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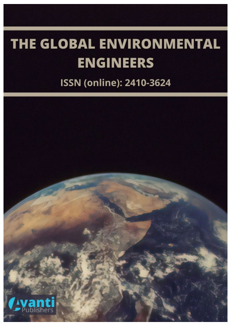

Enhanced Mechanism of Nano Zero-Valent Iron Activated Persulfate for Persistent Organic Pollutants in the Environment: A Critical Review

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ABSTRACT

The advanced oxidation process based on persulfate has a broad application prospect in the remediation of organic pollutants. As an effective, low-cost and environmentally friendly material, nano-zero-valent iron (nZVI) can effectively activate persulfate (nZVI/PS) to generate strongly oxidizing sulfate radical for removing organic pollutants in the environment. In this review, we first clarify the activation pathway of nZVI activated persulfate including direct activation and indirect activation. Direct activation means that the electrons released by nZVI directly participate in the activation of PS; indirect activation means that Fe^0 corrodes to generate Fe^{2+}, and Fe^{2+} further activate the persulfate. Then, the mechanism of nZVI/PS system to degrade organic pollutants including electron transfer, hydrogen extraction and addition reactions are also discussed. Finally, combined with the activation pathway and the mechanism of degrading organic pollutants, we propose several prospects for the future research direction of nZVI activated persulfate. As a result, this review provides a theoretical basis for the nZVI/PS advanced oxidation system to remediate actual sites contaminated with organic pollutants.

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1. Introduction

With the rapid development of industry, agriculture and urbanization, organic pollutants flowing into the natural environment are becoming more and more diverse and abundant. Persistent Organic Pollutants escape into the environment, accumulate in plants and animals, and endanger life in groundwater and soil. They will enter the human body along the food chain, causing varying degrees of damage to human organs, and even threatening human's life [1]. Currently, methods of removing organic pollutants include absorption [2, 3], adsorption [4, 5], membrane separation [6, 7] and advanced oxidation process [8, 9]. Among these treatment methods, the advanced oxidation process (AOP) is widely used in the treatment of some difficult to remove organic pollutants due to its good treatment effect and short treatment cycle.

AOP refers to that highly reactive free radicals (i.e. hydroxyl radicals, sulfate radicals) decompose organic pollutants into small molecules, even carbon dioxide and water [10, 11]. Sulfate radical ($SO_4^{-}\bullet$) can degrade most organic pollutants with a fast reaction rate and excellent degradation performance. At present, advanced oxidation technology based on persulfate (PS) has attracted extensive attention from researchers [12-14]. The traditional methods of activating persulfate include ultraviolet activation technology [15], metal ion activation technology [16-18], thermal activation technology [19], ultrasonic activation technology [20, 21] and alkali activation technology [22]. However, these activation technologies require a large amount of energy consumption, strict pH conditions and cause secondary pollution. In order to overcome these shortcomings, nano-zero-valent iron (nZVI) activated PS technology (nZVI/PS) emerged as an ideal activation method. nZVI has the characteristics of large specific surface area but small particle size, high reactivity and strong reduction ability [23-25]. Additional, nZVI activated persulfate technology has mild reaction conditions, no extra heat and light source, environmental protection, simple equipment [26]. At present, studies have shown that nZVI activated persulfate can effectively remove organic pollutants [27-30].

In this paper, the activation pathway and degradation mechanism of organic pollutants are discussed in detail, including electron transfer, hydrogen extraction reaction and the addition reaction. The application of the nZVI/PS system to degrade organic pollutants is also investigated. And the prospect of nZVI/PS advanced oxidation system is importantly proposed combined with the above discussion. It has been proved that nano-zero-valent iron activated persulfate is very promising for the degradation of organic pollutants.

2. The Pathway of Activation of Persulfate by Nano-Zero-Valent Iron

Persulfate is mainly divided into peroxymonosulfate (PMS) and peroxodisulfate (PS) [31-33]. A comparison of PMS and PS on the degradation of organic pollutants in the past three years is shown in Table1. PMS is a compound salt, the impurities produced in the reaction process will cause a serious influence on the degradation. Therefore, compared with PMS, PS is commonly used in laboratory research due to its properties of water-soluble, stable, cheap and easy to transport [34]. However, persulfate ($S_2O_8^{2-}$ E_0=2.01V) has low activity and a slow reaction rate in water. After activation, it can generate strong oxidizing sulfate radicals, which is beneficial to the degradation of organic matter [35]. Kang *et al*. [36] studied the degradation effects of 1,4-dioxane (1,4-D) and As(III) in the three oxidation systems of nZVI/PS, nZVI/PMS and nZVI/hydrogen peroxide. The results showed that the removal effect of nZVI/PS system was optimal under the same conditions. The standard redox potential of $SO_4^{-}\bullet$ (2.5-3.1V) is greater than that of •OH (1.8-2.7V), and the half-life of $SO_4^{-}\bullet$ (4s) is thousands of times that of the hydroxyl radical (1μs). At the same time, $SO_4^{-}\bullet$ can also make up for the limitation of •OH that cannot degrade some organic matter. Therefore, advanced oxidation technology based on $SO_4^{-}\bullet$ has become the preferred method for pollutant degradation in recent years. nZVI activated persulfate is divided into direct and indirect activation. Direct activation refers to the direct activation of persulfate by electrons released from nZVI; indirect activation refers to the indirect activation of persulfate by reducing Fe^{2+} produced by Fe^0 corrosion [37]. At present, the degradation of organic matter by $SO_4^{-}\bullet$ generated by nZVI/PS system has become a research trend.

2.1. Direct Action of Persulfate Activated by nZVI

The essence of nZVI activation of persulfate is to break the O-O bond to form $SO_4^{-}\bullet$. During the activation process, the lost electrons of Fe^0 directly participate in the activation of persulfate to form $SO_4^{-}\bullet$, along with the generation of Fe^{2+} and SO_4^{2-} (Equation (1)). The generated SO_4^{-}• reacts with water to further generate •OH and H^+(Equation (2)). This lowers the pH of the reaction system and facilitates the degradation of pollutants. However, the increasing concentration of SO_4^{2-} during the reaction will occupy the active sites on the surface of nZVI particles and suppress the release of electrons and Fe^{2+}, thereby hindering the activation process.

Table 1: A comparison about PMS and PS on the degradation of organic pollutants.

Target Pollutant	Activator/Condition	PS	PMS	Reference
Imidacloprid	UV	90%	66.7%	[38]
ethyl paraben	UV	98.10%	81.30%	[39]
Benzene, toluene, ethylbenzene and o-xylene (BTEX)	Ultrasound (US)	98%	97%	[40]
acid orange 7 (AO7)	Fe-0	PS>PMS (pH=4/7)	PS>PMS (pH=4/7)	[41]
Tyrosol(TSL)	UV-254	PS >PMS	PS>PMS	[42]
brilliant green (BG)	UV	47%	63.1%	[43]
1,4-dioxane (1,4-D) and As(III)	nZVI	PS>PMS	PS>PMS	[36]
toxic organic contaminants in wastewater and actual industrial wastewater	microwave-ultraviolet catalyzed oxidation system (MW-UV)	PS>PMS	PS>PMS	[44]

nZVI will occur an oxidation reaction in the natural environment, losing electrons to generate ferrous ions (Equations (3), (4)) [45]. Moreover, the concentration of OH^- in the reaction system increases as the reaction progresses, so the pH value of the system increases. In an alkaline environment, some of SO_4^{-}• will react with OH^- (Equation (5)) to generate hydroxyl radicals [46]. The Fe^{2+} and Fe^{3+} formed by Fe^0 oxidation continue to react with sulfate radicals, in which Fe^{3+} is reduced by Fe^0 to produce Fe^{2+} and SO_4^{2-}, and Fe^{2+} occurs oxidation reaction to produce Fe^{3+} and SO_4^{2-} (Equation (6)) [47]. The above reactions realized the balance of Fe^{2+} and Fe^{3+} in the reaction system.

$$Fe^0+2S_2O_8^{2-}+2e^-\rightarrow Fe^{2+}+SO_4^{-}\cdot+2SO_4^{2-} \quad (1)$$

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

$$2Fe^0+O_2+2H_2O\rightarrow Fe^{2+}+4OH^- \quad (3)$$

$$2Fe^0+2H_2O\rightarrow Fe^{2+}+2OH^-+H_2 \quad (4)$$

$$SO_4^{-}\cdot+OH^-\rightarrow SO_4^{2-}+\cdot OH+H^+ \quad (5)$$

$$Fe^{2+}+SO_4^{-}\cdot\rightarrow SO_4^{2-}+Fe^{3+} \quad (6)$$

nZVI is a low-cost, low-toxic and environmentally friendly material [48]. Simultaneously, nZVI as an activator can efficiently and quickly activate persulfate to degrade organic matters. Nano-zero-valent iron is easily oxidized under natural conditions to form iron oxides, such as Fe_2O_3, Fe_3O_4 and FeO [49, 50]. These oxides will be deposited on the surface of nZVI, hinder the electron transfer between nZVI core-shell, and inhibit the activation of persulfate by nZVI.

Under acidic and neutral conditions, nZVI can quickly activate persulfate to generate SO_4^{-}•, which can promote the degradation of pollutants. However, under strong acid conditions, the SO_4^{-}• (2.5-3.1v) will occur a self-quenching reaction, resulting in the generation of relatively weak oxidizing $S_2O_8^{2-}$• (E_0=2.01V). Under alkaline conditions, nZVI will react with persulfate to generate hydroxyl radicals (Equation (7)), hydroxyl radicals and sulfate radicals will synergistically degrade organic pollutants. The above discussion indicates that under different conditions, the pathways of nZVI to activate PS are different.

$$Fe^{0}+S_2O_8^{2-}+OH^{-}\rightarrow Fe^{2+}+\cdot OH+2SO_4^{2-} \tag{7}$$

2.2. Indirect Effect of Persulfate Activated by nZVI

Persulfate exists in the form of $S_2O_8^{2-}$ and HSO_5^- ions in the solution. The indirect effect of nZVI activating persulfate is that the Fe^0 loses electrons during the reaction to generate ferrous ions, and the persulfate is activated by the ferrous ions to further generate sulfate radicals (Equation (8)). The sources of Fe^{2+} will be discussed in the following four aspects: (1) In the process of activation of persulfate through electron transfer by nZVI, not only sulfate radical but also Fe^{2+} is generated. (2) Fe^0 itself will dissolve and produce a small amount of Fe^{2+}; (3) Fe^{3+} generated in the reaction process is reduced by Fe^0 to Fe^{2+} [51]; (4) nZVI loses electrons to form Fe^{2+} during corrosion in both aerobic and anaerobic environments. Fe^{2+} mainly comes from the corrosion of Fe^0, which can maintain the continuous generation of Fe^{2+}.

Dissolved Fe^{2+} plays a major role in the activation of persulfate by nZVI. Compared with the activation of persulfate by Fe^{2+} alone, the merits of nZVI as an activator are as follows:(1) nZVI can slowly generate Fe^{2+}, reducing the occurrence of $SO_4^{-}\bullet$ quenching reaction, and improving the utilization rate of $SO_4^{-}\bullet$. (2) nZVI activated persulfate can avoid interference caused by the addition of other ions and improve the degradation efficiency of pollutants [52]. Additionally, Fe^0 can continuously reduce Fe^{3+} in the reaction system to Fe^{2+} (Equation (9)) [53]. Here, Fe^{3+} reacts with OH^- to generate $Fe(OH)_3$ deposited on the surface of nZVI particle [54]. During the process of continuous corrosion, the surface of nZVI will become uneven, and the generated iron oxides are not conducive to the release of sulfate radicals. In addition, another unfavourable factor is the excessively high persulfate concentration. Excessive persulfate will cause a self-quenching reaction of sulfate radicals before they can react with pollutants, causing the consumption of sulfate radicals. In addition, the reaction of sulfate radicals and persulfate will also cause the loss of $SO_4^{-}\bullet$. (Equation (11)) [55]. However, the reaction of $SO_4^{-}\bullet$ with itself will produce $S_2O_8^{2-}$ (Equation (10)), which realizes the regeneration of $S_2O_8^{2-}$.

$$Fe^{2+}+S_2O_8^{2-}\rightarrow Fe^{3+}+SO_4^{-}\cdot+SO_4^{2-} \tag{8}$$

$$Fe^{0}+2Fe^{3+}\rightarrow 3Fe^{2+} \tag{9}$$

$$SO_4^{\cdot-}+SO_4^{\cdot-}\rightarrow S_2O_8^{2-} \tag{10}$$

$$SO_4^{\cdot-}+S_2O_8^{2-}\rightarrow SO_4^{2-}+S_2O_8^{\cdot-} \tag{11}$$

For PMS, the Fe^{2+} loses electrons and activates the PMS to produce 1 molecule of sulfate radical (Equation (12)). In particular, Rodriguez-Chueca *et al*. [56] proposed that Fe^{3+} can activate PMS through uneven electron transfer to generate $SO_4^{-}\bullet$ and $SO_5^{-}\bullet$ (Equations (13)).

$$HSO_5^{-}+Fe^{2+}\rightarrow SO_4^{-}\cdot+Fe^{3+}+OH^{-} \tag{12}$$

$$HSO_5^{-}+Fe^{3+}\rightarrow SO_5^{-}\cdot+Fe^{2+}+H^{+} \tag{13}$$

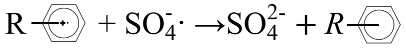
Studies have shown that nZVI can efficiently activate persulfate. Li *et al*. [57]activated PS by nZVI to remove nitrobenzene, the results found that higher temperature and acidic conditions are more conducive to the removal of nitrobenzene, and the removal rate can reach 99%. Wu *et al*. [58] used nanoscale zero-valent iron supported on the organo-montmorillonite composite to activate PS, and the degradation rate of sulfamethazine can reach 97% within ten minutes. Zhang *et al*. [59] investigated the ultrasound-enhanced nano-zero-valent iron activated persulfate for degradation of chloramphenicol (CAP). The results showed that both sulfates radical and hydroxyl radical played a role in CAP degradation, but the contribution of sulfate radicals is greater.

3. The Mechanism of nZVI Activating Persulfate to Degrade Organic Pollutants

As mentioned above, nZVI activates persulfate through direct and indirect effects, generating reactive oxygen species (ROS) including $SO_4^{-}\bullet$ and •OH are involved in the degradation of organic pollutants. $SO_4^{-}\bullet$ with strong oxidizing ability has a lone-pair of electrons, the standard oxidation-reduction potential is higher than that of •OH. •OH are highly selective for organic pollutants, so there are very few organic pollutants available for degradation. Compared with •OH, SO_4^{-}• has a strong oxidizing ability and low selectivity to organic pollutants, so most pollutants can be degraded [60]. Similar to the mechanism of •OH, SO_4^{-}• degrades organic matter into H_2O, CO_2 and other small molecules through electron transfer, hydrogen extraction reaction and addition reaction.

3.1. Electronic Transfer

Lone pair electrons on sulfate radical are electrophilic groups. When reacting with organic pollutants, sulfate radicals capture electrons from organic molecules and form SO_4^{2-} (Equation (14)). SO_4^{-}• is more prone to electron transfer reactions than •OH. Organic compounds such as aromatic compounds, amine compounds, usually occur oxidation reaction through electron transfer. This is because these organic compounds contain multiple electron-donating groups, including hydroxyl group (-OH), amino group (-NH_2), alkoxy group (-OR), etc. The presence of these electron-donating groups can promote electron transfer between sulfate radicals and target organic pollutants. Simultaneously, organic compounds contain electron-gaining groups, such as carboxyl groups (C=O) and nitro groups (-NO_2) [61]. The presence of these electron-gaining groups will compete with the SO_4^{-}• for electrons. This is not conducive to the degradation of target pollutants [62].



（14）

Nitroaromatic compounds as a kind of important chemical raw materials are widely used in dyes, medicine, pesticides and other industrial production [63, 64]. Nitroaromatic compounds have the characteristics of stable structure, poor biodegradability and strong toxicity, and their existence will cause serious pollution to water bodies. An advanced oxidation system of persulfate activated by nZVI can efficiently degrade nitroaromatic compounds. Wang *et al*. [65] studied the green synthesis of biochar loaded with nano-zero-valent iron combined with persulfate to degrade p-nitrophenol (PNP) in water. The reduction effect of nano-zero-valent iron reduces nitrobenzene to aniline, and SO_4^{-}• oxidizes aniline through electron transfer. Du *et al*. [66] studied the mechanism of simultaneous activation of hydrogen peroxide and persulfate by nZVI to degrade p-nitrophenol (PNP). •OH and SO_4^{-}• jointly degrade p-nitrophenol. SO_4^{-}• mainly oxidizes and degrades p-nitrophenol through electron transfer.

3.2. Hydrogen Extraction Reaction

Organic substances containing saturated bonds are prone to hydrogen extraction reactions. Such organic compounds include alkane compounds, alcohol compounds, ethers, and lipid compounds. When SO_4^{-}• reacts with these types of pollutants, active free radicals will deprive the hydrogen atoms of the C-H bond in the organic pollutants, causing the organic matter to occur decarbonization and chain scission (Equation (15)). Anipsitakis *et al*. [67] found that lipid compounds are prone to hydrogen extraction reactions.

$$SO_4^{-}\cdot + RH \rightarrow HSO_4^{-} + R \qquad (15)$$

Dong *et al*. [68] investigated the degradation of Trichloroethylene (TCE) by sulfided nano-zero-valent iron activated persulfate, and proposed a possible degradation mechanism (Figure **1**). •OH and SO_4^{-}• attack the TCE molecules together, so that the hydrogen atoms on TCE are taken away, then SO_4^{-}• and •OH are converted into HSO_4^{-} and H_2O. Ding *et al*. [69] prepared attapulgite-loaded nano-zero-valent iron composites to activate PMS to degrade quincloric acid. Quincloric acid contains -COOH and -Cl electrophilic groups, which is not conducive to sulfate radical attacking quincloric acid through electron transfer. Studies have found that quincloric acid mainly forms small molecular substances by capturing hydrogen atoms, oxidizing and ring-opening. Wu *et al*. [70] synthesized a composite material of nano-zero-valent iron and graphene, and explored the degradation mechanism of the herbicide atrazine by composite material/persulfate system. The result has found that SO_4^{-}• degrades atrazine through hydrogen extraction. Li *et al*. [71] applied biochar loaded nano-zero-valent iron (BC-nZVI) to activate persulfate to remove decabromodiphenyl ether (BDE209). The results of batch experiments showed that the molar ratio of PS/BC-nZVI, the pH value of the PS solution and the temperature of the reaction system are all factors that affect the degradation efficiency of BDE209 (Figure **2**). The possible degradation pathway of this system is also proposed as shown in Figure **3**. In addition, the quenching experiment used in this research further proves that sulfate radicals play a dominate role under acidic and neutral conditions, while hydroxyl radicals play a dominant role under alkaline conditions.

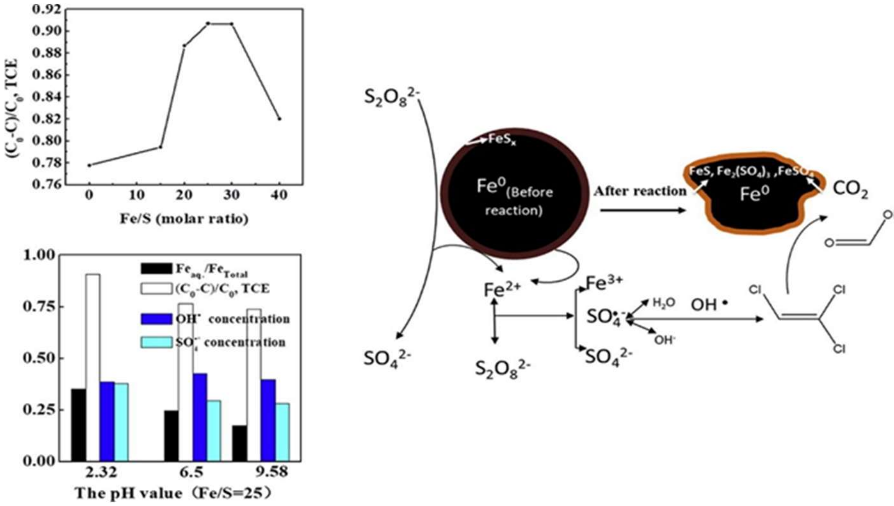
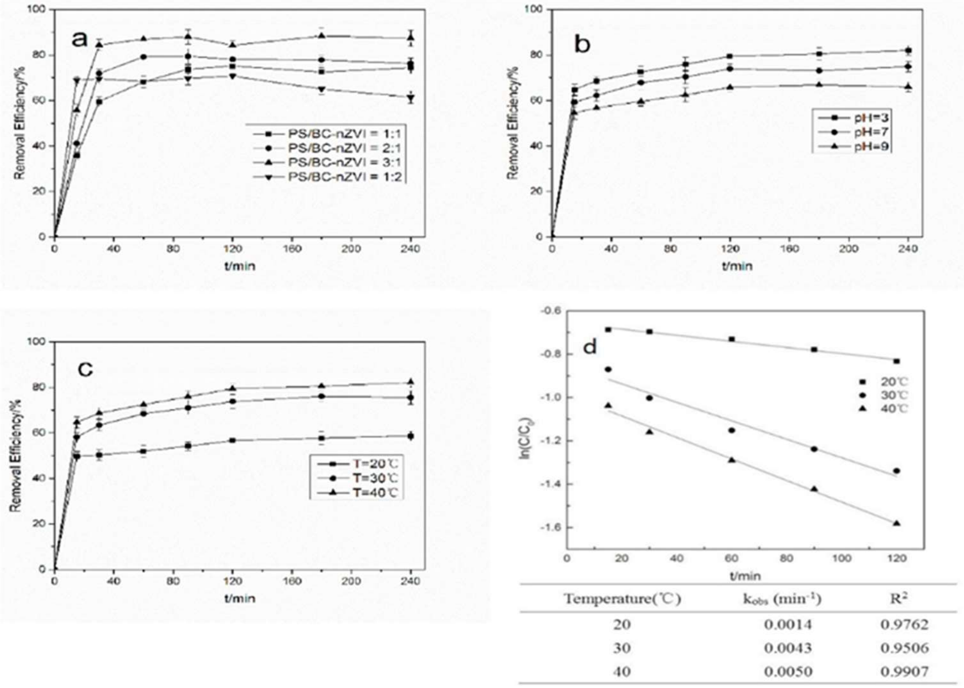


Figure 1: Mechanism of removing TCE by sulfided nano-zero-valent iron ([68]).



Temperature(℃)	k_{obs} (min^{-1})	R^2
20	0.0014	0.9762
30	0.0043	0.9506
40	0.0050	0.9907

Figure 2: The effect of PS/BC-nZVI molar ratio (a); pH value of PS (b) and temperature (c) on the removal of BDE209; (d) kinetic study under different temperature conditions ([71]).

3.3. The Addition Reaction

Addition reaction refers to that under certain conditions, the organics containing unsaturated bonds have broken the double bond (C=C, C=O) or triple bond, and other atoms or atomic groups are added to both ends of the broken bond. The strongly oxidizing sulfate radical provides electrons to unsaturated hydrocarbon organics and the addition reaction occurs. The reaction mechanism is as follows:

$$SO_4^{-}\cdot + H_2C{=}CHR \rightarrow {}^{-}OSO_2OCH\text{-}CHR \quad (16)$$

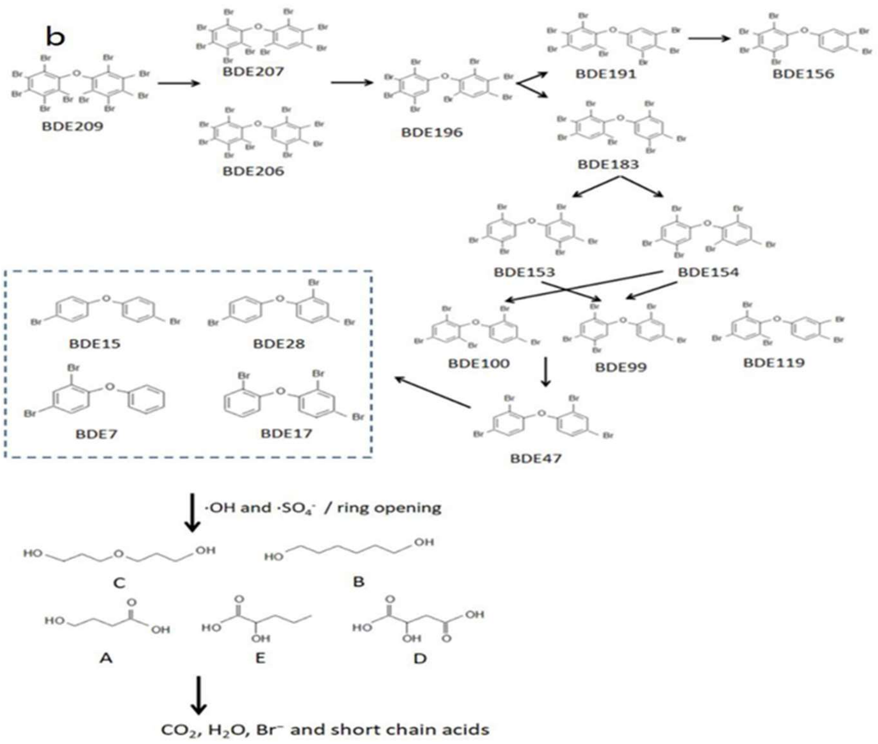


Figure 3: The degradation of BDE209 by BC-nZVI/PS ([71]).

Huang *et al*. [72] investigated the degradation of 59 kinds of organic compounds by persulfate oxidation process and found that persulfate oxidation process is more likely to occur addition reaction to organic compounds containing C=C double bond.

In general, nZVI activated persulfate degrades organic pollutants not by a single action, but by a combination of several actions. The specific mechanism of synergistic degradation of organic matter needs further study. In the degradation of norfloxacin (NOR), Zhu *et al*.[73] found that the presence of biochar-loaded nZVI/Ni bimetallic materials (BC@nZVI/Ni) can effectively activate PS to produce sulfate radicals by the electron paramagnetic resonance spectrum (EPR) test (Figure **4**). Moreover, the acidic conditions and the increase of reaction temperature are conducive to the removal of NOR. In addition, the presence of humic acid (HA), SO_4^{2-} and NO_3^- has inhibition on the degradation of NOR, but HCO_3^- and Cl^- can promote the degradation of NOR (Figure **5**).

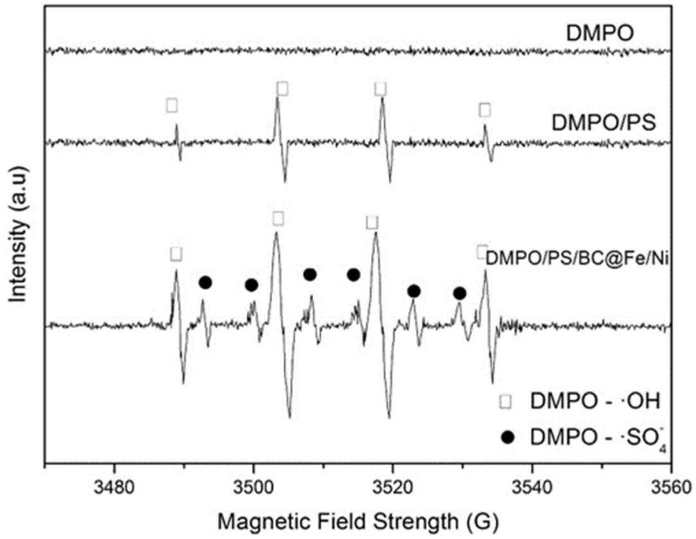


Figure 4: EPR spectra in the BC@nZVI/Ni/PS system([73]).

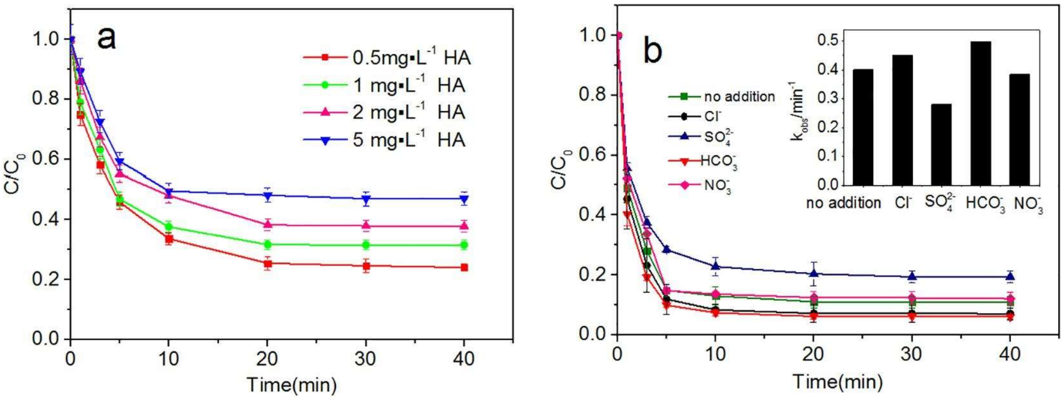


Figure 5: The effect of HA (a) and coexisting anions (b) on the degradation of NOR in the BC@nZVI/Ni/PS system([73]).

4. Conclusion and Prospect

The advanced oxidation technology of persulfate activated by nZVI has been widely used in the field of environmental remediation due to its strong oxidation and low selectivity. Sulfate radicals can maintain stable activity in acidic, neutral and alkaline environments. nZVI activated persulfate advanced oxidation technology is simple, has good degradation performance, is environmentally friendly and wide range of applications. Nano-zero-valent iron activated persulfate still have great potential for development in the future. Therefore, future research should focus on the following aspects :(1) Fe^{2+} is the key to activating persulfate, and how to effectively control the corrosion rate of nZVI and improve the utilization rate of Fe^{2+} should be considered in the future. (2) At present, the degradation effect of nano-zero-valent-iron activated persulfate on organic pollutants only focuses on the removal rate and degree of mineralization, and the degradation mechanism should be further discussed in the future. (3) Advanced oxidation technology based on persulfate can be further studied in combination with other oxidation technologies, which can improve the degradation rate and expand the degradation range of pollutants.

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