A Review of Activation Persulfate by Iron-Based Catalysts for Degrading Wastewater

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Abstract: Advanced oxidation technology of persulfate is a new method to degrade wastewater. As the economy progresses and technology develops, increasingly more pollutants produced by the paper industry, printing and dyeing, and the chemical industry are discharged into water, causing irreversible damage to water. Methods and research directions of activation persulfate for wastewater degradation by a variety of iron-based catalysts are reviewed. This review describes the merits and demerits of advanced oxidation techniques for activated persulfate by iron-based catalysts. In order to promote the development of related research work, the problems existing in the current application are analyzed.

Keywords: iron-based catalysts; activation persulfate; degrading wastewater

1. Introduction

With people’s yearning for a better life, increasingly more new materials are used in the petrochemical, medical, and pharmaceutical industries. As a result, huge amounts of organic pollutants are produced [1–3]. Advanced oxidation processes (AOPs) can generate a variety of free radical ions, which can gradually decompose large organic matter into small organic matter until mineralization occurs. At present, advanced oxidation methods include Fenton oxidation [4–6], ozone oxidation [7,8], photolysis [9–11], photocatalysis [12,13], and ferrate (VI) catalytic oxidation [14–16], etc. It is worth mentioning that advanced oxidation technology (sulfate radical-based AOPs, SR-AOPs) based on persulfate (PS) that can produce sulfate radical ion (SO\textsuperscript{4}–) is also attracting increasing attention [17,18].

In recent years, sulfonamides antibiotics (SAs) have been widely detected in urban and agricultural wastewater and its receiving water in many regions of the world [19], and it is estimated that about 12 t of sulfamethoxazole (SMX) is discharged into the South China Sea via the Mekong River every year [20]. When it enters the water body, it affects the survival and growth of the microbial community and microfauna, and even induces antibiotic resistance, which will eventually destroy the virtuous cycle of the entire ecosystem [21]. SR-AOPs have shown a great result in this regard [22,23]. This technology not only has a good effect in the treatment of antibiotic wastewater, but also shows excellent performance in the treatment of oilfield wastewater [24].

Common persulfates include peroxymonosulfate (peroxymonosulfate, PMS) and peroxodisulfate (peroxodisulfate, PDS). Owing to the high redox potential (2.5–3.1 V) [25] of the sulfate radical ion, it can effectively oxidize organic pollutants into H\textsubscript{2}O and CO\textsubscript{2} as a powerful oxidant. It can also be applied over a wide range of pH, from 3 to 8 [22,26,27]. Although PS is a strong oxidant, without the action of catalyst the number of collisions with organic pollutants is reduced, which greatly reduces the effect of the chemical agent [28].
Iron is a transition metal, less toxic than copper and manganese. At present, there are many reports about the application of various [29] iron-based catalysts such as CuFe$_2$O$_4$ [30–32] in the activation of persulfate [33–35]. In this paper, the role of various iron-based catalysts in the activation of persulfate is reviewed. Then, we introduce the advanced oxidation technology of persulfate, as well as the current problems and development prospects, so as to promote the sustainable development of this technology.

2. Activation Persulfate by Various Iron-Based Catalysts

2.1. MeFe$_2$O$_4$ (Me = Cu, Co, Zn, etc.)

In terms of activation mechanism, transition metal compounds react with PS to produce a large amount of ·SO$_4$$^-$; the reaction equation follows:

\[ M^{n+} + S_2O_8^{2-} \rightarrow M^{(n+1)+} + \cdot SO_4^- + SO_4^{2-} \]  \hspace{1cm} (1)

As can be seen from the above reaction, metal ions are in a free state dispersed in the solution during the reaction process. Although the wastewater can be degraded by the activation persulfate mechanism, it belongs to homogeneous catalysis; metal ions will be dissolved in the aqueous solution, which causes difficult separation from solution. Therefore, the production cost is greatly increased due to its difficult recycling nature, and it is easy to cause secondary pollution to the environment. Therefore, MeFe$_2$O$_4$ with a low metal leaching rate has become a new research direction. Through PS/PMS [36] heterogeneous catalytic technology, these problems can be effectively solved [22,37,38].

At present, there are several common methods for preparing iron-based catalysts: hydrothermal, solvothermal, sol–gel preparation, and coprecipitation methods.

In the hydrothermal method, the solute is dispersed into the solution, stirred, and heated in the reactor, and finally washed and dried to obtain the required product [39].

Similar to the hydrothermal method, the solvothermal method changes water into an organic solvent. By dissolving one or more precursors in a nonaqueous solvent, the reaction occurs in liquid phase or supercritical conditions [40].

The sol–gel method is to dissolve the metal alkoxides in organic solvents, form homogeneous solutions, add other components, react at a certain temperature to form gels, and finally make products by drying [41].

Coprecipitation is an important method to prepare composite oxide ultrafine powder containing a large variety of metal elements [42].

The electron transfer between transition metal oxides is much higher [43] than that between single transition metal oxides. Generally, AB$_2$O$_4$ [44,45] structure is referred to as spinel structure. CuFe$_2$O$_4$ is a typical spinel ferrite with a magnetic structure, which has high chemical stability and low metal leaching rate. Taking CuFe$_2$O$_4$ as an example, compared with single transition metal oxides, Fe and Cu elements can play a role in the reaction; respectively, they can also activate PS to produce ·OH and ·SO$_4$$^-$. G. Xian et al. [46] comprehensively compared the catalytic degradation effects of CoFe$_2$O$_4$, CuFe$_2$O$_4$, MnFe$_2$O$_4$, and ZnFe$_2$O$_4$. In detail, CuFe$_2$O$_4$ presented the best and fastest catalytic performance in organics removal. Almost 87.6% azo dye acid orange 7 (AO7) was removed in PS solution coupled with CuFe$_2$O$_4$ [46]. Additionally, it was known that CuFe$_2$O$_4$ had the best catalytic effect. Moreover, through the quenching experiment, it was not ·OH but ·SO$_4$$^-$ that played a major role in the reaction.

Table 1 shows the degradation effects of some different MeFe$_2$O$_4$-activated PS/PMS on different kinds of wastewater. It can be seen from the table that the iron-based catalyst with spinel structure mainly acts on ·SO$_4$$^-$ in the mechanism of activation persulfate; the effect of ·OH is slightly worse [47]. Of course, there are also some nonfree radical pathways, which degrade pollutants in water by generating singlet oxygen $^1$O$_2$ [48–50].
Table 1. Effect of Different MoFe$_2$O$_4$-activated PMS on degradation of different wastewater [39–42,47,51–53].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pollution</th>
<th>Main Mechanism</th>
<th>Pollutant Concentration</th>
<th>Catalyst Concentration</th>
<th>Oxidant</th>
<th>Oxidation Concentration</th>
<th>T/min</th>
<th>Degradation Rate/%</th>
<th>Number of Cycles</th>
<th>Synthesis Techniques</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbFe$_2$O$_4$</td>
<td>Thionine</td>
<td>$^{1}$O$_2$</td>
<td>10 µM</td>
<td>0.4 g/L</td>
<td>PMS</td>
<td>400 µM</td>
<td>20</td>
<td>100</td>
<td>Not mentioned</td>
<td>Solution combustion</td>
<td>[51]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$-loaded quartz sand</td>
<td>Sulfachloropyridazine sodium</td>
<td>-SO$_4^-$OH</td>
<td>2 g/L</td>
<td>10 g</td>
<td>PMS</td>
<td>75 mg/L</td>
<td>150</td>
<td>90</td>
<td>Not mentioned</td>
<td>Citrate combustion</td>
<td>[52]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$-SAC</td>
<td>Norfloxacin (NOF)</td>
<td>-SO$_4^-$OH</td>
<td>10 mg/L</td>
<td>0.1 g/L</td>
<td>PMS</td>
<td>0.15 g/L</td>
<td>120</td>
<td>TOC reduction 81</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
<td>[47]</td>
</tr>
<tr>
<td>The biochar loaded with CoFe$_2$O$_4$ nanoparticles</td>
<td>Bisphenol A (BPA)</td>
<td>-SO$_4^-$OH</td>
<td>10 mg/L</td>
<td>0.05 g/L</td>
<td>PMS</td>
<td>0.5 g/L</td>
<td>8</td>
<td>93</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
<td>[39]</td>
</tr>
<tr>
<td>C$_3$N$_4$@MnFe$_2$O$_4$-graphene</td>
<td>Metronidazole</td>
<td>-SO$_4^-$OH</td>
<td>20 mg/L</td>
<td>1.0 g/L</td>
<td>PS</td>
<td>0.01 M</td>
<td>90</td>
<td>94.5</td>
<td>TOC reduction 81</td>
<td>Solvothermal</td>
<td>[40]</td>
</tr>
<tr>
<td>Zr$<em>{0.18}$Cu$</em>{0.82}$Fe$_2$O$_4$</td>
<td>Atrazine</td>
<td>-SO$_4^-$</td>
<td>4.4 µM</td>
<td>200 mg/L</td>
<td>PS</td>
<td>0.5 mM</td>
<td>30</td>
<td>95</td>
<td>Not mentioned</td>
<td>Sol-gel</td>
<td>[41]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$/O$_3$</td>
<td>Dichlorophenoxycetic acid (2,4-D)</td>
<td>Not mentioned</td>
<td>20 mg/L</td>
<td>0.20 g/L</td>
<td>PMS</td>
<td>O$_3$</td>
<td>16.0 mg/L</td>
<td>40</td>
<td>88.9</td>
<td>Coprecipitation</td>
<td>[42]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>Atrazine (ATZ)</td>
<td>-SO$_4^-$</td>
<td>10 mg/L</td>
<td>0.4 g/L</td>
<td>PMS</td>
<td>0.8 mM</td>
<td>30</td>
<td>&gt;99</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
<td>[53]</td>
</tr>
</tbody>
</table>
2.2. MeFe$_2$O$_4$ Combined with the Carrier

As mentioned above, the carrier recombination method can increase the specific surface area and increase the contact of chemical sites [54], thus greatly improving the rate of chemical reaction. At present, SiO$_2$ [54,55], black phosphorus [56,57], and rGO [58,59] (reduced graphene oxide) are commonly used as carriers. After compositing with the carrier, it is closely combined with the carrier by van der Waals force [58] or electrostatic interaction [60], making it difficult to fall off the surface of the carrier.

Pure graphene is a benzene-ring-like two-dimensional nanomaterial consisting of sp$^2$ hybrid orbitals. However, its high production cost limits its large-scale application. Afterward, by improving Hummer’s method, a large number of oxygen-containing functional groups were linked at the edge of the plane by a strong oxidant, hence the name GO (graphene oxide) (Figure 1); rGO (Figure 2) was obtained by sodium borohydride and other means of reduction, which has low synthesis cost and is suitable for use as a good carrier of catalysis.

![Figure 1. Plane structure (left) and solid structure (right) of GO (bond line type).](image1.png)

![Figure 2. Plane structure (left) and solid structure (right) of rGO (bond line type).](image2.png)

Taking CuFe$_2$O$_4$, a representative of MeFe$_2$O$_4$, as an example, by comparing the effect of pure CuFe$_2$O$_4$ with that of CuFe$_2$O$_4$ combined with the carrier, it can be seen that the latter has a stronger catalytic effect under acidic and photoinduced conditions [61]. CuFe$_2$O$_4$ in CuFe$_2$O$_4$–rGO is closely combined with the oxygen-containing groups on rGO through electrostatic interaction, as shown in Figure 3. Images from a scanning electron microscope are shown in Figure 4.

Table 2 shows the degradation effects of some CuFe$_2$O$_4$ and rGO composite materials on different kinds of wastewater. It can be seen from the table that the composite catalyst can still produce good effects even without the presence of PS. Not only the Cu, Fe, and other elements in the catalyst can produce pure chemical catalytic effect, but the carrier rGO can produce electron transition under the light condition, promoting the transfer of electrons, and plays a part of the photocatalytic effect [62,63]. Table 2 contains some other carriers, which can also greatly influence degradation of different kinds of wastewater.
Table 2. Effects of partial MeFe$_2$O$_4$ and carrier composite materials on degradation of different kinds of wastewater [61,64–70].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pollution</th>
<th>Main Mechanism</th>
<th>Pollutant Concentration</th>
<th>Catalyst Concentration</th>
<th>Oxidant</th>
<th>Oxidation Concentration</th>
<th>T/min</th>
<th>Degradation Rate (%)</th>
<th>Number of Cycles</th>
<th>Synthesis Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$-20%rGO</td>
<td>Methylparaben</td>
<td>SO$_4^-$ -OH</td>
<td>10 mg/L</td>
<td>0.2 mg/L</td>
<td>PS</td>
<td>5 mM</td>
<td>120</td>
<td>96</td>
<td>Not mentioned</td>
<td>Sol-gel [64]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$-1% (w/w) rGO</td>
<td>Phenol</td>
<td>-OH</td>
<td>20 ppm</td>
<td>5 mL</td>
<td>30% H$_2$O$_2$</td>
<td>6 mg/L</td>
<td>240</td>
<td>100</td>
<td>Not mentioned</td>
<td>Coprecipitation [61]</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$/g-C$_3$N$_4$</td>
<td>Propranolol</td>
<td>SO$_4^-$</td>
<td>0.02 mM</td>
<td>1 g/L</td>
<td>PS</td>
<td>1 mM</td>
<td>120</td>
<td>82.2</td>
<td>Not mentioned</td>
<td>Sol-gel [65]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/CCNF</td>
<td>Dimethyl phthalate</td>
<td>SO$_4^-$</td>
<td>0.05 mM</td>
<td>0.5 g/L</td>
<td>PMS</td>
<td>1.5 mM</td>
<td>60</td>
<td>&gt;90</td>
<td>5 (&gt;90%)</td>
<td>Sol-gel [66]</td>
</tr>
<tr>
<td>TiO$_2$@CuFe$_2$O$_4$/UV</td>
<td>2,4-D</td>
<td>SO$_4^-$</td>
<td>20 mg/L</td>
<td>0.1 g/L</td>
<td>PMS</td>
<td>0.3 mM</td>
<td>60</td>
<td>97.2</td>
<td>5 (&gt;90%)</td>
<td>Sol-gel [67]</td>
</tr>
<tr>
<td>ZnS-ZnFe$_2$O$_4$</td>
<td>Rhodamine B</td>
<td>SO$_4^-$</td>
<td>20 mg/L</td>
<td>20 mg</td>
<td>PS</td>
<td>5 mg</td>
<td>90</td>
<td>97.67</td>
<td>3 (&gt;95%)</td>
<td>Hydrothermal [68]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@CoFe$_2$O$_4$</td>
<td>NOF</td>
<td>SO$_4^-$ -OH</td>
<td>15 µM</td>
<td>0.3 g/L</td>
<td>PMS</td>
<td>0.4 mM</td>
<td>25</td>
<td>89.8</td>
<td>4 (90%)</td>
<td>Hydrothermal [69]</td>
</tr>
<tr>
<td>Nitrogen and sulfur codoped CNTs-COOH loaded CuFe$_2$O$_4$</td>
<td>Phenylbenzimidazole-5-sulfonic acid</td>
<td>SO$_4^-$</td>
<td>5 mg/L</td>
<td>50 mg/L</td>
<td>PMS</td>
<td>1:100 (molar ratio)</td>
<td>40</td>
<td>98</td>
<td>5 (&gt;95%)</td>
<td>Coprecipitation [70]</td>
</tr>
</tbody>
</table>

@: the composite of two materials.
2.3. Activation Persulfate by Fe$^0$

In recent years, activation persulfate based on Fe$^0$ (zero-valent iron, ZVI) have been widely used in chemical production and environmental remediation [71,72]. As mentioned above, the activation persulfate/Fe (II) mechanism can cause secondary pollution to water, so ZVI/PS [73,74] is used instead to reduce a series of problems caused by the reduction of Fe$^{2+}$ content due to the change of pH and other factors in water [71].

ZVI/PS system has strong reducibility (Fe$^0$, $E^0_0$ = −0.44 V) [75]. Compared with CuFe$_2$O$_4$, its reaction process is more complex, as shown in Figure 5. Fe$^0$ is first converted to Fe$^{2+}$ in the presence of acid and oxidant, then further oxidized to Fe$^{3+}$ by Fe$^{2+}$, and finally to Fe(IV) [76,77]. The reaction mechanism follows [78]: According to the reaction equation, the reaction is easily affected by pH, and the reaction will gradually slow with the increase of pH. Weng et al. [79] point out that the Fe$^0$/PS system exhibits two-stage kinetics. The kinetic first stage is mostly attributed to a heterogeneous reaction occurring on the surface of the Fe$^0$ aggregate. As the reaction proceeds, decolorization shifts from the slow kinetic first stage to the fast kinetic second stage when sufficient Fe$^{2+}$ ions are maintained in the system [80].

$$\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad (2)$$

$$2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^- \quad (3)$$

$$\text{Fe}^0 + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} \quad (4)$$

$$\text{Fe}^0 + \text{HSO}_5^- \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + \text{OH}^- \quad (5)$$
Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + \cdot SO_4^- \quad (6)

Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{2-} + \cdot SO_4^- \quad (7)

Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^- + SO_4^{2-} \quad (8)

Fe^0 + 2 HSO_5^- \rightarrow Fe^{2+} + 2OH^- + 2SO_4^- \quad (9)

Fe^{2+} + S_2O_8^{2-} + H_2O \rightarrow Fe^{IV}O_2^+ + 2SO_4^{2-} + 2H^+ \quad (10)

Fe^{2+} + HSO_5^- \rightarrow Fe^{IV}O_2^+ + SO_4^{2-} + H^+ \quad (11)

Figure 5. Schematic of the formation of \cdot SO_4^- and Fe(IV) in nZVI/persulfate systems containing methyl phenyl sulfoxide [81].

Figure 6 shows the proposed degradation pathway of 2,4-D [82]. By examining Figure 6, it can further confirm that macromolecular organic matter is decomposed into small molecular organic matter, which is gradually mineralized.

Table 3 shows the degradation effects of various types of polluted water bodies activated by PS/PMS based on elemental iron. Usually, an appropriate amount of H_2O_2 [83] will be added to the water when PS is activated by Fe^0, so as to reduce the cost of oxidant. Through the analysis of the table, it can be seen that the effect of ZVI when used alone [84] is worse than when it is combined with the carrier or when other conditions exist.
Table 3. Degradation effect of different kinds of wastewater based on PS/PMS activated by different kinds of iron [85–92].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pollutant</th>
<th>Main Mechanism</th>
<th>Pollutant Concentration</th>
<th>Catalyst Concentration</th>
<th>Oxidant</th>
<th>Oxidation Concentration</th>
<th>T/min</th>
<th>Degradation Rate %</th>
<th>Number of Cycles</th>
<th>Synthesis Techniques</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>nZVI</td>
<td>Sulfamethazine</td>
<td>·OH ·SO₄⁻ ·SO₄⁻</td>
<td>50 mg/L</td>
<td>2 mM</td>
<td>PS</td>
<td>1 mM</td>
<td>30</td>
<td>96</td>
<td>Not mentioned</td>
<td>Sol-gel [88]</td>
<td></td>
</tr>
<tr>
<td>CN-Fe</td>
<td>Sulfamethazine</td>
<td>·OH ·SO₄⁻ ·1O₂⁻</td>
<td>50 µM</td>
<td>0.5 g/L</td>
<td>PMS</td>
<td>1 mM</td>
<td>15</td>
<td>82</td>
<td>Not mentioned</td>
<td>Carbothermal [87]</td>
<td></td>
</tr>
<tr>
<td>Carbon-coated nZVI</td>
<td>4-chlorophenol</td>
<td>·SO₄⁻ ·1O₂⁻ ·SO₄⁻</td>
<td>150 µM</td>
<td>0.25 g/L</td>
<td>PMS</td>
<td>1 mM</td>
<td>120</td>
<td>96</td>
<td>Not mentioned</td>
<td>Commercially available [86]</td>
<td></td>
</tr>
<tr>
<td>US-nZVI</td>
<td>Chloramphenicol</td>
<td>·SO₄⁻ ·1O₂⁻ ·OH</td>
<td>5 mg/L</td>
<td>0.5 g/L</td>
<td>PMS</td>
<td>1 mM</td>
<td>90</td>
<td>98.1</td>
<td>Not mentioned</td>
<td>Liquid phase reduction [85]</td>
<td></td>
</tr>
<tr>
<td>Feₐ@Fe₃O₄</td>
<td>Dibutyl phthalate</td>
<td>·OH ·SO₄⁻ ·OH</td>
<td>18 µM</td>
<td>0.5 g L⁻¹</td>
<td>PS</td>
<td>1.8 mM</td>
<td>180</td>
<td>94.7</td>
<td>(&gt;68%)</td>
<td>Calcination [89]</td>
<td></td>
</tr>
<tr>
<td>Feₐ@Fe₃O₄</td>
<td>Atrazine</td>
<td>·OH ·SO₄⁻ ·SO₄⁻</td>
<td>500 µg/L</td>
<td>25 mg/L</td>
<td>PMS</td>
<td>1 mM</td>
<td>2</td>
<td>100</td>
<td>Not mentioned</td>
<td>Reduction [90]</td>
<td></td>
</tr>
<tr>
<td>Fo@C</td>
<td>Bisphenol S</td>
<td>·OH ·SO₄⁻ ·SO₄⁻</td>
<td>5 mg/L</td>
<td>0.5 g/L</td>
<td>PMS</td>
<td>1.0 mM</td>
<td>60</td>
<td>92.8</td>
<td>Not mentioned</td>
<td>Resin carbonization [91]</td>
<td></td>
</tr>
<tr>
<td>Fe@C/PB</td>
<td>2,4-Dichlorophenol</td>
<td>·OH ·SO₄⁻ ·SO₄⁻</td>
<td>20 mg/L</td>
<td>0.6 g/L</td>
<td>PMS</td>
<td>2.0 g/L</td>
<td>50</td>
<td>99.4</td>
<td>Not mentioned</td>
<td>Calcination [92]</td>
<td></td>
</tr>
</tbody>
</table>

®: the composite of two materials.
2.4. Fe$_3$O$_4$

Fe$_3$O$_4$ magnetite, also known as magnetic iron oxide, is a black crystal with a rotating spinel structure (Figure 7). In magnetite, Fe$^{2+}$ and Fe$^{3+}$ are disordered on the ferrite octahedron, so electrons can transfer rapidly between Fe$^{2+}$ and Fe$^{3+}$; thus, reversible redox reactions can occur at the same position on the octahedron.

![Figure 7. Crystal structure of Fe$_3$O$_4$.](image)

However, since Fe$_3$O$_4$ is easy to accumulate in solution and contact sites are reduced after agglomeration, single Fe$_3$O$_4$ is rarely used. Using the composite carrier method [93] can not only solve these problems, but also speeds the reaction rate, making it more cost effective when applied in industrial production. He et al. [94] pointed out that the Fe$_3$O$_4$/GO/Ag composite microspheres are formed using magnetic Fe$_3$O$_4$ as cores, followed by coating an internal layer of GO and an outer layer of Ag nanoparticles, as Figure 8 shows. The synthesized Fe$_3$O$_4$/GO/Ag composite catalyst under the action of NaBH$_4$, methylene blue, and ciprofloxacin can be completely degraded within 12 min. Figure 8 shows SEM images of Fe$_3$O$_4$/GO/Ag composite catalyst. In Figure 9, we can clearly observe that Ag has been completely attached to the Fe$_3$O$_4$/GO surface, which can increase the specific surface area and improve the chemical reaction rate.

Table 4 shows the research progress of Fe$_3$O$_4$ and its composite materials on the degradation of different pollutants reported at present. According to the data in the table, when Fe$_3$O$_4$ is compounded with the carrier, the catalytic performance is greatly improved.

![Figure 8. Illustration of the fabrication of Fe$_3$O$_4$/GO/Ag composite microspheres.](image)
Table 4. Effects of Fe\textsubscript{3}O\textsubscript{4} and its composite-material-activated PS/PMS on degradation of different kinds of wastewater [95–101].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pollution</th>
<th>Main Mechanism</th>
<th>Pollutant Concentration</th>
<th>Catalyst Concentration</th>
<th>Oxidant</th>
<th>Oxidation Concentration</th>
<th>T/min</th>
<th>Degradation Rate /%</th>
<th>Number of Cycles</th>
<th>Synthesis Techniques</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>BPA</td>
<td>(\text{SO}_4^-\cdot\text{OH})</td>
<td>20 mg/L</td>
<td>2.0 g/L</td>
<td>PMS</td>
<td>5 mM</td>
<td>30</td>
<td>27.53</td>
<td>Not mentioned</td>
<td>Commercially available [95]</td>
<td></td>
</tr>
<tr>
<td>CuO-Fe\textsubscript{3}O\textsubscript{4}-BC</td>
<td>BPA</td>
<td>(\text{SO}_4^-\cdot\text{OH})</td>
<td>20 mg/L</td>
<td>2.0 g/L</td>
<td>PMS</td>
<td>5 mM</td>
<td>30</td>
<td>100 (˃85%)</td>
<td>4</td>
<td>Coprecipitation [96]</td>
<td></td>
</tr>
<tr>
<td>rGO-Fe\textsubscript{3}O\textsubscript{4}</td>
<td>NOF</td>
<td>(\text{SO}_4^-\cdot\text{OH})</td>
<td>20 mg/L</td>
<td>0.5 g/L</td>
<td>PS</td>
<td>1 g/L</td>
<td>30</td>
<td>89.69</td>
<td>Not mentioned</td>
<td>Coprecipitation [96]</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>Sulfamonomethoxine</td>
<td>(\text{SO}_4^-)</td>
<td>0.06 mM</td>
<td>2.4 mM</td>
<td>PS</td>
<td>1.2 mM</td>
<td>15</td>
<td>100</td>
<td>Not mentioned</td>
<td>Coprecipitation [96]</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}@Zn/Co-ZIFs</td>
<td>Carbamazepine</td>
<td>(\text{SO}_4^-)</td>
<td>5 mg/L</td>
<td>25 mg/L</td>
<td>PMS</td>
<td>0.4 mM</td>
<td>30</td>
<td>100</td>
<td>Not mentioned</td>
<td>Solvothermal [98]</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}/microwave irradiation (3 kW/L)</td>
<td>p-Nitrophenol</td>
<td>(\text{SO}_4^-)</td>
<td>20 mg/L</td>
<td>2.5 g/L</td>
<td>PS</td>
<td>15:1 (molar ratio)</td>
<td>28</td>
<td>94.2</td>
<td>Not mentioned</td>
<td>Not mentioned [99]</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}/MC</td>
<td>p-Hydroxybenzoic acid</td>
<td>(\text{SO}_4^-)</td>
<td>1.0 g/L</td>
<td>0.2 g/L</td>
<td>PS</td>
<td>1.0 g/L</td>
<td>30</td>
<td>100</td>
<td>Not mentioned</td>
<td>Sol-gel [100]</td>
<td></td>
</tr>
<tr>
<td>Fe\textsubscript{3}O\textsubscript{4}/graphene aerogels</td>
<td>Malachite green</td>
<td>Not mentioned</td>
<td>20 mg/L</td>
<td>0.2 g/L</td>
<td>PS</td>
<td>1.0 mM</td>
<td>12</td>
<td>91.7</td>
<td>Not mentioned</td>
<td>Sol-gel [101]</td>
<td></td>
</tr>
</tbody>
</table>

®: the composite of two materials.
Figure 9. Typical FESEM images of (a) Fe₃O₄, (b) Fe₃O₄/GO, (c) Fe₃O₄/GO/Ag, and (d) Fe₃O₄/Ag microspheres. Inserts are magnified FESEM images of Fe₃O₄/GO/Ag and Fe₃O₄/Ag microspheres [94].

3. Comparison of the Performance of Different Iron-Based Catalysts

Different catalysts and contaminants are described above. We select representative pollutants, 2,4-D, NOF, and BPA, as examples to illustrate the performance of various kinds of catalysts.

As one type of auxin analogue, 2,4-D is the most applied herbicides in the world. If overused, it pollutes the water body and harms crops [102]. Figure 10 shows that when the concentration of 2,4-D was 20 mg/L, all three iron-based catalysts showed excellent degradation rate and fast degradation time. The best material is Fe@C/PB, which can degrade 99.4% of the 2,4-D in 50 min [92].

Figure 10. Degradation of 2,4-D by three iron-based catalysts: (a) CuFe₂O₄/O₃ [42], (b) TiO₂@CuFe₂O₄/UV [69], and (c) Fe@C/PB [92].

Antibiotics are currently extensively used in human medicine, animal farming, agriculture, and aquaculture, and their residue has become a global environmental problem [103]. NOF is the third generation of quinolone antibiotic. It has certain antibacterial action [104]. Figure 12 shows that when the concentration of NOF was 15 μM, Fe₂O₃@CoFe₂O₄ was 0.3 g/L. In 25 min, the degradation rate could reach 89.8% [69]. Compared with the degra-
dation rate of other pollutants, it has a greater improvement. Piezoelectric catalysis can be used to further enhance performance.

BPA is a very common chemical product. It is widely found in plastics used in our daily life. It can lead to endocrine disorders, and cancer is also considered to be associated with BPA [105]. Figure 11 shows that when the concentration of BPA was 10 mg/L, the degradation rate of (a) the biochar loaded with CoFe$_2$O$_4$ nanoparticles can reach 93% [39] in 8 min.

![Figure 11. Degradation of BPA by three iron-based catalysts: (a) biochar loaded with CoFe$_2$O$_4$ nanoparticles [39], (b) Fe$_3$O$_4$ [87], and (c) CuO–Fe$_3$O$_4$–BC [88].](image)

Figure 12. Degradation of NOF by three iron-based catalysts: (a) CoFe$_2$O$_4$–SAC [47], (b) Fe$_3$O$_4$@CoFe$_2$O$_4$ [69], and (c) rGO–Fe$_3$O$_4$ [88].
4. Coupling Activation of Iron-Based Catalysts under Auxiliary Action

4.1. Photocatalytic Activation

Transition metal compounds with lower states can effectively activate PMS, and the reaction mechanism follows:

\[ \text{M}^{n^+} + \text{HSO}_5^- \rightarrow \text{M}^{(n+1)^+} + \cdot\text{SO}_4^- + \cdot\text{OH} \]  \hspace{1cm} (12)

\[ \text{M}^{n^+} + \text{HSO}_5^- \rightarrow \text{M}^{(n+1)^+} + \text{SO}_{42^-} + \cdot\text{OH} \]  \hspace{1cm} (13)

Currently, photocatalytic activation of PS can be done either through direct exposure to ultraviolet light, or through the reaction of light with the photocatalyst to excite the photoinduced electrons on its surface [106]. According to many studies, the efficiency of Fenton-like degradation of pollutants by iron-based catalyst can be improved under the condition of light [107,108]. As an efficient catalyst to activate persulfate, Fe\(^{2+}\) also shows good performance under dark conditions, but there are still problems such as the reduction of utilization rate caused by the mutual transformation of Fe\(^{2+}\) and Fe\(^{3+}\). Benkelberg et al. [109] found in their study that under ultraviolet light, the transformation of Fe\(^{3+}\) into Fe\(^{2+}\) in the solution was accelerated, and the Fe(OH)\(_2\) generated by the reaction would greatly absorb ultraviolet light and produce Fe\(^{2+}\) and \cdot\text{OH}. The reaction mechanism follows:

\[ \text{Fe(OH)}_2 \xrightarrow{h\nu} \text{Fe}^{2+} + \cdot\text{OH} \]  \hspace{1cm} (14)

However, as described above, homogeneous catalysis based on Fe\(^{2+}\) is prone to many problems. Therefore, heterogeneous catalysis based on an iron catalyst is relatively more convenient to recycle and is environmentally friendly. Regardless of the form the iron-based catalyst enters the solution, it will be converted to Fe\(^{2+}\) to activate PS and degrade the pollutants in the water. It is Fe\(^{2+}\) that plays a vital role in activating persulfate. Part of the ions converted to Fe\(^{3+}\) will also be converted to Fe\(^{2+}\) through illumination and other ways to speed the reaction process.

Table 5 shows the degradation effects of different iron-based catalysts on different pollutants under UV lamp irradiation. The data in the Table show that the degradation effect is the best under UV lamp irradiation (UV–Vis) within the visible range.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pollutant</th>
<th>Concentration</th>
<th>Catalyst Concentration</th>
<th>Oxidant</th>
<th>Oxidant Concentration</th>
<th>T/min</th>
<th>Degradation Rate (%)</th>
<th>Number of Cycles</th>
<th>Synthesis Techniques</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/Fe(^{2+})</td>
<td>Lindane</td>
<td>3.43 mM</td>
<td>50 mM</td>
<td>PMS</td>
<td>250 mM</td>
<td>180</td>
<td>92.2</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available</td>
</tr>
<tr>
<td>CuO-UV/Fe(<em>{2}O</em>{3})</td>
<td>2,4-D</td>
<td>50 mg/L</td>
<td>0.5 g/L</td>
<td>PMS</td>
<td>3 mM</td>
<td>60</td>
<td>90.2</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
</tr>
<tr>
<td>UV-Vis /Fe(II)</td>
<td>Carbazepine</td>
<td>0.05 mM</td>
<td>0.1 mM</td>
<td>PMS</td>
<td>0.2 mM</td>
<td>30</td>
<td>100</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available</td>
</tr>
<tr>
<td>UV/Fe(^{2+})</td>
<td>Lindane</td>
<td>3.43 mM</td>
<td>0.25 mM</td>
<td>PMS</td>
<td>0.25 mM</td>
<td>720</td>
<td>78.4</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available</td>
</tr>
<tr>
<td>UV/Fe(^{2+})</td>
<td>Atrazine</td>
<td>18.56 µM</td>
<td>17.91 µM</td>
<td>PS</td>
<td>1856 µM</td>
<td>Not mentioned</td>
<td>62.94</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available</td>
</tr>
<tr>
<td>UV-Vis /Fe(II)</td>
<td>Diclofenac, Sulfamethoxazole</td>
<td>Compound = 50 µM</td>
<td>1 mM</td>
<td>PMS</td>
<td>2 mM</td>
<td>60</td>
<td>&gt;70</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available</td>
</tr>
<tr>
<td>Vis/ZnFe(<em>{2}O</em>{4})</td>
<td>Orange II</td>
<td>20 mg L(^{-1})</td>
<td>0.1 g L(^{-1})</td>
<td>PMS</td>
<td>0.5 g L(^{-1})</td>
<td>80</td>
<td>100</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available</td>
</tr>
<tr>
<td>Vis/ZnFe(<em>{2}O</em>{4})</td>
<td>Orange II</td>
<td>100 mg L(^{-1})</td>
<td>0.5 g L(^{-1})</td>
<td>PS</td>
<td>1.0 g L(^{-1})</td>
<td>300</td>
<td>50.5</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Sol-gel</td>
</tr>
</tbody>
</table>

4.2. Piezoelectric Catalytic Activation

Piezoelectrics are a noncentrosymmetric crystal structure that separates positive and negative charges under the action of external forces, resulting in a corresponding piezopotential [116–118]. Piezocatalysis refers to the conversion of mechanical energy into chemical energy. When using an iron-based catalyst piezoelectric material or coupled with other photocatalysts, an electric field near the piezoelectric material assists in charge separation [119].
Vibration is a very common motion that produces mechanical energy. Compared with commonly used oxidation methods such as Fenton reaction and photoelectric catalysis, piezoelectric catalytic activation is more resource-saving. Even a very small vibration can drive a deformation of nano/micrometer materials to generate a potential [120]. The degradation mechanism of piezoelectric catalysis follows [121]:

\[
\text{(Piezo-materials) + vibration} \rightarrow \text{(Piezo-materials)}(h^+ + e^-) \tag{15}
\]

\[
O_2 + e^- \rightarrow \cdot O^2^- \tag{16}
\]

\[
h^+ + OH^- \rightarrow \cdot OH \tag{17}
\]

\[
h^+ / e^- / \cdot OH / \cdot O^2^- + \text{pollutants} \rightarrow \text{degradation products} \tag{18}
\]

Ultrasound (US) is the most common wave that can generate mechanical energy. PS is converted into \(\cdot \text{SO}_4^-\) under the action of ultrasound; the reaction equation follows [122]:

\[
\text{S}_2\text{O}_8^{2-} + \text{US} \rightarrow 2\cdot \text{SO}_4^- \tag{19}
\]

\[
\text{H}_2\text{O} + \text{US} \rightarrow \text{H}^+ + \cdot \text{OH} \tag{20}
\]

\[
\cdot \text{SO}_4^- + \text{H}_2\text{O} + \cdot \text{OH} \rightarrow \text{H}^+ + \text{SO}_4^{2-} \tag{21}
\]

The study of Xu et al. [123] indicated that in the ultrasonic environment, activation persulfate based on foamed zero-valent iron (Fe\(^{0f}\)) could remove the oxide film on the surface of Fe\(^{0f}\) in the reaction process. Thus, more Fe\(^{0f}\) is exposed to the solution to increase the contact area and speeds the reaction. In the persulfate/chlorite Fe\(^{0f}\) system, a large number of \(\cdot \text{SO}_4^-\), \(\cdot \text{OH}\) and other free radical ions can be generated through ultrasonic action. The possible reaction mechanism is shown in Figure 13 [123].

![Figure 13](image_url)

**Figure 13.** The possible reaction mechanism of US/Fe\(^{0f}\)-PS [123].

As an activation method of piezoelectric catalysis, an ultrasonic wave is partially used as an example in the Table 6 to degrade different kinds of wastewater through the activation persulfate mechanism.
Table 6. Under the action of ultrasound, iron-based catalysts degrade different kinds of wastewater by activation persulfate [37,88,123–128].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Condition of US</th>
<th>Pollution</th>
<th>Pollutant Concentration</th>
<th>Catalyst Concentration</th>
<th>Oxidant</th>
<th>Oxidation Concentration</th>
<th>T/min</th>
<th>Degradation Rate /%</th>
<th>Number of Cycles</th>
<th>Synthesis Techniques</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>US/PS/Fe&lt;sub&gt;0&lt;/sub&gt;</td>
<td>30 W L&lt;sup&gt;−1&lt;/sup&gt; 28 kHz</td>
<td>Tmp&lt;sub&gt;FG&lt;/sub&gt;</td>
<td>50 µM</td>
<td>0.214 mM</td>
<td>PS</td>
<td>1.45 mM</td>
<td>40</td>
<td>100</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Commercially available [123]</td>
</tr>
<tr>
<td>US/Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>140 W L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>SD</td>
<td>20 mg/L</td>
<td>1.3 mM</td>
<td>PS</td>
<td>1.3 mM</td>
<td>30</td>
<td>97.4</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
<td>[124]</td>
</tr>
<tr>
<td>US/Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>60 W L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>SMT</td>
<td>0.05 mM</td>
<td>0.1 mM</td>
<td>PS</td>
<td>1 mM</td>
<td>30</td>
<td>100</td>
<td>Not mentioned</td>
<td>Magnetization</td>
<td>[125]</td>
</tr>
<tr>
<td>US/Fe&lt;sup&gt;2+&lt;/sup&gt; (pH = 3.5)</td>
<td>40 kHz</td>
<td>Azorubine</td>
<td>20 mg L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>4 mM</td>
<td>PS</td>
<td>4 mM</td>
<td>60</td>
<td>66.5</td>
<td>Not mentioned</td>
<td>Commercially available</td>
<td>[126]</td>
</tr>
<tr>
<td>US/Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>20 kHz</td>
<td>Azo dye</td>
<td>0.06 mM</td>
<td>0.4 g/L</td>
<td>PMS</td>
<td>3 mM</td>
<td>30</td>
<td>90</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
<td>[127]</td>
</tr>
<tr>
<td>US/nZVI</td>
<td>360 W L&lt;sup&gt;−1&lt;/sup&gt; 40 kHz</td>
<td>Chloramphenicol</td>
<td>5 mg/L</td>
<td>0.5 g/L</td>
<td>PS</td>
<td>1 mM</td>
<td>90</td>
<td>98.1</td>
<td>Not mentioned</td>
<td>Hydrothermal</td>
<td>[88]</td>
</tr>
<tr>
<td>US/Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;@MOF-2</td>
<td>200 W L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>Diazinon</td>
<td>30 mg/L</td>
<td>0.7 g/L</td>
<td>PS</td>
<td>10 mM</td>
<td>120</td>
<td>98</td>
<td>Not mentioned</td>
<td>Commercially available</td>
<td>[128]</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;/US</td>
<td>40 kHz</td>
<td>Carbamazepine</td>
<td>1.0 mg L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>0.4 g L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>PDS</td>
<td>0.4 g L&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>60</td>
<td>98.4</td>
<td>Not mentioned</td>
<td>Commercially available</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Tmp<sub>FG</sub>: a triphenylmethane derivative; SD: sulfadiazine; SMT: sulfamethazine. @: the composite of two materials.
4.3. Summary

The coupling activation of two iron-based catalysts under auxiliary action was introduced above. Both methods can accelerate the activation effect of iron-based catalysts on activation persulfate to a certain extent.

At present, the problem of photocatalysis is how to strengthen the application range of the photocatalyst. The treatment of industrial wastewater is generally conducted outdoors under complicated conditions. Some single photocatalysts, such as few-layered graphitized graphitic carbon nitride composite (GrCN), can be used in the degradation process together with PMS and photothermal catalysis [129]. The maximum reaction rate is 0.044 min\(^{-1}\). The light source used for the data given in Table 5 is ultraviolet light, although sunlight contains only 5–7% of the ultraviolet spectrum. Therefore, how to improve the practicability of materials in the visible light range has become a new research direction.

Furthermore, if GrCN is used alone to degrade wastewater, not to mention the effect, recycling becomes a large problem. Therefore, it is a better method to compound it with a magnetic carrier. By combining magnetic iron oxide nanoparticles with the carrier, not only can the excellent catalytic effect of iron oxide be brought into play, but it can also facilitate the recovery of GrCN as a carrier, so that the two substances complement each other [130].

Piezoelectric catalysis, as a newly developed technology in recent years, still has a great space for development. Through ultrasonic and other methods that can generate vibration, oxidants and catalysts can be evenly dispersed into sewage to increase the contact point of chemical reaction, and more electrons can be generated by promoting piezoelectric materials to increase the concentration of free radicals and accelerate the progress of chemical reaction.

Table 7 shows the advantages and disadvantages of representative five iron–base catalysts mentioned above.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe(_2)O(_4)</td>
<td>CoFe(_2)O(_4) exhibited an excellent performance for ATZ removal (over 99%).</td>
<td>It has a good effect in activating PMS, but in activating PS and H(_2)O(_2); its recycling rate is not good due to the leaching of metal ions and loss of active sites.</td>
<td>[53]</td>
</tr>
<tr>
<td>CuFe(_2)O(_4)-20%rGO</td>
<td>Increase of specific surface area and chemical reaction activation sites.</td>
<td>The most suitable pH is 6.5; the application is limited.</td>
<td>[64]</td>
</tr>
<tr>
<td>Fe(_0)@Fe(_3)O(_4)</td>
<td>It has high reactivity for atrazine degradation (near 100% removal in 2 min) and is highly stable in air. Under the action of UV light, it shows an improved regeneration of Fe(_{2+}), causing a fast generation of highly reactive -SO(_4)- and -OH. The reaction rate was improved by coupling activation. Compared with pure catalyst, the degradation rate is also improved.</td>
<td>Its applicable pH range is low (under 4). Too much catalyst will also reduce the reaction rate, so the use of catalyst needs to be strictly controlled.</td>
<td>[90]</td>
</tr>
<tr>
<td>UV/Fe(_2+)</td>
<td></td>
<td>It is easily affected by the action of other anions in the solution (Cl(^-), NO(_3)(^-)). Moreover, the effect of PMS alone is not good, and additional H(_2)O(_2) is needed to better degrade pollutants.</td>
<td>[110]</td>
</tr>
<tr>
<td>US/ Fe(_0)</td>
<td></td>
<td></td>
<td>[125]</td>
</tr>
</tbody>
</table>

\(@:\) the composite of two materials.
5. Conclusions and Prospect

Activation persulfate technology based on iron-based catalysts has attracted wide attention in recent years. As for iron-based catalysts themselves because the central atom is Fe, their electron configuration is not in a full or partially full state, so their chemical properties are relatively active, and they are susceptible to not only pH but also various ions in water. SR-AOPs-PMS/PDS technology is new, and several metal ions mentioned above can activate persulfate. In terms of the current problems, several ideas and possibilities for improvement are proposed:

Adopt the multimetal composite method in the advanced oxidation technology of bimetal coordination. Taking iron as the core, screen and compare other metal ions of transition elements, and compound new iron-based catalyst.

Based on the data above, it is not difficult to see that the AOPs technology of nonfree radicals also has ideal effects. Compared with the generation of \( \cdot \text{SO}_4^- \), the degradation effect of \( \cdot \text{O}_2 \) produced by nonfree radicals is better to find a new nonfree radical reaction pathway to degrade wastewater.

After the reaction stops, the solubility of some iron-based catalysts or metal leaching may produce iron slag and other wastes. If the subsequent treatment is improper, it is easy to cause secondary pollution to the water body; at the same time, there is metal valency reaction in the reaction process, which reduces the collision of effective molecules and has more side reactions. How to improve the effective ion concentration for the reaction has become an urgent problem to be solved.

The persulfate used in the reaction is strongly oxidizing. If stored improperly or used in excess, it will produce a large toxic effect on organisms.

Most of the iron-based catalyst reaction conditions are acidic and create a strong acid environment. It is not applicable in a neutral environment. If used for degraded wastewater, the pH of water needs to be adjusted, and if there is acid intolerance or acid decomposition substances in the water, then it is easy to produce adverse consequences. Furthermore, the pH of water should be adjusted after the reaction is terminated, which greatly increases the cost.

Coupled catalysis based on iron-based catalysts with auxiliary action has played a good role in activation persulfate, and it is worthy of further study to improve the degradation effect by applying additional conditions. We can try to improve the performance of the materials with poor degradation effect among the 12 different iron-based catalysts mentioned above by photocatalysis, piezoelectric catalysis, and other methods.

Piezoelectric catalysis, as a research hotspot in recent years, is in its infancy at present. More kinds of catalysts can be produced by attempting to combine other transition metals and oxides with iron-based materials.

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