

Article

Phosphogypsum-Supported CoFe_2O_4 for Peroxymonosulfate Activation and Bisphenol AF Degradation: Performance and Mechanistic Assessment

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Abstract

Bisphenol AF (BPAF), a highly persistent fluorinated substitute for bisphenol A with endocrine-disrupting risks, resists conventional water treatment. To simultaneously address recalcitrant fluorinated pollutant removal and phosphogypsum (PG) valorization, we synthesized a CoFe_2O_4 @PG composite catalyst via sol-gel using industrial PG as support, and applied it to activate peroxymonosulfate (PMS) for BPAF degradation. CoFe_2O_4 was successfully loaded onto PG, forming densely packed quasi-spherical aggregates. Under optimal conditions, the 10% CoFe_2O_4 @PG/PMS system removed 99.17% of BPAF within 60 min, outperforming CoFe_2O_4 /PMS and confirming that PG loading enhances catalytic activity. The system tolerated pH variations; Cl^- had some interference, while CO_3^{2-} , SO_4^{2-} , and HPO_4^{2-} showed limited effects. The Co(II)/Co(III) and Fe(II)/Fe(III) redox cycles play a key role in the activation of PMS to generate reactive oxygen species (ROS), with the sulfate radical ($\text{SO}_4^{\bullet-}$) and singlet oxygen ($^1\text{O}_2$) being the primary reactive species. The catalyst exhibited broad pH adaptability, anti-interference, and cycling stability; after five cycles, removal decreased by only 15.48%, and metal leaching complied with Chinese national standards. This work offers a new strategy for fluorinated-pollutant remediation and PG valorization.

Keywords: bisphenol AF; phosphogypsum; CoFe_2O_4 @PG; peroxymonosulfate; advanced oxidation processes

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1. Introduction

Bisphenol AF (BPAF), a fluorinated alternative to BPA with a hexafluoroisopropyl moiety, is widely used in electronic components, fluoroelastomers, and optical resins due to its thermal and corrosion resistance [1]. It has been detected in water (0–3080 ng L⁻¹), sludge (0–275 ng g⁻¹), and sediment (0–4.13 ng g⁻¹) [2,3]. With global restrictions on BPA, BPAF production and use are increasing, likely leading to greater environmental release. Moreover, its trifluoromethyl groups confer persistence and endocrine-disrupting toxicity [4,5]. Conventional biological and coagulation processes cannot effectively mineralize or remove BPAF, and long-term accumulation may threaten aquatic ecosystems and human

endocrine systems. Therefore, developing efficient and cost-effective advanced degradation technologies for BPAF has become a critical research priority in water remediation.

Sulfate radical-based advanced oxidation processes (SR-AOPs) using peroxymonosulfate (PMS) offer a high oxidation potential, a broad applicable pH range, and good oxidant stability during storage and transportation, and have therefore become a major technology for treating refractory fluorinated phenolic contaminants [6,7]. Although homogeneous cobalt ions activate PMS efficiently, free Co ions can cause secondary heavy-metal contamination and generate metal-containing sludge after treatment, limiting engineering applications. Heterogeneous transition-metal oxide catalysts enable rapid solid-liquid separation and substantially reduce the risk of metal leaching. Among them, spinel CoFe_2O_4 efficiently activates PMS through $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ bimetallic redox cycles without external energy input, while offering magnetic recoverability and good chemical stability; [8,9] reported that nanoscale CoFe_2O_4 removed 99.8% of moxifloxacin within 30 min at a catalyst dosage of 0.1 g L^{-1} and a PMS concentration of 0.25 mM, with a pseudo-first-order rate constant of 0.194 min^{-1} . Nevertheless, unsupported nanoscale CoFe_2O_4 has a high surface energy and readily agglomerates during reaction, blocking active sites and substantially reducing catalytic capacity. Long-term cycling in the absence of a support can also result in appreciable metal-ion leaching, while coexisting cations and anions in water may directly occupy surface catalytic sites and weaken treatment performance in practical waters [10,11].

To mitigate CoFe_2O_4 particle agglomeration and improve resistance to matrix interference and cycling stability, previous studies have used biochar [12,13], layered double hydroxides [14], and clay minerals [15] as supports to disperse the active components. The biochar loaded with CoFe_2O_4 nanoparticles ($\text{CoFe}_2\text{O}_4/\text{HPC}$), prepared via pyrolysis, exhibits strong magnetism, hierarchically porous structure, and graphitic structure. The degradation performance of $\text{CoFe}_2\text{O}_4/\text{HPC}$ for BPA is significantly superior to that of pristine CoFe_2O_4 [16]. Fan et al. [17] developed a novel CoFe_2O_4 -coated carbon nanotube composite ($\text{CoFe}_2\text{O}_4/\text{CNT}$) through a modified impregnation-sintering method, achieving 95.3% degradation of the antibiotic florfenicol (FLO) within 30 min. However, carbon-based supports are costly and prone to oxidative loss at high temperatures, while modified clays have limited pore structures, highlighting the need for low-cost supports from bulk solid wastes [18]. Phosphogypsum (PG), a bulk waste from wet-process phosphoric acid production, is stockpiled in large quantities annually; open-air storage can cause fluoride and phosphorus contamination [19]. As an inorganic solid mainly composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, PG can serve as a low-cost support for metal-oxide composites. However, thermal treatment alters its hydration state, and impurities may affect catalytic performance and environmental behavior. Research on PG-supported CoFe-based oxides for PMS activation remains scarce, and key factors relevant to practical water matrices—such as coexisting ions, pH, and cycling stability—have not been systematically investigated.

Thus, PG-supported $\text{CoFe}_2\text{O}_4/\text{PG}$ catalysts with varying loading ratios were prepared via sol-gel and evaluated for PMS activation using BPAF as the target pollutant. The materials were characterized by SEM, FTIR, and XPS for morphology, phase composition, and surface elemental valence states. The effects of reaction system, catalyst dosage, PMS concentration, pH, and coexisting anions on degradation were examined. Cycling tests and ICP-based metal-leaching measurements assessed stability and environmental safety. Quenching experiments identified the main reactive species and elucidated the synergistic activation mechanism. This work provides a novel solid-waste-based catalytic material for fluorinated pollutant treatment.

2. Results and Discussion

2.1. Material Characterization

2.1.1. SEM and EDS Analysis

The surface morphologies of the prepared samples were characterized by SEM. As shown in Figure 1a,b, the PG predominantly exhibits an orthorhombic prismatic habit with a typical rhombic plate-like morphology, a rough surface, and some agglomerated particles attached, which are inferred to be residual impurities from the original material [20]. CoFe_2O_4 exhibits an irregular cubic spinel structure, with pronounced agglomeration among particles (Figure 1c,d) [21]. After CoFe_2O_4 loading (Figure 1e,f), the surface morphology of PG undergoes significant changes. The CoFe_2O_4 particles are tightly coated on the PG surface, forming spherical-like aggregates, and the overall packing is dense. EDS mapping analysis results (Figure S1) show that the main elements in the $\text{CoFe}_2\text{O}_4/\text{PG}$ composite are Ca, O, S, Co, and Fe. Among them, Co and Fe are heterogeneously distributed on PG, confirming the successful synthesis of the $\text{CoFe}_2\text{O}_4/\text{PG}$ composite.

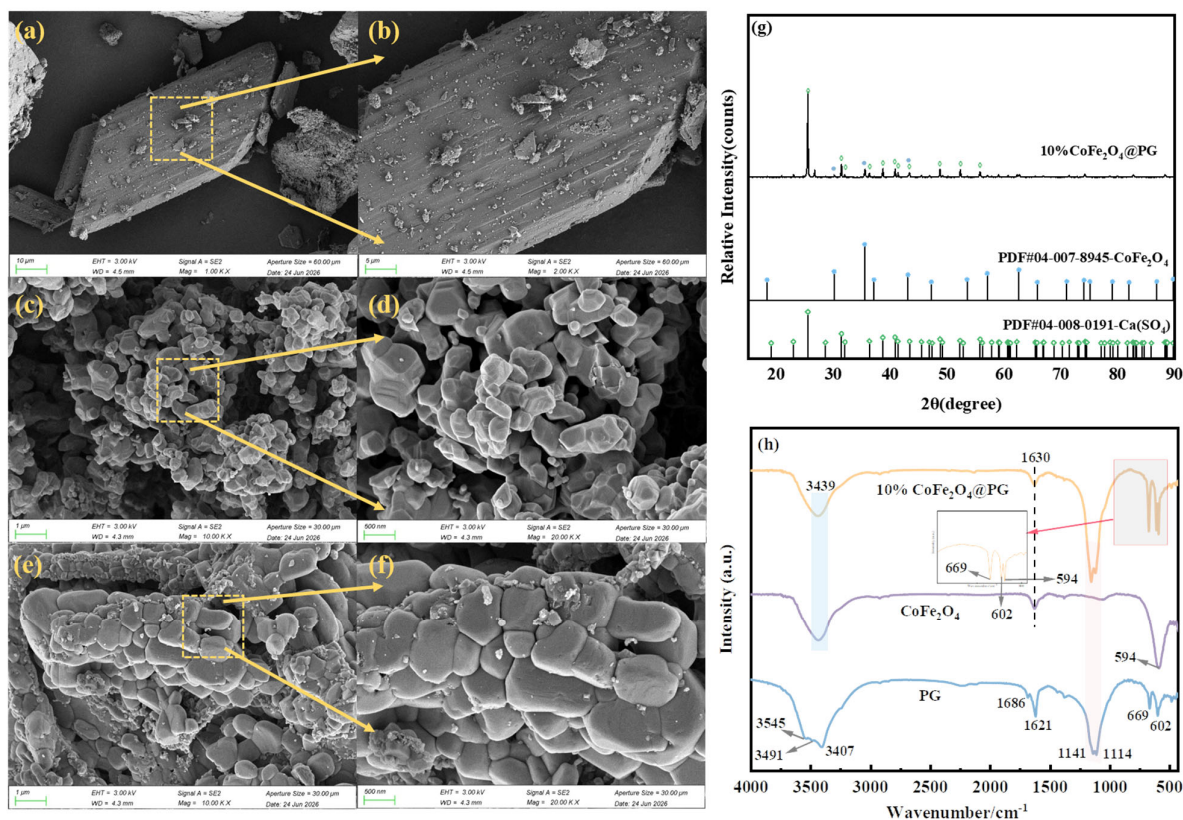


Figure 1. SEM images of (a,b) PG; (c,d) CoFe_2O_4 ; (e,f) 10% $\text{CoFe}_2\text{O}_4/\text{PG}$; XRD patterns of the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ (g); FTIR spectra of the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ (h).

2.1.2. XRD and FTIR Analysis

The samples were characterized by XRD, and the results are shown in Figure S2. The main component in PG was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (PDF#04-008-9805). The diffraction peaks at $2\theta = 30.1^\circ, 35.6^\circ, 37.2^\circ, 43.2^\circ, 53.6^\circ, 57.1^\circ$, and 62.7° are assigned to the (220), (311), (222), (400), (422), (511), and (440) planes of CoFe_2O_4 , respectively (PDF#04-007-8945), confirming the formation of CoFe_2O_4 [21]. After CoFe_2O_4 was loaded onto PG (Figure 1g), characteristic reflections of both CoFe_2O_4 and CaSO_4 (PDF#04-008-0191) are detected in the composite,

supporting the successful synthesis of $\text{CoFe}_2\text{O}_4/\text{PG}$. The conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in PG to CaSO_4 is likely caused by the loss of crystal water during high-temperature calcination [22].

The FTIR spectra of the materials are presented in Figure 1h. As shown in the figure, the bands at 3545, 3491, and 3407 cm^{-1} are assigned to O-H stretching vibrations in PG, whereas those at 1686 and 1621 cm^{-1} arise from O-H bending vibrations [20]. The absorption bands at 1141, 1114, 669, and 602 cm^{-1} are attributed to SO_4^{2-} vibrations [12]. The strong characteristic peak of CoFe_2O_4 at 594 cm^{-1} is attributed to the metal–oxygen (Co–O and Fe–O) stretching vibrations, indicating the successful preparation of CoFe_2O_4 [23]. In addition, its surface is readily covered by hydroxyl groups in water, giving rise to absorption peaks of –OH at 3439 and 1630 cm^{-1} . After loading CoFe_2O_4 onto PG (Figure 1h), the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ sample exhibits absorption peaks of Co–O and Fe–O at 594 cm^{-1} , indicating the successful loading of CoFe_2O_4 onto PG.

2.2. BPAF Degradation Performance of $\text{CoFe}_2\text{O}_4/\text{PG}$

2.2.1. Comparison of Different Loading Ratios of CoFe_2O_4

The effect of the CoFe_2O_4 loading ratio on PMS activation for BPAF degradation was first examined (Figure 2a). Within 60 min, catalysts with loading ratios of 10%, 20%, 50%, and 70% achieved BPAF removal efficiencies of 99.17%, 97.98%, 95.92%, and 95.90%, respectively, indicating only small overall differences in performance. Excessive metal loading can promote particle agglomeration and mask surface active sites, thereby limiting further enhancement of organic-pollutant degradation [24]. A comparison of their kinetic data revealed that the K values for 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ and 20% $\text{CoFe}_2\text{O}_4/\text{PG}$ were 0.07829 min^{-1} and 0.08257 min^{-1} , respectively, with little difference between the two (Figure S3a). Considering both preparation cost and catalytic performance, the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ catalyst was selected for subsequent experiments.

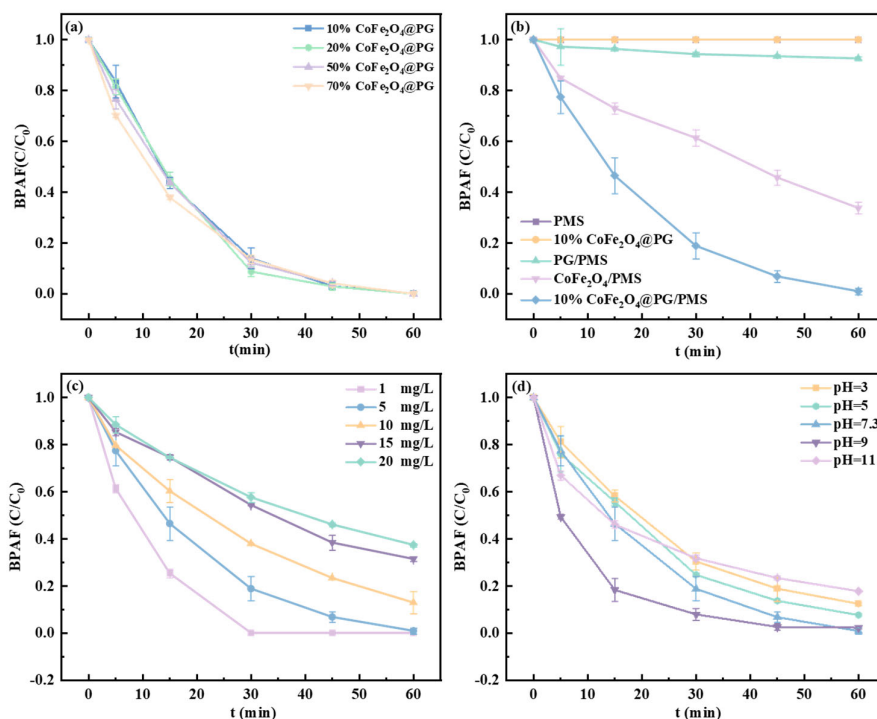


Figure 2. (a) Degradation of BPAF with different CoFe_2O_4 loadings. (b) Degradation of BPAF with different catalyst systems. (c) Degradation of BPAF at different BPAF concentrations. (d) Degradation of BPAF under different initial pH values.

2.2.2. Comparison of Different Reaction Systems

To clarify the synergistic catalytic effect of the composite, control experiments were conducted using different reaction systems (Figures 2b and S3b). PMS alone produced negligible BPAF degradation, indicating limited direct oxidation by PMS under the tested conditions. BPAF concentration also showed no appreciable decrease in the presence of 10% CoFe₂O₄@PG alone, confirming that adsorption by the catalyst contributed little to BPAF removal. The PG/PMS system achieved only 7.44% removal, indicating that PG itself had negligible activity toward PMS activation. Within 60 min, the CoFe₂O₄/PMS system achieved a BPAF removal efficiency of 66.28%, while the 10% CoFe₂O₄@PG/PMS system achieved a BPAF removal efficiency of 99.17% and exhibited a kinetic constant significantly higher than that of the individual materials, indicating that its catalytic performance is far superior to that of the CoFe₂O₄/PMS system. This suggests that composite materials are more effective at activating PMS.

2.2.3. Influence of the Initial BPAF Concentrations, Catalyst Dosage, PMS Concentration and pH

Figures 2c and S3c shows the effect of the initial BPAF concentration over 1–20 mg/L. The degradation rate decreased progressively as the initial BPAF concentration increased. At a BPAF concentration of 1 mg/L, there are relatively abundant oxidation and catalytic sites, allowing for nearly complete removal within 30 min. At a concentration of 5 mg/L, a degradation rate of 99.17% can still be achieved within 60 min. When the initial concentration was further increased to 10, 15, and 20 mg/L, the residual BPAF concentration after the same reaction time increased markedly. This trend may be explained by the finite number of catalytic sites available for electron transfer at fixed catalyst and PMS dosages. At higher BPAF concentrations, BPAF molecules competed for these limited surface sites, while degradation intermediates could accumulate on the catalyst surface and further restrict site accessibility, thereby lowering the removal efficiency. Therefore, 5 mg/L was chosen as the initial concentration. Figure S4a,c systematically examined the effect of 10% CoFe₂O₄@PG dosage in the range of 0.2–1.0 g/L on BPAF degradation in the PMS system. When the catalyst dosage increased from 0.2 to 0.6 g/L, both the degradation rate and final removal efficiency increased markedly. At 0.2 g/L, the limited number of catalytic sites restricted PMS activation, resulting in only 81.74% BPAF removal within 60 min. Increasing the catalyst dosage supplied more sites for PMS activation and consequently accelerated BPAF oxidation [25]. When the catalyst concentration was 0.6 g/L, the removal rate reached 99.17%, which is equivalent to the nearly complete removal of BPAF. Increasing the concentration from 0.6 g/L to 0.8 g/L did not result in a significant improvement in the final removal rate, and the degradation rate constant remained essentially unchanged; therefore, 0.6 g/L was selected as the catalyst concentration for subsequent experiments. The effect of PMS dosage on BPAF removal is shown in Figure S4b,d. Over the investigated range of 0.05–0.60 mM, BPAF removal increased continuously with increasing PMS concentration. Increasing the PMS concentration supplied more precursor for reactive-species generation and markedly accelerated BPAF degradation [26]. When the PMS concentration reached 0.40 mM and 0.60 mM, BPAF was almost completely removed. The degradation rate constants were 0.0745 min^{−1} and 0.0770 min^{−1}, respectively, with little difference between the two. After considering both removal efficiency and economic costs, this study decided to use a PMS concentration of 0.40 mM. Compared with relevant reports in the literature (Table S2), the 10% CoFe₂O₄@PG prepared in this study exhibited good performance in degrading BPAF and demonstrated certain advantages.

The initial pH of the solution can regulate the surface charge of the catalyst, the generation of reactive species, and the existing form of BPAF, making it an important parameter affecting catalytic degradation performance. Therefore, the effect of initial pH on

BPAF removal by 10% CoFe₂O₄@PG was investigated in this study, and the results are shown in Figures 2d and S3d. Within the pH range of 3–11, the BPAF removal efficiency by 10% CoFe₂O₄@PG exceeded 80%. However, the removal efficiencies decreased to 87.56%, 92.35%, and 82.17% under strongly acidic (pH = 3), weakly acidic (pH = 5), and strongly alkaline (pH = 11) conditions, respectively. This is mainly because PMS is more stable under acidic conditions, which hinders the conversion of PMS to reactive oxygen species (ROS) and thus reduces the catalytic activity [25]. Under strongly alkaline conditions (pH ≥ 11), the generated SO₄^{•−} may be quenched by OH[−], leading to a decrease in catalytic performance [21]. At pH = 7.3, the maximum BPAF removal efficiency reached 99.17%. In addition, as shown in Figure S5, we observed the pH changes in a reaction system with an initial pH of 7.3 and found that the pH dropped significantly after the addition of PMS; as the reaction proceeded, the final pH reached 3.85. Relevant studies have indicated that after the reaction, when the initial solution's pH is adjusted to acidic or neutral conditions, the final solution remains acidic with a pH < 4; this is referred to as the system's buffering capacity. As the initial solution's pH is further increased to strongly alkaline conditions, the reaction system exhibits limited buffering capacity, and the buffering effect is completely lost when the initial pH is 11.0 [27,28]. Overall, the 10% CoFe₂O₄@PG/PMS system exhibits wide pH applicability, which lays a foundation for its practical application.

2.2.4. Influence of Different Inorganic Ions

Natural waters commonly contain inorganic anions that can interfere with advanced oxidation processes by scavenging reactive radicals or occupying surface active sites. Typical anions, including Cl[−], CO₃^{2−}, SO₄^{2−}, and HPO₄^{2−}, were therefore selected to evaluate their effects at concentrations of 0.1–1.0 mM on BPAF removal by the 10% CoFe₂O₄@PG/PMS system (Figure 3a,d).

Compared with the anion-free control, the addition of Cl[−] markedly decreased BPAF removal, and the inhibitory effect intensified as the Cl[−] concentration increased from 0.1 to 1.0 mM. At 0.1 mM Cl[−], BPAF removal after 60 min was 60.44%; at 1.0 mM Cl[−], it decreased to 35.44%. This inhibition was attributed to the reaction of Cl[−] with •OH and SO₄^{•−}, which generated less reactive chlorine-containing radicals [29]. When the CO₃^{2−} concentration increased from 0.1 mM to 1 mM, the BPAF removal efficiency still showed little change. The inhibitory effect of SO₄^{2−} on the reaction was relatively mild (Figure 3c). In the concentration range of 0.1–1.0 mM, the BPAF degradation curves only exhibited a slight upward shift; even at 1.0 mM, a removal efficiency of 93.42% could still be achieved within 60 min. SO₄^{2−} is relatively inert in oxidation and is only slightly adsorbed onto the catalyst surface, causing site competition without significantly consuming the reactive radicals in the system, thus having limited interference with the overall degradation kinetics. In contrast, HPO₄^{2−} slightly promoted BPAF degradation, mainly because HPO₄^{2−} can accelerate pollutant degradation through a buffering effect [30]. Overall, the order of influence of different ions on BPAF removal efficiency is as follows: Cl[−] > SO₄^{2−} > CO₃^{2−} > HPO₄^{2−}.

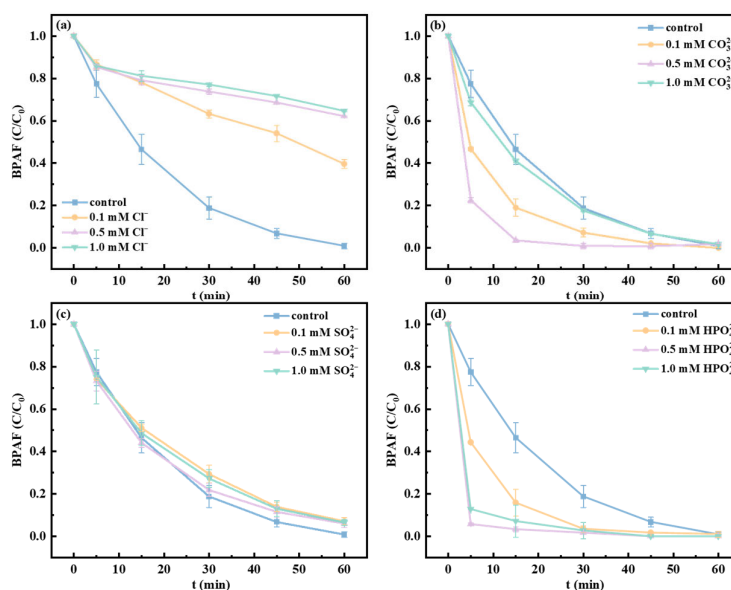


Figure 3. Effect of common anions on the degradation of BPAF by 10% CoFe₂O₄@PG/PMS system, (a) Cl[−], (b) CO₃^{2−}, (c) SO₄^{2−}, (d) HPO₄^{2−}.

2.3. Reaction Mechanisms

2.3.1. XPS Analysis

XPS analysis was performed on the prepared 10% CoFe₂O₄@PG to verify the elemental composition and valence state changes on the material surface, aiming to elucidate the catalytic mechanism. As shown in Figure S6, characteristic peaks of Co, Fe, O, Ca, C, and S were observed in the composite before the reaction. After the reaction, the peaks of Co and Fe were enhanced, which is consistent with the SEM and XRD results, indicating that the CoFe₂O₄ deposited within PG was exposed after the reaction.

Figure 4a presents the Co 2p spectra of the 10% CoFe₂O₄@PG composite before and after the reaction. Before the reaction, the two peaks of Co 2p_{3/2} were located at 779.78 eV and 782.17 eV, corresponding to Co(III) and Co(II), respectively [31], with relative contents of 63.5% and 36.5%. Compared with the fresh CoFe₂O₄@PG composite, the Co 2p_{3/2} peaks of the spent composite shifted slightly to 780.11 eV and 782.78 eV, and the relative content of Co(III) increased from 63.5% to 66.4%, while that of Co(II) decreased from 36.5% to 33.6%, indicating that electron transfer occurred during the catalytic process [12]. Figure 4b displays the Fe 2p spectra of the 10% CoFe₂O₄@PG composite before and after the reaction. Before the reaction, the peaks at 710.80 and 724.52 eV were attributed to Fe(II), while those at 714.06 and 726.86 eV were assigned to Fe(III) [32]. After the reaction, the relative content of Fe(II) decreased from 66.8% to 62.0%, whereas that of Fe(III) increased from 33.2% to 38.0%. These results indicate that Co(II)/Co(III) and Fe(II)/Fe(III) valence state cycling occurs during the activation of PMS by the CoFe₂O₄@PG composite [33]. The changes observed in the XPS data confirm that the Co(II)/Co(III) and Fe(II)/Fe(III) redox pairs are the key driving forces behind PMS activation and the generation of reactive oxygen species [34].

Figure 4c presents the O 1s spectra of the 10% CoFe₂O₄@PG composite before and after the reaction. Before the reaction, the O 1s spectrum of CoFe₂O₄@PG could be deconvoluted into three components: the peak at 529.73 eV was assigned to lattice oxygen (O_{lat}) corresponding to Co–O and Fe–O bonds; the peak at 531.88 eV was attributed to surface

hydroxyls (O_{surf}); and the peak at 534.03 eV was ascribed to adsorbed oxygen (O_{ads}), originating from water molecules adsorbed on the catalyst surface or within the pores [35,36]. The peak area of O_{lat} (Fe–O/Co–O) increased from 4.94% to 23.04%, while the peak area of O_{surf} decreased from 89.15% to 58.50%. This is because, during the degradation process, the activation of Fe–O/Co–O bonds in PMS leads to increased generation of reactive oxygen species (ROS) [37,38]. The relative content of O_{ads} increased from 5.6% to 18.5%, which could be ascribed to the adsorption of water molecules from the reaction solution, as well as the deposition and adsorption of BPAF degradation intermediates on the catalyst surface. In addition, after BPAF removal, the Ca 2p spectrum shifted to lower binding energy (Figure 4d), suggesting that the Ca in PG may promote the reduction of Co(III) and Fe(III) to Co(II) and Fe(II), thereby facilitating the redox cycles of Co(II)/Co(III) and Fe(II)/Fe(III) and enhancing the activation efficiency of PMS. Similar phenomena have been observed in the study by Lu et al. [39].

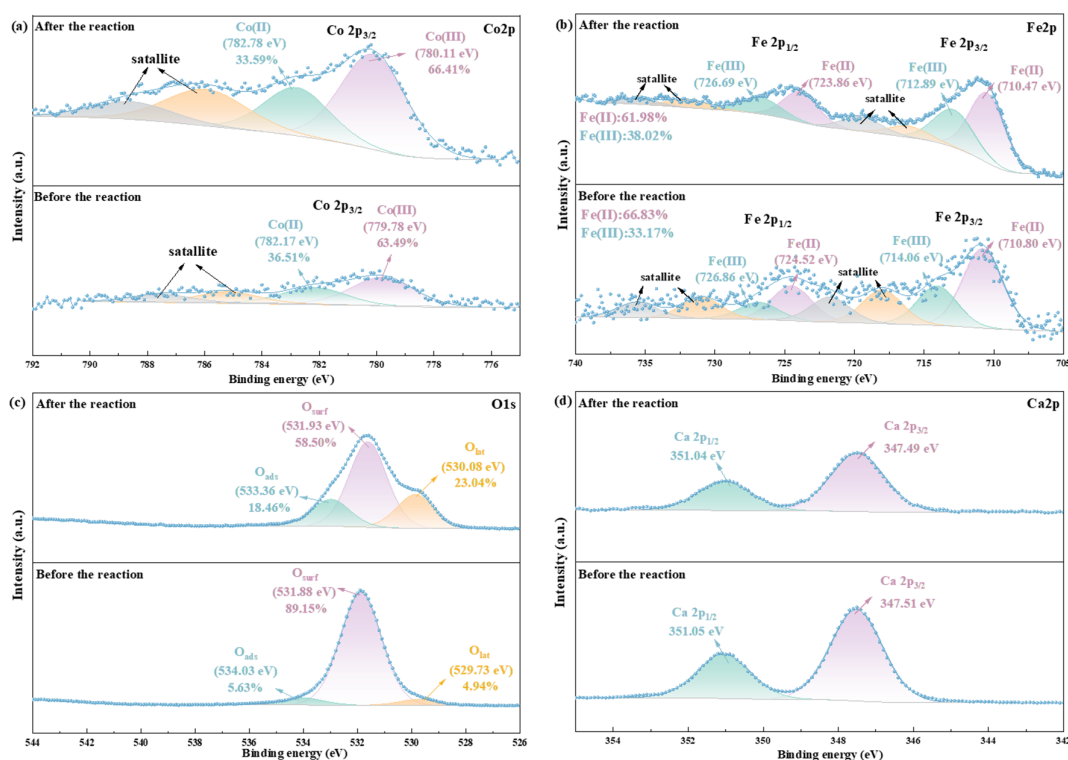


Figure 4. XPS spectra of the 10% CoFe₂O₄@PG before and after reaction. (a) Co 2p; (b) Fe 2p; (c) O 1s; (d) Ca 2p.

2.3.2. Analysis of ROS

EPR analysis was employed to identify the ROS generated in the 10% CoFe₂O₄@PG/PMS system. As shown in Figure S7a–c, characteristic signals of DMPO–•OH, DMPO–SO₄•[−], DMPO–O₂•[−], and TEMP–¹O₂ were observed, indicating that •OH, SO₄•[−], O₂•[−], and ¹O₂ were simultaneously produced in the 10% CoFe₂O₄@PG/PMS system.

To further confirm the contribution of each reactive species to BPAF degradation in the 10% CoFe₂O₄@PG/PMS system, radical quenching experiments were carried out. MeOH and TBA can rapidly react with •OH, with reaction rate constants of $k_{OH/MeOH} = 9.7 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$ and $k_{OH/TBA} = 3.8\text{--}7.6 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$, respectively. Due to the presence of α -hydrogen, SO₄•[−] reacts faster with MeOH than with TBA ($k_{SO_4^{\bullet-}/MeOH} = 2.5 \times 10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{SO_4^{\bullet-}/TBA} = 4\text{--}9.5 \times 10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$) [40,41]. BQ and L-histidine ($k_{\bullet OH/L-His} = 7.1 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$, $k_{^1O_2/L-His} = 3.2 \times 10^7 \text{ M}^{-1}\cdot\text{s}^{-1}$) were used as quenchers for O₂•[−] and ¹O₂, respectively [42,43]. As

shown in Figure 5a, increasing the MeOH concentration from 10 mM to 100 mM significantly inhibited BPAF degradation, indicating that both $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ may participate in the degradation process. In contrast, after the addition of 100 mM TBA, the BPAF degradation efficiency remained at 91.8% (Figure 5b), showing only slight inhibition, suggesting that the contribution of $\bullet\text{OH}$ to BPAF degradation was very limited and further indicating that $\text{SO}_4^{\bullet-}$ might be the dominant reactive species involved in the degradation process. With increasing BQ concentration (0.1–1.0 mM), BPAF degradation efficiency remained at 87.2% (Figure 5c), indicating that $\text{O}_2^{\bullet-}$ participated in the degradation but with a limited contribution. However, upon the addition of L-histidine, BPAF degradation was significantly suppressed; after the addition of 10 mM L-histidine, the degradation efficiency dramatically decreased to 17.5% (Figure 5d), indicating that $^1\text{O}_2$ also plays a major role in BPAF degradation. In summary, $\text{SO}_4^{\bullet-}$ and $^1\text{O}_2$ likely play dominant roles, while $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ play minor roles in the degradation of BPAF by the 10% $\text{CoFe}_2\text{O}_4/\text{PG}/\text{PMS}$ system.

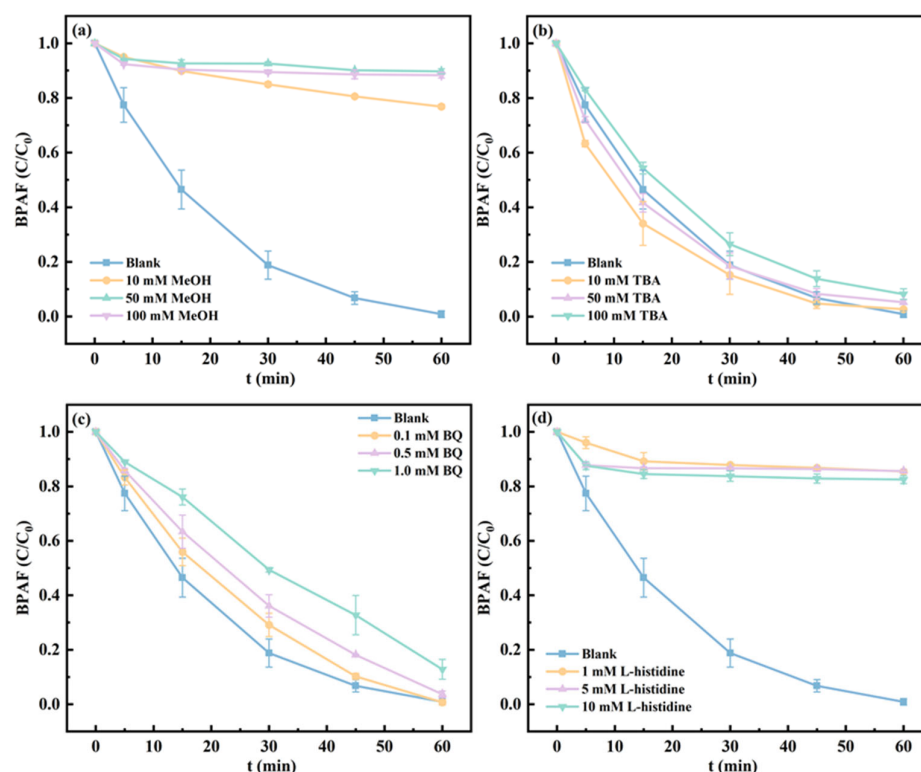


Figure 5. Quenching tests for different reactive oxygen species. (a) MeOH; (b) TBA; (c) BQ; (d) L-histidine.

2.3.3. Intermediates of BPAF

The intermediates generated during BPAF degradation were identified by LC–MS (Figure S8). The fluoride ion release in the aqueous solution after the reaction was measured at 0.53 mg/L, with a fluoride removal rate of 31.26%. In addition, to determine the degree of mineralization of the BPAF, TOC analysis was performed; the results are shown in the Figure S9 [44]. Based on theoretical and experimental results, the proposed degradation pathways of BPAF in the 10% $\text{CoFe}_2\text{O}_4/\text{PG}/\text{PMS}$ system are illustrated in Figure 6. In Pathway 1, $\text{SO}_4^{\bullet-}$ attacks the phenolic group with the highest molecular orbital, promoting the formation of hydroxylated BPAF (TP1). Subsequent β -scission of the C–C bond between the hexafluoroisopropyl group and the benzene ring generates intermediates P1–P3. Thereafter, intermediates P1 and P2 are further oxidized to P4, P5, and P6, respectively.

[45,46]. In Pathway 2, BPAF undergoes oxidative coupling to form intermediate TP2, which is then converted into intermediates P7, P8, and phenol (P9) through hydrogenation and C–C bond cleavage. Subsequently, P7 and P8 are further transformed into p-hydroxybenzoic acid (P10) and 3-hydroxyphthalic acid (P11) [47]. In Pathway 3, the adjacent C–F bonds or F₃C–C bonds on BPAF may be oxidized to C=O double bonds by ¹O₂. Then, the para-positioned C–C bond between the isopropyl group and the benzene ring is cleaved, leading to further conversion into P12, P13, P9, P14, P15, and P16 [45]. Finally, these intermediates are further oxidized to P17, P18, and P19, which are ultimately mineralized into CO₂ and H₂O.

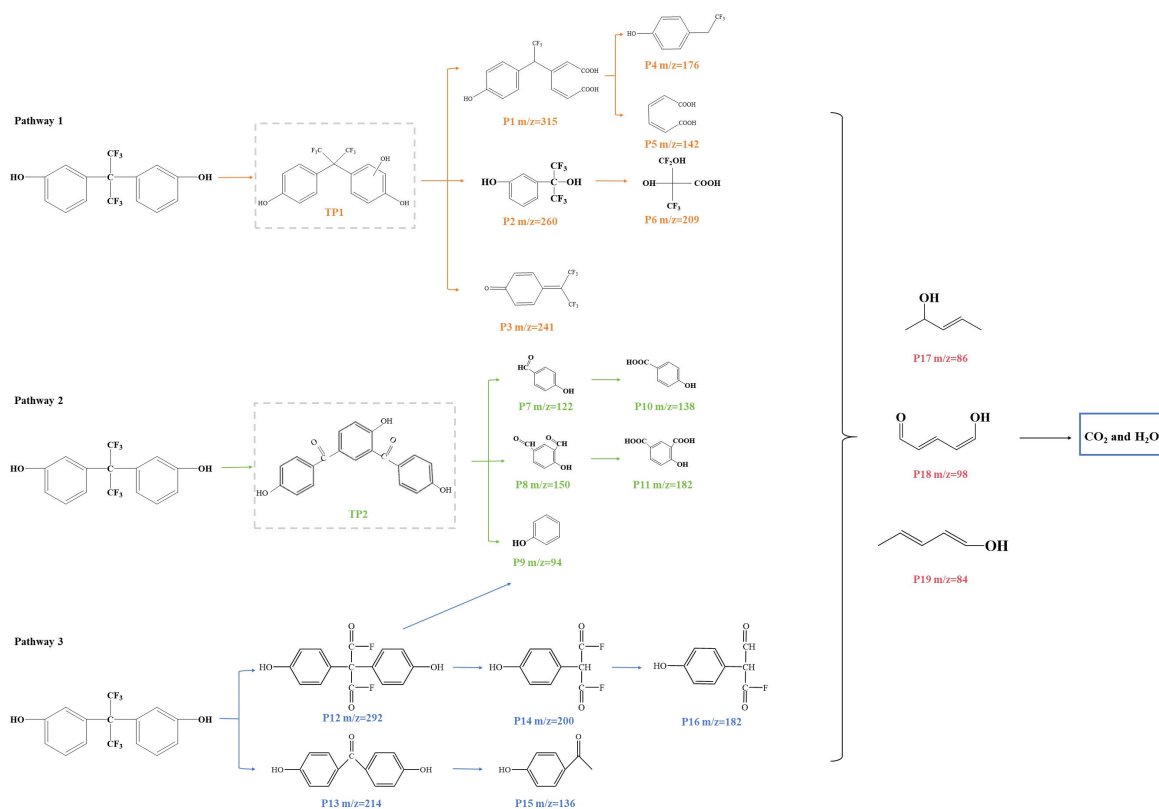


Figure 6. The possible degradation pathway of BPAF by 10% CoFe₂O₄@PG/PMS system.

2.3.4. Mechanism of BPAF Degradation by 10% CoFe₂O₄@PG/PMS

Based on the experimental results, SO₄^{•−} and ¹O₂ are the dominant reactive oxygen species responsible for BPAF degradation in the 10% CoFe₂O₄@PG/PMS system, while O₂^{•−} and •OH play minor roles (Figure 5). The valence cycles of Co(II)/Co(III) and Fe(II)/Fe(III) serve as the core active sites (Figure 4), and Ca ions play a role in electron transfer. Accordingly, a reaction mechanism for BPAF degradation over the 10% CoFe₂O₄@PG/PMS system is proposed, as illustrated in Figure 7.

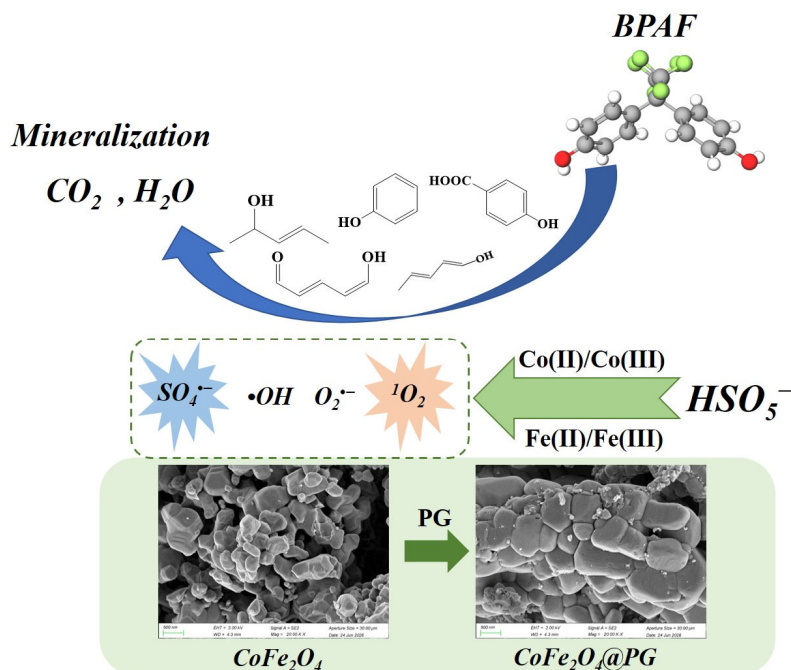
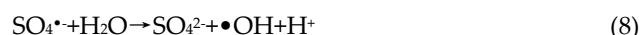
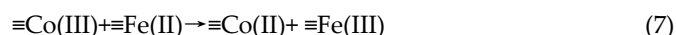
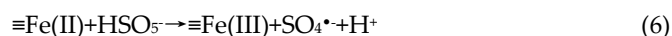
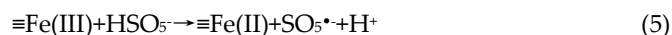
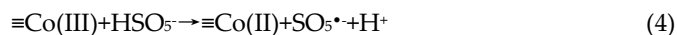
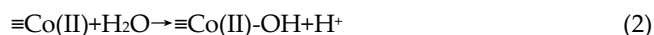
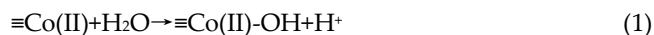
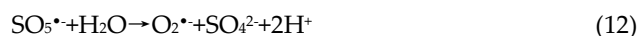
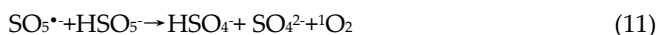
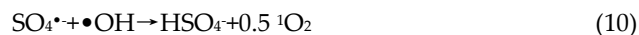


Figure 7. Schematic diagram of the removal mechanism of BPAF by CoFe₂O₄@PG/PMS system.

First, Co on CoFe₂O₄@PG acts as a Lewis acid site to adsorb H₂O, forming ≡Co(II)–OH (Equation (1)). Upon addition of PMS, ≡Co(II)–OH reacts with HSO₅^{•-} to generate SO₄^{•-} and CoO⁺ (Equation (2)) [48,49]. Subsequently, in the presence of H⁺, the generated CoO⁺ is oxidized to ≡Co(III) (Equation (3)). Meanwhile, the generated ≡Co(III) can also be reduced to ≡Co(II) by PMS (Equation (4)). In addition to the Co(II)/Co(III) cycle, Fe(II)/Fe(III) also plays an important role in the catalytic oxidation process. ≡Fe(III) on CoFe₂O₄@PG can react with PMS to produce ≡Fe(II) (Equation (5)). The generated or inherent ≡Fe(II) can donate electrons to PMS, promoting the generation of SO₄^{•-} (Equation (6)). Furthermore, ≡Fe(II) can participate in the regeneration of ≡Co(II), because the reduction of ≡Co(III) by ≡Fe(II) is thermodynamically favorable (Equation (7)). Besides, the generated SO₄^{•-} and SO₅^{•-} can be further converted into •OH, ¹O₂, and O₂^{•-} (Equations (8)–(12)) [50]. Finally, under the combined action of SO₄^{•-}, ¹O₂, O₂^{•-}, and •OH, BPAF is oxidized to small molecule products such as CO₂ and H₂O (Equation (13)).





2.4. Reusability and Universality of 10% CoFe₂O₄@PG

To evaluate the practical application potential of the 10% CoFe₂O₄@PG composite, its reusability was investigated through five consecutive cycles of BPAF degradation. After each cycle, the catalyst was recovered by membrane filtration, thoroughly washed with deionized water and anhydrous ethanol, dried, and reused. The removal rates over five cycles are shown in Figure 8a. After five cycles, the removal efficiency decreased from 99.17% to 80.69%, a drop of 18.48%. Thus, the composite maintained stable catalytic activity during repeated use, demonstrating good reusability. To investigate the root cause of the decline in the catalyst's degradation performance after cycling, the morphology and crystal structure of the cycled catalyst were characterized. Scanning electron microscopy (SEM) images (Figure S10a,b) showed that after five cycles, the crystal edges of the composite became more distinct, while the overall framework remained intact. Fine particles had accumulated on the surface, likely due to residual degradation products. The XRD spectra before and after the reaction (Figure S10c) showed that the diffraction peaks of CoFe₂O₄ in the composite material increased, while the diffraction peaks of CaSO₄ decreased. This was likely due to the reaction exposing the CoFe₂O₄ that was originally deposited inside the PG, which was consistent with the SEM observation results. In addition, a comparison of the FTIR spectra before and after the reaction (Figure S10d) reveals that the sulfate-related absorption peaks (at 1141, 1114, 669, and 602 cm⁻¹) in the 10% CoFe₂O₄@PG sample were significantly weakened, likely due to the reaction products covering the PG. While the intensities of some peaks fluctuated slightly, the positions of the characteristic absorption peaks did not change significantly, indicating that the composite catalyst possesses a certain degree of stability. In addition, to further evaluate the performance of the catalyst-activated PMS in degrading BPAF in real-world water samples, we prepared BPAF solutions using tap water and lake water, respectively. As shown in Figure S11, the catalyst still demonstrated good degradation performance in these real-world water samples.

Moreover, the Co ion leaching concentrations in the five cycles were 0.3090, 0.1708, 0.1269, 0.1356, and 0.1675 mg/L (Figure 8b), all far below the surface water quality standard limit of 1.00 mg/L (GB 3838-2002) [51]. Fe ion leaching concentrations were 0.0889, 0.0433, 0.0364, 0.0299, and 0.0235 mg/L (Figure 8b), also well below the limit of 0.30 mg/L (GB 3838-2002)(GB 3838-2002; Environmental quality standards for surface water. China, 2002). Furthermore, the leaching concentrations of both metals declined with increasing cycles. This is likely because unstable surface metals were largely lost in the first cycle, after which the remaining active components were immobilized by the PG support, suppressing further leaching. In summary, the 10% CoFe₂O₄@PG composite exhibits low metal leaching risk and good structural stability.

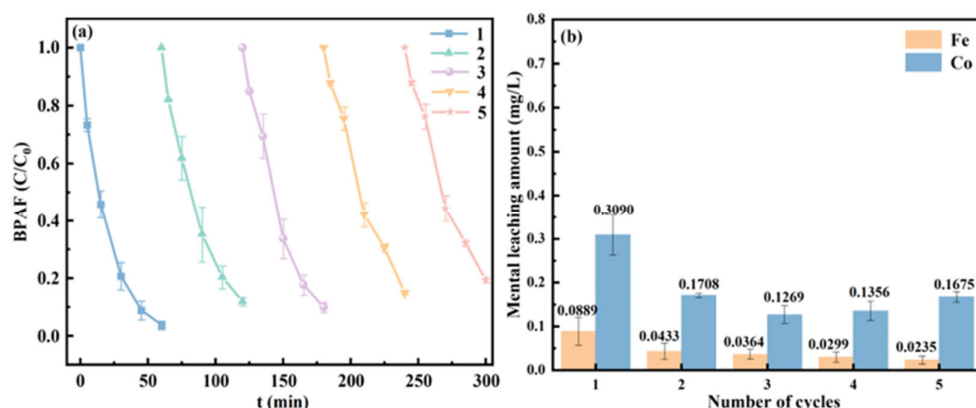


Figure 8. (a) Recycling test on the 10% CoFe₂O₄@PG/PMS system; (b) Leaching Concentrations of Cobalt and Iron Ions in Different Cycles

3. Materials and Methods

3.1. Materials

Phosphogypsum (PG) was supplied by Guizhou Wengfu Group Co., Ltd., China. The PG was ground and passed through a 100-mesh sieve. As shown in Table S1, it consisted predominantly of Ca and S, with Si, Al, and Fe present as impurities. Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), citric acid (C₆H₈O₇), potassium peroxydisulfate triple salt (KHSO₅·0.5KHSO₄·0.5K₂SO₄), bisphenol AF (BPAF, C₁₅H₁₀F₆O₂), methanol (CH₃OH), ethylene glycol (C₂H₆O₂), furfuryl alcohol (C₅H₆O₂), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na₂CO₃), sodium sulfate (Na₂SO₄), disodium hydrogen phosphate (Na₂HPO₄), 1,4-benzoquinone (C₆H₄O₂), L-histidine (C₆H₉N₃O₂), and tert-butanol (C₄H₁₀O) were obtained from Chengdu Kelong Chemical Co., Ltd. and Shanghai Aladdin Biochemical Technology Co., Ltd., China. All chemicals were of analytical grade and used without further purification.

3.2. Sample Preparation

A series of CoFe₂O₄@PG catalysts were prepared using the sol-gel method and tube furnace calcination. In brief, 0.808 g of Fe(NO₃)₃·9H₂O and 0.291 g of Co(NO₃)₂·6H₂O were weighed out and dissolved in 200 mL of ultrapure water. The theoretical mass of CoFe₂O₄ produced was calculated, and different masses of PG were then added to achieve CoFe₂O₄ loading levels of 10 wt%, 20 wt%, 50 wt%, and 70 wt%. The suspensions were stirred for 10 min. Citric acid was then added as a chelating agent, and the mixture was heated and stirred continuously in a 90 °C water bath for 2 h to form a uniform sol. The resulting sol was dried in a 120 °C oven to obtain the CoFe₂O₄@PG precursor. Finally, the dried precursor was calcined in a muffle furnace at 700 °C for 4 h to obtain the CoFe₂O₄@PG material. Unloaded CoFe₂O₄ was prepared using the same method, except without the addition of PG.

3.3. Evaluation of the BPAF Removal Performance

In a typical experiment, the CoFe₂O₄@PG catalyst was used at a concentration of 0.6 g/L, PMS at 0.4 mM, the initial BPAF concentration was 5 mg/L, the reaction temperature was 25 °C, the reaction time was 60 min, and the BPAF solution volume was 100 mL. To investigate the effects of catalyst dosage and PMS dosage on BPAF removal by the CoFe₂O₄@PG/PMS system, the catalyst dosage was varied from 0.2 to 0.8 g/L, and the PMS

dosage was varied from 0.05 to 0.60 mM. To explore the effect of initial BPAF concentration on BPAF removal, the initial BPAF concentration was set in the range of 1–20 mg/L. The experimental data were analyzed using a first-order kinetic model to figure out the degradation rate [52,53]. To examine the effect of pH on BPAF removal, the pH of the BPAF solution was adjusted from 3 to 11. To evaluate the effect of coexisting anions on BPAF removal, the concentrations of Cl^- , CO_3^{2-} , SO_4^{2-} , and HPO_4^{2-} were set in the range of 0.1–1.0 mM. To assess the contribution of radicals to BPAF removal, quenching experiments were conducted using methanol (MeOH), tert-butanol (TBA), 1,4-benzoquinone (BQ), and L-histidine as quenchers for $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$, respectively. In addition, recycling experiments were performed to evaluate the stability of the $\text{CoFe}_2\text{O}_4/\text{PG}$ catalyst. After each reaction cycle, the catalyst was recovered by membrane filtration, washed sequentially with deionized water and anhydrous ethanol, dried, and then used in the next cycle. All experiments were conducted in triplicate, and the results are expressed as mean $\pm$ standard deviation.

3.4. Characterization Methods

Characterization methods are described in the Supplementary Material.

4. Conclusions

In this study, a $\text{CoFe}_2\text{O}_4/\text{PG}$ catalyst was prepared using solid waste as feedstock to establish a highly efficient PMS oxidation system for the degradation of BPAF. The 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ catalyst removed 99.17% of BPAF within 60 min. The ROS involved in BPAF degradation include $\bullet\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$, among which $\bullet\text{SO}_4^{\bullet-}$ and $^1\text{O}_2$ are the primary active species, while $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ play auxiliary roles. The redox cycle between $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ensures the continuous generation of reactive oxygen species (ROS), driving PMS activation. Based on the analysis of degradation intermediates, three BPAF degradation pathways were proposed. This composite exhibits stable performance under different pH and anion conditions, with good reusability and environmental safety; however, its recovery methods still have certain limitations. Overall, this study provides a feasible solution for treating contaminated water and achieves the resource utilization of phosphogypsum through a “waste-to-waste” approach. In future studies, we will simultaneously monitor the leaching of multiple components from the phosphogypsum carrier in the cyclic experiments, in order to comprehensively clarify its stability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16100882/s1>. Figure S1. EDS mapping of 10% $\text{CoFe}_2\text{O}_4/\text{PG}$; Figure S2 XRD of CoFe_2O_4 and PG; Figure S3 (a) Effects of different CoFe_2O_4 loading levels on the degradation kinetics of BPAF; (b) Effects of different catalyst systems on the degradation kinetics of BPAF; (c) Effects of different BPAF concentrations on the degradation kinetics of BPAF; (d) Effects of different initial pH values on the degradation kinetics of BPAF; Figure S4 Effect of (a) catalyst dosage and (b) PMS concentration on BPAF removal in the 10% $\text{CoFe}_2\text{O}_4/\text{PG}/\text{PMS}$ system; degradation rate constants (kobs) for the catalyst dosage(c) and PMS concentration(d); Figure S5 Evolution of pH values along with thereaction time; Figure S6 XPS spectra of the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ before and after reaction; Figure S7 EPR characterization results of $\text{DMPO}\cdot\bullet\text{OH}$, $\text{DMPO}\cdot\text{O}_2^{\bullet-}$, and $\text{TEMP}\cdot^1\text{O}_2$ of 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ system; Figure S8. Intermediate products of BPAF degradation by the 10% $\text{CoFe}_2\text{O}_4/\text{PG}/\text{PMS}$ system identified via HPLC-MS; Figure S9 The mineralization rate of BPAF; Figure S10 SEM images of (a-b) 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ after the reaction; (c) XRD patterns of the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ before and after reaction; (d) FTIR spectra of the 10% $\text{CoFe}_2\text{O}_4/\text{PG}$ before and after reaction; Figure S11 Degradation of BPAF in various water systems; Table S1 Analysis of the composition of phosphogypsum; Table S2 Comparison of the degradation efficiencies of various catalysts for pollutants. References [54–57] are cited in Supplementary Materials.

Author Contributions: J.Z., writing—review & editing, funding acquisition, conceptualization, supervision; N.W., data curation, writing—original draft, methodology; C.D., writing—review & editing; Y.C., methodology; J.X., investigation, formal analysis; H.L. (Hetian Li), formal analysis, validation; B.Z., software; H.L. (Huarong Liu), validation; B.F., investigation; Y.X., investigation. All authors have read and agreed to the published version of the manuscript.

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References

- Chen, D.; Kannan, K.; Tan, H.; Zheng, Z.; Feng, Y.L.; Wu, Y.; Widelka, M. Bisphenol Analogues Other Than BPA: Environmental Occurrence, Human Exposure, and Toxicity—A Review. *Environ. Sci. Technol.* **2016**, *50*, 5438–5453.
- Choi, Y.J.; Lee, L.S. Partitioning Behavior of Bisphenol Alternatives BPS and BPAF Compared to BPA. *Environ. Sci. Technol.* **2017**, *51*, 3725–3732.
- Liu, J.; Liang, S.; Xiang, T.; Li, L.; Gao, P.; Zhou, J. S-vacancy-rich MoS₂ for enhanced BPA degradation involved peroxymonosulfate activation: Sustainable transformation of toxic V(V) into a homogeneous catalytic system. *J. Water Process Eng.* **2025**, *77*, 108542.
- Sun, Q.; Wang, Y.; Li, Y.; Ashfaq, M.; Dai, L.; Xie, X.; Yu, C. Fate and mass balance of bisphenol analogues in wastewater treatment plants in Xiamen City, China. *Environ. Pollut.* **2017**, *225*, 542–549.
- Zhang, H.; Zhang, Y.; Zhao, Y.; Liang, T.; Wei, W.; Zhang, W.; Li, J.; Liu, Y.; Tao, H. Magnetic biochar derived from dairy manure for peroxymonosulfate activation towards bisphenol A degradation: Kinetics, electron transfer mechanism, and environmental toxicity. *J. Water Process Eng.* **2022**, *50*, 103314.
- Kohantorabi, M.; Moussavi, G.; Giannakis, S. A review of the innovations in metal- and carbon-based catalysts explored for heterogeneous peroxymonosulfate (PMS) activation, with focus on radical vs. non-radical degradation pathways of organic contaminants. *Chem. Eng. J.* **2021**, *411*, 127957.
- Deng, D.; Chen, R.; Zhong, Q.; Xiong, B.; Deng, J.; Zhang, N.; Xie, S. Bicarbonate ions enhanced surface Fe(II) regeneration and peroxymonosulfate activation on stainless-steel scrubber cathode for BPA degradation. *J. Water Process Eng.* **2025**, *78*, 108739.
- Liu, L.; Zhan, R.; Zhang, M.; Li, J.; Wang, Z.; Mi, H.; Zhang, Y. Insights into the performance, mechanism, and ecotoxicity of levofloxacin degradation in CoFe₂O₄ catalytic peroxymonosulfate process. *J. Environ. Chem. Eng.* **2022**, *10*, 107435.
- Liu, L.; Mi, H.; Zhang, M.; Sun, F.; Zhan, R.; Zhao, H.; He, S.; Zhou, L. Efficient moxifloxacin degradation by CoFe₂O₄ magnetic nanoparticles activated peroxymonosulfate: Kinetics, pathways and mechanisms. *Chem. Eng. J.* **2021**, *407*, 127201.
- Gan, L.; Zhong, Q.; Geng, A.; Wang, L.; Song, C.; Han, S.; Cui, J.; Xu, L. Cellulose derived carbon nanofiber: A promising biochar support to enhance the catalytic performance of CoFe₂O₄ in activating peroxymonosulfate for recycled dimethyl phthalate degradation. *Sci. Total Environ.* **2019**, *694*, 133705.
- Li, Y.; Chen, Z.; Qi, J.; Kang, J.; Shen, J.; Yan, P.; Wang, W.; Bi, L.; Zhang, X.; Zhu, X. Degradation of bisphenol S by peroxymonosulfate activation through monodispersed CoFe₂O₄ nanoparticles anchored on natural palygorskite. *Sep. Purif. Technol.* **2021**, *277*, 119492.
- Li, J.; Liu, Z.; Zhao, Y.; Lin, C.; Song, C.; Zhi, Z.; Wang, S.; Tan, C.; Song, M. Heat enhanced bisphenol AF degradation in CoFe₂O₄@BC activated peroxymonosulfate process: Mechanism and the role of inorganic anions. *Sep. Purif. Technol.* **2024**, *342*, 126968.
- Wang, Y.; Wang, Y.; Xie, Y.; Chen, X.; Ma, X.; Wang, X. Application of novel magnetic biochar: Material performance and mechanisms for efficient persulfate activation in sulfamethoxazole degradation. *Environ. Res.* **2026**, *296*, 123974.
- Li, J.; Chen, F.; Zhang, L.; Lei, W.; Zhang, L.; Chen, H.; Xue, C.; Xu, L. Peroxymonosulfate Activation by CoFe₂O₄/MgAl-LDH Catalyst for the Boosted Degradation of Antibiotic. *J. Inorg. Mater.* **2025**, *40*, 440–448.

15. Li, M.; Li, Y.-W.; Yu, P.-F.; Zhao, H.-M.; Xiang, L.; Feng, N.-X.; Li, Q.-K.; He, K.-Y.; Luo, X.; Cai, Q.-Y.; et al. Exploring degradation mechanism of tetracycline via high-effective peroxymonosulfate catalysts of montmorillonite hybridized CoFe composites and safety assessment. *Chem. Eng. J.* **2022**, *427*, 130930.
16. Li, Y.; Ma, S.; Xu, S.; Fu, H.; Li, Z.; Li, K.; Sheng, K.; Du, J.; Lu, X.; Li, X.; et al. Novel magnetic biochar as an activator for peroxymonosulfate to degrade bisphenol A: Emphasizing the synergistic effect between graphitized structure and CoFe₂O₄. *Chem. Eng. J.* **2020**, *387*, 124094.
17. Fan, Y.; Zhu, R.; Liu, J.; Yang, J.; Zhong, J.; Ding, D.; Ma, Y.; Liang, Y.; Chen, R.; Xia, Y.; et al. Carbon nanotube-coated cobalt-iron spinel ceramic membrane activated peroxymonosulfate for the removal of florfenicol based on singlet oxygen catalysis. *Sep. Purif. Technol.* **2026**, *397*, 138148.
18. Zhu, J.; Wang, S.; Yang, Z.; Pan, B. Robust polystyrene resin-supported nano-CoFe₂O₄ mediated peroxymonosulfate activation for efficient oxidation of 1-hydroxyethane 1,1-diphosphonic acid. *J. Hazard. Mater.* **2023**, *443*, 130281.
19. Millan-Becerro, R.; Perez-Lopez, R.; Canovas, C.R.; Macias, F.; Leon, R. Phosphogypsum weathering and implications for pollutant discharge into an estuary. *J. Hydrol.* **2023**, *617*, 128943.
20. Zhao, L.; Zhang, Q.; Li, X.; Ye, J.; Chen, J. Adsorption of Cu(II) by phosphogypsum modified with sodium dodecyl benzene sulfonate. *J. Hazard. Mater.* **2020**, *387*, 121808.
21. Deng, J.; Shao, Y.S.; Gao, N.Y.; Tan, C.Q.; Zhou, S.Q.; Hu, X.H. CoFe₂O₄ magnetic nanoparticles as a highly active heterogeneous catalyst of oxone for the degradation of diclofenac in water. *J. Hazard. Mater.* **2013**, *262*, 836–844.
22. Li, X.; Zhang, Q. Dehydration behaviour and impurity change of phosphogypsum during calcination. *Constr. Build. Mater.* **2021**, *311*, 125328.
23. Gormez, O.; Yakar, E.; Gozmen, B.; Kayan, B.; Khataee, A. CoFe₂O₄ nanoparticles decorated onto graphene oxide and graphitic carbon nitride layers as a separable catalyst for ultrasound-assisted photocatalytic degradation of Bisphenol-A. *Chemosphere* **2022**, *288*, 132663.
24. Seeharaj, P.; Pasupong, P.; Choojun, K. Magnetically separable CeO₂/CoFe₂O₄ heterojunction photocatalysts for dye degradation: Characterization and mechanism. *J. Asian Ceram. Soc.* **2024**, *12*, 44–58.
25. Wang, P.; Zhang, Y.; Zhu, J.; Wei, J.; Qi, J.; Cao, T.; Yang, M. Catalytic degradation of BPA by bamboo leaf-derived KOH-activated porous biocarbon loaded with CoFe₂O₄-activated peroxymonosulfate. *Chem. Eng. J.* **2024**, *492*, 151886.
26. Qi, J.; Zhu, K.; Li, M.; Liu, Y.; Duan, P.; Huang, L. Efficient Tetracycline Hydrochloride Degradation by Urchin-Like Structured MoS₂@CoFe₂O₄ Derived from Steel Pickling Sludge via Peroxymonosulfate Activation. *Molecules* **2025**, *30*, 3194.
27. Hu, L.; Zhang, G.; Liu, M.; Wang, Q.; Wang, P. Enhanced degradation of Bisphenol A (BPA) by peroxymonosulfate with Co₃O₄-Bi₂O₃ catalyst activation: Effects of pH, inorganic anions, and water matrix. *Chem. Eng. J.* **2018**, *338*, 300–310.
28. Dung, N.T.; Thu, T.V.; Van Nguyen, T.; Thuy, B.M.; Hatsukano, M.; Higashimine, K.; Maenosono, S.; Zhong, Z. Catalytic activation of peroxymonosulfate with manganese cobaltite nanoparticles for the degradation of organic dyes. *RSC Adv.* **2020**, *10*, 3775–3788.
29. Pei, S.; Liu, F.; Li, Z.; Duan, Z.; Lu, H.; Xu, W.; Zhu, Y.; Liu, X. Chitosan hydrogel supported Fe-Co bimetallic metal organic framework for efficient peroxymonosulfate activation: Levofloxacin degradation and catalytic mechanism. *Sep. Purif. Technol.* **2026**, *398*, 138106.
30. Li, N.; Wang, Y.; Cheng, X.; Dai, H.; Yan, B.; Chen, G.; Hou, L.A.; Wang, S. Influences and mechanisms of phosphate ions onto persulfate activation and organic degradation in water treatment: A review. *Water Res.* **2022**, *222*, 118896.
31. Nalina, S.; Kavya, K.; Srinivas, M.; Ramesh, K.B.; Munirathnam, K. Synthesis of sulphur doped CoFe₂O₄ by calcination process in air and their photocatalytic activity in the presence of visible light. *Results Surf. Interfaces* **2024**, *14*, 100153.
32. Ma, T.; Guo, M.; Cao, Y.; Zhong, W.; Ding, C.; Ye, H.; Chen, L.; Xu, H.; Fang, Z.; He, W. Switch PMS activation pathway from free radical to non-radical by introducing hexagonal boron nitride in supported CoFe₂O₄: The role of lattice oxygen and PMS adsorption. *J. Environ. Chem. Eng.* **2024**, *12*, 114823.
33. Xiong, M.; Sun, Y.; Chai, B.; Fan, G.; Song, G. Efficient peroxymonosulfate activation by magnetic CoFe₂O₄ nanoparticle immobilized on biochar toward sulfamethoxazole degradation: Performance, mechanism and pathway. *Appl. Surf. Sci.* **2023**, *615*, 156398.
34. Jiang, X.; Wang, P.; Mei, R.-X.; Chu, H.-Y.; Dong, X.-F.; Lv, X.-L.; Liu, Z.-Y.; Li, K.-X.; Sheng, X.-Y.; Wang, A.; et al. Immobilized ZIF-62(Co) glass on Ni foam for peroxymonosulfate activation and pollutant degradation. *Appl. Catal. B Environ. Energy* **2027**, *400*, 127241.
35. Liu, D.; Chen, D.; Hao, Z.; Tang, Y.; Jiang, L.; Li, T.; Tian, B.; Yan, C.; Luo, Y.; Jia, B. Efficient degradation of Rhodamine B in water by CoFe₂O₄/H₂O₂ and CoFe₂O₄/PMS systems: A comparative study. *Chemosphere* **2022**, *307*, 135935.

36. Wang, C.; Zhao, B.-H.; Zhang, B.-Y. Synergism of adsorption and catalytic degradation of levofloxacin by exfoliated vermiculite anchored with CoFe_2O_4 particles activating peroxymonosulfate. *J. Environ. Chem. Eng.* **2025**, *13*, 115090.
37. Ren, Y.; Lin, L.; Ma, J.; Yang, J.; Feng, J.; Fan, Z. Sulfate radicals induced from peroxymonosulfate by magnetic ferrosphenel MFe_2O_4 ($\text{M}=\text{Co}$, Cu , Mn , and Zn) as heterogeneous catalysts in the water. *Appl. Catal. B Environ.* **2015**, *165*, 572–578.
38. Chen, P.; Cheng, Z.; Zhang, X.; Yan, C.; Wei, J.; Qiu, F.; Liu, Y. Fe–Mn bimetallic catalyst to activate peroxymonosulfate (PMS) for efficient degradation of tetracycline: Mechanism insights and application for pharmaceutical wastewater. *J. Clean. Prod.* **2024**, *445*, 141365.
39. Lu, Z.; Luo, R.; Chen, S.; Fu, D.; Sun, G.; Zhao, Z.-J.; Pei, C.; Gong, J. Alkaline-earth ion stabilized sub-nano-platinum tin clusters for propane dehydrogenation. *Chem. Sci.* **2024**, *15*, 1046–1050.
40. Gao, P.; Tian, X.; Fu, W.; Wang, Y.; Nie, Y.; Yang, C.; Deng, Y. Copper in LaMnO_3 to promote peroxymonosulfate activation by regulating the reactive oxygen species in sulfamethoxazole degradation. *J. Hazard. Mater.* **2021**, *411*, 125163.
41. Wang, Y.; Sun, H.; Ang, H.M.; Tade, M.O.; Wang, S. 3D-hierarchically structured MnO_2 for catalytic oxidation of phenol solutions by activation of peroxymonosulfate: Structure dependence and mechanism. *Appl. Catal. B-Environ.* **2015**, *164*, 159–167.
42. Kong, Y.; Dai, S.; Chen, Q.; Nie, Y.; Ma, J. Enhanced oxidation and in-situ coagulation $\text{Fe(II)}/\text{peroxymonosulfate-Mn(VII)}$ process for carbamazepine removal: Multiple promoting effects of Mn and direct/indirect regulation of Cl^- on active substances transformation. *J. Hazard. Mater.* **2025**, *485*, 136933.
43. Duan, P.; Qi, Y.; Feng, S.; Peng, X.; Wang, W.; Yue, Y.; Shang, Y.; Li, Y.; Gao, B.; Xu, X. Enhanced degradation of clothianidin in peroxymonosulfate/catalyst system via core-shell FeMn @ N-C and phosphate surrounding. *Appl. Catal. B Environ.* **2020**, *267*, 118717.
44. Dhakal, O.B.; Dahal, R.; Iqbal, Z.; Choi, E.H. Synergistic degradation of tetracycline using plasma-activated persulfate: Roles of hydroxyl and sulfate radicals. *J. Environ. Chem. Eng.* **2026**, *14*, 122955.
45. Wang, N.; Zhang, J.; Peng, Z.; Zhang, Y.; Li, W.; Cheng, F.; Pan, Z.; Liu, Y. Iron molybdate catalyzed activation of peroxymonosulfate for bisphenol AF degradation via synergetic non-radical and radical pathways. *Sci. Total Environ.* **2021**, *797*, 149151.
46. Li, M.; Liu, J.; Shi, Y.; Yang, J.; Zhang, H.; Xie, H.; Xia, D. Built-in electric field-enhanced electron super-exchange interactions for non-radical activation in ultra-thin $\text{FeOCl/g-C}_3\text{N}_4$ nanosheets. *J. Environ. Chem. Eng.* **2024**, *12*, 114805.
47. Liu, C.; Zhang, J.; Li, K.; Wang, Y. Bisphenol AF degradation by persulfate activation based on $\text{Mn}_3\text{O}_4/\text{BiOI}$ composite catalyst. *Environ. Sci. Eur.* **2026**, *38*, 57.
48. Li, X.; Liu, X.; Lin, C.; Zhang, H.; Zhou, Z.; Fan, G.; Ma, J. Cobalt ferrite nanoparticles supported on drinking water treatment residuals: An efficient magnetic heterogeneous catalyst to activate peroxymonosulfate for the degradation of atrazine. *Chem. Eng. J.* **2019**, *367*, 208–218.
49. Zheng, C.; Wu, J.; Zhang, Y.; Yang, Q.; Yang, Y. Walnut Shell Loaded with Cobalt Ferrite as Efficient Peroxymonosulfate Activator to Degrade Ofloxacin. *Water Air Soil Pollut.* **2023**, *234*, 305.
50. Zhang, R.; Yang, C.; Niu, Q.; Yang, J. Removal of humic acid by peroxymonosulfate active with MnO_x from the backwashing sludge of a filter for manganese removal. *J. Environ. Chem. Eng.* **2023**, *11*, 110515.
51. Bai, Y.; Zhang, G.; Liu, M.; Hou, S.; Zheng, S.; Yang, S.; Zhu, C.; Xu, H. Spatial axial oxygen coordination of $\text{CoSA-N}_2\text{O}_1/\text{MXene}$ single-atom catalyst with electron-depleted active site for selective $^1\text{O}_2$ generation. *Appl. Catal. B-Environ. Energy* **2025**, *374*, 125378.
52. Khalifa, A.; Faramawy, A.M.; Attia, Y.A.; Swillam, M.A. Synthesis and photocatalytic improvement for methylene blue degradation of $\text{MgO/g-C}_3\text{N}_4$ and $\text{ZnO/g-C}_3\text{N}_4$ composites. *Discov. Mater.* **2025**, *5*, 258.
53. Faramawy, A.M.; Sattar, A.A.; El-Sayed, H.M.; Nessem, R.G. Detailed study of enhancing the electrical, optical, and photodegradation properties of MnZn/CdZn spinel ferrite core/shell nanostructures. *J. Mater. Sci.* **2026**, *61*, 21070–21092.
54. Deng, M.; Shi, Y.; Li, M.; Zhang, H.; Deng, H.; Xia, D., Enhanced non-radical activation of peroxymonosulfate by g- C_3N_4 modulated N-doped biochar: The role of extrinsic defects and oxygen-containing functional groups. *Journal of Water Process Engineering* **2025**, *70*, 106940.
55. Xie, Y.; Yu, J.; Li, Y.; Zhang, Y.; Tang, Q.; Li, F.; Wang, Y.; Chen, B., Waste Baijiu Distillers' Grain-Derived Porous Biochar: A Promising Material for Bisphenol AF Removal from Water Through Both Adsorption and Advanced Oxidation Process. *Molecules* **2026**, *31*, 1713.

56. Wang, Q.; Zeng, H.; Liang, Y.; Cao, Y.; Xiao, Y.; Ma, J., Degradation of bisphenol AF in water by periodate activation with FeS (mackinawite) and the role of sulfur species in the generation of sulfate radicals. *Chemical Engineering Journal* 2021, 407, 126738.
57. Mu, F.; Dai, B.; Dai, C.; Chu, X.; Xu, J.; Shen, J.; Zhao, W.; Dong, G., Novel 2D/1D MXene/Bi₅O₇I Schottky junction for photocatalytic degradation of bisphenol AF by peroxymonosulfate-assisted photocatalysis. *Chinese Chemical Letters* 2026, 37 (9), 111866.

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