years, CBMs has been used in the heterogeneous activation of PS because of its relatively low cost, no additional energy consumption, recyclability and environmental friendliness. Similar to TMMs, which is also used for heterogeneous activation, the pathways of PS activation by CBMs can be divided into radical and non-radical pathways, and both pathways may be involved in the same reaction system.

(1) Radical pathway: Oxygen-containing functional groups (OCGs) on the CBMs surface serve as significant active sites, include carbonyl (—C=O), hydroxyl (—OH), carboxyl (—COOH), among others. OCGs can combine with PMS or PDS to form the intermediate —C=O—HO—O—SO_3, which can be further cleaved to form $SO_4^{\bullet -}$ involved in the degradation of APs. Meanwhile, OCGs themselves can be oxidized to the substable $[—C=O]^+$ and immediately reduced to —C=O by the remaining PMS or PDS, forming a redox cycle (Eqs. (21)-(22) in the case of PMS). In addition to OCGs, the off-domain Π electrons and surface defects (vacancies, sawtooth edges, sp^2 hybridized carbon, etc.) of CBMs can also become active sites, contributing to the generation of $SO_4^{\bullet -}$ (Eqs. (23)-(24)). Additionally, CBMs can be modified by doping with heteroatoms, such as introducing N atoms to create more active sites(graphite N, pyrrole N and pyridine N). Among these, graphite N presents the most superior impact because of its high electron transfer capacity which has the capability to modulate the charge distribution of Carbon atoms. This ultimately results in the formation of positively charged sites on the surface of the activated material which aid in promoting the combination with negatively charged Oxygen atoms present in the PS. [24]

$$—C=O + HSO_5^- \rightarrow —C=O—HO—O—O—SO_3 + SO_4^{\bullet -} + OH^- \quad (21)$$

$$[—C=O]^+ + HSO_5^- \rightarrow —C=O + SO_5^{\bullet -} + H^+ \quad (22)$$

$$C-\pi + HSO_5^- \rightarrow C-\pi^+ + SO_4^{\bullet -} + OH^- \quad (23)$$

$$C-\pi^+ + HSO_5^- \rightarrow C-\pi + SO_4^{\bullet -} + H^+ \quad (24)$$

(2) Non-radical pathway: Unlike other activation modes, CBMs can often enhance the dominance of the non-radical pathway during PS activation, which mainly consists of two pathways: generation of $^1O_2$ and surface electron transfer.

Generation of $^1O_2$: The production of $^1O_2$ is believed to primarily occur at the oxygen-containing functional group C=O located on the surface of BC, which is because C=O can act as a Lewis basic site with a lone electron, providing an exceeding redox potential for BC. In the case of PMS, for example, C=O can react with HSO_5^- to form an intermediate and further form an epoxy bond (Eqs. (25)-(27)), which breaks in the presence of HSO_5^- to produce $^1O_2$ (Eq. (28)). Interestingly, the surface of certain carbon materials is relatively lacking in C=O, such as CNT, but the study by Cheng et al. [25] still detected the presence of a large amount of $^1O_2$ during CNT-activated PMS, which further confirms the indication that defective structures in CNT can also produce $^1O_2$. In addition, the introduction of reactive sites, such as graphite N, can also contribute to the production of $^1O_2$ by PMS/PDS (Eqs. (29)-(30)).[]

$$Carbon=O + HSO_5^- \rightarrow HO—Carbon\cdots O—O—SO_3^- \quad (25)$$

$$HO—Carbon\cdots O—O—SO_3^- + OH^- \rightarrow {}^-O—Carbon\cdots O—O—SO_3^- + H_2O \quad (26)$$

$${}^-O—Carbon\cdots O—O—SO_3^- \rightarrow \text{epoxy groups} + SO_4^{2-} \quad (27)$$

$$SO_5^- + \text{epoxy groups} \rightarrow Carbon=O + SO_4^{2-} + {}^1O_2 \quad (28)$$

$$BC—N\cdots SO_3—O—O—SO_3^{2-} \rightarrow BC—N + 2SO_4^{2-} + {}^1O_2 \quad (29)$$

$$BC—N\cdots O—O—SO_3^{2-} + SO_5^{2-} \rightarrow BC—N + HSO_4^- + SO_4^{2-} + {}^1O_2 \quad (30)$$

Surface electron transfer: carbon materials usually have good adsorption capacity, which can form PS substable complexes with PMS/PDS in solution [26] (Eqs. (31)-(32)) and can act as an electron conductor (transfer medium) during the surface electron transfer process, which prompts the PS substable complexes to complete the electron transfer process with adsorbed APs as electron donors. Lee et al. [27] found that graphitized nanodiamond could achieve electron transer from phenol to PDS by forming complexes on the surface. Ren et al [28] also found electron transfer to CNTs-activated PDS complexes in the reaction system, confirming the main pathway of surface electron transfer leading to pollutant degradation. Numerous studies have been initiated with the aim of enhancing the efficiency of surface electron transfer. These studies focused on modifying carbon-based materials to create more active reaction sites, with a particular emphasis in recent years on heteroatom doping modification, especially nitrogen doping. Wang et al. [43] pointed out that the pyrrole N and pyridine N in the N-doped BC/PDS system could improve the charge distribution of BC and generating more active sites to promote the formation of substable complexes. Since then, it has been found that graphite N also has a significant effect on the surface electron transfer. Qi et al. [30] found that during the degradation of sulfamethoxazole, graphite N can disrupt the intrinsic conjugated graphitic network to facilitate electron transfer and the introduction of graphite N can also weaken the O—O bond, prompting electron rearrangement to form a substable complex.

$$C + HSO_5^- \rightarrow [C \cdots HSO_5^-]^* \quad (31)$$

$$C + S_2O_8^{2-} \rightarrow [C \cdots S_2O_8^{2-}]^* \quad (32)$$

4. Conclusions

PS-AOPs have received extensive attention in the management of ACW. In this paper, the activation mechanism and the activation mode of PS are reviewed. APs are activated and degraded by PS in this process through two pathways: the radical pathway (mainly the radicals with high redox potentials such as •OH and $SO_4^{\bullet -}$ produced in the solution system) and the non-radical pathway (mainly through the generation of $^1O_2$ with strong selectivity or the surface electron transfer mechanism). In order to further enhance the removal of APs, scholars are continuously exploring the development of activation techniques for PS-AOPs. Thermal activation and radiation activation mainly promote the activation of the radical pathway by exogenous input of energy, which can break the O—O bond in PS and generates free radicals, such as •OH and $SO_4^{\bullet -}$. Non-heterogeneous activation based on TMMs and CBMs has been developed more rapidly in recent years, and their activation mechanisms are more complex, involving the generation of active species on the one hand, and direct degradation of pollutants by surface electron transfer on the other, which involves the formation of surface electron transfer complexes.

For the current research, this paper summarizes the following four suggested research directions at the end and analyzes the difficulties of the current directions,

aiming to provide theoretical directions for the subsequent research:

(1) Optimization of detection methods of activation mechanism and regulation of different activation pathways: The current study focuses less on the numerical examination of the activation of radicals and non-radical pathways in APs degradation.

(2) Selection of different activation methods: The disadvantages of different activation effects should be fully considered. Thermal activation and radiation activation imply energy consumption; the stability and reusability of materials need to be considered for CBMs non-heterogeneous activation.

(3) Toxicity assessment and risk control:There are many types of antibiotics, some APs have complex structures, and their degradation (non-mineralized) products may still have high toxicity. Therefore, toxicity assessment can be added to the study.

(4) Application promotion in actual water bodies: Actual water bodies contain background substances such as soluble organic matter (DOM), $NO2^{--}$ and $HCO3^{--}$, which may react with the active species generated by PS (especially $SO4^{\bullet -}$), leading to the degradation effect of target

pollutants being affected, which is one of the difficulties in engineering application that makes it difficult to carryout many researches at present.

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