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\textsuperscript{0} corrodes to generate Fe\textsuperscript{2+}, and Fe\textsuperscript{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$_4^{•-}$) 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$_2$O$_8^{2−}$: 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$_4^{•−}$ (2.5-3.1V) is greater than that of •OH (1.8-2.7V), and the half-life of SO$_4^{•−}$ (4s) is thousands of times that of the hydroxyl radical (1μs). At the same time, SO$_4^{•−}$ can also make up for the limitation of •OH that cannot degrade some organic matter. Therefore, advanced oxidation technology based on SO$_4^{•−}$ 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$_4^{•−}$ 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$_4^{•−}$. During the activation process, the lost electrons of Fe$^{0}$ directly participate in the activation of persulfate to form SO$_4^{•−}$, 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.

\[
\begin{align*}
Fe^0 + 2S_2O_5^{2−} + 2e^- & \rightarrow Fe^{2+} + SO_4^{•} + 2SO_4^{2−} \\
SO_4^{•} + H_2O & \rightarrow SO_4^{2−} + •OH + H^+ \\
2Fe^0 + O_2 + 2H_2O & \rightarrow 2Fe^{2+} + 4OH^- \\
2Fe^0 + 2H_2O & \rightarrow Fe^{2+} + 2OH^- + H_2 \\
SO_4^{•} + OH^- & \rightarrow SO_4^{2−} + OH + H^+ \\
Fe^{2+} + SO_4^{2−} & \rightarrow SO_4^{2−} + Fe^{3+}
\end{align*}
\]

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$_2$O$_3$, Fe$_3$O$_4$ 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$_2$O$_8^{2•}$ (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.
2.2. Indirect Effect of Persulfate Activated by nZVI

Persulfate exists in the form of \( \text{S}_2\text{O}_8^{2-} \) and \( \text{HSO}_5^- \) 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\(_4^{2-}\)• quenching reaction, and improving the utilization rate of SO\(_4^{2-}\)•. (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\(_4^{2-}\)•. (Equation (11)) [55]. However, the reaction of SO\(_4^{2-}\)• with itself will produce S\(_2\)O\(_8^{2-}\) (Equation (10)), which realizes the regeneration of S\(_2\)O\(_8^{2-}\).

\[
\begin{align*}
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} & (8) \\
\text{Fe}^{0} + 2\text{Fe}^{3+} &\rightarrow 3\text{Fe}^{2+} & (9) \\
\text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{S}_2\text{O}_8^{2-} + \text{S}_2\text{O}_8^{2-} & (10) \\
\text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} &\rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} & (11)
\end{align*}
\]

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\(_4^{2-}\)• and SO\(_5^{2-}\)• (Equations (13)).

\[
\begin{align*}
\text{HSO}_5^- + \text{Fe}^{2+} &\rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{OH}^- & (12) \\
\text{HSO}_5^- + \text{Fe}^{3+} &\rightarrow \text{SO}_5^{2-} + \text{Fe}^{2+} + \text{H}^+ & (13)
\end{align*}
\]

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\(_4^{2-}\)• and •OH are involved in the degradation of organic pollutants. SO\(_4^{2-}\)• 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, SO₄• has a strong oxidizing ability and low selectivity to organic pollutants, so most pollutants can be degraded [60]. Similar to the mechanism of •OH, SO₄• degrades organic matter into H₂O, CO₂ 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 SO₄²⁻ (Equation (14)). SO₄• 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 (-NH₂), 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 (-NO₂) [61]. The presence of these electron-gaining groups will compete with the SO₄• for electrons. This is not conducive to the degradation of target pollutants [62].

\[
R \underset{\text{SO₄•}}{\longrightarrow} + SO₄²⁻ \rightarrow SO₄⁴⁻ + R \underset{\text{•OH}}{\longrightarrow}
\]

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 SO₄• 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 SO₄• jointly degrade p-nitrophenol. SO₄• 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 SO₄• 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 decarboxylation and chain scission (Equation (15)). Anipsitakis et al. [67] found that lipid compounds are prone to hydrogen extraction reactions.

\[
SO₄⁺RH→HSO₄+R
\]

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 SO₄• attack the TCE molecules together, so that the hydrogen atoms on TCE are taken away, then SO₄• and •OH are converted into HSO₄⁻ and H₂O. Ding et al. [69] prepared attapulgite-loaded nano-zero-valent iron composites to activate PMS to degrade quinclorac acid. Quinclorac acid contains -COOH and -Cl electrophilic groups, which is not conducive to sulfate radical attacking quinclorac acid through electron transfer. Studies have found that quinclorac 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 SO₄• 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]).

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:

$$\text{SO}_4^2- + \text{H}_2\text{C}=\text{CHR} \rightarrow \text{OSO}_2\text{OCH}-\text{CHR}$$

(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]).
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.

References

[1] Li Q, Chen ZS, Wang HH, Yang H, Wen T, Wang SQ, Hu BW, Wang XK, Removal of organic compounds by nanoscale zero-valent iron and its composites, Sci Total Environ 2021; 792: 148546. https://doi.org/10.1016/j.scitotenv.2021.148546.

[2] Zhu F, He SY, Shang ZF, Effect of vegetables and nano-particle hydroxyapatite on the remediation of cadmium and phosphatase activity in rhizosphere soil through immobilization, International Journal Of Phytoremediation 2019; 21: 610-616. https://doi.org/10.1080/15226514.2018.1546276.

[3] Qin Y, Xue CL, Yu HR, Wen YT, Zhang LN, Li Y, The construction of bio-inspired hierarchically porous graphene aerogel for efficiently organic pollutants adsorption, Journal Of Hazardous Materials 2021; 419: 126441. https://doi.org/10.1016/j.jhazmat.2021.126441.

[4] Fu LN, Li J, Wang GY, Luan YN, Dai W, Adsorption behavior of organic pollutants on microplastics, Ecotoxicology And Environmental Safety 2021; 217: 112207. https://doi.org/10.1016/j.ecoenv.2021.112207.

[5] Li BY, Wei DN, Li ZQ, Zhou YM, Li YJ, Huang CH, Long JM, Huang HL, Tie BQ, Lei M, Mechanistic insights into the enhanced removal of roxarsone and its metabolites by a sludge-based, biochar supported zerovalent iron nanocomposite: Adsorption and redox transformation, Journal Of Hazardous Materials 2020; 389: 122091.https://doi.org/10.1016/j.jhazmat.2020.122091.

[6] Rajeswari A., Christy E. Jackcina Stobel, Mary G. Ida Celine, Jayaraj K, Pius Anitha, Cellulose acetate based biopolymeric mixed matrix membranes with various nanoparticles for environmental remediation-A comparative study, Journal Of Environmental Chemical Engineering 2019; 7: 103278. https://doi.org/10.1016/j.jece.2019.103278.

[7] Chang XQ, Lin T, Chen W, Hu X, Tao H, Wu YH, Zhang QW, Yao SZ, A new perspective of membrane fouling control by ultraviolet synergic ferrous iron catalytic persulfate (UV/Fe(II)/PS) as pretreatment prior to ultrafiltration, Sci Total Environ 2020; 737: 139711.https://doi.org/10.1016/j.scitotenv.2020.139711.

[8] Zheng JT, Zhu CS, Jiang B, Uses of activated carbon fibers and advanced oxidation technologies in the remediation of water, New Carbon Materials 2015; 30: 519-532. https://doi.org/10.1016/j.ncm.2015.06.003.

[9] Ma S, Lee S, Kim K, Im J, Jeon H, Purification of organic pollutants in cationic thiazine and azo dye solutions using plasma-based advanced oxidation process via submerged multi-hole dielectric barrier discharge, Separation And Purification Technology 2021; 255: 117715. https://doi.org/10.1016/j.seppur.2020.117715.
Enhanced Mechanism of Nano Zero-Valent Iron Activated Persulfate  
Iribagiza et al.

[10] Behin J, Akbari A, Mahmoudi M, Khajeh M, Sodium hypochlorite as an alternative to hydrogen peroxide in Fenton process for industrial scale, Water Research 2017; 121: 120-128. https://doi.org/10.1016/j.watres.2017.05.015.

[11] Tan J, Li ZF, Li J, Wu JX, Yao XL, Zhang TT, Graphitic carbon nitride-based materials in activating persulfate for aqueous organic pollutants degradation: A review on materials design and mechanisms, Chemosphere 2021; 262: 127675. https://doi.org/10.1016/j.chemosphere.2020.127675.

[12] Zhou Z, Ma J, Liu XT, Lin CY, Sun K, Zhang Hj, Li XW, Fan GX, Activation of peroxysulfate by nanoscale zero-valent iron for sulfamethoxazole removal in agricultural soil: Effect, mechanism and ecotoxicity, Chemosphere 2019; 223: 196-203. https://doi.org/10.1016/j.chemosphere.2019.02.074.

[13] Wang SL, Wu JF, Lu XQ, Xu WX, Gong Q, Ding JQ, Dan BS, Xie PC, Removal of acetalaminophen in the Fe2+/persulfate system: Kinetic model and degradation pathways, Chemical Engineering Journal 2019; 358: 1091-1100. https://doi.org/10.1016/j.cej.2018.09.145.

[14] Ma J, Ding Y, Chi LP, Yang X, Zhong YJ, Wang Zh, Shi Q, Degradation of benzotriazole by sulfate radical-based advanced oxidation process, Environmental Technology 2021; 42: 238-247. https://doi.org/10.1080/09593330.2019.1625959.

[15] Liu YQ, He XX, Fu YS, Dionysiou DD, Kinetics and mechanism investigation on the destruction of oxytetracycline by UV-254 nm activation of persulfate, Journal of Hazardous Materials 2016; 305: 229-239. https://doi.org/10.1016/j.jhazmat.2015.11.043.

[16] Monteagudo JM, Duran A, Gonzalez R, Exposito AJ, In situ chemical oxidation of carbamazepine solutions using persulfate simultaneously activated by heat energy, UV light, Fe2+ ions, and H2O2, Appl. Catal. B-Environ. 2015; 176: 120-129. https://doi.org/10.1016/j.apcatb.2015.03.055.

[17] Liang CJ, Bruell Clifford J, Marley Michael C, Sperry Kenneth L, Persulfate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulfate-thiosulfate redox couple, Chemosphere 2004; 55: 1213-1223. https://doi.org/10.1016/j.chemosphere.2004.01.029.

[18] He DQ, Cheng Y, Zeng YF, Luo HW, Luo K, Li J, Pan XL, Barcelo D, Crittenden JC, Synergistic activation of peroxymonosulfate and persulfate by ferrous ion and molybdenum disulfide for pollutant degradation: Theoretical and experimental studies, Chemosphere 2020; 240: 124979. https://doi.org/10.1016/j.chemosphere.2019.124979.

[19] Waldemer RH, Tratnyek PG, Johnson RL, Nurmi JT, Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products, Water Environment Research 2015; 87: 656-659. https://doi.org/10.2175/106143015x14338845154986.

[20] He SY, Zhu F, Li LW, Ma SY, Shang ZF, Effect factors, kinetics and thermodynamics of remediation in the chromium contaminated soils by nanoscale zero valent Fe/Cu bimetallic particles, Chemical Engineering Journal 2016; 302: 663-669. https://doi.org/10.1016/j.cej.2016.05.072.

[21] He SY, Zhu F, Li LW, Ren WT, Box-Behnken design for the optimization of the removal of Cr(VI) in soil leachate using nZVI/Ni bimetallic particles, Soil & Sediment Contamination 2018; 27: 658-673. https://doi.org/10.1080/105320383.2018.1502744.

[22] Zhu F, Li LW, Ren WT, Deng QX, Liu T, Effect of pH, temperature, humic acid and coexisting anions on reduction of Cr(VI) in the soil leachate by nZVI/Ni bimetal material, Environmental Pollution 2017; 227: 444-450. https://doi.org/10.1016/j.envpol.2017.04.074.

[23] Shan A, Idrees A, Zaman WQ, Abbas Z, Ali M, Rehman MSU, Hussain S, Danish M, Gu XG, Lyu SG, Synthesis of nZVI-Ni@BC composite as a stable catalyst to activate persulfate: Trichloroethylene degradation and insight mechanism, Journal Of Environmental Chemical Engineering 2021; 9: 104808. https://doi.org/10.1016/j.jece.2020.104808.

[24] Yan JC, Han L, Gao WG, Xue S, Chen MF, Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene, Bioresource Technology 2015; 175: 269-274. https://doi.org/10.1016/j.biortech.2014.10.103.

[25] Ahmad A, Gu XG, Li L, Lv SG, Xu YS, Guo XH, Efficient degradation of trichloroethylene in water using persulfate activated by reduced graphene oxide-iron nanocomposite, Environ. Sci. Pollut. Res. 2015; 22: 17876-17885. https://doi.org/10.1007/s11356-015-5034-1.

[26] Hussain I, Li MY, Zhang YQ, Li YC, Huang SB, Du XD, Liu GQ, Hayat W, Anwar N, Insights into the mechanism of persulfate activation with nZVI/BC nanocomposite for the degradation of nonylphenol, Chemical Engineering Journal 2017; 311: 163-172. https://doi.org/10.1016/j.cej.2016.11.085.

[27] Huang JY, Yi SP, Zheng CM, Lo IMC, Persulfate activation by natural zeolite supported nanoscale zero-valent iron for trichloroethylene degradation in groundwater, Sci Total Environ 2019; 684: 351-359. https://doi.org/10.1016/j.scitotenv.2019.05.331.

[28] Gu MB, Sui Q, Farooq U, Zhang X, Qiu ZF, Lyu SG, Degradation of phenanthrene in sulfate radical based oxidative environment by nZVI-PDA functionalized rGO catalyst, Chemical Engineering Journal 2018; 354: 541-552. https://doi.org/10.1016/j.cej.2018.08.039.

[29] Chen XY, Wang WP, Xiao H, Hong CL, Zhu FX, Yao YL, Xue ZY, Accelerated TiO2 photocatalytic degradation of Acid Orange 7 under visible light mediated by peroxymonosulfate, Chemical Engineering Journal 2012; 193: 290-295. https://doi.org/10.1016/j.cej.2012.04.033.
Zhang YL, Su YM, Zhou XF, Dai CM, Keller Arturo A., A new insight on the core-shell structure of zerovalent iron nanoparticles and its effect on sludge characteristics and reaction mechanisms, Research on Chemical Intermediates 2018; 44: 5501-5519. https://doi.org/10.1007/s11164-018-3436-7.

Kang YG, Yoon H, Lee W, Kim EJ, Chang YS, Comparative study of peroxide oxidants activated by nZVI: Removal of 1,4-Dioxane and arsenic(III) in contaminated waters, Chemical Engineering Journal 2018; 334: 2511-2519. https://doi.org/10.1016/j.cej.2017.11.076.

Qu GZ, Chu RJ, Wang H, Wang TC, Zhang ZQ, Qiang H, Liang DL, Hu SB, Simultaneous removal of chromium(VI) and tetracycline hydrochloride from simulated wastewater by nanoscale zero-valent iron/copper-activated persulfate, Environmental Science And Pollution Research 2020; 27: 40826-40836. https://doi.org/10.1007/s11356-020-10120-8.

Wang QF, Rao PH, Li GH, Dong L, Zhang X, Shao YS, Gao NY, Chu WH, Xu B, An N, Deng J, Degradation of imidacloprid by UV-activated persulfate and peroxymonosulfate processes: Kinetics, impact of key factors and degradation pathway, Ecotoxicology And Environmental Safety 2020; 187: 109779. https://doi.org/10.1016/j.ecoenv.2019.109779.

Dhaka S, Kumar R, Lee SH, Kurade MB, Jeon BH, Degradation of ethyl paraben in aqueous medium using advanced oxidation processes: Efficiency evaluation of UV-C supported oxidants, Journal Of Cleaner Production 2018; 180: 505-513. https://doi.org/10.1016/j.jclepro.2018.01.197.

Fedorov K, Plata-Gryl M, Khan JA, Boczka J, Ultrasound-assisted heterogeneous activation of persulfate and peroxymonosulfate by asphaltene for the degradation of BTEX in water, Journal Of Hazardous Materials 2020; 397: 122804. https://doi.org/10.1016/j.jhazmat.2020.122804.

Wang ZH, Ai LY, Huang Y, Zhang JK, Li ST, Chen JW, Yang F, Degradation of azo dye with activated peroxygens: when zero-valent iron meets chloride, Rsc Advances 2017; 7: 30941-30948. https://doi.org/10.1039/c7ra03872k.

Kilic MY, Abdelraheem WH, He XX, Kestigolu K, Dionysiou DD, Photochemical treatment of tyrosol, a model phenolic compound present in olive mill wastewater, by hydroxyl and sulfate radical-based advanced oxidation processes (AOPs), Journal Of Hazardous Materials 2019; 367: 734-742. https://doi.org/10.1016/j.jhazmat.2018.06.062.

Rehman F, Sayed M, Khan JA, Shah NS, Khan HM, Dionysiou DD, Oxidative removal of brilliant green by UV/S2O82-, H2O2 and UV/H2O2 processes in aqueous media: A comparative study, Journal Of Hazardous Materials 2018; 357: 506-514. https://doi.org/10.1016/j.jhazmat.2018.06.012.

Zuo SY, Li DY, Xu HM, Xia DS, An integrated microwave-ultraviolet catalysis process of four peroxides for wastewater treatment: Free radical generation rate and mechanism, Chemical Engineering Journal 2020; 380: 122434. https://doi.org/10.1016/j.cej.2019.122434.

Yan JC, Qian LB, Gao WG, Chen Y, Ouyang D, Chen MF, Enhanced Fenton-like Degradation of Trichloroethylene by Hydrogen Peroxide Activated with Nanoscale Zero Valent Iron Loaded on Biochar, Scientific Reports 2017; 7: 43051. https://doi.org/10.1038/srep43051.

Liang CQ, Su HW, Identification of Sulfate and Hydroxyl Radicals in Thermally Activated Persulfate, Industrial & Engineering Chemistry Research 2009; 48: 5558-5562. https://doi.org/10.1021/ie9002848.

Dong HR, Wang B, Li L, Wang YY, Ning Q, Tian R, Li R, Chen J, Xie QQ, Activation of persulfate and hydrogen peroxide by using sulfide-modified nanoscale zero-valent iron for oxidative degradation of sulfamethazine: A comparative study, Separation And Purification Technology 2019; 218: 113-119. https://doi.org/10.1016/j.seppur.2019.02.052.

Wang W, Li SL, Lei H, Pan BC, Zhang WX, Enhanced separation of nanoscale zero-valent iron (nZVI) using polyacrylamide: Performance, characterization and implication, Chemical Engineering Journal 2015; 260: 616-622. https://doi.org/10.1016/j.cej.2014.09.042.

Zhu F, He SY, Liu T, Effect of pH, temperature and co-existing anions on the Removal of Cr(VII) in groundwater by green synthesized nZVI, Ecotoxicology And Environmental Safety 2018; 163: 544-550. https://doi.org/10.1016/j.ecoenv.2018.07.082.

Zhu F, Liu T, Zhang ZC, Liang WJ, Remediation of hexavalent chromium in column by green synthesized nanoscale zero-valent iron/nickel: Factors, migration model and numerical simulation, Ecotoxicology And Environmental Safety 2021; 207: 111572. https://doi.org/10.1016/j.ecoenv.2020.111572.

Kim C, Ahn JY, Kim TY, Shin WS, Hwang I, Activation of Persulfate by Nanosized Zero-Valent Iron (NZVI): Mechanisms and Transformation Products of NZVI, Environmental Science & Technology 2018; 52: 3625-3633. https://doi.org/10.1021/acs.est.7b05847.

Wu LB, Lin QT, Fu HY, Luo HY, Zhong QF, Li JQ, Chen YJ, Role of sulfide-modified nanoscale zero-valent iron on carbon nanotubes in nonradical activation of peroxysulfate, Journal Of Hazardous Materials 2022; 422: 126949. https://doi.org/10.1016/j.jhazmat.2021.126949.

Li H, Song L, Han BH, Song HW, Improved sludge dewaterability using persulfate activated by humic acid supported nanoscale zero-valent iron: effect on sludge characteristics and reaction mechanisms, Environmental Science-Water Research & Technology 2018; 4: 1480-1488. https://doi.org/10.1039/c8ew00379c.

Zhang YL, Su YM, Zhou XF, Dai CM, Keller Arturo A., A new insight on the core-shell structure of zerovalent iron nanoparticles and its application for Pb(II) sequestration, Journal Of Hazardous Materials 2013; 263: 685-693. https://doi.org/10.1016/j.jhazmat.2013.10.031.
Enhanced Mechanism of Nano Zero-Valent Iron Activated Persulfate: Inhibiting Wastewater Pollution

[55] Lin CC, Chen YH, Feasibility of using nanoscale zero-valent iron and persulfate to degrade sulfamethazine in aqueous solutions, Separation And Purification Technology 2018; 194: 388-395. https://doi.org/10.1016/j.seppur.2017.10.073.

[56] Rodriguez-Chueca J, Guerra-Rodriguez S, Raiz JM, Lopez-Munoz MJ, Rodriguez E, Assessment of different iron species as activators of S2O8 2− and HO2− for inactivation of wild bacteria strains, Applied Catalysis B-Environmental 2019; 248: 54-61. https://doi.org/10.1016/j.apcatb.2019.02.003.

[57] Li LX, Zhang SS, Lu B, Zhu F, Cheng J, Sun ZH, Nitrobenzene reduction using nanoscale zero-valent iron supported by polystyrene microspheres with different surface functional groups, Environmental Science And Pollution Research 2018; 25: 7916-7923. https://doi.org/10.1007/s11356-017-0854-9.

[58] Wu JX, Wang B, Blaney L, Peng GL, Chen P, Cui YZ, Deng SB, Wang YJ, Huang J, Yu G, Degradation of sulfamethazine by persulfate activated with organo-montmorillonite supported nano-zero valent iron, Chemical Engineering Journal 2019; 361: 99-108. https://doi.org/10.1016/j.cej.2018.12.024.

[59] Zhang TT, Yang YL, Gao JF, Li X, Yu HK, Wang N, Du P, Yu R, Li H, Fan XY, Zhou ZW, Synergistic degradation of chloramphenicol by ultrasound-enhanced nanoscale zero-valent iron/persulfate treatment, Separation And Purification Technology 2020; 240: 116575. https://doi.org/10.1016/j.seppur.2020.116575.

[60] Han WL, Dong LY, Activation Methods of Advanced Oxidation Processes Based on Sulfate Radical and Their Applications in The Degradation of Organic Pollutants, Progress In Chemistry 2021; 33: 1426-1439. https://doi.org/10.7536/pc200771.

[61] Xia SQ, Gu ZL, Zhang ZQ, Zhang J, Hermanowicz SW, Removal of chloramphenicol from aqueous solution by nanoscale zero-valent iron particles, Chemical Engineering Journal 2014; 257: 98-104. https://doi.org/10.1016/j.cej.2014.06.106.

[62] Luo S, Wei ZS, Spinney R, Villamena FA, Dionysiou DD, Chen D, Tang CJ, Chai LY, Xiao RY, Quantitative structure-activity relationships for reactivities of sulfate and hydroxyl radicals with aromatic contaminants through single-electron transfer pathway, Journal Of Hazardous Materials 2018; 344: 1165-1173. https://doi.org/10.1016/j.jhazmat.2017.09.024.

[63] Ma B, Wang YY, Tong XL, Guo XN, Zheng ZF, Guo XY, Graphene-supported CoS2 particles: an efficient photocatalyst for selective hydrogenation of nitroaromatics in visible light, Catalysis Science & Technology 2017; 7: 2805-2812. https://doi.org/10.1039/c7cy00356k.

[64] Zhang DJ, Li Y, Sun AW, Tong SQ, Jiang XB, Mu Y, Li JS, Han WQ, Sun XY, Wang LJ, Shen JY, Optimization ofS/Fe ratio for enhanced nitrobenzene biological removal in anaerobic System amended with Sulfide-modified nanoscale zerovalent iron, Chemosphere 2020; 247: 125832. https://doi.org/10.1016/j.chemosphere.2020.125832.

[65] Wang B, Zhu C, Ai D, Fan ZP, Activation of persulfate by green nano-zero-valent iron-loaded biochar for the removal of p-nitrophenol: Performance, mechanism and variables effects, Journal Of Hazardous Materials 2021; 417: 126106. https://doi.org/10.1016/j.jhazmat.2021.126106.

[66] Du JK, Wang Y, Faheem, Xu TT, Zheng H, Bao JG, Synergistic degradation of PNP via coupling H2O2 with persulfate catalyzed by nano zero valent iron, Rsc Advances 2019; 9: 20323-20331. https://doi.org/10.1039/c9ra02901j.

[67] Anipsitakis, George P, Dionysiou, Dionysios D, Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt, Environmental science & technology 2003; 37: 4790-7. https://doi.org/10.1021/es0263792.

[68] Dong HR, Hou KJ, Qiao WW, Cheng YJ, Zhang LH, Wang B, Li L, Wang YY, Ning Q, Zeng GM, Insights into enhanced removal of TCE utilizing sulfide-modified nanoscale zero-valent iron activated persulfate, Chemical Engineering Journal 2019; 359: 1046-1055. https://doi.org/10.1016/j.cej.2018.11.080.

[69] Ding CX, Xiao SJ, Lin YJ, Yu P, Zhong ME, Yang LH, Wang H, Su L, Liao CJ, Zhou YY, Deng YC, Gong DX, Attapulgite-supported nano-Fe0/peroxymonsulfate for quinclorac removal: Performance, mechanism and degradation pathway, Chemical Engineering Journal 2019; 360: 104-114. https://doi.org/10.1016/j.cej.2018.11.189.

[70] Wu SH, He HJ, Li X, Yang CP, Zeng GM, Wu B, He SY, Lu L, Insights into atrazine degradation by persulfate activation using composite of nanoscale zero-valent iron and graphene: Performances and mechanisms, Chemical Engineering Journal 2018; 341: 126-136. https://doi.org/10.1016/j.cej.2018.01.136.

[71] Li HH, Zhu F, He SY, The degradation of decabromodiphenyl ether in the e-waste site by biochar supported nanoscale zero-valent iron/persulfate, Ecotoxicology And Environmental Safety 2019; 183: 109540. https://doi.org/10.1016/j.ecoenv.2019.109540.

[72] Huang KC, Zhao ZQ, Hoag GE, Dahmani A, Block PA, Degradation of volatile organic compounds with thermally activated persulfate oxidation, Chemosphere 2005; 61: 551-560. https://doi.org/10.1016/j.chemosphere.2005.02.032.

[73] Zhu F, Wu YY, Liang YK, Li HH, Liang WJ, Degradation mechanism of norfloxacin in water using persulfate activated by BC@nZVI/Ni, Chemical Engineering Journal 2020; 389: 124276. https://doi.org/10.1016/j.cej.2020.124276.