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Enhanced activation of PMS by a novel Fenton-like composite Fe$_3$O$_4$/S-WO$_3$ for rapid chloroxylenol degradation

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ABSTRACT

Chloroxylenol (PCMX) is widely used as disinfectant since the epidemic outbreak due to its effective killing of Covid-19 virus. Its stable chemical properties make it frequently detected in surface water. Herein, we successfully modified Fe$_3$O$_4$ nanoparticles with S-WO$_3$ (X-Fe$_3$O$_4$/S-WO$_3$) to accelerate the Fe$^{3+}$/Fe$^{2+}$ cycle. The composite has outstanding PCMX degradation and peroxymonosulfate (PMS) decomposition efficiency over a wide pH range (3.0 ~ 9.0). 80-Fe$_3$O$_4$/S-WO$_3$/PMS system not only increased PMS decomposition efficiency from 27.7% to 100.0%, but also realized an enhancement of PCMX degradation efficiency by 16 times in comparison with that of Fe$_3$O$_4$ alone. The catalyst utilization efficiency reached 0.3506 mmol·g$^{-1}$·min$^{-1}$ which stands out among most Fenton-like catalysts. The composite has excellent degradation ability to a variety of emerging pollutants, such as antibiotics, drugs, phenols and endocrine disrupters, and at least a 90% removal efficiency reached in 10 min. The degradation of PCMX was dominated by HO$^-$, SO$_4^{2-}$ and O$_2$·. The degradation pathways of PCMX were analyzed in detail. The component WS$_2$ in S-WO$_3$ plays a co-catalytic role instead of WO$_3$. And the exposed active W$^{4+}$surf. efficiently enhanced the Fe$^{3+}$/Fe$^{2+}$ cycle, thereby complete PMS decomposition and high catalytic efficiency were achieved. Our findings clarify that applying two-dimensional transition metal sulfide WS$_2$ to modify heterogeneous Fe$_3$O$_4$ is a feasible strategy to improve Fenton-like reaction and provide a promising catalyst for PCMX degradation.

1. Introduction

Although the rapid development of industry has greatly improved daily lives, a variety of emerging contaminations (ECs) are quietly discharged into environment [1]. For instance, chloroxylenol (PCMX) is widely added in hand sanitizer to sterilize [2]. PCMX has been proven to be highly effective in inhibiting Covid-19 virus [3,4]. Thereby, the demand for disinfectants containing PCMX has greatly increased during the epidemic [3]. Data shows that the concentration of PCMX in hand sanitizers is generally between 0.18 and 0.22%(w/w) [5]. However, ECs like PCMX are usually chemically stable and not easily biodegradable [6,7]. Conventional municipal wastewater treatment systems (CMWTs) have limited capacity to treat these ECs. Consequently, PCMX was continuously detected in CMWTs effluent and the concentration of PCMX reached 1.46–5.59 μg/L [5,8]. It was reported that PCMX is neurotoxic and genotoxic to aquatic organisms. The discharge of antibacterial agents poses a threat to the life and health of aquatic organisms and the human bodies. Therefore, it poses new challenges to traditional wastewater treatment systems to remove ECs efficiently.

Persulfate (including peroxydisulfate (PDS) and peroxymonosulfate (PMS)) based advanced oxidation processes (AOPs) is an effective method to degrade refractory organic pollutants [6,9]. Dionysiou first found that Co$^{2+}$ could efficiently activate PMS to degrade pollutants in 2003 [10]. PMS is safer to store and transport as compared to H$_2$O$_2$. Up to now, numerous methods such as UV, ultrasound, homogeneous metal ions (Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, etc.), heterogeneous metal compounds (Fe$^{3+}$, Fe$_2$O$_3$, Fe$_3$O$_4$, Mn$_2$O$_3$, etc.) [11] and carbon-based materials (graphene oxide, carbon nanotubes, biochar, etc.) are applied for PMS activation [12-16]. Heterogeneous iron-based compounds are the most promising PMS activator thanks to the wide distribution of iron element on the earth and the low biological toxicity. For instance, Fe$_3$O$_4$ has a certain PMS activation ability [6,13], since its molecular structure is rich...
in Fe$^{2+}$ ions [6]. Although iron-based heterogeneous catalysts attract a lot of attention in AOPs, it’s practical application still hindered by following two aspects. On the one hand, the key issue is the low Fe$^{2+}$/Fe$^{3+}$ cyclic efficiency which limited the catalytic efficiency. On the other hand, relatively low oxidants decomposition and utilization efficiency lead to the waste of oxidants.

Recently, introducing external electrons through electron-rich materials has become a promising strategy to promote the regeneration of Fe$^{2+}$ and increase the oxidant utilization efficiency. These electron-rich materials including reducing agent (hydroxylamine [17]), chelating agent (citric acid [7] and L-cysteine [18]) and carbon material (graphene [13]). Near recently, two-dimensional transition metal sulfides have received more and more concern, such as MoS$_2$ and WS$_2$. WS$_2$ and MoS$_2$ have similar physical and chemical properties, but few studies applied WS$_2$ in Fenton-like reactions. The role and effect of WS$_2$ in iron-based heterogeneous Fenton-like reactions still need to be further verified and explored. It’s worth noting that WS$_2$, as an important mineral element, has relatively low toxicity and environmental impact [19]. To our knowledge, Dong et al. first found that commercial WS$_2$ is an outstanding co-catalyst in 2018. It can efficiently improve the reaction efficiency of Fe$^{2+}$/H$_2$O$_2$ reaction. The decomposition efficiency of H$_2$O$_2$ improved about 3 times as compared to Fenton reaction. It is because the exposed W$^{4+}$ on WS$_2$ surface dramatically accelerates the reduction of Fe$^{3+}$ to Fe$^{2+}$ [20]. It was also demonstrated that WS$_2$ can improve the catalytic efficiency of Fe$^{3+}$/PMS [21], Fe$^{2+}$/PDS and Fe$^{3+}$/PDS systems [22]. Wang et al. found that the Mo and W can promote the cycle of Fe$^{2+}$/Fe$^{3+}$, and the PMS decomposition efficiency of Mo/FeSO$_4$/PMS system was 10 times higher than that of FeSO$_4$/PMS system [23]. The above results confirm that WS$_2$ is an excellent co-catalyst for improving the efficiency of Fenton/Fenton-like reactions. As far as we know, there are no reports on modification heterogeneous Fenton-like catalysts by WS$_2$. Therefore, we suppose that the heterogeneous Fe$_3$O$_4$/WS$_2$ composite can promote the Fe$^{2+}$/Fe$^{3+}$ cycle through the reduction effect of WS$_2$ thereby improving the reaction efficiency and PMS decomposition efficiency. However, the synthesis of pure WS$_2$ is a complex process, which requires higher temperature and pressure. Considering the energy conservation and safety, it’s feasible to prepare partially Vulcanized WO$_3$ (S-WO$_3$) at a lower temperature. WS$_2$ and WO$_3$, as two important components of S-WO$_3$, could act as cocatalyst and metal nanoparticle carrier, respectively.

In this study, the Fe$_3$O$_4$/S-WO$_3$ composite was successfully synthesized for the first time. The physical and chemical properties of the material were analyzed by different characterization methods. The catalytic performance, including catalyst’s utilization efficiency, PMS utilization efficiency, and the stability of the material were also investigated. The interaction between Fe$_3$O$_4$ and S-WO$_3$ and the activation mechanism of PMS were further explored. Moreover, the degradation pathway of PCMX were also analyzed in detail.

2. Materials and methods

The detailed chemicals and reagents information was listed in Supplementary Information (Text S1). The detailed characterization and analysis methods were listed in Supplementary Information (Text S2).

2.1. Synthesis procedures of the X-Fe$_3$O$_4$/S-WO$_3$

The X-Fe$_3$O$_4$/S-WO$_3$ composites were synthesized by two steps (Scheme 1). S-WO$_3$ (partial Vulcanization WO$_3$) was prepared based on ref. [24]. Briefly, 1.0 g WCl$_6$ and 1.92 g TAA were dissolved in 60 mL ultra-pure water and then kept in an oven for 24 h at 210 °C. The black product was collected by centrifugation, washed with water and ethanol, and then dried in a vacuum oven. In the next step, 50 mg S-WO$_3$ powder was distributed in 10 mL ultra-pure water first, different amounts of FeSO$_4$·7H$_2$O and excessive NH$_4$OH were added in the above solution successively. The solution was kept in an oven at 90 °C for 6 h to make the Fe$_3$O$_4$ nanoparticles grow and crystallize. The product was washed alternately with ethanol/water for several times and then dried at 60 °C in a vacuum oven. The products were named 40-Fe$_3$O$_4$/S-WO$_3$, 60-Fe$_3$O$_4$/S-WO$_3$ and 80-Fe$_3$O$_4$/S-WO$_3$ based on the dosage of FeSO$_4$·7H$_2$O during synthesis (40/60/80 mg), respectively.

As shown in Scheme 1, during the process of preparing WS$_2$, W source was first oxidized into WO$_3$ intermediate. As the reaction proceeded in the presence of TAA under high temperature and pressure, intermediate WO$_3$ was slowly and partially Vulcanized to WS$_2$ [24]. Based on the literature, WO$_3$ will be completely Vulcanized to WS$_2$ when the reaction temperature is higher than 265 °C [24]. In this experiment, the S-WO$_3$ (partially Vulcanized WO$_3$) matrix formed at a lower reaction temperature (210 °C). WO$_3$ is an excellent carrier for metal nanoparticles, which has a high specific surface area and is rich in

![Scheme 1. Synthesis processes of Fe$_3$O$_4$/S-WO$_3$ and detailed formation mechanism of S-WO$_3$.](image-url)
hydroxyl functional groups [25].

2.2. Degradation experiments

All the experiments were carried out in a 100 mL flask at room temperature (20 ± 1 °C). All the degradation experiments were carried out under mechanical stirring to evenly disperse the catalysts (500 r/min). A certain amount of the as-prepared catalyst (0.4 g/L) was dispersed into the pollutant solution (20 mg/L) by ultrasonic. Start and time the Fenton-like reaction after adding the PMS powder. The initial pH value of the pollutant solution was adjusted by 0.1 M H₂SO₄ or NaOH solution. At different intervals, 1.0 mL solution was sampled and mixed with another 1.0 mL methanol (MeOH) immediately to quench the Fenton-like reaction, then filtered through a 0.22 μm syringe filter. For the reusability experiments, the catalyst was collected by a magnet after each cycle and reused in next cycle without wash and drying. All the experiments were repeated three times.

3. Results and discussion

3.1. Characterization of X-Fe₃O₄/S-WO₃

As shown in Fig. 1a, there are elements W, O and S in S-WO₃. The as-prepared S-WO₃ is flower-like nanosheets (Fig. 1b-c). Fe elements were appeared in EDS image of 80-Fe₃O₄/S-WO₃ (Fig. 1d). It can be seen small Fe₃O₄ nanoparticles in the FESEM and TEM images of 80-Fe₃O₄/S-WO₃ (Fig. 1e-f, h). As shown in Fig.S1 (HAADF-mapping), the four elements of Fe, W, O and S are evenly distributed in the composite 80-Fe₃O₄/S-WO₃. It is proved that Fe₃O₄ nanoparticles were uniformly loaded.

As shown in Fig. 1g, the XRD diffraction peaks of the pure Fe₃O₄ nanoparticles are consistent with that of the standard card: PDF #89–2355. The peaks appearing at 18.3, 30.1, 35.4, 43.1, 53.1, 56.9, 62.5 correspond to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) crystal faces of Fe₃O₄, respectively. The (3 1 1) lattice fringes (spacing 0.25 nm) of Fe₃O₄ were observed in HRTEM (Fig. 1i). The main component of the as-prepared carrier is WO₃, which is consistent with the XRD standard card PDF#85–2459. The peaks located near 14°, 28.1, 31.6, 49.8 and 55.6 correspond to the (1 0 0), (0 0 2), (2 0 0), (2 0 2), (2 2 0) and (2 2 2) crystal faces of WO₃, respectively. And the (1 0 0) and (2 0 0) lattice fringes of WO₃ were observed in HRTEM image (Fig. 1i), and the lattice fringe spacings were 0.63 and 0.32 nm, respectively. Comparing the EDS image, there was no XRD diffraction peak of WS₂ in the S-WO₃ which may be due to insufficient reaction [24]. After loading a layer of Fe₃O₄ nanoparticles on the surface of S-WO₃, 80-Fe₃O₄/S-WO₃ showed faint Fe₃O₄ diffraction peaks. As shown in Fig. 1g, 80-Fe₃O₄/S-WO₃ had weak diffraction peaks at 30.1°, 43.1°, 53.1°, 56.9°, 62.5°. Due to the diffraction peaks of WO₃ in 80-Fe₃O₄/S-WO₃ disappeared, X-ray photoelectron spectroscopy (XPS) was introduced to further characterize its structure.

Fig. 2a is the spectrum of W 4f, it was obviously seen that element W has two valence states of +6 and +4. W with +6 valence comes forms WO₃, while W with +4 valence comes forms WS₂. Peaks located at 35.3 eV (W⁶⁺ 4f₅/₂) and 37.5 eV (W⁶⁺ 4f₇/₂) are typical peaks of WO₃. Peaks

![Image](https://via.placeholder.com/150)
located at 31.8 eV (W 4f1/2) and 33.9 eV (W 4f3/2) are typical peaks of WS2 [26]. Meanwhile, Fig. 2b shows the S 2p spectrum of 80-Fe2O3/S-WO3. The peak at 161.3 eV (S 3/2– 2p3/2), 162.6 eV and 163.7 eV (S 1/2– 2p1/2) correspond to the W-S bond of WS2 [27]. The peak around 168.5 eV is the SO4 2– or S6+ which indicates that part of the S atoms were oxidized to SO4 2– and doped in the WO3 lattice [6]. Studies showed that compared with S 2– to replace O2– in WO3 to form WS2, S6+ is easier to replace W6+ in WO3 [28]. Therefore, the as-prepared S-WO3 support is partially sulfurized WO3 which maybe doped with a small amount of S. The formation process of WS2 in hydrothermal method is complex. It was reported that WCl6 was first oxidized to WO3 intermediate in hydrothermal method, and the WO3 intermediate was gradually vulcanized to WS2 in the presence of TAA. Combined with XRD and HRTEM images, the vulcanized part of WO3 is amorphous WS2. Amorphous structure of WS2 makes the electrons in a more active state, and the electron transport ability is stronger, which is conducive to the process of catalysis. Fig. 2c shows the Fe 2p spectrum. Peaks located at 710.6 eV, 712.8 eV, 724.2 eV and 726.7 eV are Fe2+ 2p3/2, Fe3+ 2p3/2, Fe2+ 2p1/2 and Fe3+ 2p1/2, respectively. Peaks located near 718.1 eV and 733.0 eV are the satellite peaks of Fe 2p3/2 and Fe 2p1/2, respectively [9]. Fig. 2d shows the O 1 s spectrum. Peaks located at 530.1 eV is the lattice oxygen (O2–), which is the Fe-O bond and W-O bond of the composite [29]. Peak located at 531.4 eV is the O–H bond which was formed by the adsorbed oxygen on the surface of the material. The peak at 532.9 eV is H2O which may be derived from crystal water in the composite or water vapor in the air [30]. According to previous reports, WO3 intermediates are first generated, and then WO3 continues to be vulcanized to WS2 in hydrothermally processes [24]. The vulcanization process requires high temperature and high pressure. Yang et al. carried out hydrothermal method to prepare WS2 at 265 °C for 24 h using WCl6 and TAA. And the product was annealed at 300 °C to improve the crystallinity of WS2. It was observed some impurity peaks including WO3, and they disappeared after annealing [24]. Therefore, amorphous WS2 was successfully prepared at 210 °C in this experiment.

In summary, the S-WO3 matrix (partially vulcanized WO3) was successfully prepared and loaded with Fe3O4 nanoparticles. The vulcanized part is amorphous WS2 and amorphous structure is more conducive to the catalytic activity of the material.

3.2. Degradation activity of X-Fe2O3/S-WO3

Fig. 3a and b showed the effect of Fe3O4 loading amounts on PCMX degradation in X-Fe2O3/S-WO3/PMS systems and corresponding first-order rate constants, respectively. The degradation efficiencies of 40/60/80-Fe2O3/S-WO3 for PCMX were 93%, ~100% and ~100%, respectively. Meanwhile, the first-order kinetic model (Fig. 3b) and second-order kinetic model (Fig.S2) were used to fit the degradation of PCMX in the X-Fe2O3/S-WO3/PMS systems, respectively. k1 (min−1) and k2 (L/mg·min) are first-order rate constant and second-order rate constant, respectively (The detailed model equations were listed in Text S3). The details of the fitted data can be found in Table S1. It can be found that the correlation coefficients (R2) of the first-order kinetic model of the catalytic systems are all larger than that of the second-order kinetic model. Therefore, the degradation of PCMX in the X-Fe2O3/S-WO3/PMS system is a first-order reaction. The order of degradation rate constants of the catalysts is 40-Fe2O3/S-WO3 < 60-Fe2O3/S-WO3 < 80-Fe2O3/S-WO3. The degradation rate constant of PCMX reached 1.0982 min−1 in 80-Fe2O3/S-WO3/PMS system, which is much higher than that of most Fenton-like catalysts (Table 1). In order to further determine the catalytic activity of the composite, the Eq.1 was applied to calculate the utilization efficiency of the as-prepared catalysts [31]. ηCat represents the molar mass of pollutants degraded by one gram catalyst in one
minute. As shown in Table 1 and Fig. 3d, 80-Fe₃O₄/S-WO₃ has much higher utilization efficiency (0.3506 mmol·g⁻¹·min⁻¹) as compared to MoS₂/CuFe₃O₄ (0.1143 mmol·g⁻¹·min⁻¹) [32], FeMgAl-MoS₄ (0.0347 mmol·g⁻¹·min⁻¹) [33], CuCo@ZnO (0.0538 mmol·g⁻¹·min⁻¹) [34] and other Fenton-like catalysts. In our previous work, metal sulfide MoS₂ was also applied for modification of Fe₃O₄ nanoparticles (Fe₃O₄@MoS₂) [6], and the utilization efficiency of Fe₃O₄@MoS₂-3 reached 0.3832 mmol·g⁻¹·min⁻¹ which is comparable with that of 80-Fe₃O₄/S-WO₃. The above results demonstrated that using metal sulfide to modify iron-based Fenton-like catalysts is a feasible strategy for improving the degradation rate constants and catalyst’s utilization efficiency.

Fig. 3. (a) Effect of Fe₃O₄ loading amounts on PCMX degradation and (b) corresponding first-order degradation rate constants in X-Fe₃O₄/S-WO₃/PMS systems. (c) Percentage of iron mass of X-Fe₃O₄/S-WO₃. (d) Comparison of utilization efficiency of different catalysts. Conditions: [Cat.] = 0.4 g/L, [PMS] = 1.0 mM, [PCMX] = 20 mg/L, initial pH = 7.1 (without adjustment) and T = 20 ± 1 ℃.

Table 1

Comparison of PMS decomposition and pollutants degradation by different Fenton-like systems.

| Catalysts          | Pollutant            | Conditions                                      | Removal efficiency | Rate constant k₁ (min⁻¹) | ηCat. (mmol·g⁻¹·min⁻¹) | Decomposition efficiency of PMS | ηPMS (%) | Ref. |
|--------------------|----------------------|------------------------------------------------|--------------------|-------------------------|------------------------|-------------------------------|----------|-----|
| PC-MnO₄            | acid orange 7 (20 mg/L) | [Cat.] = 0.4 g/L, [PMS] = 2 mM, pH₆ = 7.0 | 95% in 30 min      | 0.0955                  | 0.0129                 | 55%                           | 0.049    | [35]|
| Fe³⁺/MgAl-MoS₄     | 4-chlorophenol (10 mg/L) | [FeCl₃·6H₂O] = 5 mg/L, [Cat.] = 0.1 g/L, [PMS] = 2 mM | 100% in 60 min     | 0.072                   | —                      | 81%                           | 0.048    | [33]|
| FeMgAl-MoS₄        | parahydroxy benzoic acid (10 mg/L) | [Cat.] = 0.25 g/L, [PMS] = 5 mM | 100% in 60 min     | 0.12                    | 0.0347                 | 50%                           | 0.028    | [36]|
| CuCo@ZnO           | 4-chlorophenol (40 mg/L) | [Cat.] = 0.2 g/L, [PMS] = 2 mM, pH₆ = 7.0 | 96% in 80 min      | 0.036                   | 0.0538                 | 74.7%                         | 0.2      | [34]|
| Fe³⁺/WS₂           | Carbazalpine (8 mg/L) | [FeCl₃·6H₂O] = 0.1 mM, [WS₂] = 0.4 g/L, [PMS] = 1.5 mM, pH₆ = 4.0 | 100% in 20 min      | 0.564                   | —                      | —                             | —        | [21]|
| MoS₂/CuFe₃O₄       | fluoxetine (20 mg/L) | [Cat.] = 0.1 g/L, [PMS] = 1 mM, pH₆ = 6.9 | 97.7% in 20 min     | 0.1810                  | 0.1143                 | —                             | —        | [32]|
| Fe₃O₄@MoS₂⁻⁻       | SA (20 mg/L)         | [Cat.] = 0.4 g/L, [PMS] = 1 mM, pH₆ = 6.5 | 99.8% in 15 min     | 1.3225                  | 0.3832                 | 100%                          | 0.116    | [6] |
| Ce-MoS₂            | BPA (2 mg/L)         | [Cat.] = 0.025 g/L, [PMS] = 50 mg/L, pH₆ = 5.0 | 96.7% in 30 min     | 0.65                    | 0.2203                 | —                             | —        | [31]|
| 80-Fe₃O₄/S-WO₃     | PCMX (20 mg/L)       | [Cat.] = 0.4 g/L, [PMS] = 1.0 mM, pH₆ = 7.1 | 100% in 5 min       | 1.0982                  | 0.3506                 | 100%                          | 0.128    | This work |

The values of ηCat. and ηPMS were calculated by Eq.1 and 2, respectively.
different catalysts. (d) Total organic carbon (TOC) removal efficiency of PCMX in 80-Fe
adsorption capacity may be attributed to the specific surface area of the
exhibited a certain adsorption capacity, 14.1% PCMX (adsorption ca
As shown in Fig. 3c, the ICP data shows that the mass ratios of iron in
40/60/80-Fe
loading amount of Fe
constants also increased with the increasing of the loading
of Fe
also occurred in our previous work [6].
In order to better demonstrate the catalytic activity of the composite
80-Fe
the degradation performance of Fe
S-WO
and 80-
Fe
S-WO
as compared to PC-MnO
Fe
system (81% in 60
Fe
system (0.049) [35], Fe
MgAl-MoS
CuCo@ZnO (0.2) [34], Fe
0.116 [6] and other reported excellent catalysts. Thanks to the interaction
between Fe
S-WO
the catalytic ability of the composite was dramatically enhanced. WS
the surface of S-WO
can quickly and continuously regenerate Fe
S-WO
have limited activation effect on PMS. The residual concentration of
PMS was further determined. As shown in Fig. 4b, pure Fe
S-WO
can decompose about 27.7% and 17.0% of PMS within 10 min, respectively. However, the degradation efficiency of PCMX by these two catalysts were only 6.2% and 2.2%, respectively. The possible reason is that PMS molecules were adsorbed or only decomposed into sulfate, rather than converted into active oxygen species (ROSs). The composite 80-Fe
S-WO
can decompose PMS continuously, and 53.0% of PMS was decomposed within 1 min. PMS was completely decomposed in 5 min. To further understanding the catalytic activity of as-prepared cata-
yysts, the PMS decomposition efficiency was compared with other catalysts reported in the literature. As shown in Table 1 and Fig. 4c, 80-
Fe
S-WO
could completely decompose PMS molecular in 5 min, while other Fenton-like catalysts can’t efficiently activate PMS, such as PC-MnO
(55% in 30 min) [35], Fe
MgAl-MoS
were 26%, 29% and 32%, respectively. With
the increasing of the dosage of iron salt during the preparation process,
the loading amount of Fe
also increased. The degradation rate con-
stants of the composites also increased with the increasing of the loading
of Fe
3
1.0 mM, [PMS] = 1.0 mM, [PCMX] = 20 mg/L, initial pH = 7.1 (without adjustment) and T = 20 ± 1 °C.

\[
\eta_{\text{cat}} \left( \frac{\text{mmol}}{g \cdot \text{min}} \right) = \frac{\Delta \text{[pollutant]}}{[\text{Cat.}]} \times k_1
\]

Where \( \Delta \text{[pollutant]} \) represents the molar mass of degraded pollutants (mmol). [Cat.] represents the dosage of used catalyst in the Fenton-like reaction (g/L). And \( k_1 \) is the first-order rate constant (min\(^{-1}\)).

Fig. 4. (a) Degradation efficiency of PCMX by different catalysts. (b) Residual PMS concentration in different systems. (c) Comparison of PMS utilization efficiency of different catalysts. (d) Total organic carbon (TOC) removal efficiency of PCMX in 80-Fe
S-WO
PMS system. Conditions: [Cat.] = 0.4 g/L, [PMS] = 1.0 mM, [PCMX] = 20 mg/L, initial pH = 7.1 (without adjustment) and T = 20 ± 1 °C.
efficiency of Fe$^{2+}$/Fe$^{3+}$ and catalytic activity [6,20]. The degree of mineralization is also an important parameter in AOPs. TOC removal of PCMX over time in the 80-FeO$_4$/S-WO$_3$/PMS system was determined (Fig. 4d). 31.3% mineralization efficiency achieved in 1 min, 38.8% in 5 min, and 45.4% after 10 min reaction. It proves that the system can rapidly and continuously mineralize pollutants.

$$\eta_{\text{PMS}} = \frac{\Delta [\text{pollutant}]}{\Delta [\text{PMS}]}$$

(2)

Where $\Delta [\text{pollutant}]$ represents the molar mass of degraded pollutants (mmol). $\Delta [\text{PMS}]$ represents the concentration of decomposed PMS (mmol).

The degradation efficiencies of different pollutants by 80-FeO$_4$/S-WO$_3$ were performed to investigate degradation selectivity of the composite. Antibiotics or drugs (sulfonamides (SA), sulfadiazine (SDZ) and PCMX), phenols (phenol and 2,4-dichlorophenol (2,4-DCP)) and endocrine disrupters (bisphenol S (BPS) and bisphenol A (BPA)) were chosen as model pollutants (Fig. 5). 80-FeO$_4$/S-WO$_3$/PMS system exhibited excellent catalytic activity. At least a 90% removal efficiency was achieved within 10 min. Among them, almost all the PCMX, 2,4-DCP, SDZ and BPA can be degraded, and the degradation efficiencies of BPS, SA and phenol were 94.5%, 97.5% and 91.1%, respectively. It can be concluded that 80-FeO$_4$/S-WO$_3$ is not selective for the degradation of different types of pollutants. However, there is difference in the degradation rate constants between them. The degradation rate constants are ranked by $k_{\text{SA}}$(phenol) < $k_{\text{SDZ}}$(phenol) < $k_{\text{BPS}}$(phenol) (the degradation rate constants of other pollutants have little difference). SA and phenol have smaller degradation constant, and the possible reason is that their relatively simple molecular structures are resistant to the attack of ROSs [6,37]. In summary, the composite 80-FeO$_4$/S-WO$_3$ has excellent catalytic activity, fast degradation rate, outstanding PMS utilization efficiency, high mineralization, and no selectivity for the degradation of different types of pollutants.

3.3. Effect of PMS dosage and initial pH

The effect of PMS dosage (0.25 ~ 1.0 mM) on the degradation of PCMX by 80-FeO$_4$/S-WO$_3$ and corresponding degradation rate constants were investigated. When the dosages of PMS were 0.25, 0.50, 0.75 and 1.0 mM, the degradation efficiencies of PCMX were 66.58%, 91.85%, 98.13% and ~ 100%, respectively (Fig. 6a). The degradation efficiency of PCMX and corresponding degradation rate constants increased with the increasing of PMS dosage. When the dosages of PMS were 0.25, 0.50, 0.75 and 1.0 mM, the degradation rate constants of 80-FeO$_4$/S-WO$_3$ to PCMX were 0.1062, 0.2384, 0.3777 and 1.0982 min$^{-1}$, respectively (Fig. 6b). The degradation rate constant of the system increased by about 10 times when the dosage of PMS increased from 0.25 mM to 1.0 mM. It indicates that the catalyst contains numerous active sites, which can quickly activate PMS molecules, generate strong oxidizing ROSs and rapidly degrade pollutants.

Fig. 6c shows the effect of different initial pH values on the degradation of PCMX by 80-FeO$_4$/S-WO$_3$. The acidic environment is conducive to the progress of the catalytic reaction [9]. In acidic environment (pH$_0$ = 3.0 and 5.0), the degradation rate constants of PCMX were faster than that of other initial pH conditions (Fig. 5d). When the initial pH was between 3.0 and 9.0, the removal efficiencies of PCMX reached ~ 100%. And the degradation rate constants follow this order: $k$(pH$_0$ = 3.0) > $k$(pH$_0$ = 5.0) > $k$(pH$_0$ = 7.1) > $k$(pH$_0$ = 9.0). The unsaturated S on the surface of WS$_2$ can react with H$^+$ in acidic environment to generate HS$^-$, so that the active ingredient W$^{4+}$/surf. can be exposed [20]. Active W$^{4+}$ promotes the reduction of Fe$^{2+}$ to Fe$^{3+}$ and dramatically increase the decomposition efficiency of PMS (Eq.3) [20]. It’s worth noting that the redox cycle of W$^{4+}$/W$^{5+}$ is also achievable. As shown in Eq.3 and 4, after W$^{4+}$ is oxidized, HS$^-$ or generate lower reactivity SO$^-$ radicals can react with OH$^-$ to generate HO$^*$ (Eq.5) [38]. The side reactions between free radicals and PMS molecules could consume free radicals or generate lower reactivity SO$^-$ radicals (Eq.6 ~ 8) [6,39]. Nevertheless, the catalyst still showed certain catalytic activity when pH$_0$ = 10.0, 70% degradation efficiency was achieved within 10 min reaction. Since the pH of the solution gradually decreased to 3.3 as the progresses of the reaction, the active sites of the catalyst were gradually released [6]. In this experiment, all pH$_0$ were less than 3.3. Lu et al. [6] and Sun et al. [40] also observed the similar phenomenon in FeO$_4$@MoS$_2$-rGO/PMS system and FeS@nZVI-rGO/PMS system, respectively. Firstly, PMS will produce a large number of HSO$_4$ ions in the reaction.

![Fig. 5. (a) Structures of different pollutants, (b) Degradation efficiency of different pollutants and (c) corresponding first-order degradation rate constants in 80-FeO$_4$/S-WO$_3$/PMS system. Conditions: [Cat.] = 0.4 g/L, [PMS] = 1.0 mM, [PCMX] = 20 mg/L, initial pH = 7.1 (without adjustment) and T = 20 ± 1 °C.](image-url)
process, resulting in the decrease of pH of the solution. Secondly, metal sulfides are acidic in solution [41]. Yan et al. observed that MoS$_{2.0}$ is acidic in solution [41]. WS$_{3.0}$ is also an acidic catalyst, which makes the solution acidic. In summary, 80-Fe$_{3.0}$/S-WO$_3$ is an excellent catalyst, which showed excellent catalytic ability in a wide pH range of 3.0 ~ 9.0.

$$\begin{align*}
W^{6+}_{\text{surf}} + 2\text{Fe}^{2+}_{\text{surf}} &\rightarrow 2\text{Fe}^{3+}_{\text{surf}} + W^{6+}_{\text{surf}}. \\
W^{6+}_{\text{surf}} + 2\text{HSO}_3^- &\rightarrow W^{4+}_{\text{surf}} + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{SO}_4^{2-} + \text{OH}^- &\rightarrow \text{SO}_3^- + \text{HO}^- \\
\text{SO}_4^{2-} + \text{HO}^- &\rightarrow \text{SO}_3^- + 1/2 \text{O}_2 \\
\text{HSO}_3^- + \text{HO}^- &\rightarrow \text{SO}_3^- + \text{H}_2\text{O} \\
\text{HSO}_3^- + \text{SO}_4^{2-} &\rightarrow \text{SO}_3^- + \text{HSO}_3^- 
\end{align*}$$

3.4. Mechanism of 80-Fe$_{3.0}$/S-WO$_3$/PMS system

Four different scavengers (TBA, MeOH, CF, FFA) were used to capture ROSs in the 80-Fe$_{3.0}$/S-WO$_3$/PMS system. As shown in Fig. 7a, all the quenchers had inhibitory effect on the degradation of PCMX. The order of the inhibitory effect of the quenchers is FFA > MeOH > TBA > CF. It can be concluded that the HO$^\bullet$, SO$_4^{\cdot\cdot}$, O$_2$ and 1O$_2$ coexisted in the 80-Fe$_{3.0}$/S-WO$_3$/PMS system. The degradation efficiency of PCMX was inhibited by 27.8% in the presence of 100 mM TBA, and the degradation efficiency of PCMX was inhibited by 43.0% in the presence of 100 mM MeOH. From the point of view of the inhibitory effect, the main free radicals in the system were HO$^\bullet$ and SO$_4^{\cdot\cdot}$. CF had a certain inhibitory effect on the degradation of PCMX, indicating that there was a small amount of O$_2$ in the system. FFA is considered as a well-known quencher of O$_2$ (k = 1.2 × 10$^8$ M$^{-1}$ s$^{-1}$) [43]. The degradation of PCMX was greatly inhibited in the presence of FFA (the degradation efficiency of PCMX was only 10.3%), which indicates the existence of O$_2$ in the system. It’s worth noting that FFA is also an efficient quencher for HO$^\bullet$ and SO$_4^{\cdot\cdot}$ [44,45]. The HO$^\bullet$ and SO$_4^{\cdot\cdot}$ scavenger, MeOH added in 100-fold molar excess of PMS inhibited PCMX degradation by 43.0%. Meanwhile, only 5 mM FFA inhibited PCMX degradation by 89.7%. Therefore, 1O$_2$ is involved in the degradation of PCMX. HO$^\bullet$, SO$_4^{\cdot\cdot}$ and 1O$_2$ are the main ROSs in the 80-Fe$_{3.0}$/S-WO$_3$/PMS system. Moreover, 1O$_2$ is likely to be the main source of 1O$_2$ (Eq.9) [46].

EPR was applied to further verify the ROSs in this system. As shown in Fig. 7b, all the S-WO$_3$/PMS, Fe$_{3.0}$/O$_3$/PMS and 80-Fe$_{3.0}$/S-WO$_3$/PMS systems had detected the typical 1:2:2:1 peaks, which were the signals of HO$^\bullet$ [18]. And the 80-Fe$_{3.0}$/S-WO$_3$/PMS system had the strongest HO$^\bullet$ intensity. It is consistent with the degradation efficiency of PCMX and the residual concentration of PMS (Fig. 4a and b). Due to the pure Fe$_{3.0}$/O$_3$ and S-WO$_3$ had low ability to decompose PMS, the signal intensity of HO$^\bullet$ radicals in S-WO$_3$/PMS and Fe$_{3.0}$/O$_3$/PMS systems was much smaller than that in 80-Fe$_{3.0}$/S-WO$_3$/PMS system. At the same time, typical SO$_4^{\cdot\cdot}$ with a typical shape of 1:1.1:1:1:1 was observed in the 80-Fe$_{3.0}$/S-WO$_3$/PMS system [21]. This is consistent with the results of quenching experiments that the inhibitory effect of MeOH on the degradation of PCMX was stronger than that of TBA. No obvious SO$_4^{\cdot\cdot}$ were observed in...
WO$_3$/PMS and Fe$_3$O$_4$/PMS systems. The composite 80-Fe$_3$O$_4$/S-WO$_3$ could activate PMS to produce SO$_4^-$ and HO$^*$ through Eq. (10) \( \sim 11 \ [27,47] \). The possibility of the existence of O$_2$ in the system was further verified. As shown in Fig. 7c, obvious O$_2$ signals were observed in the 80-Fe$_3$O$_4$/S-WO$_3$/PMS system, which may be generated by Eq. (12) \( \sim 14 \ [48] \). However, O$_2$ signals were not detected in S-WO$_3$/PMS and Fe$_3$O$_4$/PMS systems. It indicates that there was synergy effect between S-WO$_3$ and Fe$_3$O$_4$ in the composite, and the metal activity of the composite was dramatically improved. The presence of O$_2$ was further verified by EPR using spin trapping agent TEMP. It was reported that the EPR signal of TEMPO radicals may not accurately represent the presence of O$_2$ [49]. In this study (Fig. 7d), the intensity of the O$_2$ peak of the 80-Fe$_3$O$_4$/S-WO$_3$/PMS system (9.4 \( \times 10^5 \)) is about 2.5 times that of the S-WO$_3$/PMS (3.6 \( \times 10^5 \)) and Fe$_3$O$_4$/PMS systems (3.7 \( \times 10^5 \)). From the point of view of signal strength, the O$_2$ signal can be ruled out as a false positive result, which also indicates the existence of O$_2$. Based on the quenching experiments and EPR analysis, it can be known that HO$^*$, SO$_4^-$ and O$_2$ play the dominated role.

\[
\begin{align*}
\text{Fe}^{2+} + \text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{O}_2^* \\
\text{Fe}^{2+} + \text{H}^+ & + \text{SO}_4^- \rightarrow \text{Fe}^{3+} + \text{H}^+ + \text{SO}_4^-
\end{align*}
\]

After clarifying the main ROSs in 80-Fe$_3$O$_4$/S-WO$_3$/PMS system, the main active components of the composite were further investigated. There are three components, Fe$_3$O$_4$, WO$_3$ and WS$_2$ in the composite 80-Fe$_3$O$_4$/S-WO$_3$. Undoubtedly, Fe$_3$O$_4$ is the main active component to activate PMS. The role of WO$_3$ and WS$_2$ in the composite was further verified by comparative experiments. Pure WO$_3$ can be prepared under the same preparation conditions of S-WO$_3$ but without adding TAA. As shown in Fig. 8c, pure WO$_3$ is light yellow powder with cubic microstructure [52,53], which is consistent with WO$_3$ standard card.
As shown in Fig. 8a, the removal performance of WO3 and S-WO3 on PCMX differs greatly. WO3 itself adsorbed and removed about 13.3% of PCMX within 10 min. The adsorption performance of the composite 80-Fe2O3/WO3 was minimal for PCMX. Meanwhile, the removal efficiency of PCMX by WO3/PMS and 80-Fe2O3/WO3/PMS systems were only 28.9% and 24.1%, respectively. Studies have shown that the transfer of electrons from the surface of WO3 to PMS is thermodynamically feasible, so WO3 can activate part of the PMS to degrade pollutants [54]. The catalytic ability of WO3 and 80-Fe2O3/WO3 to PMS was obviously insufficient, indicating that WO3 does not play a primary role in the composite. After Vulcanization, the adsorption and catalytic performance of S-WO3 was minimal. It showed that S-WO3 itself does not have catalytic ability. After loading Fe3O4 nanoparticles, the performance of the composite had been dramatically improved. Compared with the pure Fe3O4/PMS and S-WO3/PMS system, the 80-Fe2O3/S-WO3 had increased the degradation efficiency of PCMX by approximately 16 times and 45 times, respectively. Therefore, S-WO3 plays a dominate role as a promoter in the composite, and the main active component is WS2 in S-WO3.

After determining the co-catalytic effect of WS2, XPS was applied to analyze the changes in the content of Fe3+surf and W4+surf on the surface of the catalyst 80-Fe2O3/S-WO3 before and after the reaction, as shown in Table 2 (XPS analysis of the used catalyst was shown in Fig S3). After the reaction, the content of Fe3+surf increased by about 3.16%, and the W4+surf content decreased by 9.64%. The data proved that the active component WS2 on the catalyst surface reacted with Fe3O4. As shown in Eq.3 and Fig. 9, W4+surf on the surface of WS2 reduced Fe3+surf to Fe2+surf, which increased the decomposition efficiency of PMS and thus improved the catalytic efficiency. Fe3+/Fe2+ redox cycles are also observed in the Fenton-like systems such as WS2/PMS/Fe3+ [21] and WS2/H2O2/Fe2+ [20].

In summary, the main active component in the composite 80-Fe2O3/S-WO3 is Fe3O4, which participates in the decomposition of PMS. The Vulcanized part WS2 in S-WO3 is the main co-catalyst, which participates in Fe3+/Fe2+ cycles on the surface of Fe3O4. The degradation of PCMX and other ECs is dominated by HO•, SO4•− and 1O2.  

3.5. The recyclability of 80-Fe2O3/S-WO3

The cyclic performance is an important parameter for investigating the practical application of a catalyst. Thus, cyclic experiments were carried out. The composite was collected without washing after each cycle, followed by adding the PCMX solution and PMS directly to start a new cycle. As shown in Fig S4a, the composite exhibited a certain degree of recyclability. The removal efficiencies of PCMX during the 5 cycles...
During the first two cycles, the activity of the catalyst gradually decreased from the third cycle. Only about 50% of the reactivity was remained after 5 cycles reaction. In our previous research, it was found that the performance of Fe\textsubscript{3}O\textsubscript{4}-based composites will inevitably decline during the cyclic experiments \cite{7,14}. Many factors will affect the cycling performance of 80-Fe\textsubscript{3}O\textsubscript{4}/S-WO\textsubscript{3}. a) As shown in Fig.S4b, the concentration of total dissolved iron ions reached 1.2 mg/L in the first cycle. PMS is acidic in the aqueous solution, and it corrodes Fe\textsubscript{3}O\textsubscript{4} nanoparticles to a certain degree and resulting in a decrease in activity \cite{7,55}. b) The leaching of the W element is also inevitable. Moreover, active W\textsuperscript{6+}\text{surf.} itself was oxidized to inert W\textsuperscript{6+}\text{surf.}, when Fe\textsuperscript{3+}\text{surf.} was reduced to Fe\textsuperscript{2+}\text{surf.} And W\textsuperscript{6+}\text{surf.} is difficult to be reduced to W\textsuperscript{4+}\text{surf.}, which resulting WS\textsubscript{2} loses its co-catalytic activity \cite{21}. c) The loss of catalyst is also inevitable during the experiments \cite{14}. The above factors are the reasons that lead to the decrease of the catalytic activity. In future research, more attention should be focused on how to improve the stability and recyclability of metal-based composites \cite{56}.

### 3.6. Degradation pathways of PCMX

Through HPLC-MS and literature analysis, 52 intermediate products of PCMX were identified. The mass spectrum of PCMX solution after X-Fe\textsubscript{3}O\textsubscript{4}/S-WO\textsubscript{3}/PMS treatment and the m/z spectra of the intermediates were listed in Fig.S5 and Fig.S6, respectively. Fig. 10 shows the possible degradation pathways of PCMX in the 80-Fe\textsubscript{3}O\textsubscript{4}/S-WO\textsubscript{3}/PMS system. Six possible degradation pathways were identified. According to the literature, the benzene ring and phenolic hydroxyl group of PCMX are more susceptible to be attacked by free radicals \cite{8}. Pathway III is the addition reaction of phenolic hydroxyl group under the attack of free radicals. As for pathway IV, V and VI, the benzene ring of the PCMX molecule was directly opened by free radicals and the opening positions are the C4-C5, C3-C4 and C2-C3 bond. After the benzene ring was opened, the C at the end of the molecular was continuously oxidized to generate a variety of carboxylic acids \cite{8}. In pathway I, Cl10 was directly dechlorinated and oxidized to hydroxyl, and in pathway II, C9 of the PCMX benzene ring side chain was oxidized to ketone. Under the attack of ROSs, these intermediates undergo a) dechlorination, b) ring-opening, c) benzene ring side chain oxidation and other reactions, generating a variety of ketones, aldehydes and carboxylic acids and small molecular organic matters until it was mineralized \cite{57,58}. The complexity of PCMX degradation pathways may be the result of the combined action of multiple ROSs. If these intermediates are directly discharged, they will inevitably cause hidden risks to the ecological environment \cite{59}. Therefore, further advanced treatment is necessary to increase the mineralization of the PCMX effluent.

### 4. Conclusion

In summary, the composite Fe\textsubscript{3}O\textsubscript{4}/S-WO\textsubscript{3} was successfully synthesized by simple solvothermal method for PCMX removal. The component WS\textsubscript{2} in S-WO\textsubscript{3} plays the role of co-catalytic effect. Active element W\textsuperscript{6+}\text{surf.} takes participate in the reduction of Fe\textsuperscript{3+}\text{surf.} and facilitates the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} redox cycle. Thereby, outstanding PMS decomposition (100%) and utilization efficiency (0.128), high PCMX degradation efficiency (100%), fast degradation rate (1.0982 min\textsuperscript{-1}) and excellent catalytic utilization efficiency (0.3506 mmol\textsuperscript{-1}g\textsubscript{cat.}\textsuperscript{-1}min\textsuperscript{-1}) were achieved. Compared with Fe\textsubscript{3}O\textsubscript{4} alone, the composite improved the PMS decomposition and PCMX degradation efficiency by 4 and 16 times, respectively. What’s more, the composite showed high reactivity over a wide pH rage (3.0 ~ 9.0) and had no degradation selectivity for a variety of emerging pollutants, such as antibiotics, drugs, phenols and endocrine disrupters. 52 intermediates of PCMX were formed through six pathways in 80-Fe\textsubscript{3}O\textsubscript{4}/S-WO\textsubscript{3}/PMS system. Further advanced treatment is
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Fig. 10. Possible degradation pathways of PCMX in 80-Fe$_3$O$_4$/S-WO$_3$/PMS system.

recommended for PCMX degradation effluent to reduce its potential risk. Our finding demonstrated Fe$_3$O$_4$/S-WO$_3$ is an excellent catalyst for PCMX degradation, and applying metal sulfides to modify iron-based materials is a feasible strategy for constructing heterogeneous catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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