Activation Persulfate by Various Iron-Based Catalysts

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Contributor: Keke Zhi

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 entry 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.

iron-based catalysts activation persulfate degrading wastewater

1. $MeFe_2O_4$ (Me = Cu, Co, Zn, etc.)

In terms of activation mechanism, transition metal compounds react with PS to produce a large amount of $\cdot SO_4^-$; the reaction equation follows:

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

(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, $MeFe_2O_4$ with a low metal leaching rate has become a new research direction. Through PS/PMS [1] heterogeneous catalytic technology, these problems can be effectively solved [2][3][4].

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 [5].

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 [6].

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 [7].

Coprecipitation is an important method to prepare composite oxide ultrafine powder containing a large variety of metal elements [8].

The electron transfer between transition metal oxides is much higher [9] than that between single transition metal oxides. Generally, AB_2O_4 [10][11] structure is referred to as spinel structure. $CuFe_2O_4$ is a typical spinel ferrite with a magnetic structure, which has high chemical stability and low metal leaching rate. Taking $CuFe_2O_4$ 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 $\cdot SO_4^-$.

G. Xian et al. [12] comprehensively compared the catalytic degradation effects of $CoFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, and $ZnFe_2O_4$. In detail, $CuFe_2O_4$ 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 $CuFe_2O_4$ [12]. Additionally, it was known that $CuFe_2O_4$ had the best catalytic effect. Moreover, through the quenching experiment, it was not ·OH but $\cdot SO_4^-$ that played a major role in the reaction.

Table 1 shows the degradation effects of some different $MeFe_2O_4$-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 $\cdot SO_4^-$ in the mechanism of activation persulfate; the effect of ·OH is slightly worse [13]. Of course, there are also some nonfree radical pathways, which degrade pollutants in water by generating singlet oxygen $^1O_2$ [14][15][16].

Table 1. Effect of Different $MeFe_2O_4$-activated PMS on degradation of different wastewater [5][6][7][8][13][17][18][19].

Catalyst	Pollution	Main Mechanism	Pollutant Concentration	Catalyst Concentration	Oxidant	Oxidation Concentration	T/min	Degradation Rate/%	Number of Cycles	Synthesis Techniques	Ref.
$PbFe_2O_4$	Thionine	$^1O_2$	10 μM	0.4 g/L	PMS	400 μM	20	100	Not mentioned	Solution combustion	[17]
$CoFe_2O_4$–loaded quartz sand	Sulfachloropyridazine sodium	$\cdot SO_4^-$ ·OH	2 g/L	10 g	PMS	75 mg/L	150	90	Not mentioned	Citrate combustion	[18]
$CoFe_2O_4$-SAC	Norfloxacin (NOF)	$\cdot SO_4^-$ ·OH	10 mg/L	0.1 g/L	PMS	0.15 g/L	120	TOC reduction 81	5 (>80%)	Hydrothermal	[13]
The biochar loaded with $CoFe_2O_4$ nanoparticles	Bisphenol A (BPA)	$\cdot SO_4^-$ ·OH	10 mg/L	0.05 g/L	PMS	0.5 g/L	8	93	Not mentioned	Hydrothermal	[5]

Catalyst	Pollution	Main Mechanism	Pollutant Concentration	Catalyst Concentration	Oxidant	Oxidation Concentration	T/min	Degradation Rate/%	Number of Cycles	Synthesis Techniques	Ref.
C_3N_4@$MnFe_2O_4$-graphene	Metronidazole	$\cdot SO_4^-$ ·OH	20 mg/L	1.0 g/L	PS	0.01 M	90	94.5	5 (>80%)	Solvothermal	[6]
$Zn_{0.8}Cu_{0.2}Fe_2O_4$	Atrazine	$\cdot SO_4^-$	4.4 μM	200 mg/L	PS	0.5 mM	30	95	Not mentioned	Sol–gel	[7]
$CuFe_2O_4/O_3$	2,4-Dichlorophenoxyacetic acid (2,4-D)	Not mentioned	20 mg/L	0.20 g/L	PMS O_3	PMS 2.0 mM; O_3 16.0 mg/L;	40	88.9	5 (>80%)	Coprecipitation	[8]
$CoFe_2O_4$	Atrazine (ATZ)	$\cdot SO_4^-$	10 mg/L	0.4 g/L	PMS	0.8 mM	30	>99	5 (>60%)	Hydrothermal	[19]

2 4 ical sites [20] 2 [20][21] [22][23] and rGO [24][25] (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 [24] or electrostatic interaction [26], 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.

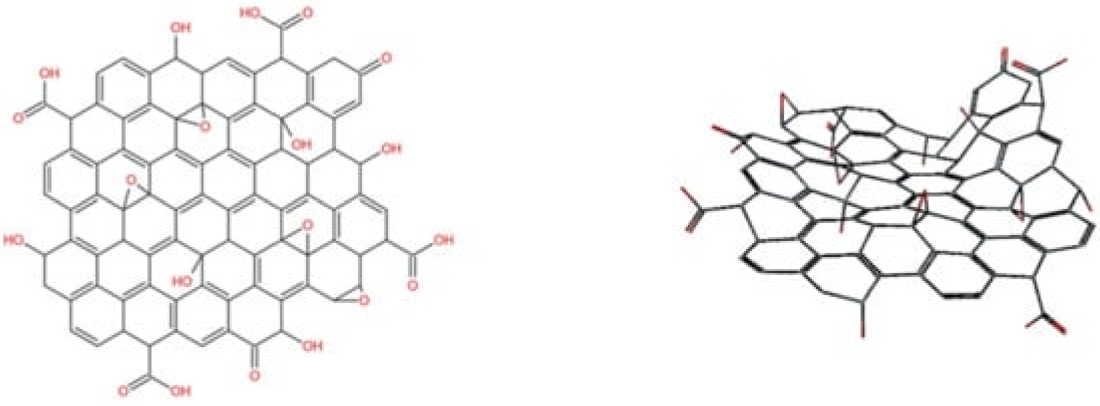

Figure 1. Plane structure (**left**) and solid structure (**right**) of GO (bond line type).

Figure 2. Plane structure (**left**) and solid structure (**right**) of rGO (bond line type).

Taking $CuFe_2O_4$, a representative of $MeFe_2O_4$, as an example, by comparing the effect of pure $CuFe_2O_4$ with that of $CuFe_2O_4$ combined with the carrier, it can be seen that the latter has a stronger catalytic effect under acidic and photoinduced conditions [27]. $CuFe_2O_4$ in $CuFe_2O_4$–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**.

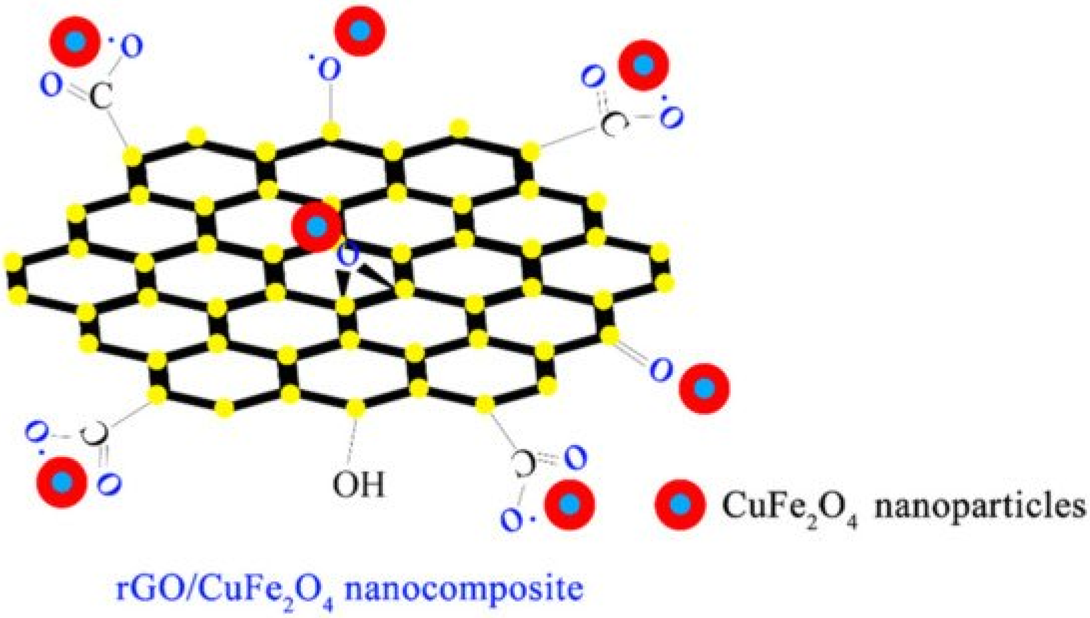

Figure 3. Chemical structural formula of $CuFe_2O_4$-rGO [26].

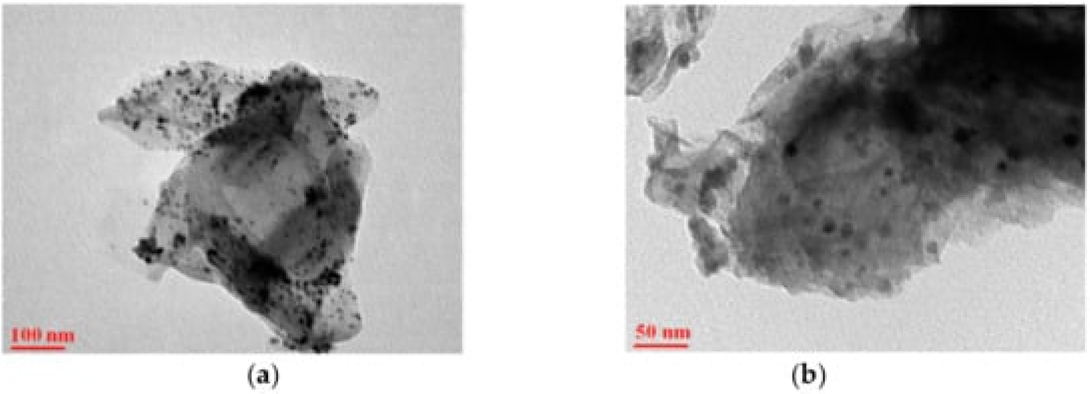

Figure 4. TEM images of (**a**,**b**) rGO/$CuFe_2O_4$ nanostructures under different magnifications [26].

Table 2 shows the degradation effects of some $CuFe_2O_4$ 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 [28][29]. **Table 2** contains some other carriers, which can also greatly influence degradation of different kinds of wastewater.

Table 2. Effects of partial $MeFe_2O_4$ and carrier composite materials on degradation of different kinds of wastewater [27][30][31][32][33][34][35][36].

Catalyst	Pollution	Main Mechanism	Pollutant Concentration	Catalyst Concentration	Oxidant	Oxidation Concentration	T/min	Degradation Rate /%	Number of Cycles	Synthesis Techniques	Ref.
$CuFe_2O_4$-20%rGO	Methylparaben	$SO_4^{-}\cdot$ $\cdot OH$	10 mg/L	0.2 mg/L	PS	5 mM	120	96	Not mentioned	Sol-gel	[30]
$CuFe_2O_4$-1% (*w*/*w*) rGO	Phenol	$\cdot OH$	20 ppm	5 mL	30% H_2O_2	6 mg/L	240	100	Not mentioned	Coprecipitation	[27]
$CuFe_2O_4$/g-C_3N_4	Propranolol	$SO_4^{-}\cdot$	0.02 mM	1 g/L	PS	1 mM	120	82.2	Not mentioned	Sol-gel	[31]
$CoFe_2O_4$/CCNF	Dimethyl phthalate	$SO_4^{-}\cdot$	0.05 mM	0.5 g/L	PMS	1.5 mM	60	>90	5 (>90%)	Sol-gel	[32]
TiO_2@$CuFe_2O_4$/UV	2,4-D	$SO_4^{-}\cdot$	20 mg/L	0.1 g/L	PMS	0.3 mM	60	97.2	5 (>90%)	Sol-gel	[33]
ZnS-$ZnFe_2O_4$	Rhodamine B	$SO_4^{-}\cdot$	20 mg/L	20 mg	PS	5 mg	90	97.67	3 (>95%)	Hydrothermal	[34]
Fe_2O_3@$CoFe_2O_4$	NOF	$SO_4^{-}\cdot$ $\cdot OH$	15 μM	0.3 g/L	PMS	0.4 mM	25	89.8	4 (90%)	Hydrothermal	[35]
Nitrogen and sulfur codoped CNTs-COOH loaded $CuFe_2O_4$	2-Phenylbenzimidazole-5-sulfonic acid	$SO_4^{-}\cdot$	5 mg/L	50 mg/L	PMS	1:100 (molar ratio)	40	98	5 (>95%)	Coprecipitation	[36]

@: the composite of two materials.

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 [37][38]. As mentioned above, the activation persulfate/Fe (II) mechanism can cause secondary pollution to water, so ZVI/PS [39][40] 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 [37].

ZVI/PS system has strong reducibility (Fe^0,E^0 = −0.44 V) [41]. Compared with $CuFe_2O_4$, 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) [42][43]. The reaction mechanism follows [44]: 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. [45] 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 [46].

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$$

(2)

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$$

(3)

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-}$$

(4)

$$Fe^{0} + HSO_5^{-} \rightarrow Fe^{2+} + SO_4^{2-} + OH^{-}$$

(5)

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

(6)

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

(7)

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

(8)

$$Fe^{0}+2\ HSO_5^{-} \rightarrow Fe^{2+} + 2OH^{-} + 2\cdot SO_4^{-}$$

(9)

$$Fe^{2+} + S_2O_8^{2-} + H_2O \rightarrow Fe^{IV}O^{2+} + 2SO_4^{2-} + 2H^{+}$$

(10)

$$Fe^{2+} + HSO_5^{-} \rightarrow Fe^{IV}O^{2+} + SO_4^{2-} + H^{+}$$

(11)

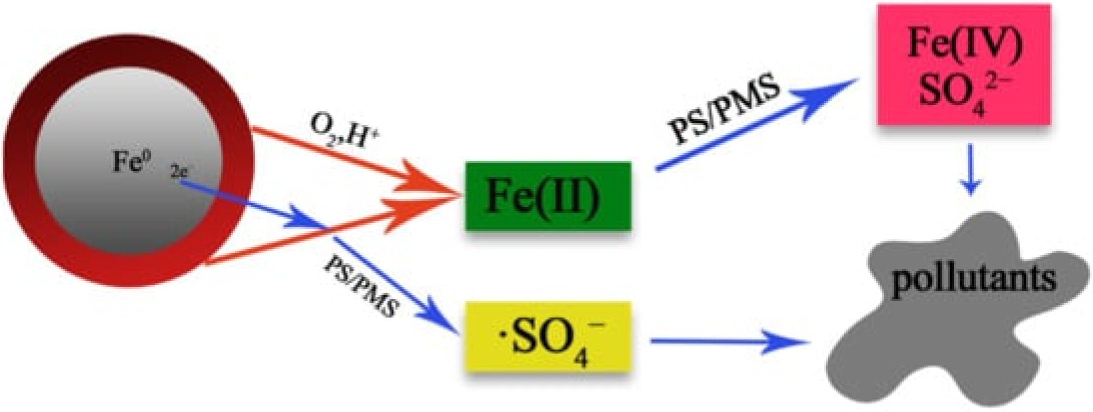

Figure 5. Schematic of the formation of $\cdot SO_4^{-}$ and Fe(IV) in nZVI/persulfate systems containing methyl phenyl sulfoxide [47].

Figure 6 shows the proposed degradation pathway of 2,4-D [48]. By examining **Figure 6**, it can further confirm that macromolecular organic matter is decomposed into small molecular organic matter, which is gradually mineralized.

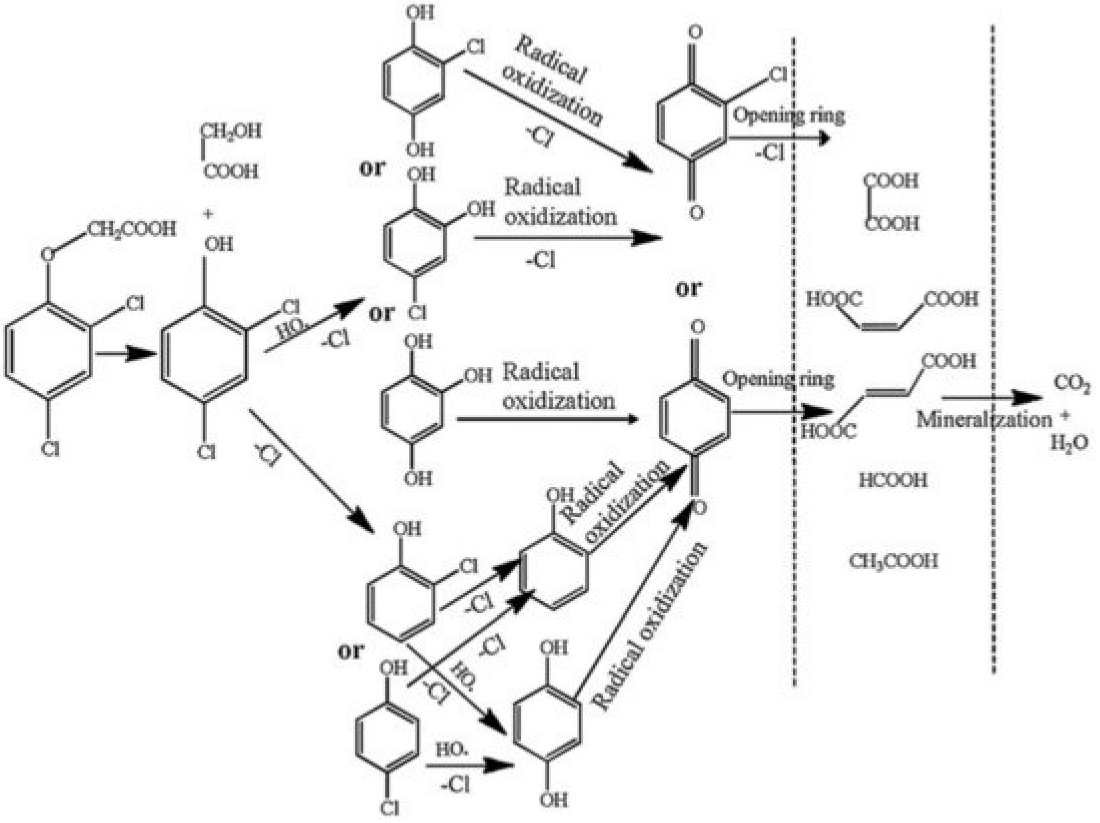

Figure 6. The proposed degradation pathway of 2,4-D [48].

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 [49] 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 [50] 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 [51][52][53][54][55][56][57][58].

Catalyst	Pollution	Main Mechanism	Pollutant Concentration	Catalyst Concentration	Oxidant	Oxidation Concentration	T/min	Degradation Rate /%	Number of Cycles	Synthesis Techniques	Ref.
nZVI	Sulfamethazine	$\cdot OH$ $\cdot SO_4^-$	50 mg/L	2 mM	PS H_2O_2	1 mM 0.5 mM	30	96	Not mentioned	Sol-gel	[54]
CN-Fe	Sulfamethazine	$\cdot SO_4^-$ $\cdot OH$ $^1O_2$	50 μM	0.5 g/L	PMS	1 mM	15	82	Not mentioned	Carbothermal	[53]
Carbon-coated	4-chlorophenol	$\cdot SO_4^-$ $\cdot OH$	150 μM	0.25 g/L	PMS	1 mM	120	96	Not mentioned	Commercially available	[52]

Catalyst	Pollution	Main Mechanism	Pollutant Concentration	Catalyst Concentration	Oxidant	Oxidation Concentration	T/min	Degradation Rate /%	Number of Cycles	Synthesis Techniques	Ref.
nZVI											
US-nZVI	Chloramphenicol	$\cdot SO_4^-$ $\cdot OH$	5 mg/L	0.5 g/L	PMS	1 mM	90	98.1	Not mentioned	Liquid phase reduction	[51]
$Fe^0@Fe_3O_4$	Dibutyl phthalate	$\cdot OH$ $\cdot SO_4^-$	18 μM	0.5 g L^{-1}	PS	1.8 mM	180	94.7	6 (>68%)	Calcination	[55]
$Fe^0@Fe_3O_4$	Atrazine	$\cdot OH$ $\cdot SO_4^-$	500 μg/L	25 mg/L	PMS	1 mM	2	100	Not mentioned	Reduction	[56]
Fe@C	Bisphenol S	$\cdot OH$ $\cdot SO_4^-$	5 mg/L	0.5 g/L	PMS	1.0 mM	60	92.8	Not mentioned	Resin carbonization	[57]
Fe@C/PB	2,4-DichloroPhenol	$\cdot OH$ $\cdot SO_4^-$	20 mg/L	0.6 g/L	PMS	2.0 g/L	50	99.4	Not mentioned	Calcination	[58]

3 4

Fe_3O_4 magnetite, also known as magnetic iron oxide, is a black crystal with a rotating spinel structure (**igure 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.

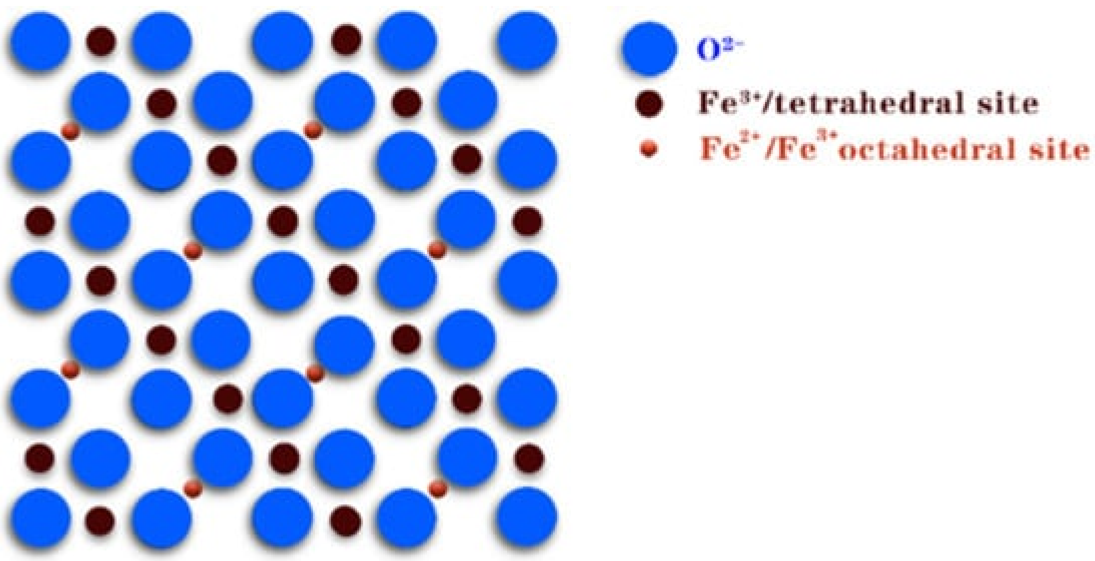

Figure 7. Crystal structure of Fe_3O_4.

However, since Fe_3O_4 is easy to accumulate in solution and contact sites are reduced after agglomeration, single Fe_3O_4 is rarely used. Using the composite carrier method [59] 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. [60] pointed out that the Fe_3O_4/GO/Ag composite microspheres are formed using magnetic Fe_3O_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_3O_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_3O_4/GO/Ag composite catalyst. In **Figure 9**, we can clearly observe that Ag has been completely attached to the Fe_3O_4/GO surface, which can increase the specific surface area and improve the chemical reaction rate.

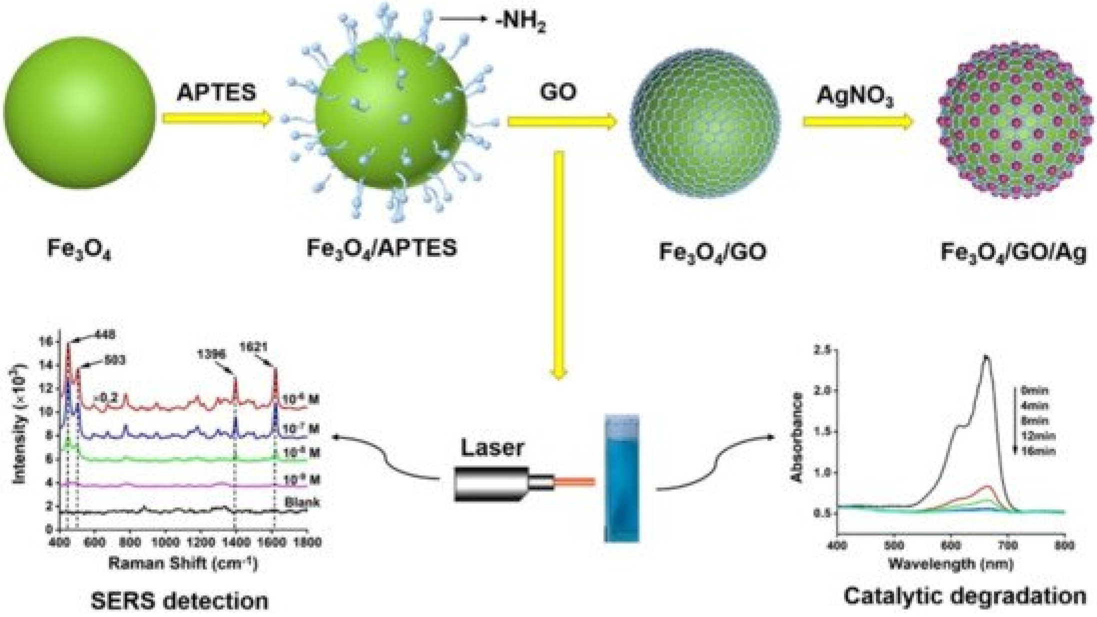

Figure 8. Illustration of the fabrication of Fe_3O_4/GO/Ag composite microspheres [60].

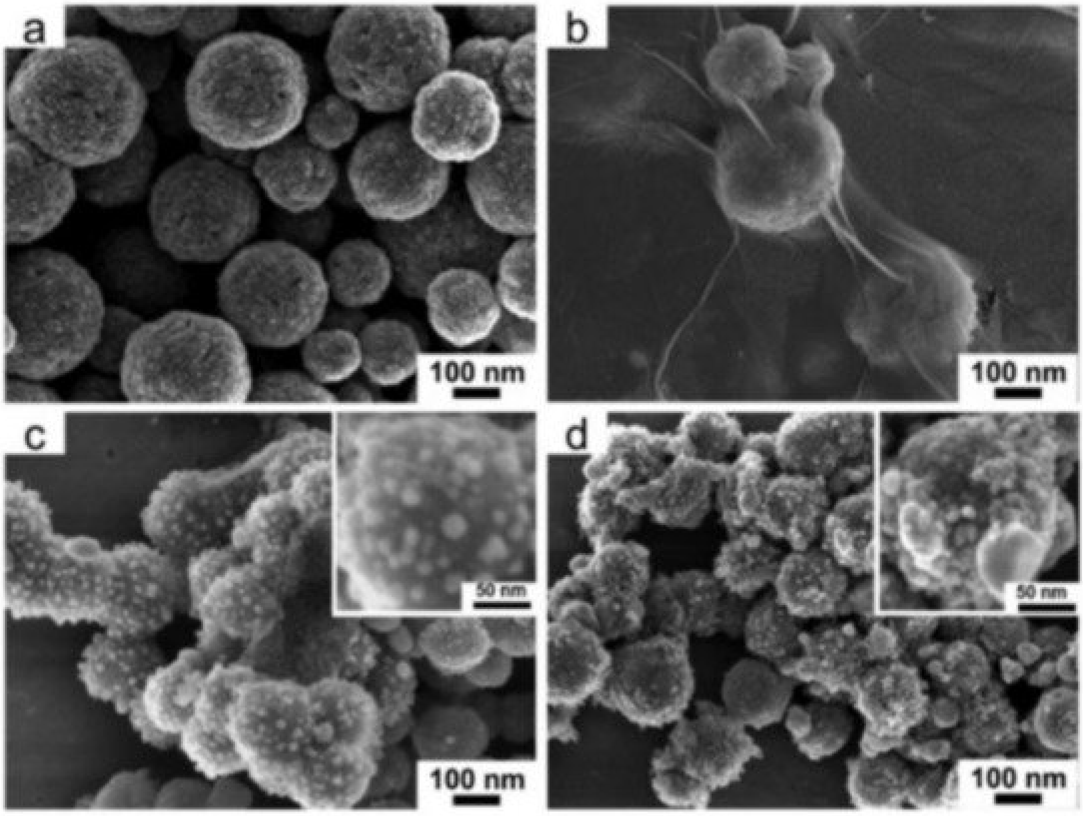

Figure 9. Typical FESEM images of (**a**) Fe_3O_4, (**b**) Fe_3O_4/GO, (**c**) Fe_3O_4/GO/Ag, and (**d**) Fe_3O_4/Ag microspheres. Inserts are magnified FESEM images of Fe_3O_4/GO/Ag and Fe_3O_4/Ag microspheres [60].

Table 4 shows the research progress of Fe_3O_4 and its composite materials on the degradation of different pollutants reported at present. According to the data in the table, when Fe_3O_4 is compounded with the carrier, the catalytic performance is greatly improved.

Table 4. Effects of Fe_3O_4 and its composite-material-activated PS/PMS on degradation of different kinds of wastewater [61][62][63][64][65][66][67].

Catalyst	Pollution	Main Mechanism	Pollutant Concentration	Catalyst Concentration	Oxidant	Oxidation Concentration	T/min	Degradation Rate /%	Number of Cycles	Synthesis Techniques	Ref.
Fe_3O_4	BPA	$\cdot SO_4^-$ $\cdot OH$	20 mg/L	2.0 g/L	PMS	5 mM	30	27.53	Not mentioned	Commercially available	[61]
CuO-Fe_3O_4-BC	BPA	$\cdot SO_4^-$ $\cdot OH$	20 mg/L	2.0 g/L	PMS	5 mM	30	100	4 (>85%)	Coprecipitation	[62]
rGO-Fe_3O_4	NOF	$^1O_2$ $\cdot OH$ $\cdot SO_4^-$	20 mg/L	0.5 g/L	PS	1 g/L	30	89.69	Not mentioned	Coprecipitation	[62]
Fe_3O_4	Sulfamonomethoxine	$\cdot SO_4^-$	0.06 mM	2.4 mM	PS	1.2 mM	15	100	Not mentioned	Coprecipitation	[63]
Fe_3O_4@Zn/Co-ZIFs	Carbamazepine	$\cdot SO_4^-$	5 mg/L	25 mg/L	PMS	0.4 mM	30	100	Not mentioned	Solvothermal	[64]
Fe_3O_4/microwave irradiation (3 kW/L)	p-Nitrophenol	$\cdot SO_4^-$	20 mg/L	2.5 g/L	PS	15:1 (molar ratio)	28	94.2	Not mentioned	Not mentioned	[65]
Fe_3O_4/MC	p-Hydroxybenzoic acid	$\cdot SO_4^-$	1.0 g/L	0.2 g/L	PS	1.0 g/L	30	100	Not mentioned	Sol-gel	[66]
Fe_3O_4/graphene aerogels	Malachite green	Not mentioned	20 mg/L	0.2 g/L	PS	1.0 mM	12	91.7	Not mentioned	Sol-gel	[67]

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@: the composite of two materials.

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