

Peroxymonosulfate Activation by CoFe₂O₄/MgAl-LDH Catalyst for the Boosted Degradation of Antibiotic

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Abstract: Owing to outstanding hydrophilicity and ionic interaction, layered double hydroxides (LDHs) have emerged as a promising carrier for high performance catalysts. However, the synthesis of new specialized catalytic LDHs for degradation of antibiotics still faces some challenges. In this study, a CoFe₂O₄/MgAl-LDH composite catalyst was synthesized using a hydrothermal coprecipitation method. Comprehensive characterization reveals that the surface of MgAl-LDH is covered with nanometer CoFe₂O₄ particles. The specific surface area of CoFe₂O₄/MgAl-LDH is 82.84 m²·g⁻¹, which is 2.34 times that of CoFe₂O₄. CoFe₂O₄/MgAl-LDH has a saturation magnetic strength of 22.24 A·m²·kg⁻¹ facilitating efficient solid-liquid separation. The composite catalyst was employed to activate peroxymonosulfate (PMS) for the efficient degradation of tetracycline hydrochloride (TCH). It is found that the catalytic performance of CoFe₂O₄/MgAl-LDH significantly exceeds that of CoFe₂O₄. The maximum TCH removal reaches 98.2% under the optimal conditions ([TCH] = 25 mg/L, [PMS] = 1.5 mmol/L, CoFe₂O₄/MgAl-LDH = 0.20 g/L, pH 7, and *T* = 25 °C). Coexisting ions in the solution, such as SO₄²⁻, Cl⁻, H₂PO₄⁻, and CO₃²⁻, have a negligible effect on catalytic performance. Cyclic tests demonstrate that the catalytic performance of CoFe₂O₄/MgAl-LDH remains 67.2% after five cycles. Mechanism investigations suggest that O₂^{·-} and ¹O₂ produced by CoFe₂O₄/MgAl-LDH play a critical role in the catalytic degradation.

Key words: magnetic composite catalyst; peroxymonosulfate; CoFe₂O₄/MgAl-LDH; advanced oxidation process; antibiotic

TCH is a broad-spectrum antibiotic widely used in medicine and animal husbandry. However, the increasing use of TCH poses a serious threat to the ecological environment^[1]. Significant amounts of TCH have been released into aquatic ecosystems, such as rivers and lakes, due to excessive or inappropriate use^[2]. TCH molecules in water seriously threatened the health of aquatic animals and aquatic plants, even human being^[3-5]. TCH is chemically stable and tends to accumulate in water^[6]. Therefore, it is hard to be eliminated by natural purification. It is an urgent task to find efficient ways to remove TCH from water. Significant works have been dedicated to this issue and developed various methods to

purify TCH from water, including biodegradation, adsorption, extraction, and ion exchange^[7]. However, most of the techniques can only transfer or partially degrade TCH molecules, leading to secondary pollution^[8-9].

Advanced oxidation processes (AOPs) based on sulfate radicals (SR-AOPs) are increasingly recognized as an effective method for the degradation of refractory organic contaminants featuring efficiency, convenience for storage, and mobility^[10-11]. Generally, SR-AOPs take PMS as an oxidant. PMS is activated by external energy sources, *e.g.*, ultraviolet illumination, thermal, electrochemical, ultrasonic and microwave, generating activated reactive oxygen species (ROS)^[12]. Depending on the catalysts and

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reaction conditions used, various ROS, including sulfate radicals (SO₄^{•−}), hydroxyl radicals (•OH), superoxide radicals (O₂^{•−}) and singlet oxygen (¹O₂), can be produced^[13–14]. These ROS possess strong oxidizing properties, making them capable of effectively degrading recalcitrant organic pollutants in a wide pH range of 2–8^[15]. They can mineralize organic pollutants into CO₂, H₂O, and inorganic salts through non-selective degradation pathways.

SR-AOPs can be classified into homogeneous and heterogeneous systems. Within homogeneous systems, metal ions have attracted much attention as promising activators due to their high availability and affordability^[16]. However, the generation of metal hydroxide sludge presents an obstacle to their further utilization due to the risk of secondary pollution. To address this issue, the metal ion-based heterogeneous catalysts have emerged as alternatives for activating PMS, benefiting from convenient operation, mild reaction conditions, high generation rates and ease of recycling^[17–19]. CoFe₂O₄ has been recognized as an efficient heterogeneous metal ion-based catalyst, due to its excellent magnetic properties, high specific surface area, insolubility and cost-effectiveness^[20]. Due to the presence of variable valence states (Co³⁺/Co²⁺ and Fe³⁺/Fe²⁺ pairs) on the surface of CoFe₂O₄, electrons can be provided to spontaneously activate the PMS without external energy, endowing CoFe₂O₄ with high catalytic activity^[21].

However, nano-sized CoFe₂O₄ particles are prone to agglomerate during the degradation of target pollutants due to their high surface energy, which reduces the available reaction sites^[22]. Additionally, the adsorption of organic molecules by CoFe₂O₄ is limited, hindering the degradation process. To mitigate these problems, CoFe₂O₄ was loaded onto various materials with high specific surface area and superior dispersibility to improve its catalytic activity and stability^[23–24]. The properties of the selected carrier have a significant influence on the catalytic effect^[25–26]. LDHs are inorganic non-metallic minerals with a large specific surface area and strong anion exchange capacity, along with excellent thermal stability, dispersion, structural stability and resistance to strong acid and alkali corrosion, making them ideal carrier materials^[27].

In this study, a magnetic CoFe₂O₄/MgAl-LDH composite catalyst was designed and synthesized by the one-pot co-precipitation hydrothermal method. The magnetic properties, chemical composition, surface morphology and structure were characterized. The catalytic degradation performance of CoFe₂O₄/MgAl-LDH/PMS system for TCH was carefully studied, and the catalytic mechanism was discussed. This work expands the application

potential of spinel ferrites and LDHs for the treatment of organic pollutants in aquatic environments.

1 Experimental

1.1 Preparation of MgAl-LDH

MgAl-LDH was prepared by the hydrothermal co-precipitation method. Typically, 30 mmol Mg(NO₃)₂·6H₂O and 10 mmol Al(NO₃)₃·9H₂O were dissolved in 50 mL deionized water to obtain solution A. Then, 10 mmol NaOH and 5 mmol Na₂CO₃ were dissolved in 30 mL deionized water to obtain solution B. Solution B was added into solution A drop by drop and stirred simultaneously. The solution pH was adjusted to 10 and stirred at room temperature for 3 h. Then the mixture was put into a hydrothermal reaction kettle and placed at 105 °C for 18 h. After the reaction, it was filtered, and the precipitate was washed to be neutral. Then the precipitate was dried in an oven to obtain MgAl-LDH.

1.2 Preparation of CoFe₂O₄/MgAl-LDH

8 mmol Co(NO₃)₂·6H₂O and 4 mmol Fe(NO₃)₃·9H₂O were put into a 50 mL deionized water beaker, and it was agitated for 10 min. 1 g MgAl-LDH was added into the solution and mixed. Then, 25 mL NaOH solution (2 mol/L) was added into the mixture drop by drop. The combined solution was transferred into a hydrothermal reactor and kept at 180 °C for 12 h. After the reaction, the solution was filtered, and the precipitate was rinsed to neutral. The precipitate was then dried in an oven to yield CoFe₂O₄/MgAl-LDH. Information about the chemicals, equipment, and characterization techniques used in this study is available in supporting materials.

1.3 Determination of the catalytic performance

To evaluate the catalytic performance of CoFe₂O₄/MgAl-LDH, TCH was used as the degradation target. In order to determine the concentration of TCH, the functional relationship between its absorbance and concentration was investigated. The concentration of TCH was calculated by measuring the absorbance of the solution. Details are available in the supporting materials. Degradation experiments were conducted as follows. Certain catalysts and PMS were poured into 200 mL TCH solution (25 mg/L) simultaneously under continuous stirring. At regular intervals, 4 mL of the solution was removed and filtered through a 0.22 μm membrane, and its absorbance was immediately measured by an ultraviolet visible spectrophotometer at 357 nm. To study the effect of pH on the catalytic performance, pH of the TCH solution was regulated using 2 mol/L NaOH solution and 2 mol/L HCl solution.

On the basis of optimization of experimental parameters, the catalytic performance and TCH degradation were investigated by placing 0.04 g $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$, 0.2 mmol PMS, and 0.04 g $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}/0.2$ mmol PMS into 200 mL TCH solution (25 mg/L), respectively, and the absorbance was determined after 45 min. A magnet was used to recover the used catalyst from the TCH solution. The effects of solution pH, catalyst dosage, oxidant concentration, and numerous typical anions on the TCH removal were also comprehensively examined. The recyclability of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ and the main ROS produced in $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}/\text{PMS}$ oxidation system were studied *via* five groups of cyclic experiments. To quickly quench $^1\text{O}_2$, $\text{O}_2^{\cdot-}$, $\text{SO}_4^{\cdot-}$, and $\cdot\text{OH}$ independently, furfuryl alcohol (FFA), p-benzoquinone (p-BQ), methyl alcohol (MeOH), and tert-butanol (TBA) were chosen as their quenchers.

2 Results and discussion

2.1 Characterization of the catalysts

X-ray diffraction (XRD) analysis was performed to investigate the crystal structure of the catalysts. As shown in Fig. 1(a), the diffraction peaks at $2\theta=11.49^\circ$, 22.90° , 34.74° , 46.28° , and 60.46° correspond to the (003), (006), (009), (018), and (110) planes of MgAl-LDH (JCPDS# 14-0109), respectively. The dominant peaks at $2\theta=30.08^\circ$, 35.43° , 43.06° , 56.94° , and 62.53° correspond to the (104), (113), (024), (125), and (208) planes of CoFe_2O_4 (JCPDS#79-1744), respectively. This indicates that the obtained sample is composed of CoFe_2O_4 and MgAl-LDH . $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ possesses magnetic properties resulting from the strong ferromagnetism of CoFe_2O_4 . As shown in Fig. 1(b), the magnetism is $22.24 \text{ A}\cdot\text{m}^2\cdot\text{kg}^{-1}$, facilitating efficient magnetic separation. 99% (mass fraction) of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ could be gathered using a hand magnet, as depicted in the inset of Fig. 1(b).

Scanning electron microscopy (SEM) images of

MgAl-LDH and $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ are shown in Fig. 2. The surface of MgAl-LDH is relatively smooth with a typical layered structure, which is advantageous for adsorption, as shown in Fig. 2(a, b). After composition with CoFe_2O_4 , numerous nanoparticles were observed covering the surface of MgAl-LDH (Fig. 2(c, d)), thereby forming a porous structure layer. The energy dispersive spectroscopy (EDS) mappings (Fig. 2(e-j)) reveal that the sample primarily consists of five elements: O, Mg, Al, Fe, and Co. The Mg and Al elements are associated with MgAl-LDH , while Co and Fe are associated with CoFe_2O_4 . The distribution of Co and Fe indicates that CoFe_2O_4 is uniformly coated on the surface.

To further elucidate the structure and morphology of the composite catalyst, transmission electron microscope (TEM) and high resolution TEM (HRTEM) imaging were conducted on $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$. As shown in Fig. 3(a), CoFe_2O_4 nanoparticles with a diameter of 5–20 nm are uniformly dispersed on the surface of MgAl-LDH . Fig. 3(b) displays the neatly arranged lattice stripes without structural defects, indicating good crystallinity of the nanoparticles. The measured stripe spacing is 0.2099 nm, corresponding to the (024) crystal plane of CoFe_2O_4 , further confirming the formation of CoFe_2O_4 on the surface of MgAl-LDH .

The surface chemical component and state of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ were examined by an X-ray photoelectron spectroscope (XPS). The survey spectrum demonstrates that $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ contains O, Mg, Al, Fe, and Co elements (Fig. 4(a)). The peaks at 724.5 and 710.8 eV in the $\text{Fe}2\text{p}$ spectrum correspond to $\text{Fe}2\text{p}_{1/2}$ and $\text{Fe}2\text{p}_{3/2}$, respectively (Fig. 4(b)), indicating the presence of Fe^{3+} and the absence of Fe^{2+} on the surface. The $\text{Co}2\text{p}$ spectrum exhibits two primary peaks at approximately 780.4 and 796.4 eV, which correspond to $\text{Co}2\text{p}_{3/2}$ and $\text{Co}2\text{p}_{1/2}$, respectively, as shown in Fig. 4(c). Two satellite peaks were observed at 786.1 and 802.2 eV. It is strong evidence for the existence of Co^{2+} rather than Co^{3+} [28]. In

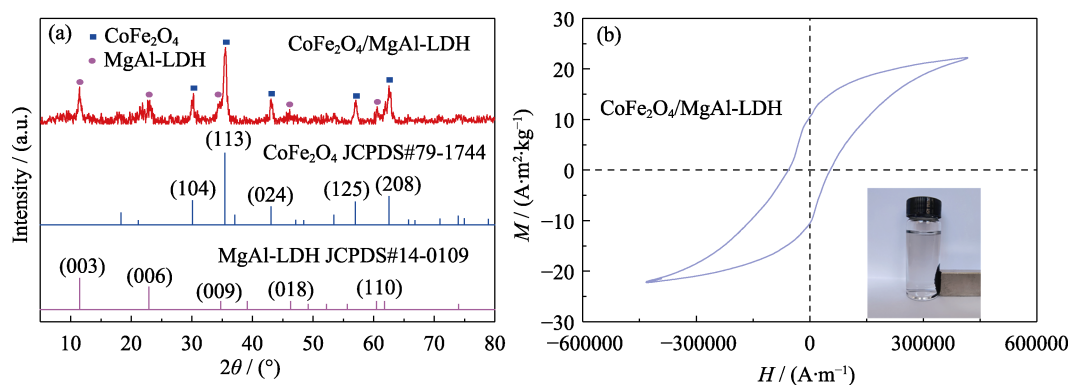


Fig. 1 XRD patterns (a) and hysteresis loop (b) of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$
Insert in (b) showing the magnetic recovery of the sample by a hand magnet

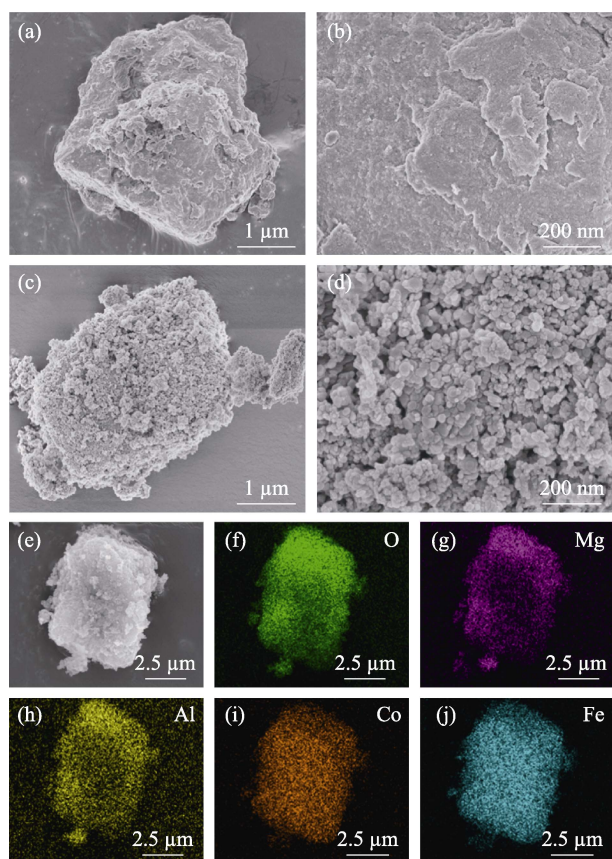


Fig. 2 SEM images of MgAl-LDH and $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$, and EDS mappings of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$
(a, b) SEM images of MgAl-LDH; (c, d) SEM images of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$; (e) EDS scanning area; (f-j) EDS mappings of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$

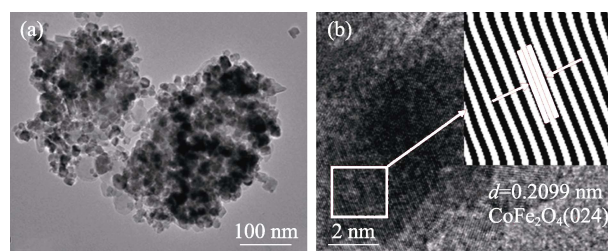


Fig. 3 TEM (a) and HRTEM (b) images of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$

the O1s spectrum (Fig. 4(d)), a prominent envelope peak can be deconvoluted to three peaks at 529.7, 530.9, and 532.2 eV. These peaks are attributed to lattice oxygen ($\text{O}_{\text{Latt.}}$), adsorbed oxygen ($\text{O}_{\text{Ads.}}$), and surface oxygen ($\text{O}_{\text{Surf.}}$)^[29]. This provides additional evidence for the formation of CoFe_2O_4 .

The N_2 adsorption-desorption isotherms and pore sizes of the composite catalysts were evaluated by N_2 adsorption-desorption measurements, as shown in Fig. 5. The specific surface areas of CoFe_2O_4 , MgAl-LDH, and $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ are 35.42, 138.78, and 82.84 $\text{m}^2\cdot\text{g}^{-1}$, respectively. The specific surface area of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ is 2.34 times that of CoFe_2O_4 . Fig. 5(a-c) shows that the shapes of the adsorption-desorption curves of three samples are similar, indicating a typical class IV isotherm. The adsorption and desorption branches do not overlap, which is attributed to the coalescence of capillaries, confirming that $\text{CoFe}_2\text{O}_4/$

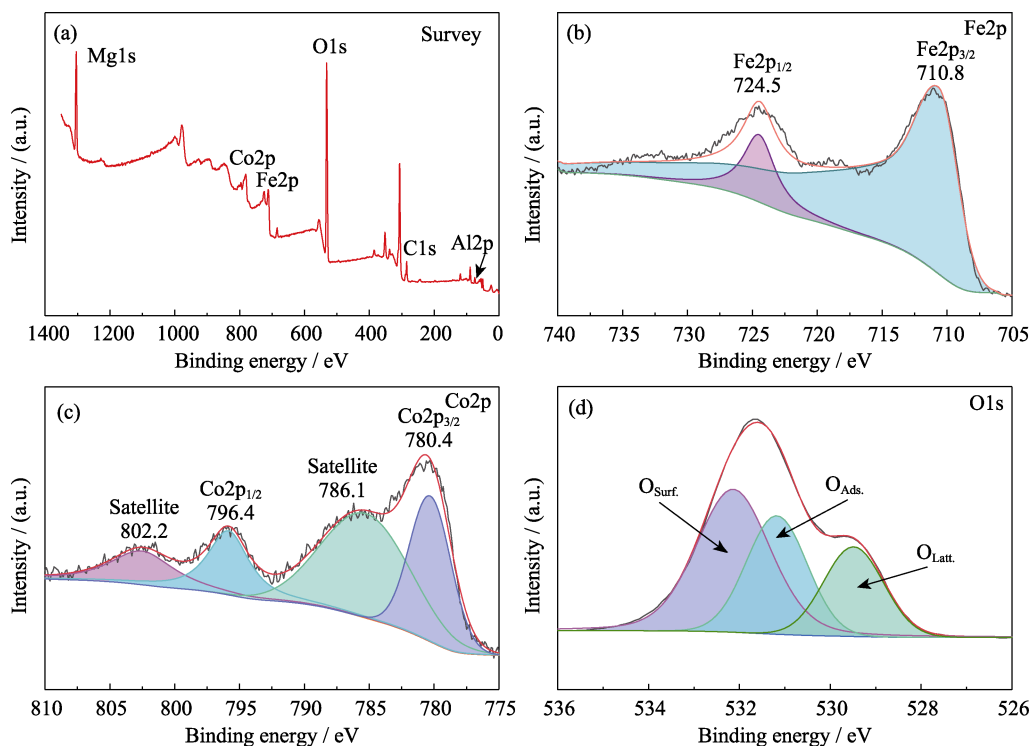


Fig. 4 XPS spectra of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$
(a) Survey spectrum; (b-d) Spectra of (b) Fe2p, (c) Co2p, and (d) O1s

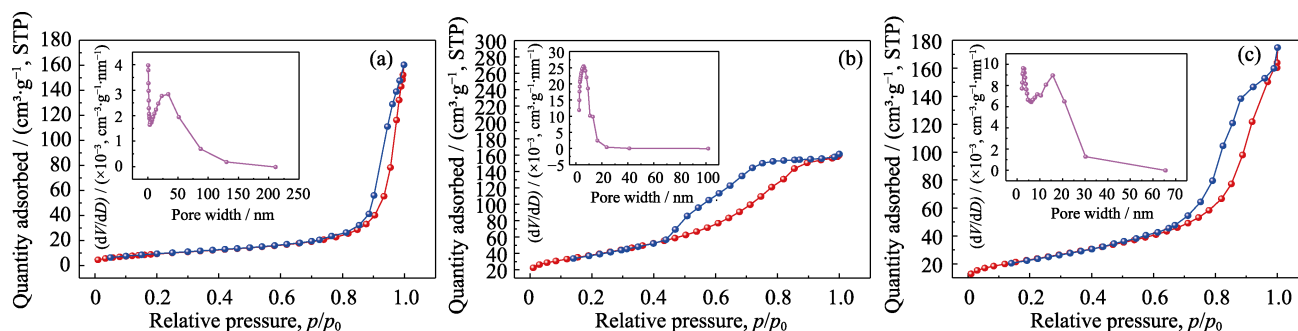


Fig. 5 N_2 adsorption-desorption isotherms of $CoFe_2O_4$ (a), $MgAl-LDH$ (b) and $CoFe_2O_4/MgAl-LDH$ (c)

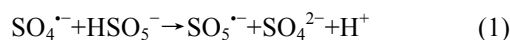
$MgAl-LDH$ exhibits a mesoporous structure. The hysteresis loop is classified as type H3 according to the International Union of Pure and Applied Chemistry (IUPAC) classification, indicating that narrow fracture pores distribute in the samples. Corresponding pore size distribution curves reveal that pore size distribution is narrow and primarily concentrated within the mesopore region^[30-31]. The specific surface area and pore structure parameters of the samples, determined using Brunauer-Emmett-Teller (BET) formula and Barret-Joyner-Halenda (BJH) algorithm, are listed in Table S1. Compared with $CoFe_2O_4$, $CoFe_2O_4/MgAl-LDH$ has a significantly higher specific surface area, indicating more active sites in $CoFe_2O_4/MgAl-LDH$ composite catalyst.

2.2 Evaluation of catalytic activity of $CoFe_2O_4/MgAl-LDH$

Catalysts with different mass ratios of $CoFe_2O_4$ to $MgAl-LDH$ were prepared, and their capacities to activate PMS were explored. Results presented in Fig. 6(a) showed that all of them catalyzed more effectively than pure $CoFe_2O_4$ (68.7%). The best TCH removal rate of 98.2% was obtained at the mass ratio of $CoFe_2O_4$ to $MgAl-LDH$ of 1 : 1. At the mass ratios of $CoFe_2O_4$ to $MgAl-LDH$ of 2 : 1 and 1 : 2, the degradation rates of TCH were 83.4% and 95.2%, respectively. This indicates that the proportion of $CoFe_2O_4$ to $MgAl-LDH$ affects the composite structure and the synergy of two parts, significantly affecting TCH degradation. For the convenience of systematic study, samples with a mass ratio of 1 : 1 are selected in subsequent studies. The effect of catalyst doses ranging from 0.05 to 0.25 g/L on TCH degradation was investigated. As shown in Fig. 6(b), a TCH degradation rate of 83.7% was obtained with minimal addition of 0.05 g/L of $CoFe_2O_4/MgAl-LDH$. This finding indicates that $CoFe_2O_4/MgAl-LDH$ has a strong catalytic effect on PMS. The notable adsorption properties of $MgAl-LDH$ facilitated the accumulation of PMS and TCH molecules at the solid-liquid interface, and the variable-valence reaction of Co and Fe ions enhanced the generation of ROS from PMS^[32]. The TCH removal rates increased

from 83.7% to 98.2% when the $CoFe_2O_4/MgAl-LDH$ doses increased from 0.05 to 0.20 g/L. $CoFe_2O_4/MgAl-LDH$ offered more active sites for catalytic reaction, thereby improving the generation of ROS and promoting TCH degradation. Nevertheless, further addition of catalyst did not yield a substantial increase in TCH degradation. As shown in Fig. 6(b), the TCH degradation rate remained at 98.2% with a catalyst dosage of 0.25 g/L. Considering the economic cost and practical application, 0.20 g/L of catalyst dose was chosen for the following studies.

Moreover, the dosage of PMS has an effect on TCH degradation. As shown in Fig. 6(c), when the PMS concentration increased from 0.5 to 2.5 mmol/L, TCH degradation rate increased from 87.9% to 98.7%. The TCH degradation rate rose slightly from 98.2% to 98.7% when the PMS content increased from 1.5 to 2.5 mmol/L. This indicates that an optimal concentration of PMS is necessary for PMS based AOPs. The more PMS added, the more TCH degraded, owing to the generation of more active species to attack TCH molecules. However, excess PMS did not further promote the degradation, presumably because the excess PMS served as SO_4^{2-} scavengers, resulting in the reduction of oxidative $SO_4^{\cdot-}$ (Eq. (1)). In the following, 1.5 mmol/L PMS addition was determined as the best PMS dose.



The influence of pH on TCH degradation was shown in Fig. 6(d). High TCH degradation rate was obtained across a broad pH range (pH 3–11) in $CoFe_2O_4/MgAl-LDH/PMS$ system. The degradation was more than 80% at all pH levels, except pH 3. At pH 3, the degradation decreased to 67.8%, mainly due to two factors. First, the molecular stability of PMS is enhanced in acidic environments, hindering the conversion of PMS to ROS group, thereby reducing catalytic activity. Second, electrostatic repulsion between the catalyst and TCH reduces the adsorption, consequently lowering the degradation^[33-35]. The maximum degradation rate of TCH reached 98.2% at pH 7. The wide pH range of $CoFe_2O_4/MgAl-LDH/PMS$ system is expected to expand its application field.

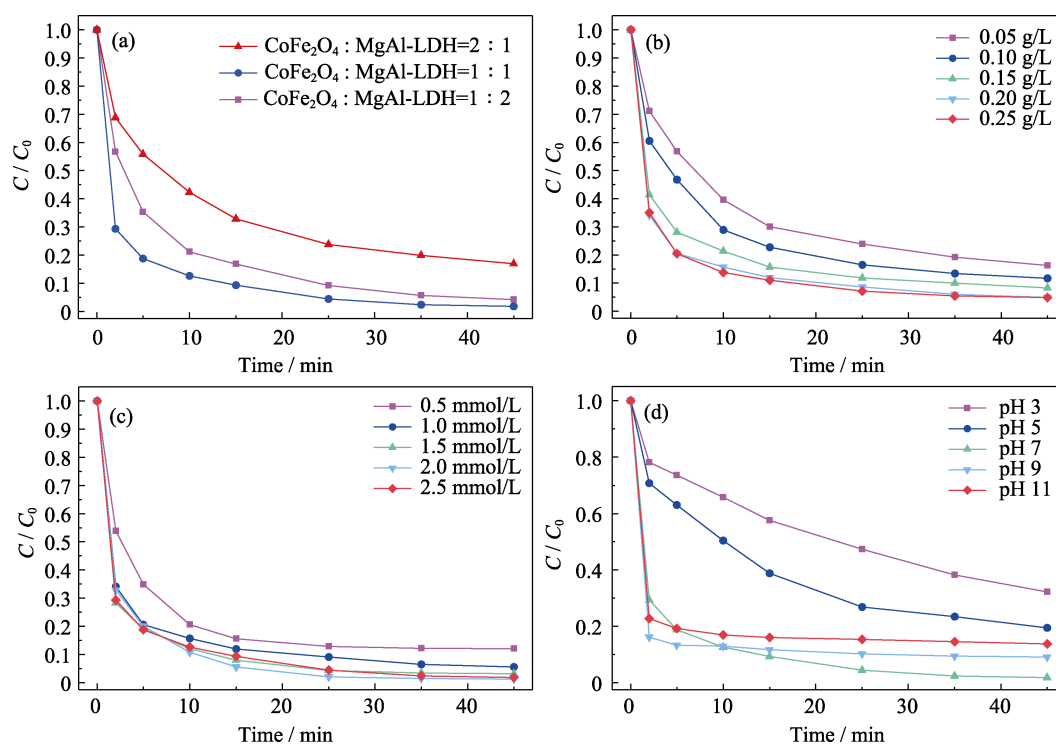


Fig. 6 Effects of different factors on TCH removal
(a) Mass ratio of CoFe₂O₄ to MgAl-LDH; (b) Catalyst dosage; (c) PMS concentration; (d) pH
([TCH]=25 mg/L, [PMS]=1.5 mmol/L, CoFe₂O₄/MgAl-LDH=0.20 g/L, pH 7 and $T=25\text{ }^{\circ}\text{C}$)

2.3 Effect of coexisting anions on CoFe₂O₄/MgAl-LDH

Given the natural water bodies often contain various anions that may affect the degradation process of AOP, experiments assessing the effects of coexisting ions are necessary. In this study, 50 mg/L concentrations of SO_4^{2-} , Cl^- , H_2PO_4^- , and CO_3^{2-} were employed to investigate the effects on the catalytic activity of CoFe₂O₄/MgAl-LDH. The maximum removal rate of TCH under optimal conditions was set as 98.2% in the control group. As shown in Fig. 7(a), the presence of SO_4^{2-} , Cl^- , H_2PO_4^- , and CO_3^{2-} reduced the TCH removal rate to 96.5%, 95.2%, 94.3%, and 87.9%, respectively. These results suggest that SO_4^{2-} , Cl^- , and H_2PO_4^- have little effect on the degradation, whereas CO_3^{2-} has a comparatively

larger impact. It could be due to an increase in pH caused by the addition of carbonates. This effect can be consistent with the results shown in Fig. 6(d).

2.4 Reusability and stability evaluation of CoFe₂O₄/MgAl-LDH

Recycling experiments were conducted to investigate the reusability and stability of CoFe₂O₄/MgAl-LDH. Owing to its magnetic properties, CoFe₂O₄/MgAl-LDH could be efficiently separated using magnetic separation techniques. Following appropriate treatment, the catalyst was reused many times. As shown in Fig. 7(b), the removal rate of TCH decreased to 86.7%, 73.9%, 67.6%, and 67.2% during 2nd to 5th cycles, respectively. The degradation rate of TCH gradually decreased as the number of cycles increased. After four cycles, the degradation

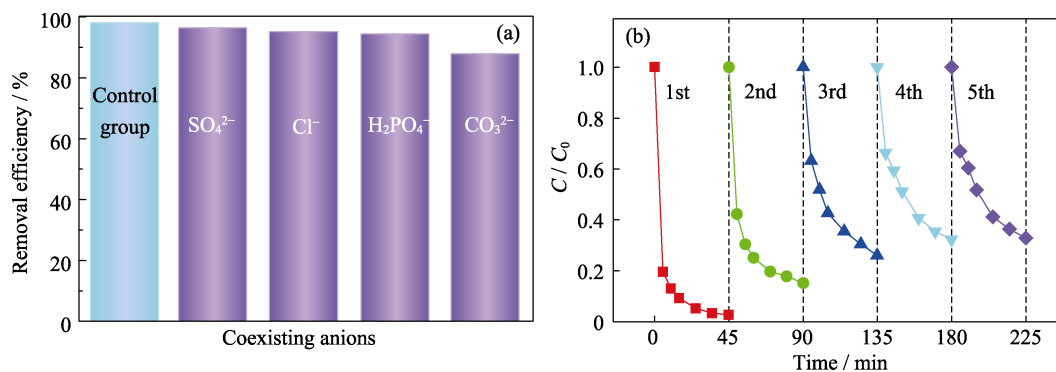


Fig. 7 Effects of coexisting anions on TCH removal (a) and cyclic experiments (b)
([TCH]=25 mg/L, [PMS]=1.5 mmol/L, CoFe₂O₄/MgAl-LDH=0.20 g/L, pH 7 and $T=25\text{ }^{\circ}\text{C}$)

rate stabilized at approximately 67%. This phenomenon may be attributed to the weakened adsorption capacity of the catalyst, and the results of the cyclic adsorption experiments of the catalyst are shown in Fig. S4.

2.5 Catalytic mechanism of CoFe₂O₄/MgAl-LDH

2.5.1 Determination of ROS

As broadly studied before, the PMS based AOPs are owing to the various ROS, including those from the radical route and non-radical pathway. Reactive species were quenched with four different scavengers to examine the critical ROS present in the CoFe₂O₄/MgAl-LDH/PMS system. MeOH, TBA, p-BQ, and FFA were employed to rapidly quench SO₄^{•−}, •OH, O₂^{•−}, and ¹O₂, respectively. As shown in Fig. 8(a), the scavengers p-BQ and FFA greatly reduced the rate of TCH degradation to 70.85% and 70.75%, respectively. According to these results, O₂^{•−} and ¹O₂ could be crucial in the degradation of TCH. Electron paramagnetic resonance (EPR) experiments with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMP) as spin-trapping agents were conducted to characterize the ROS generated in the CoFe₂O₄/MgAl-LDH/PMS system. In Fig. 8(b), the EPR signals corresponding to DMPO-•OH

and DMPO-SO₄^{•−} confirm the generation of •OH and SO₄^{•−} during PMS activation by CoFe₂O₄/MgAl-LDH. Similarly, typical signals of DMPO-O₂^{•−} and TEMP-¹O₂ appear in Fig. 8(c, d), respectively. The results align with the quenching experimental results, further confirming the existence of ROS (•OH, SO₄^{•−}, O₂^{•−}, and ¹O₂), which play a crucial role in the degradation of PMS in the CoFe₂O₄/MgAl-LDH/PMS system.

2.5.2 Mechanism of catalytic oxidation determination of ROS

The degradation of TCH in the CoFe₂O₄/MgAl-LDH/PMS system involves both the non-radical pathway and radical pathway, as illustrated above (Fig. 9). For the non-radical pathway, several routes, as outlined in Eqs. (2-13), might yield ¹O₂. For the radical pathway, O₂^{•−} might be produced by the hydrolysis of PMS (Eq. (9)), and there is no extra side reaction. In summary, TCH can be degraded by O₂^{•−} and ¹O₂ into CO₂ and H₂O (Eq. (14)). Part of these processes were catalyzed and accelerated in the CoFe₂O₄/MgAl-LDH/PMS system by the synergistic interaction between Fe³⁺/Fe²⁺, Co²⁺/Co³⁺, and PMS^[36].

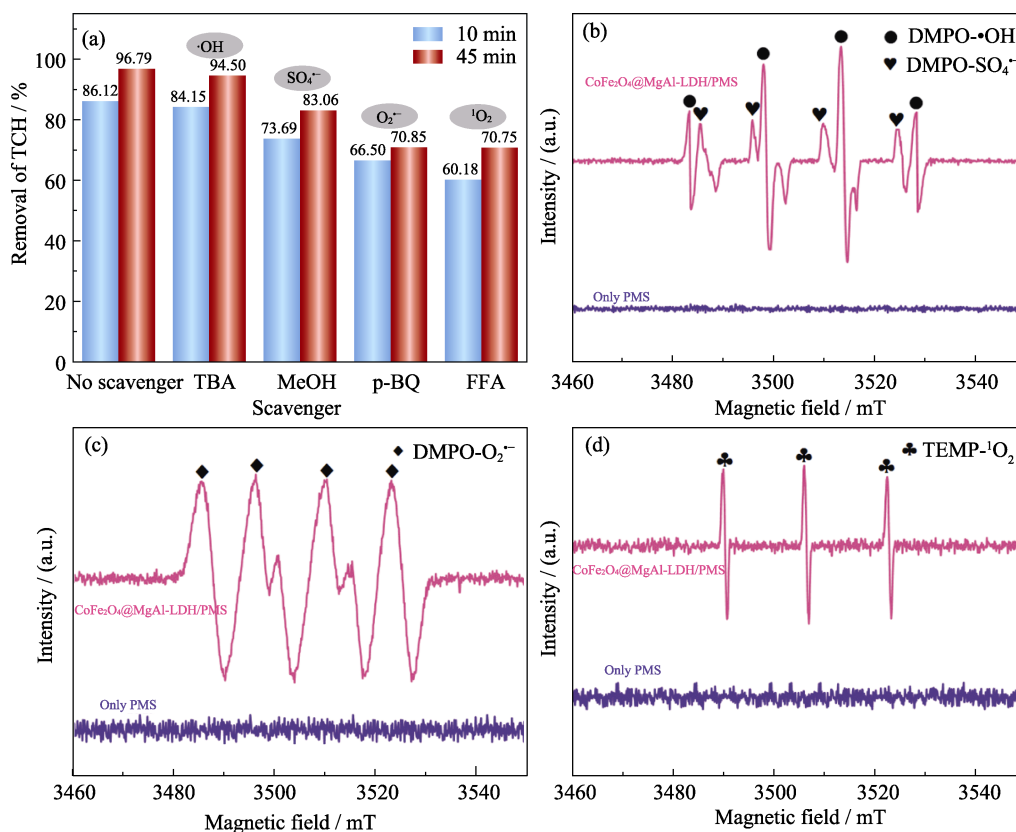


Fig. 8 Effects of ROS quenching tests on TCH removal (a) and EPR spectra of (b) DMPO-•OH and DMPO-SO₄^{•−}, (c) DMPO-O₂^{•−}, and (d) TEMP-¹O₂ ([TCH]=25 mg/L, [PMS]=1.5 mmol/L, CoFe₂O₄/MgAl-LDH=0.20 g/L, pH 7, T=25 °C and [Scavenger]=100 mmol/L)

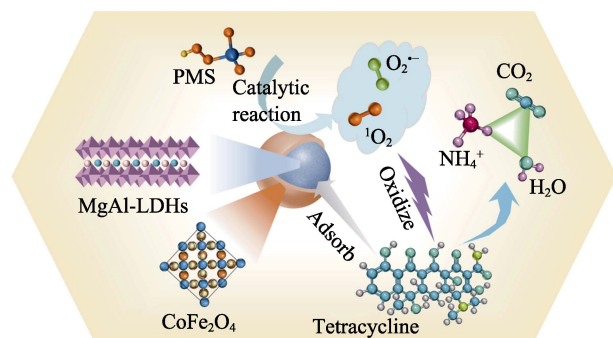
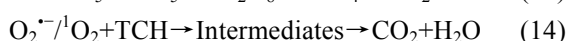
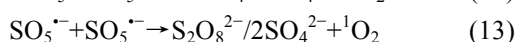
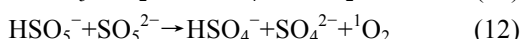
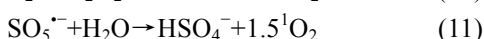
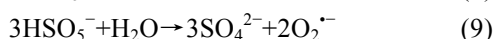
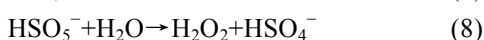
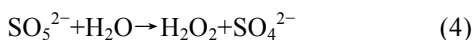


Fig. 9 Schematic illustration of catalytic oxidation process to remove pollutants



3 Conclusions

A magnetic CoFe₂O₄/MgAl-LDH catalyst with high pollutant removal rate was synthesized *via* co-precipitation hydrothermal technique and employed as a PMS activator to degrade TCH. The composite catalyst, CoFe₂O₄/MgAl-LDH, possesses an abundant porous structure due to the intrinsic porous structure of MgAl-LDH substrate and the excellent dispersion of CoFe₂O₄ on the MgAl-LDH. These porous structures enhance catalyst's adsorption on TCH, thereby improving its catalytic performance. The CoFe₂O₄/MgAl-LDH/PMS system can spontaneously catalyze the degradation of TCH, achieving an optimal TCH degradation rate of up to 98.2%. Furthermore, the coexisting ions, SO₄²⁻, Cl⁻, H₂PO₄⁻, and CO₃²⁻, present in wastewater exert negligible effects on the catalytic performance of CoFe₂O₄/MgAl-LDH. The catalyst exhibits relatively stable catalytic activity, remaining a catalytic efficiency of 67.2% after five cycles. The primary reactive oxygen species in the catalytic degradation process are O₂^{•-} and ¹O₂. This work offers novel insights into LDH-based catalysts for the degradation of organic contaminants through SR-AOPs.

Supporting Materials

Supporting materials related to this article can be

found at <https://doi.org/10.15541/jim20240222>.

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CoFe₂O₄/MgAl-LDH 催化剂活化 过氧一硫酸盐促进抗生素降解

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摘要: 层状双氢氧化物(LDH)具有优异的亲水性和离子相互作用, 是一种很有前途的高性能催化剂载体。本研究采用简单的共沉淀水热法制备了 $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ 复合催化剂。结果表明, 纳米级 CoFe_2O_4 颗粒覆盖在 MgAl-LDH 表面; $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ 的比表面积为 $82.84 \text{ m}^2 \cdot \text{g}^{-1}$, 是 CoFe_2O_4 的 2.34 倍; $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ 的饱和磁化强度为 $22.24 \text{ A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$, 可实现高效的固液分离。将催化剂用于活化过氧一硫酸盐(PMS)高效降解盐酸四环素(TCH), 发现 $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ 的催化性能明显优于 CoFe_2O_4 。在最佳条件下($[\text{TCH}] = 25 \text{ mg/L}$, $[\text{PMS}] = 1.5 \text{ mmol/L}$, $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH} = 0.20 \text{ g/L}$, $\text{pH } 7$, $T = 25^\circ \text{C}$), TCH 去除率最高可达 98.2%; 溶液中共存离子 SO_4^{2-} 、 Cl^- 、 H_2PO_4^- 和 CO_3^{2-} 对催化性能影响不大; 而且经过 5 次循环后 $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ 的催化性能仍保持在 67.2%。机理研究发现, O_2^- 和 $^1\text{O}_2$ 在催化降解过程中起主导作用。

关键词: 磁性复合催化剂; 过氧一硫酸盐; CoFe_2O_4 /水滑石; 高级氧化技术; 抗生素

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Supporting Materials

Peroxymonosulfate Activation by CoFe₂O₄/MgAl-LDH Catalyst for the Boosted Degradation of Antibiotic

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Reagents: Tetracycline hydrochloride (TCH), Mg(NO₃)₂ • 6H₂O, Al(NO₃)₃ • 9H₂O, Co(NO₃)₂ • 6H₂O and Fe(NO₃)₃ • 9H₂O were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). KHSO₅ • 0.5 KHSO₄ • 0.5K₂SO₄ (PMS), NaOH, diluted hydrochloric acid (HCl), Na₂CO₃, Na₂SO₄, NaCl, KH₂PO₄, methyl alcohol (MeOH), tert-butyl alcohol (TBA), p-benzoquinone (p-BQ) and furfuryl alcohol (FFA) were purchased from National Medicines Co., Ltd. (Shanghai, China). All the reagents above are analytical grade, and deionized water was used throughout all experiments.

Equipment or characterization methods used in this work: Vacuum drying oven (DZF-6050, China) was used to provide reaction temperature in the hydrothermal process and to dry samples. The absorbance of TCH solution was measured *via* UV-visible spectrophotometer (UV-5100, China). The crystal phase, magnetism and surface morphology of CoFe₂O₄/MgAl-LDH were characterized by X-ray diffractometer (XRD, Smartlab SE, Japan), vibrating sample magnetometer (VSM, HH-20, China) and scanning electron microscopy (SEM, ZEISS-G500, Germany), respectively. Transmission electron microscope (TEM, Tecnai G2 F20, Netherlands) was employed to further characterize the morphology and overall structure of CoFe₂O₄/MgAl-LDH. The surface composition and chemical state of CoFe₂O₄/MgAl-LDH were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, USA) and energy dispersive spectrometer (EDS). Brunauer-Emmett-Teller (BET, V-sorb2800p, China) was used to measure the N₂ adsorption-desorption isotherms, and the specific surface area was calculated based on the BET model.

Method for measuring the concentration of TCH: Before the degradation experiment, TCH solutions

with concentrations of 0, 2, 4, 6, 8 and 10 mg/L were prepared. The absorbance was measured by ultraviolet-visible spectrophotometer (UV-5100, China) at 357 nm. After linear fitting of the TCH concentration and corresponding absorbance (Fig. S1), a functional relationship can be obtained:

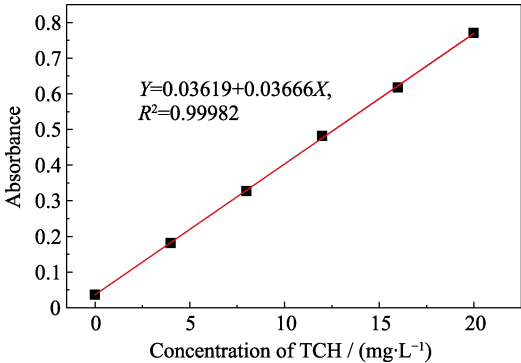


Fig. S1 Functional relationship of TCH concentration and its absorbancy

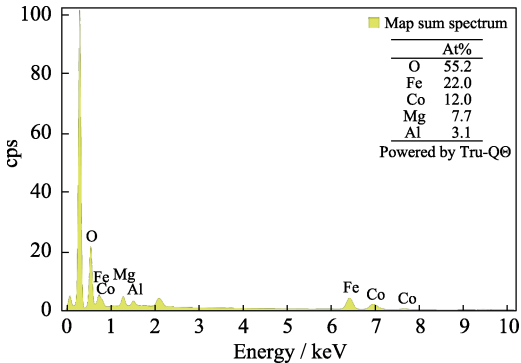


Fig. S2 EDS-mapping result of CoFe₂O₄/MgAl-LDH

Table S1 *S*_{BET} and pore size analysis data of the prepared CoFe₂O₄, MgAl-LDH and CoFe₂O₄/MgAl-LDH

Sample	<i>S</i> _{BET} /(m ² ·g ⁻¹)	Pore volume/(cm ³ ·g ⁻¹)	Pore size/nm
CoFe ₂ O ₄	35.42	0.15	10.76
MgAl-LDH	138.78	0.16	5.76
CoFe ₂ O ₄ /MgAl-LDH	82.84	0.25	23.26

$$Y=0.03619+0.03666X \quad (S1)$$

Where, Y and X are the concentration and absorbance of TCH, respectively. It can be seen from the value of R^2 that there is a good linear relationship between the concentration and absorbance of TCH.

Removal of TCH in different systems: The catalytic activity of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ was evaluated by comparing the TCH removal rates in various systems. As shown in Fig. S3(a), after 45 min of reaction, the removal rates of TCH in the $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ system and the PMS system were 34.6% and 56.8%, respectively. The removal of TCH from $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ with no oxidant mainly arises from the surface adsorption, due to the relatively high specific surface area of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$. With the absence of catalyst, the oxidation of PMS is relatively low. In the reaction system with the presence of both CoFe_2O_4 and PMS, 68.7% of TCH was degraded. This suggests that CoFe_2O_4 can activate PMS, but the catalysis capacity is limited. Furthermore, in the $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}/\text{PMS}$ system, the TCH degradation reached 90.0% within 10 min, and the final TCH removal achieved 98.2% at 45 min.

As illustrated in Fig. S3(b), the reaction rate constants of the four systems increased from 0.0061, 0.0172, and 0.0242 to 0.0771 min^{-1} . It clearly indicates that the $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}/\text{PMS}$ system had the strongest catalytic degradation ability and the highest degradation rate for TCH. As shown in Fig. S3(a), the majority of the TCH could be eliminated in the $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}/\text{PMS}$ system, whereas the TCH removal was very limited in the other systems. CoFe_2O_4 had catalytic activation with PMS because it can react with PMS to produce various ROS. After CoFe_2O_4 loading on the surface of LDH, the catalytic activity was greatly increased, which should be related to the reduction of the agglomeration of nanoparticles. The significant increase in TCH removal is owing to the synergistic effect of CoFe_2O_4 and MgAl-LDH , which increased the production of ROS.

We compared the degradation rate of TCH with different catalysts reported earlier, and the results are shown in Table S2. Compared with other catalysts, $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$ achieved higher TCH removal rate with fewer catalysts and PMS, which has good reference value for TCH degradation in wastewater.

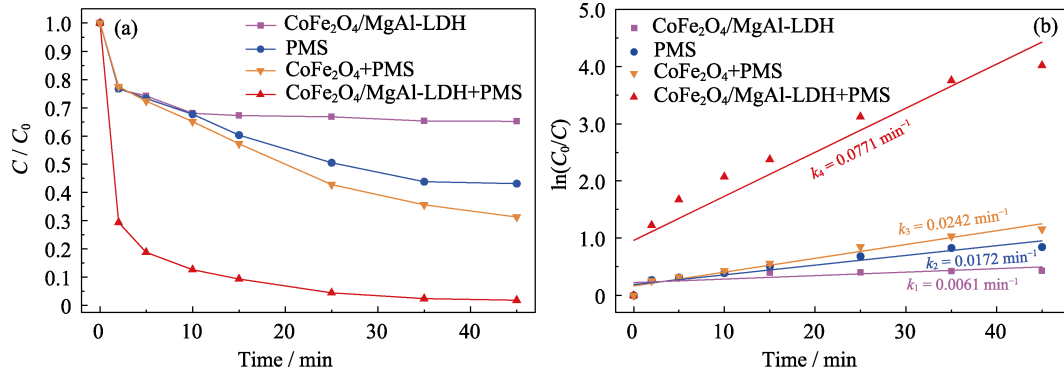
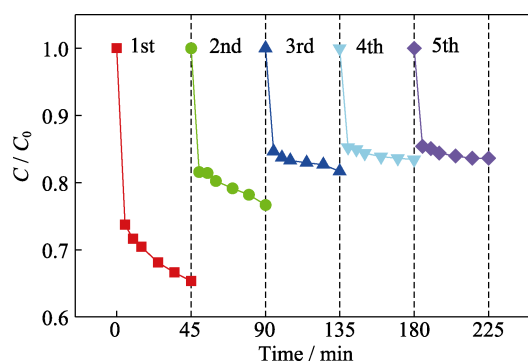


Fig. S3 Comparison of different systems
(a) TCH removal; (b) Corresponding reaction rate constant

Table S2 Comparison of the effects of different catalysts on degrading TCH

Catalyst	Tetracycline concentration/($\text{mg} \cdot \text{L}^{-1}$)	Reactant conditions/($\text{g} \cdot \text{L}^{-1}$)	Time/min	Degradation efficiency/%	Ref.
MIL-53(Fe)@AC	20	[catalyst]=0.20 [PMS]=2.00	120	92.4	[S1]
Fe-N/BC	30	[catalyst]=0.05 [PMS]=0.50	60	89.9	[S2]
Mn-MoS ₂ @AABs	20	[catalyst]=0.40 [PMS]=2.50	90	82.4	[S3]
Co@N-MC	25	[catalyst]=0.04 [PMS]=0.20	30	91.2	[S4]
ZCO-CN	20	[catalyst]=0.13 [PMS]=0.10	30	91.0	[S5]
MIL-88A/CoFe ₂ O ₄	10	[catalyst]=0.25 [PMS]=1.00	60	90.0	[S6]
CoFe ₂ O ₄ /MgAl-LDH	25	[catalyst]=0.20* [PMS]=0.23*	45	98.2	This work

*: For a more intuitive comparison, the concentration of PMS is converted here. ($1.5 \text{ mmol/L PMS} \approx 0.23 \text{ g/L PMS}$)

Fig. S4 Adsorption cyclic experiment of $\text{CoFe}_2\text{O}_4/\text{MgAl-LDH}$

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