

Article

Magnetic Co-Al Layered Double Hydroxides as Peroxymonosulfate Activator for the Removal of Pesticide Multiresidues

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Abstract

The increasing prevalence of multiclass pesticide residues in aquatic environments poses a significant threat to ecosystems and human health. To address this challenge, magnetic Fe₃O₄@Co₅Al-LDH nanoparticles were synthesized as high-performance, easily recoverable catalysts for the peroxymonosulfate (PMS)-mediated degradation of epoxiconazole, atrazine, and metalaxyl. Under optimized conditions (pH 7.0, 35 mg catalyst, and 4.0 mM PMS), the system achieved 100% degradation of the three coexisting pesticides within 15 min. Quenching experiments and electron paramagnetic resonance (EPR) spectroscopy confirmed that SO₄^{•−} and •OH radicals were the primary reactive species driving the process. Liquid chromatography–mass spectrometry (LC-MS) analysis identified four intermediates for epoxiconazole, three for atrazine, and four for metalaxyl, facilitating the proposal of distinct degradation pathways. The degradation mechanism revealed that electron transfer between Fe/Co and PMS promoted the generation of reactive oxygen species, leading to dechlorination, hydroxylation, and dealkylation of the pesticides transiently adsorbed on the surface of Fe₃O₄@Co₅Al-LDH. In summary, this study demonstrates that Fe₃O₄@Co₅Al-LDH is an easily recoverable, reusable, and cost-effective catalyst for the simultaneous remediation of complex pesticide mixtures in water.

Keywords: magnetic catalyst; cobalt–aluminum layered double hydroxide; peroxymonosulfate; multiclass pesticide residues

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1. Introduction

While pesticides are essential for crop protection and yield enhancement, their widespread and often indiscriminate use poses severe ecological environment and human health threats [1,2]. For instance, atrazine, a widely used broad-spectrum herbicide, is a prominent concern. It is classified as a Category 3 carcinogen by the IARC and exhibits significant long-term toxicity toward aquatic life [3,4]. Similarly, epoxiconazole, a prevalent triazole fungicide, is notorious for its environmental persistence, acting as an endocrine disruptor with documented reproductive toxicity [4,5]. Furthermore, the systemic fungicide metalaxyl has been shown to impair the growth and reproduction of aquatic species and may cause chronic organ damage upon prolonged exposure [3,4]. More im-

portantly, mixed pesticide residues—rather than individual compounds—are now ubiquitous in real-world environments, potentially causing synergistic toxicity and complicating risk assessment and remediation [6]. Therefore, developing safe and efficient remediation technologies for pesticide multiresidue has become an urgent global priority.

Up to now, a variety of technologies have been developed and applied to remove residual pesticides from the environment, including adsorption [5], biodegradation [7], membrane separation [8], photocatalysis [9], electrochemistry [10], and advanced oxidation technologies [11]. Compared to traditional removal techniques, advanced oxidation processes (AOPs) have broad application prospects in the field of water treatment due to their advantages such as simple operation and economy, and they continue to be optimized and developed in research and practice [12]. The fundamental principle of AOPs lies in utilizing powerful oxidants to produce reactive oxygen species in aqueous solution. These reactive oxygen species subsequently react with contaminants, ultimately achieving the goal of pollutant degradation. At present, the prevalent AOP technologies primarily comprise Fenton oxidation [13], photochemical oxidation [14], and persulfate advanced oxidation [15]. However, few studies have investigated the application of AOPs to complex pollutants.

Persulfates can be divided into peroxymonosulfate (PMS) and peroxydisulfate (PDS), which have relatively low oxidation capacity on their own. They require activation means such as light, heat, and catalysts to produce sulfate radical anions ($\text{SO}_4^{\cdot-}$) with a higher oxidation potential, thus achieving the decomposition and mineralization of refractory organic pollutants. Transition metal ions (Fe^{2+} , Co^{2+} , Mn^{2+} , Al^{3+}) and transition metal oxides are the most widely used persulfate activators at present. Their activation mechanism mainly involves utilizing the reducibility of transition metals and their oxides to reduce $\text{S}_2\text{O}_8^{2-}$ or HSO_5^- to produce $\text{SO}_4^{\cdot-}$. Research has found that persulfates can act as electron acceptors and undergo redox reactions with electron donors such as transition metals to generate $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$, and activate their reactivity through electron transfer [16]. Among them, cobalt (Co)-based catalysts are valued for their unique catalytic performance, relatively low cost, good thermal stability, and environmental compatibility [17]. Co-based catalysts are a type of catalyst with cobalt as the main active component, typically supported on carriers such as alumina, carbon materials, and diatomaceous earth to improve dispersion, stability, and activity [18].

Currently, LDH is a type of ionic clay two-dimensional (2D) material with a structure similar to hydrotalcite, possessing unique ionic exchange properties due to its anion interlayer and cationic metal layer [19]. The structure of LDHs is composed of divalent and trivalent cations, which are neutralized by exchangeable anions in the interlayer. The general formula of LDHs is $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{x+} (\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} represents divalent metal cations, M^{3+} represents trivalent metal cations, A^{n-} represents interlayer exchangeable anions (such as carbonates or nitrates), and x represents the molar ratio of metal ions [20]. The rich selection of $\text{M}^{2+}/\text{M}^{3+}$ makes LDHs efficient heterogeneous catalysts with high PMS activation capability, capable of degrading toxic organic residues in water bodies [21].

Although LDHs exhibit fast reaction rates in homogeneous transition metal-activated persulfate systems, they suffer from poor pollutant removal efficiency and difficulty in catalyst recovery. To address these issues while also exploring the application of AOPs to complex pollutants, this study employed Co_5Al -LDH as the catalyst host and composited it with magnetic Fe_3O_4 to prepare an $\text{Fe}_3\text{O}_4/\text{Co}_5\text{Al}$ -LDH catalyst with excellent PMS activation performance and facile recoverability, thereby achieving efficient removal of mixed pesticide residues from environmental water.

2. Materials and Methods

2.1. Materials and Characterization of Catalysts

Detailed information on chemicals and catalyst characterization is provided in Text S1 and Text S2 of the Supplementary Materials, respectively.

2.2. Synthesis of the Catalysts

Fe_3O_4 and $\text{Co}_5\text{Al-LDH}$ were synthesized by modifying a previously reported procedure, with detailed procedures provided in Texts S3 and S4 [22,23]. $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ was achieved by a one-step solvothermal-synthesis method. The specific steps are as follows: 0.5 mmol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2.5 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to 70 mL of deionized water under stirring. Subsequently, 8 mmol NH_4F , 12 mmol urea and 231.5 mg Fe_3O_4 nanoparticles were added to the above system. The mixed solution was transferred into a 100 mL Teflon stainless steel autoclave after 15 min of ultrasonic dispersion. The reaction was carried out at 100 °C for 5 h. The product was washed three times with deionized water and absolute ethanol after cooling to room temperature and dried in a vacuum at 60 °C.

2.3. Experimental Procedures

The catalytic experiments were carried out in a 100 mL conical bottle. Specifically, 35 mg of catalyst was added into a mixture of the target pesticides ($C_{\text{ATZ}} = C_{\text{MET}} = C_{\text{EPD}} = 30$ mg/L), and 4.0 mM of PMS was added to initiate the reaction. Ultrasonic dispersion was then conducted on a constant-temperature shaking table at a speed of 220 rpm. The conical bottles were removed at set time intervals for the reaction (1 min, 3 min, 5 min, 10 min, 15 min), and the catalyst was separated from the solution using an external magnet. Then, 500 μL of the reaction solution was extracted and mixed with 500 μL of methanol to stop the reaction. After mixing, the sample was transferred into the sample vial through a 0.22 μm filter membrane. The reusability and regeneration of the catalyst were evaluated through three cycles of degradation experiments. The used catalyst was collected from the aqueous solution using a magnet, then washed three times with methanol, and finally placed in an oven at 60 °C until completely dry before being used in the next experiment. All experiments were performed three times to ensure data reliability.

2.4. Analytical Methods

The concentrations of atrazine, metalaxyl and epoxiconazole were quantitatively analyzed by a Thermo Scientific HPLC system equipped with an automated sample injector, a quaternary solvent delivery pump, and a diode array detector (DAD). Chromatographic separation was achieved by using a Welch Ultimate® XB-C₁₈ column (5 μm $\times$ 4.6 mm $\times$ 250 mm i.d., Welch Materials, Inc, Shanghai, China) at 30 °C. The mobile phase was ultrapure water and acetonitrile (50/50, *v/v*) with a flow rate of 0.5 mL/min. The injection volume was 10 μL , and the detection wavelength was chosen at 200 nm.

The possible intermediates of the target pesticides were identified by Zeno TOF 7600 liquid chromatography (SCIEX, Marlborough, MA, USA) combined with mass spectrometry in positive ion mode at 40 °C with a Waters Acquity UPLC® HSS T3 column (1.8 μm , 2.1 μm $\times$ 100 mm, Waters Corporation, Milford, MA, USA). In this paper, water (A) and methanol (B) were used as mobile phases with a flow rate of 0.3 mL/min. Both the A and B mobile phases contained 2 mM ammonium formate and 0.01% formic acid, and the sample volume was 2 μL . Gradient elution is employed with the following gradient elution program: 0–1.0 min, 3% A, 97% B; 1.0–1.5 min, 15% A, 85% B; 1.5–2.5 min, 50% A, 50% B; 2.5–10.0 min, 30% A, 70% B; 10.0–23 min, 2% A, 98% B; 23.0–27.0 min, 2% A, 98% B; 27.0–27.1 min, 97% A, 3% B; 27.1–30 min, 97% A, 3% B.

ROS were detected using 5,5-dimethyl-1-pyrrolidinone N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidine alcohol (TEMP) as spin traps using an EPR spectrometer (Bruker EMXplus-6/1, Bruker Biospin GmbH, Rheinstetten, Germany). DMPO was used to identify $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$, and $\text{O}_2^{\bullet-}$. TEMP was chosen as the spin trap for identifying $^1\text{O}_2$. Additionally, excess free radical scavengers (tert-butanol, methanol, 1,4-benzoquinone, and L-histidine) were added in the quenching experiments to specifically remove $\cdot\text{OH}$, $\text{SO}_4^{\bullet-}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$, respectively. The concentrations of tert-butanol and methanol were 500 mM, and the concentrations of 1,4-benzoquinone and L-histidine were 10 mM.

3. Results and Discussion

3.1. Characterizations

The microstructure and internal structure of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ particles were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As depicted in Figure S1, the SEM images of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ both reveal abundant aggregated spherical structures with relatively rough surfaces, and no significant differences are observed between them. This is presumably attributed to the low loading of $\text{Co}_5\text{Al-LDH}$ and the stacking of numerous spherical particles, which makes the lamellar structure of $\text{Co}_5\text{Al-LDH}$ difficult to observe by SEM. Nevertheless, distinct structural differences between the two samples can be clearly observed in the TEM images. As shown in Figure 1, $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ not only exhibits typical spherical Fe_3O_4 particles but also possesses a sheaf-like ultrathin nanosheet structure with numerous sheets aligned in the same direction, providing direct evidence for the successful preparation of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$. Furthermore, energy-dispersive X-ray spectroscopy (EDS) analysis (Figure S2) confirms the presence of Co and Al elements on the material surface, further verifying the successful hybridization of Fe_3O_4 and $\text{Co}_5\text{Al-LDH}$.

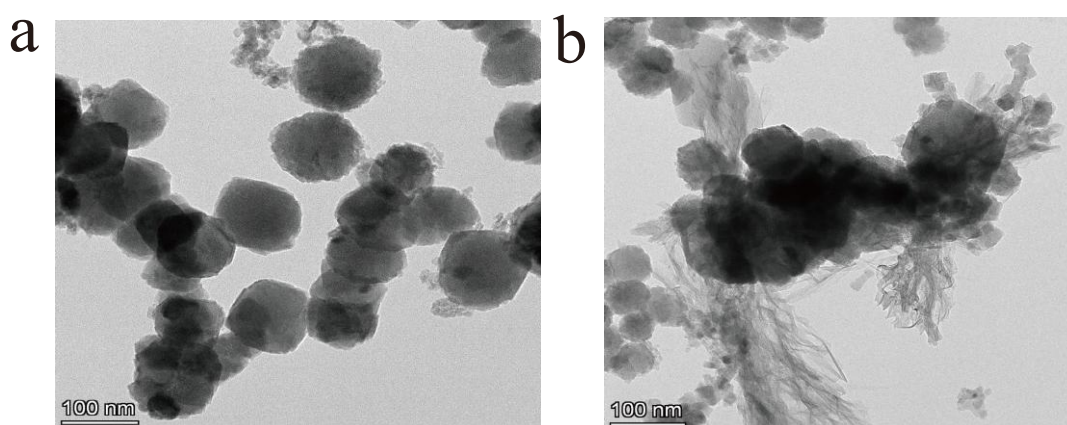


Figure 1. The TEM images of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ (b).

X-ray diffraction (XRD) is an analytical method used to study information such as the composition, atomic or molecular structure, and morphology of catalysts. In this study, XRD was employed to characterize the crystal structure. As shown in Figure 2a, the main peaks at 30.1° , 35.5° , 43.2° , 53.5° , 57.1° , and 62.6° correspond to the (220), (311), (400), (422), (511) and (440) crystal planes of Fe_3O_4 [24], respectively. After loading $\text{Co}_5\text{Al-LDH}$, new peaks appeared at 2θ values of 11.7° , 23.6° , 34.7° , 39.3° and 46.9° , corresponding to the (003), (006), (012), (015) and (018) crystal planes of CoAl-LDH (JCPDS: 51-0045) [25], respectively. Compared to the characteristic peak of Fe_3O_4 , the peak intensity of LDH was weaker, suggesting that the loading of $\text{Co}_5\text{Al-LDH}$ may be low. This was also consistent with previous assumptions and EDS results.

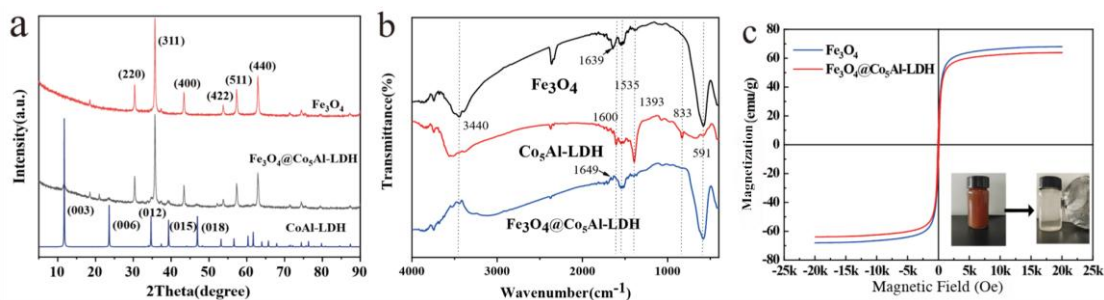


Figure 2. The XRD patterns (a) and FTIR spectra (b) of Fe₃O₄, Co₅Al-LDH and Fe₃O₄@Co₅Al-LDH and VSM image (c) of Fe₃O₄ and Fe₃O₄@Co₅Al-LDH.

The structure of functional groups on the catalyst surface was characterized by Fourier-Transform Infrared (FTIR). There is a wide peak at 3000–3500 cm⁻¹ in Figure 2b, which belongs to the bending vibration of interlayer water molecules or the tensile vibration of O-H. For the spectrum of Fe₃O₄ nanoparticles, the peaks at 591 cm⁻¹ may be caused by the stretching vibration of Fe-O bonds, while the double peaks at 1639 cm⁻¹ and 1535 cm⁻¹ may be attributed to the symmetric and asymmetric vibration of C-O [22]. For the spectrum of Co₅Al-LDH, the peaks at 1393 cm⁻¹ indicated the presence of CO₃²⁻ ions in the interlayer structure [26]. The spectral band near 800 cm⁻¹ was mainly caused by the telescopic vibration of metal–oxygen (M-O) or metal–hydroxy (M-OH) groups in the hydrotalcite lattice [23]. The spectra of Fe₃O₄@Co₅Al-LDH exhibited characteristic peaks corresponding to both Fe₃O₄ and Co₅Al-LDH, which confirmed the successful preparation of Fe₃O₄@Co₅Al-LDH.

The magnetic properties of the catalyst were characterized using a vibrating sample magnetometer (VSM). As shown in Figure 2c, the saturation magnetization of Fe₃O₄ and Fe₃O₄@Co₅Al-LDH is 68.0 emu/g and 64.0 emu/g, respectively. Compared to Fe₃O₄, the magnetic strength of Fe₃O₄@Co₅Al-LDH was slightly reduced. Moreover, the magnetization curves exhibited sufficient superparamagnetism, meeting the requirements for rapid magnetic separation between solid materials and liquid matrices [27].

To further understand the elemental composition and chemical state of the catalyst surface, the results of X-ray photoelectron spectroscopy (XPS) characterization were analyzed. Figure 3a was the elemental survey spectrum of Fe₃O₄@Co₅Al-LDH, which reveals the presence of Co, Al, and C elements, indirectly verifying the successful synthesis of Co₅Al-LDH. Figure 3b–e display the high-resolution XPS spectra of C, O, Co, and Fe elements in Fe₃O₄@Co₅Al-LDH, respectively. Specifically, the high-resolution C 1s spectrum was successfully deconvoluted into three peaks at 284.77, 286.27, and 288.42 eV in Figure 3b, corresponding to C=C, C-O, and O-C=O bonds, respectively. A large amount of oxygen-containing functional groups has formed on the catalyst surface, which may serve as a source of electron transfer for activating persulfate. In Figure 3c, the O 1s fine spectrum consists of three peaks located at 529.99, 531.31, and 532.21 eV, indicating the presence of lattice oxygen (labeled as O_L), oxygen vacancies (labeled as O_v), and adsorbed oxygen or surface hydroxyl groups (labeled as O_s) in Fe₃O₄@Co₅Al-LDH [28–30]. As shown in Figure 3d, in the Co 2p spectrum, the binding energies observed at 782.10 and 780.70 eV for Co 2p_{3/2} were attributed to Co (II) and Co (III), respectively. The peaks located at 797.50 and 796.10 eV correspond to Co 2p_{1/2}, indicating the presence of Co (II) and Co (III). These peaks represent the different oxidation states of cobalt in Fe₃O₄@Co₅Al-LDH. The Co 2p_{3/2} and Co 2p_{1/2} peaks were typically split due to spin–orbit coupling, with the Co 2p_{3/2} peak having a lower binding energy than the Co 2p_{1/2} peak [26,31,32]. Peaks at 53 eV in the Fe 2p spectrum (Figure 3e) are assigned to Fe 2p_{3/2}, indicating the presence of Fe³⁺ and Fe²⁺ oxides. The peaks at 725.99 and 724.13 eV corresponded to Fe 2p_{1/2}. Additionally, there were satellite peak features present at 732.75 and 718.73 eV [33,34]. The different binding

energies for Fe^{2+} and Fe^{3+} indicated that iron was present in multiple oxidation states within $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$, which could have implications for its catalytic properties.

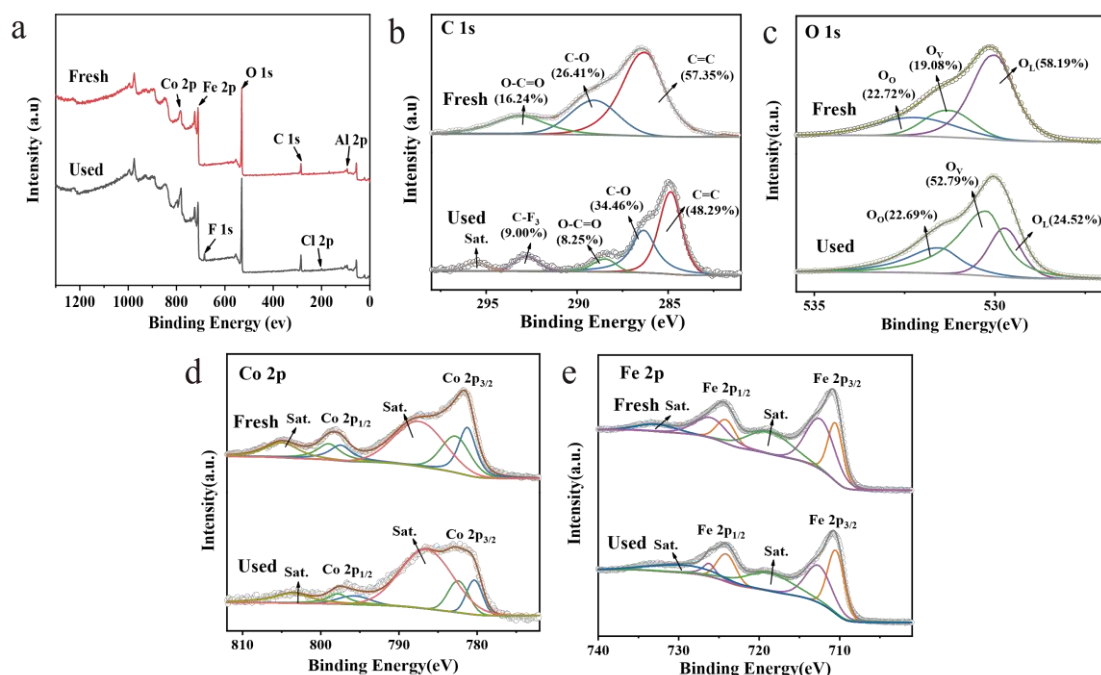


Figure 3. The XPS full-scan spectrum (a) and fine-scanned spectrum for C 1s (b), O 1s (c), Co 2p (d) and Fe 2p (e) of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ before and after reaction.

3.2. PMS Activation Performance of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$

The degradation performance of atrazine, metalaxyl and epoxiconazole was evaluated by designing different catalyst/PMS combinations, which included Fe_3O_4 alone, $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ alone, PMS alone, $\text{Fe}_3\text{O}_4/\text{PMS}$, and $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}/\text{PMS}$ systems, and the results are shown in Figure 4a–c. Apparently, the degradation rates of atrazine, metalaxyl and epoxiconazole were almost negligible (<15%) in the only- Fe_3O_4 system and only- $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ system. The above results show that the adsorption capacity of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ to remove these three pesticides was inferior. Furthermore, the removal efficiencies of atrazine, metalaxyl and epoxiconazole in the only-PMS system were 85%, 50% and 51% within 15 min, respectively. It manifested that PMS exhibited a certain level of degradation capability towards the three pesticides. Its superior performance in degrading atrazine may be attributed to its relatively simple structure. When Fe_3O_4 was used as a catalyst to activate PMS, the degradation efficiencies of atrazine and metalaxyl were only 60% within 15 min, and that of epoxiconazole was 51%. This indicated that Fe_3O_4 may have a weak ability to activate PMS to produce free radicals. In contrast, atrazine and metalaxyl were removed by 100% in the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}/\text{PMS}$ system within 10 min, and 92% of epoxiconazole was removed within 15 min, which indicated that PMS could be effectively activated by $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ and the loading of $\text{Co}_5\text{Al-LDH}$ could enhance the catalytic performance of the material.

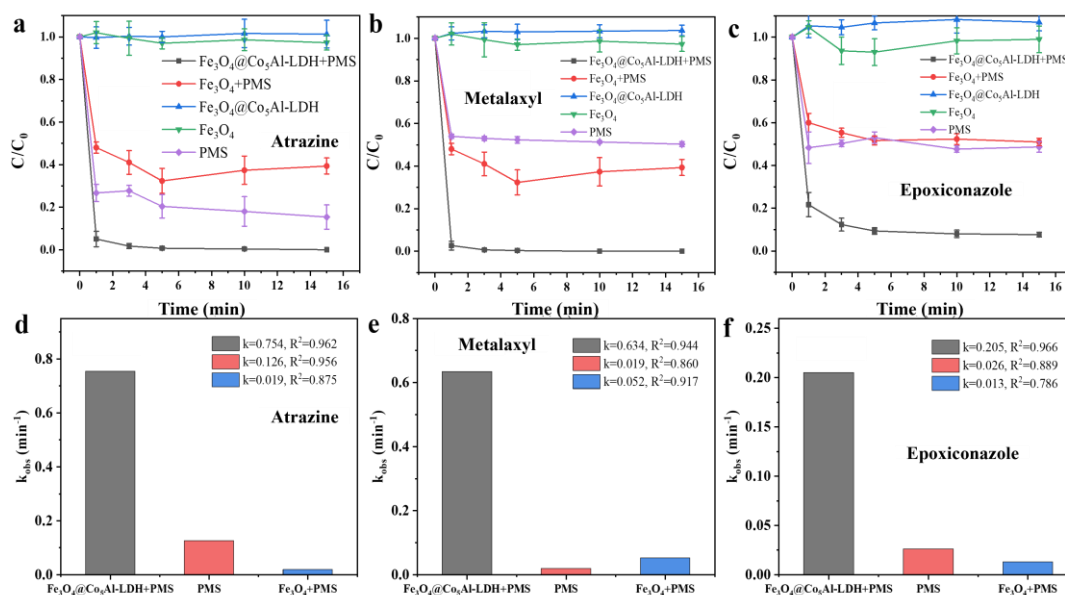


Figure 4. Degradation of atrazine (a,d), metalaxyl (b,e), and epoxiconazole (c,f) in different reaction systems and the corresponding pseudo-first-order kinetic rate constants.

To compare the catalytic degradation activities toward atrazine, metalaxyl, and epoxiconazole in different reaction systems, the degradation processes were fitted using a pseudo-first-order kinetic model. The neat Fe_3O_4 and $Fe_3O_4@Co_5Al-LDH$ systems exhibited negligible degradation and only slight adsorption, so no kinetic fitting was performed. The apparent rate constants (k) and correlation coefficients (R^2) obtained for the PMS, Fe_3O_4/PMS , and $Fe_3O_4@Co_5Al-LDH/PMS$ systems are presented in Figure 4d–f. Among the three investigated systems, the $Fe_3O_4@Co_5Al-LDH/PMS$ system showed the optimal catalytic degradation performance for all three pesticides, with k values remarkably higher than those of the Fe_3O_4/PMS and sole-PMS systems. Specifically, atrazine was degraded most rapidly in this system ($k = 0.754 \text{ min}^{-1}$). Similarly, the k value for metalaxyl in the composite system (0.634 min^{-1}) was much higher than those in the other two systems. Although epoxiconazole degraded relatively slowly, the $Fe_3O_4@Co_5Al-LDH/PMS$ system still exhibited a distinct catalytic advantage, with the rate constant enhanced by approximately 15.8-fold compared with the sole-PMS system (0.013 min^{-1}). These results clearly demonstrate that the modification of $Fe_3O_4@Co_5Al-LDH$ on the Fe_3O_4 surface combined with PMS enables a synergistic effect of active components, which efficiently activates PMS and thus enhances the catalytic degradation performance toward metalaxyl, atrazine, and epoxiconazole.

3.3. Effect of Different Factors on $Fe_3O_4@Co_5Al-LDH/PMS$ System

3.3.1. Effect of Solution pH

The PMS activation system could be significantly affected by the solution pH because the initial pH value would change the existing form of PMS and pesticides, altering the surface-active sites of the catalyst and causing free radical evolution [26]. As exhibited in Figure 5a–c, atrazine can be effectively degraded under different pH values, with the best degradation effect at a pH value of 7.0. In contrast, the effect was only poor when the pH value was 9.0, probably due to the formation of hydroxide precipitation and the conversion of $SO_4^{\bullet-}$ to the less reactive $\bullet OH$ (Equation (1)) [35,36]. In addition, the self-activation of PMS hinders catalytic performance under alkaline conditions (Equation (2)) [37]. When the pH value was 11.0, the removal effect was better than that at 9.0, probably because

atrazine was more stable in slightly alkaline media, and it was easy to hydrolyze in strong alkali media. It can be found that the removal effect of the three pesticides was the highest for the initial pH value of 7.0, and the degradation efficiency of metalaxyl and epoxiconazole was reduced by 28% and 27% when the pH was 3.0, respectively. This dramatic drop in performance was due to the fact that PMS was more stable under strongly acidic conditions, limiting the production of $\text{SO}_4^{\bullet-}$, and excessive H^+ could clear $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ under acidic conditions (Equations (3)–(5)) [26,35]. In addition, metalaxyl is stable under neutral and acidic conditions and breaks down easily when exposed to alkali. All in all, $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ could be applied under a wide range of pH conditions, and the pH value was fixed at 7.0 in the subsequent experiments.

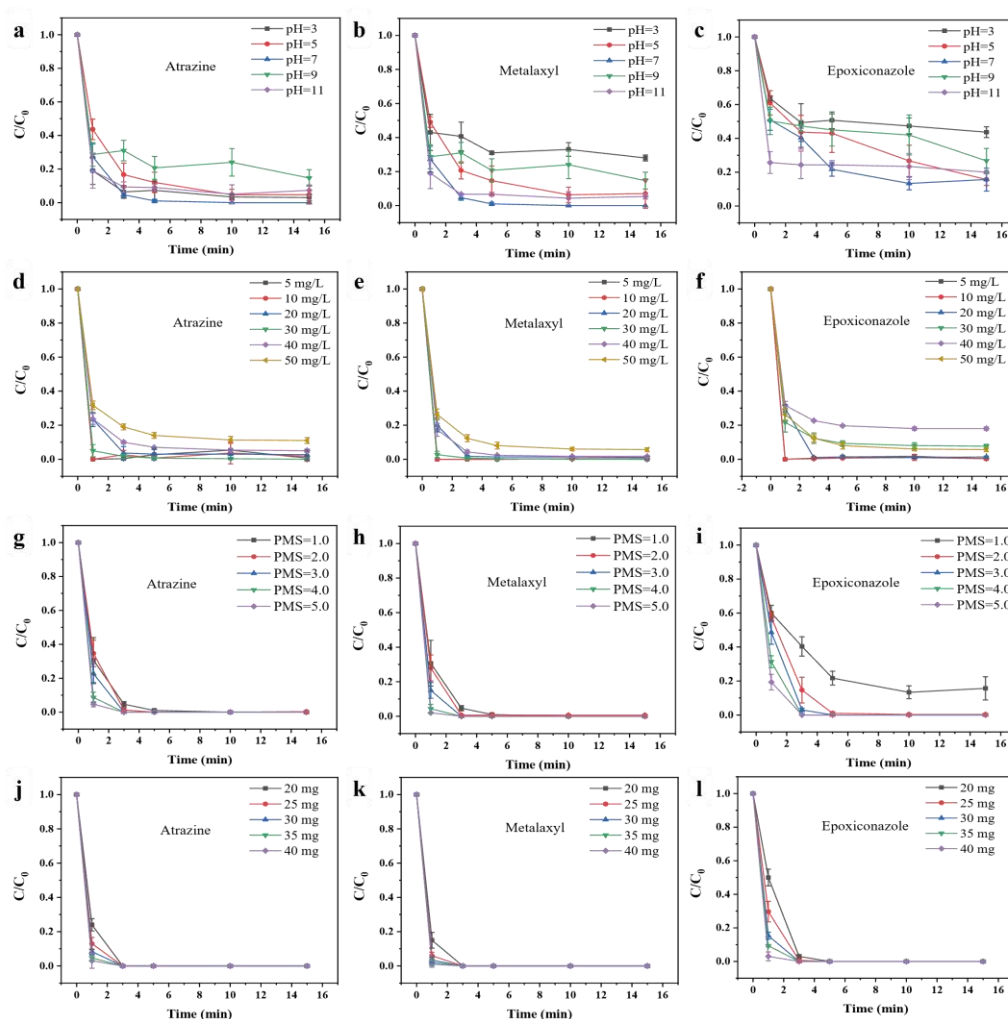
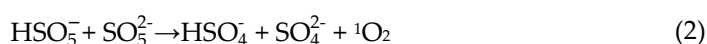


Figure 5. Effects of initial solution pH (a–c), initial pesticide concentration (d–f), PMS concentration (g–i), and catalyst dosage (j–l) on the simultaneous removal efficiency of mixed atrazine, metalaxyl, and epoxiconazole.

3.3.2. Effect of Initial Pesticide Concentration

The effect of various initial concentrations of pesticides on the degradation efficiency was also investigated. Figure 5d shows that when the initial concentration of atrazine was gradually increased from 5 mg/L to 40 mg/L, the removal efficiency also slowly decreased from 100% to 95%. When the concentration increased from 40 mg/L to 50 mg/L, the removal efficiency decreased to 89%. This may be due to the fact that there were a limited number of active sites on Fe₃O₄@Co₅Al-LDH to activate PMS efficiently, resulting in a limited number of active species to quickly break down large amounts of atrazine [38]. The same trend occurred with metalaxyl (Figure 5e), but the removal efficiency of metalaxyl still reached 95% when the concentration was 50 mg/L. In contrast, the removal efficiency of epoxiconazole was reaching the minimum value (82%) at a concentration of 40 mg/L (Figure 5f). The difference in removal efficiency between 30 mg/L and 40 mg/L has no significance. Therefore, 30 mg/L was ultimately chosen as the optimal experimental condition for subsequent experiments for saving costs.

3.3.3. Effect of PMS Concentration

In general, the concentration of PMS plays a crucial role in the oxidizing ability of AOP. The results are shown in Figure 5g–i. The removal rate of pesticides significantly increased with the rise in concentration of PMS from 1.0 mM to 4.0 mM, possibly due to the enhanced utilization of reaction sites by higher PMS amounts, leading to a faster generation of active substances for their degradation [39]. Meanwhile, when the concentration of PMS increased from 4.0 mM to 5.0 mM, the degradation efficiency improved slowly. This may be due to the self-scavenging reaction of excess SO₄^{•−} (Equation (6)), and excessive PMS could also react with SO₄^{•−} to form SO₅^{•−} (Equation (7)), which possesses weak oxidation capabilities [40]. Therefore, 4.0 mM of PMS was selected as the optimum amount in the following experiments.



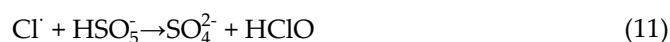
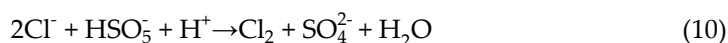
3.3.4. Effect of Catalyst Dosage

The catalyst dosage is a crucial factor influencing the pesticide degradation performance. When the dose of the catalyst increased from 20 to 35 mg, a gradual increase in the degradation rate was observed, as shown in Figure 5j–l. This might be due to the fact that an increase in the dosage of catalysts was associated with an increase in the number of active sites, which enlarged the catalytic surface area and thus significantly increased the degradation rate. When the dose was increased from 35 to 40 mg, the degradation rate increased slowly. All three pesticides exhibited a trend consistent with the description provided above. After considering the degradation efficiency and cost, 35 mg was determined to be the optimal condition for the subsequent experiments.

3.3.5. Effect of Coexisting Inorganic Ions

In natural environment water, the presence of a high concentration of anions is common, and these anions frequently compete with the target pollutants for the reactive oxygen species (ROS) generated during the catalytic process, thereby influencing the degradation rate of the target contaminants. Therefore, solutions containing five common anions at concentrations of 5.0 mM and 10.0 mM were prepared with the aim of investigating the influence on the Fe₃O₄@Co₅Al-LDH/PMS system (Figure S3). Specifically, Cl[−] exhibited an inhibitory effect on all three pesticides. The inhibition of Cl[−] was due to the reaction between PMS and Cl[−] that produced reactive chlorine species such as hypochlorous acid

(HClO) and chlorine (Cl₂), which could reduce the removal rate (Equations (8)–(11)). This inhibition became more pronounced with increases in the concentrations of Cl[−].



The inhibitory effect of CO₃^{2−} on atrazine was weak and increased with increasing concentration. This may be attributed to the reaction of CO₃^{2−} with SO₄^{•−} and [•]OH to form carbonate radical (CO₃^{•−}) (Equations (12) and (13)). It has been reported that CO₃^{•−} was less reactive than SO₄^{•−} and [•]OH, which means that the degradation effect was poor [41,42]. A total of 5.0 mM of CO₃^{2−} promoted the degradation of epoxiconazole, whereas 10.0 mM of CO₃^{2−} exhibited an inhibitory effect on its degradation. Dissolved CO₃^{2−} can act as a buffer in the reaction solution, which may help to maintain a favorable pH environment for the degradation process of epoxiconazole. However, at higher concentrations, the CO₃^{2−} might alter the reaction conditions in a way that is less conducive to degradation. CO₃^{2−} and HCO₃[−] show neither inhibitory nor promotional effects on metalaxyl.



The presence of HCO₃[−] and HPO₄^{2−} facilitated the degradation of atrazine and epoxiconazole, which might be due to the fact that these ions can convert the solution into a basic buffering solution and a weakly basic environment is favorable for the degradation of atrazine and epoxiconazole. HPO₄^{2−} has no inhibitory or promotional effect on the degradation of metalaxyl. SO₄^{2−} exhibited an inhibitory effect on all three pesticides. The mild inhibitory effect observed upon the addition of SO₄^{2−} may indeed be due to the repressive role of SO₄^{2−} in the chain reaction of simultaneously generating the active species and SO₄^{•−} [43]. It may also be due to its ability to lower the redox potential of SO₄^{•−}/SO₄^{2−}, leading to a decrease in the activation efficiency of the PMS.

3.4. Stability Studies of Catalyst

The stability and reusability of the catalyst are important evaluation indicators that affect its practicality. To investigate the catalytic stability of Fe₃O₄@Co₅Al-LDH, three cyclic degradation experiments were conducted under the same experimental conditions. After each experiment, the catalyst was collected from the aqueous solution using a magnet and then washed with methanol and dried for reuse. As shown in Figure S4, the catalytic performance of Fe₃O₄@Co₅Al-LDH remains relatively stable. After each cycle, metalaxyl and atrazine can still be removed within 15 min. However, after the third cycle of reaction, the degradation efficiency of epoxiconazole decreased by 8%. The reason for the decline may be due to the loss of a small amount of material during the degradation process, as well as the possible attachment of small-molecule intermediate products to the catalyst surface, which may reduce the activity or deactivate some active sites, hindering the reaction between the catalyst and PMS [44]. In turn, this inhibits the formation of SO₄^{•−} and [•]OH, leading to a slight decrease in the degradation efficiency of epoxiconazole. Overall, the catalyst demonstrates excellent stability and potential for repeated use.

3.5. Possible Reaction Mechanism

The types of reactive species in the reaction system are of great significance for exploring the degradation pathways of pesticides. In this study, the formation of reactive species in the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH/PMS}$ system was investigated by adding an excess of free radical quenchers to the reaction mixture. It is generally believed that $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ are active free radicals involved in the catalytic system. In addition, $^1\text{O}_2$ and $\text{O}_2\cdot^-$ could also attack organic compounds. Tert-butanol (TBA) was used as a specific scavenger for $\cdot\text{OH}$, while methanol (MeOH) was used as a specific scavenger for both $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$. Furthermore, $\text{O}_2\cdot^-$ and $^1\text{O}_2$ could be quenched by 1,4-benzoquinone (p-BQ) and L-histidine (L-his), respectively. The concentrations of tert-butanol and methanol were 500 mM, while the concentrations of 1,4-benzoquinone and L-histidine were 10 mM. As can be inferred from Figure 6a–c, compared with the blank control, the addition of MeOH and TBA to the reaction system reduced the degradation rate of atrazine by 27% and 17%, respectively, confirming the presence of $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ in the system. These radicals played significant roles in the degradation of atrazine. Moreover, it was observed that L-his and p-BQ exhibited weak inhibitory effects in the first 10 min of the reaction, indicating the possible presence of $^1\text{O}_2$ and $\text{O}_2\cdot^-$, but their role in removing atrazine can be ignored. The results of metalaxyl and epoxiconazole were more consistent with the above phenomenon. Compared to the blank control, the degradation rate of metalaxyl decreased by 26% and 9% after adding MeOH and TBA, respectively. After adding MeOH and TBA to the reaction system, the degradation rate of epoxiconazole decreased by 33% in both cases. L-his exhibited a significant inhibitory effect on the system during the first 10 min of the reaction, indicating that $^1\text{O}_2$ may have a certain contributory role in the degradation of epoxiconazole.

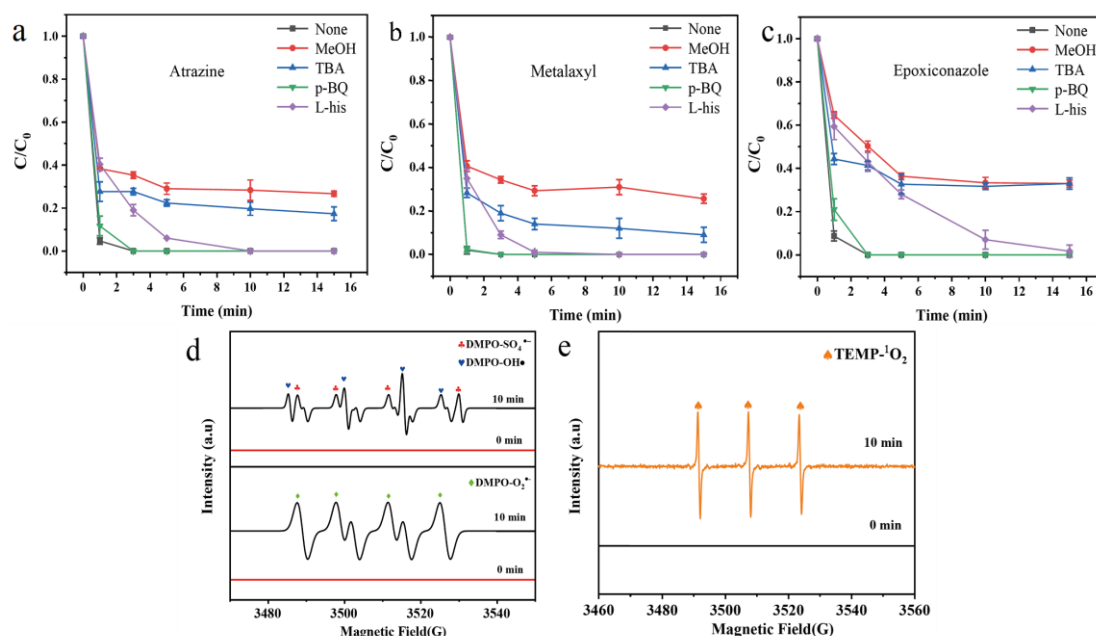


Figure 6. Effects of radical scavengers on the removal of atrazine (a), metalaxyl (b), and epoxiconazole (c) and EPR spectra for the detection of $^1\text{O}_2$ (e) $\cdot\text{OH}$, $\text{SO}_4\cdot^-$ and $\text{O}_2\cdot^-$ (d).

In addition, electron paramagnetic resonance (EPR) technology was employed to further detect possible active substances in the catalytic degradation system. The results are shown in Figure 6d–e. Signals of DMPO- $\cdot\text{OH}$ and DMPO- $\text{SO}_4\cdot^-$ were detected, indicating that both $\text{SO}_4\cdot^-$ and $\cdot\text{OH}$ coexist in the reaction system. Additionally, DMPO- $\text{O}_2\cdot^-$ was also detected. This indicated that $\text{O}_2\cdot^-$ existed within the system, but its contribution to the

degradation process of pesticides was not significant. Furthermore, a triplet peak was observed in the spectrum obtained by capturing $^1\text{O}_2$ with TEMP, which can be attributed to the $^1\text{O}_2$ produced by the decomposition of persulfate in the reaction system. The EPR results provided clear evidence for the presence of free radicals and validated the accuracy of the free radical quenching experimental data. This also confirmed that the degradation processes of these three pesticides were caused by the attack of reactive oxygen species generated in the reaction system.

To investigate the reaction mechanism of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ activating PMS for the degradation of pesticides, XPS characterization analysis was performed on $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ before and after the reaction. By comparing the changes in surface chemical composition and elemental content, possible reaction mechanisms can be inferred. As can be seen from Figure 3a, there were two new characteristic absorption bands ascribed to Cl 2p and F 1s, indicating the adsorption of atrazine and epoxiconazole on the surface of the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$. In Figure 3b, it can be observed that two new peaks at 292.76 and 295.52 eV appeared after the reaction in the C 1s spectrum, corresponding to the C-F₃ and π - π oscillation satellite peaks, respectively. The appearance of the new C-F₃ peak could indeed be indicative of the adsorption of epoxiconazole onto the surface of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$. This adsorption could be a transient step in the degradation process, where pesticides were initially adsorbed onto the surface of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$. Subsequently, the reaction with PMS led to pesticide degradation. Additionally, the content of C=C and O-C=O decreased from 57.35% and 16.24% to 48.29% and 8.25%, respectively, while the content of C-O increased from 26.41% to 34.46%. These changes in the surface chemical composition indicated that as the reaction process occurred, many CO_3^{2-} molecules were released from the LDH layer, and the double bonds may have been broken [25].

In Figure 3c, the content of lattice oxygen (O_L) decreases from 58.19% to 24.52%. There were two reasons for the reduction in O_L content. The first was that O_L , as a reactive oxygen species, may react with the pesticide during catalysis, leading to a decrease in its content. The second reason was that the decrease in O_L may be related to the formation of oxygen vacancies. During material treatment or catalytic reactions, oxygen atoms may be removed from the lattice, resulting in the formation of oxygen vacancies. In this situation, the absence of oxygen atoms directly caused a decrease in the content of O_L . Conversely, the content of oxygen vacancy (O_V) increased from 19.08% to 52.79%, suggesting that oxygen atoms may indeed be removed from the lattice to form O_V , which reacts with the pesticide during catalysis. As shown in Figure 3d, the ratios of Co^{2+} and Co^{3+} in the system were 44.43% and 55.57%, respectively. After the degradation occurred, the content of Co^{3+} in the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ system decreased to 45.81%, while the content of Co^{2+} increased to 54.19%, indicating the conversion of Co^{3+} to Co^{2+} (Equation (15)). From Figure 3e, it can be seen that the content of Fe^{2+} decreased from 61.71% to 45.46% and Fe^{3+} in the system was increased from 38.29% to 54.54% after the degradation occurred. This showed that the conversion of Fe^{2+} to Fe^{3+} occurred (Equation (16)). In addition, PMS could provide electrons to Fe^{3+} , thus completing the redox cycle (Equation (17)). Moreover, thermodynamically, Fe^{2+} promoted the conversion of Co^{3+} to Co^{2+} (Equation (18)) [45]. The above results indicate that the redox coupling of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ may be involved in the activation of PMS.

Based on the comprehensive analysis above, a possible mechanism for the activation of PMS by $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ to remove pesticides is proposed, as shown in Figure 7. The free radical pathway involved the generation of three free radicals ($\cdot\text{OH}$, $\text{SO}_4\cdot^-$ and $\text{O}_2\cdot^-$) [35]. Initially, HSO_5^- was activated by divalent metal ions $\text{Fe}^{2+}/\text{Co}^{2+}$ to generate $\text{SO}_4\cdot^-$ and the corresponding trivalent metal ions $\text{Fe}^{3+}/\text{Co}^{3+}$ (Equations (14) and (16)). Subsequently, $\text{Fe}^{3+}/\text{Co}^{3+}$ was reduced by HSO_5^- to obtain $\text{SO}_5\cdot^-$ and two divalent metal ions (Equations (15) and (17)), thus achieving a redox cycle between divalent and trivalent metal ions. Addi-

tionally, Fe^{2+} could reduce Co^{3+} to Co^{2+} (Equation (18)), thereby promoting the $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycles. At the same time, some $\text{SO}_4^{\bullet-}$ was consumed by OH^- to generate $\bullet\text{OH}$ (Equation (19)) [46]. It was reported that dissolved oxygen in the solution, lattice oxygen in the catalyst, PMS self-activation, or the conversion of $\text{O}_2^{\bullet-}$ may produce $^1\text{O}_2$ [47]. However, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ were not the primary active species in the system. The main degradation of the target pesticide was still attributed to the oxidation by $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, leading to the gradual decomposition of the parent pesticide.

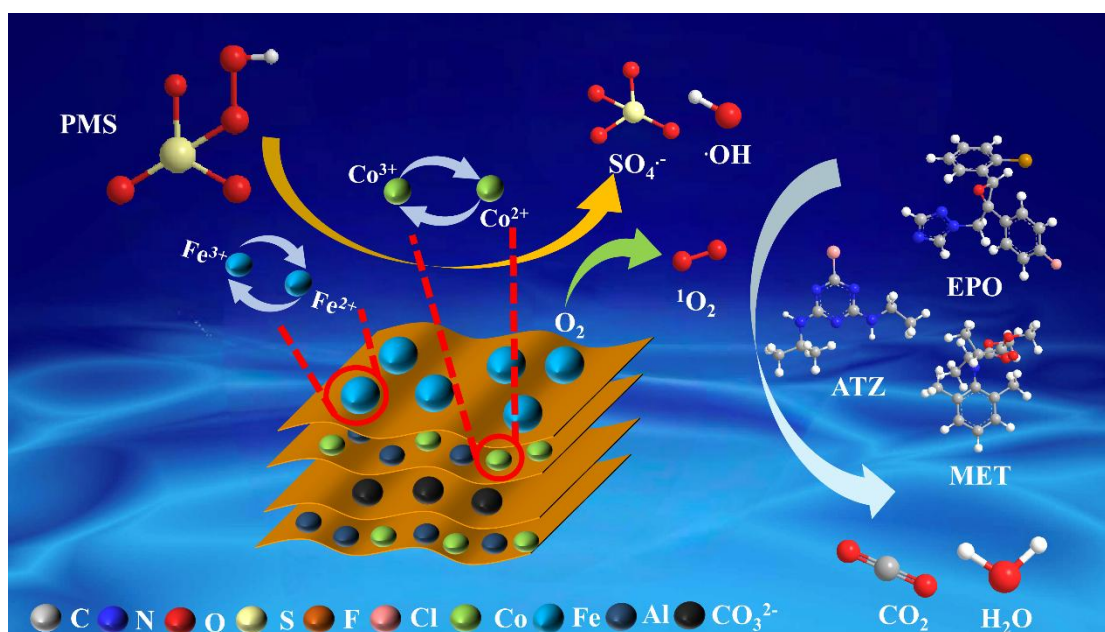
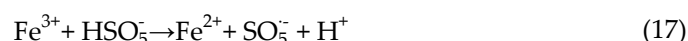
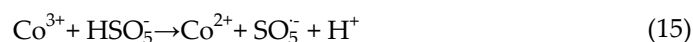


Figure 7. Proposed reaction mechanism of atrazine, metalaxyl, and epoxiconazole by $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}/\text{PMS}$ system.

3.6. Degradation Pathway of Pesticides

The main transformation products (TPs) formed by three pesticides in the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}/\text{PMS}$ system were further detected by using liquid chromatography coupled with mass spectrometry (LC-MS). Based on the detection results and previous reports, potential degradation pathways were proposed, as illustrated in Figure 8. There is a scarcity of references on the degradation pathways of metalaxyl and epoxiconazole. Here, based only on the structures of metalaxyl and epoxiconazole, their electron-rich sites, and the structures of the intermediate products, possible degradation pathways were proposed.

Four intermediates of metalaxyl were detected, and four potential degradation pathways were proposed. Pathway I involves the hydroxylative attack of free radicals on the carbon atom connected to the amide bond. Subsequently, there is a free radical substitu-

tion of the alkyl group on the benzene ring. Finally, TP1 is formed through hydrogen atom transfer. In pathway II, the attack by free radicals leads to the oxidation of the carbon atom, forming a carbonyl group and resulting in TP2. In pathway III, the alkyl groups on the benzene ring undergo substitution reactions. Meanwhile, the groups on both sides of the amide bond might experience rearrangement, recombination, and demethylation, ultimately producing TP3. Pathway IV, in contrast, involves the complete hydrolysis of the amide bond, leading to its cleavage from the benzene ring and directly forming the degradation product TP4.

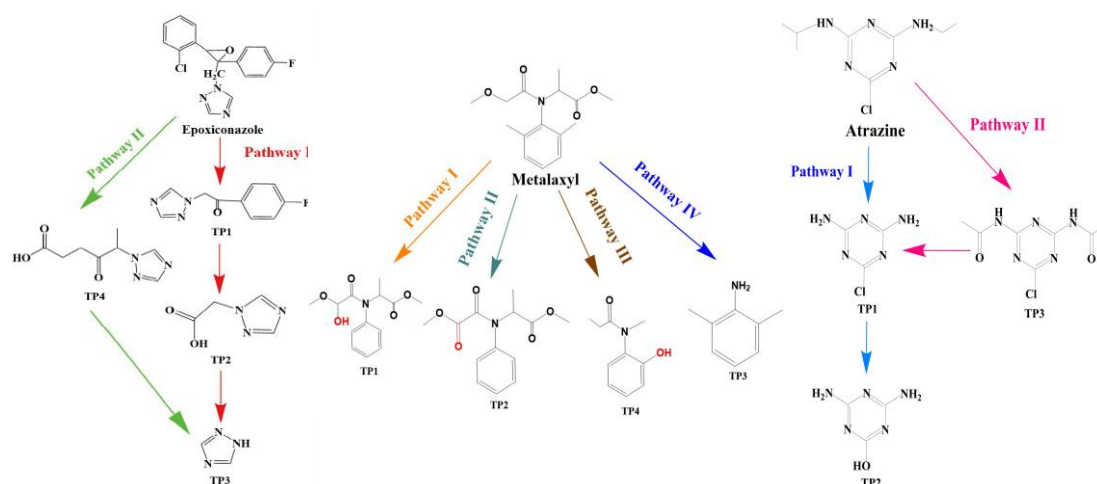


Figure 8. Proposed degradation pathways of atrazine, metalaxyl, and epoxiconazole by $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH/PMS}$ system.

The epoxide group (-O-) in the structure of epoxiconazole is a group with high electron density as it contains an oxygen atom. The lone pair of electrons of this oxygen atom can increase the electron density of adjacent carbon atoms, making these positions potential electron-rich centers as well. Although the fluorine atom on the benzene ring in the structure of epoxiconazole is a strong electron-withdrawing group, it can still affect the electron distribution on the benzene ring through conjugation effects, making the positions opposite the fluorine atom on the benzene ring potentially more electron-rich. Four potential intermediates of epoxiconazole have been identified, and two feasible degradation pathways have been proposed.

In degradation pathway I, the free radical first attacks the carbon atom connected to the epoxide group, causing the epoxide ring to open and form TP1. Subsequently, the free radical continues to attack the carbon on the benzene ring opposite the fluorine atom, leading to a hydroxyl substitution reaction and the formation of TP2. The carbon atom connected to nitrogen is also an electron-rich site, and upon attack by the free radical, the C-N bond breaks, resulting in the formation of TP3. In degradation pathway I, the free radical first attacks the carbon atom connected to the epoxy group, causing the epoxy ring to open and form a new carbon-oxygen double bond ($\text{C}=\text{O}$), resulting in the formation of TP1. Subsequently, the free radical continues to attack the carbon on the benzene ring opposite the fluorine atom, leading to a hydroxyl substitution reaction and generating TP2. The carbon atom connected to the triazole ring is also an electron-rich site, and when it is attacked by the free radical, the C-N bond breaks, yielding TP3. In degradation pathway II, the free radical first attacks the carbon atom connected to the epoxy group, causing the epoxy ring to open. After the epoxy bond is opened, an intermediate may form, which then further reacts with carboxylate ions ($-\text{COO}^-$) on the catalyst surface to form a carboxylic acid group. Meanwhile, the molecule may undergo rearrangement, which leads to the

realignment of carbon atoms, thus forming TP4. Later, the free radical continues to attack the carbon atom connected to the triazole ring, and after being attacked by the free radical, the C-N bond breaks to generate TP3.

Three potential intermediates of atrazine were recognized, and two feasible degradation pathways were proposed. The degradation reaction of atrazine mainly included dealkylation, dechlorination reactions, and alkyl chain oxidation [48]. Furthermore, the $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ both participated in the degradation process of atrazine. As an electrophilic oxidant, $\text{SO}_4^{\bullet-}$ tended to attack the electron-rich sites of atrazine (ATZ). Additionally, it has been reported that the C-N bonds in the alkyl side chains of ATZ were prone to cleavage, leading to the formation of dealkylation products [49]. In pathway I, the isopropylamine and ethylamine substituents of atrazine were attacked by $\text{SO}_4^{\bullet-}$, prompting a demethylation process that results in the formation of TP1 (CAAT). Then, $\text{SO}_4^{\bullet-}$ further attacked the C-Cl bond due to it having the longest bond length (1.734 Å) and the lowest bond polarity [50], undergoing dechlorination-hydroxylation to generate TP2 (OAAT). In pathway II, $\bullet\text{OH}$ attacked both side chains to generate a radical, which was then subjected to alkyl oxidation to form TP3 [51,52]. Next, TP3 was transformed into TP1 through an amide hydrolysis reaction, and then formed TP2 via a dechlorination reaction. TP2 would be further decomposed by reactive oxygen species, and then possibly transformed into CO_2 and H_2O [53].

4. Conclusions

In summary, the composite $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ prepared by a one-step solvothermal method can serve as a recoverable catalyst to activate PMS, thereby efficiently degrading the coexisting atrazine, metalaxyl, and epoxiconazole within the system. In the presence of the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ catalyst and PMS, 30 mg/L of the target pesticides can be completely degraded within 15 min. After three consecutive cycles of degradation experiments, the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ catalyst still maintained good catalytic activity. Based on the results of the quenching experiments and EPR spectra, active species such as $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$, and the non-radical $^1\text{O}_2$ were all involved in the degradation of pesticides in the $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ degradation system. $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ were the main reactive radicals to decompose the target pesticides. Furthermore, XPS analysis further revealed the catalytic mechanism of PMS activation by $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$, which initially activated PMS to generate $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ through the redox coupling of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$. Subsequently, $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ attacked the easily broken chemical bonds of the target pesticides, leading to their oxidative degradation into intermediates, and even possibly complete oxidation to CO_2 and H_2O . Based on the intermediates detected by LC-MS, potential transformation pathways for target pesticides were proposed. This work will deepen the understanding of the activation mechanism of the magnetic catalyst PMS system and provide a feasible strategy for designing effective oxidation processes.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/separations13070193/s1>, Text S1: Materials, Text S2: Characterization, Text S3: Synthesis of Fe_3O_4 , Text S4: Synthesis of $\text{Co}_5\text{Al-LDH}$, Figure S1: The SEM images of Fe_3O_4 (a) and $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ (b), Figure S2: The elemental mapping for C, N, O, Fe, Co and Al of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$, Figure S3: The effect of co-existing inorganic ions species on the degradation performance of atrazine (a), metalaxyl (b), and epoxiconazole (c), Figure S4: The reusability of $\text{Fe}_3\text{O}_4@\text{Co}_5\text{Al-LDH}$ for atrazine (a), metalaxyl (b) and epoxiconazole (c) degradation.

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—review & editing, Q.T., E.-C.Z. and Z.-H.Y.; Supervision, C.-X.H., Q.T., J.L., B.-Y.D. and Z.-H.Y. All authors have read and agreed to the published version of the manuscript.

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