Hydrothermal synthesis of magnetic nano-CoFe$_2$O$_4$ catalyst and its enhanced degradation of amoxicillin by activated permonosulfate

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ABSTRACT

Advanced oxidation process (AOP) has attracted widespread attention because it can effectively remove antibiotics in water, but its practical engineering application is limited by the problems of the low efficiency and difficult recovery of the catalyst. In the study, nano-spinel CoFe$_2$O$_4$ was prepared by hydrothermal method and served as the peroxymonosulfate (PMS) catalyst to degrade antibiotic amoxicillin (AMX). The reaction parameters such as CoFe$_2$O$_4$ dosage, AMX concentration, and initial pH value were also optimized. The reaction mechanism was proposed through free radical capture experiment and possible degradation pathway analysis. In addition, the magnetic recovery performance and stability of the catalyst were evaluated. Results showed that 85.5% of AMX could be removed within 90 min at optimal conditions. Sulfate radicals and hydroxyl radicals were the active species for AMX degradation. Moreover, the catalyst showed excellent magnetism and stability in the cycle experiment, which has great potential in the AOP treatment of antibiotic polluted wastewater.

Key words: amoxicillin, degradation, nano-CoFe$_2$O$_4$, peroxymonosulfate, sulfate radical

HIGHLIGHTS

- Magnetic nano-CoFe$_2$O$_4$ was fabricated by hydrothermal process.
- High activity of removing AMX in the CoFe$_2$O$_4$/PMS system.
- The recovery of nano-CoFe$_2$O$_4$ was convenient due to strong magnetics.
- The nano-CoFe$_2$O$_4$ exhibited good stability and reusability.

GRAPHICAL ABSTRACT
INTRODUCTION

Since their discovery in 1928, antibiotics have been widely used in humans and veterinary medicine to treat bacterial infections (Jung et al. 2012). Amoxicillin (AMX), a β-lactam antibiotic, has become one of the ten antibiotics with the largest consumption due to its wide range of uses, strong acid resistance and good medical effects (Marco et al. 2014; Xin et al. 2020). In fact, most antibiotics cannot be metabolized in humans and animals (Chen et al. 2021), about 80%-90% enter the environment through excretion (Bergamonti et al. 2019). Traditional sewage treatment was not effective in removing antibiotics (Manaia et al. 2018). In recent years, AMX has been frequently detected in surface water (Tlili et al. 2016), sewage plant effluent (Grzegorz et al. 2016) and even drinking water (Bergamonti et al. 2019). Although the concentration of AMX in the aquatic environment is low, at the μg/L level (Yilmaz et al. 2020), the presence of AMX is toxic to aquatic plants and leads to the emergence of drug-resistant bacteria and drug-resistant genes (Nuno et al. 2016; Vineet et al. 2018), posing a potential risk to the ecological environment and public health (Song et al. 2018; Minashree & Arun 2020). Therefore, a new technology is urgently needed to remove AMX efficiently.

A variety of techniques have been studied to remove AMX from water, such as adsorption (Kerkez-Kuyumcu et al. 2016), nanofiltration (Karimnezhad et al. 2020), photocatalytic degradation (Moreira et al. 2016) and advanced oxidation process (AOP) (Seyhani et al. 2018; Sun et al. 2021). In contrast, AOP based on sulfate radical (SO4·−) has attracted the most attention due to its high efficiency and wide range of applications (Matzek & Carter 2016). Compared with hydroxyl radical (·OH), SO4·− has stronger oxidation capacity (E0 = 2.5–3.1 V), wider range of pH values (pH = 2–9) and longer half-value period (Ghanbari & Moradi 2017). SO4·− could be generated by activating persulfate in a variety of ways, such as ultraviolet irradiation (Ghauch et al. 2017), heating (Sun et al. 2019), ultrasonic waves (Lie et al. 2019) and homogeneous (Huang et al. 2009) or heterogeneous catalysts (Xiao et al. 2018). Ultraviolet, heat or ultrasonic activation require additional external energy (Zhang et al. 2016), the difficulty of recovery of homogeneous catalyst could lead to secondary pollution and limit its application (Anapishtakis & Dionysiou 2005; Yin et al. 2016). Heterogeneous catalysis has become a research hotspot because of its stable performance, recyclability and price advantage (Oh et al. 2016; Rama et al. 2018; Zhou et al. 2020). Cobalt-based materials have exhibited excellent persulfate activation ability, but the inevitable leaching of potential carcinogen Co2+/Co3+ would cause health risks (Zhang et al. 2013). In addition, solid-liquid separation is also difficult to achieve, which might cause secondary pollution (Wan et al. 2011). Spinel cobalt ferrite (CoFe2O4) has the advantages of high catalytic activity, stable crystal structure and convenient magnetic separation (Shirsath et al. 2019). Moreover, CoFe2O4 has good Co leaching resistance due to the strong interaction between Co and Fe (Yang et al. 2009). Based on the above advantages, this study intended to use CoFe2O4 to activate PMS to degrade AMX, and currently few studies have been reported.

Herein, nano-CoFe2O4 was prepared by hydrothermal method and used to activate PMS to degrade the target pollutant AMX. The reaction parameters were optimized by investigating the main operating conditions in the CoFe2O4/PMS system, including CoFe2O4 dosage, PMS usage, AMX initial concentration, temperature, initial pH value, and coexisting ions (HCO3− and Cl−). The degradation mechanism was explored by radical quenching experiment and possible degradation pathway analysis of AMX. In addition, the reusability and stability of the samples were analyzed.

MATERIALS AND METHODS

Materials

The total chemicals used in this experiment were analytically pure, no further purification was required after purchase. Cobalt nitrate (Co(NO3)2·6H2O) and iron nitrate (Fe(NO3)3·4H2O) were bought from Shanghai zhongqin Chemical Reagent Co., Ltd (Shanghai, China). Anhydrous ethanol (CH3CH2OH), ethylene glycol (CH2OH)2, sulfuric acid (H2SO4), methanol (CH3OH) and tert-butanol (C4H10O) were supplied by Tianjin Damao Chemical Reagent Co., Ltd (Tianjin, China). Polyvinyl pyrrolidone (PVP,K30), Amoxicillin (C16H19N3O5S), Sodium Chloride (NaCl) and Sodium Bicarbonate (NaHCO3) were provided by Sinopharm Chemical Reagent Co., Ltd (Tianjin, China). Peroxymonosulfate (KHSO5·0.5KHSO4·0.5 K2SO4, PMS) were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Besides, deionized (DI) water (from Milli-Q IQ7000) was used throughout all experiments.

Fabrication of CoFe2O4 nanoparticles

The CoFe2O4 nanoparticles were prepared by hydrothermal process. Typically, 17.2 g Co(NO3)2·6H2O and 6.2 g Fe(NO3)3·9H2O were dissolved in 250 mL DI water to ensure that the molar ratio of cobalt and iron ions in the mixture was 1:2. After 15 h of
stirring, the pH was adjusted to 10 by adding 18 mol·L⁻¹ NaOH dropwise. Then 0.02 g PVP was added and the stirring was continued for 1 h. Subsequently, the mixture was divided into 3 parts and shifted to a 100 mL high pressure reactor with a lining of Teflon, then heated at 180 °C for 12 h. The black solids were gathered after natural cooling, washed several times using absolute ethanol and DI water alternately until the supernatant was neutral, then desiccated in a drying oven at 80 °C for 12 hours, and finally the product was put in a high temperature box resistance furnace at 600 °C for 3 h to get CoFe₂O₄ nanoparticles.

**Characterization of CoFe₂O₄ nanoparticles**

X-ray diffractometer (XRD, X'pert pro) was performed to study the crystal structure of the catalyst, and the scanning range (2θ) was 20–80°. The obtained spectrum was compared with the standard spectrum JCPDS (22-1086) for crystal matching analysis. The microscopic morphology was surveyed by scanning electron microscope (SEM, Apreo S). The sample elements composition was characterized by energy spectrum analyzer (EDS, EDAX). The magnetic performance of the catalyst was studied by vibrating sample magnetometer (VSM, MicroSence EVP) at 300 K.

**Degradation experiment and analysis**

The catalytic performance of the prepared nano-CoFe₂O₄ was investigated by activating PMS for degradation of AMX in water. All experiments were performed in a series of 250 mL beakers. In detail, first a certain quantity of catalyst was put into a beaker with 200 mL of AMX (10 mg·L⁻¹). After stirring for 30 min (1,200 rpm) to make the adsorption reach equilibrium, secondly an appropriate amount of PMS was added to continue stirring and start timing. At regular intervals, a certain amount of water was sampled from the beaker, then passed through a filter with an aperture of 0.45 um, and quenched with methanol. The AMX concentration was identified by an ultraviolet spectrophotometer (UV-2800A) at a wavelength of 230 nm.

The degradation of AMX could approximately follow the first-order kinetics:

\[ C_t = C_0 \exp(-k_{obs}t) \]

where \( k_{obs} \) is the first order reaction rate constant (min⁻¹); \( T \) is the reaction time (min); \( C_0 \) is the initial concentration (mg L⁻¹); \( C_t \) is the concentration of amoxicillin at t (mg L⁻¹); According to Equation (1), the first-order reaction rate constant can be calculated as follows:

\[ k_{obs} = \frac{\ln\left(\frac{C_0}{C_t}\right)}{t} \]

when studying the effects of different reaction conditions on the degradation system, the experiment and analysis followed the single variable principle. H₂SO₄ (0.1 mol·L⁻¹) and NaOH (0.1 mol·L⁻¹) were prepared to regulate the initial pH values of the solution during the experiment. To investigate the influence of quenching on the reaction, ethanol (EtOH) and tert-butanol (TBA) were selected as reaction quenchers, each quencher was added before PMS, and the other group was used as a blank. Samples were taken for testing and analysis at regular intervals after the reaction began.

The stability and reusability of prepared nano-CoFe₂O₄ were explored through cyclic degradation test. The catalyst was recovered after each reaction, washed repeatedly, and after that set in an oven at 80 °C to dry and reuse.

**RESULTS AND DISCUSSION**

**Characterization of CoFe₂O₄**

**Crystal structure**

The crystal structure of the catalyst was one of the important factors affecting its catalytic performance, and it could be identified based on the XRD data of the material. The XRD diffraction pattern of CoFe₂O₄ is displayed in Figure 1. It was observed that the diffraction maximums of the catalyst sample at 30.1°, 35.4°, 43.1°, 53.4°, 57.0°, 62.6°, 74.0° and 75.0° were in accord with (220), (311), (400), (422), (511), (440), (620) and (533) crystal planes of the spinel CoFe₂O₄ (JCPDS 22-1086), indicating that nano-CoFe₂O₄ was successfully synthesized in the experiment. In addition, the sharp diffraction peaks of the material indicated that the prepared nano-CoFe₂O₄ has a high crystallinity.
Surface topography

Figure 2 showed the SEM image and EDS measurement results of CoFe$_2$O$_4$. Clearly seen from Figure 2(a) and 2(b), the catalyst was composed of spherical nanoparticles with uniform surface morphology. However, the nanoparticles revealed slight agglomeration due to the ferromagnetism of the catalyst. According to the catalyst EDS diagram Figure 2(c), it could be seen obviously that the CoFe$_2$O$_4$ nanomaterial was composed of three elements: Fe, Co and O, indicating that the material effectively synthesized by hydrothermal method, which was in keeping with the XRD results.

Magnetic

Figure 3 displayed the hysteresis regression line of the CoFe$_2$O$_4$ sample at 300 K. As seen, the magnetization curve presented an ‘S’ shape and the magnetization intensity (Ms) was 47.2 emu g$^{-1}$. In addition, when an external magnetic field was offered, the CoFe$_2$O$_4$ sample had a strong response. The sample exhibited a large coercive force, which was mainly due to the highly anisotropic characteristics of the catalyst. In general, the catalyst sample had strong magnetic properties and could be recycled and reused in practical engineering applications by applying an external magnetic field.

Influence of reaction parameters and kinetic analysis

The process of CoFe$_2$O$_4$ activated PMS to degrade AMX was affected by a variety of reaction parameters. The main influencing factors of the reaction were systematically studied, such as CoFe$_2$O$_4$ dosage, PMS usage, AMX initial concentration, temperature, initial pH and coexisting ions (HCO$_3^-$ and Cl$^-$).

Catalyst dosage

The active sites on CoFe$_2$O$_4$ surface were very important for the activation of persulfate in the PMS/CoFe$_2$O$_4$ system. Figure S1 in Supplementary Materials describes the changes of AMX removal rate with time when the catalyst dosage was 0.05 g·L$^{-1}$, 0.1 g·L$^{-1}$, 0.2 g·L$^{-1}$ and 0.4 g·L$^{-1}$. After 90 min of reaction, the AMX removal rate and reaction rate increased from 57.8%, 9.60 × 10$^{-3}$ min$^{-1}$ to 88.3%, 2.39 × 10$^{-2}$ min$^{-1}$ with the rise of CoFe$_2$O$_4$ dosage from 0.05 to 0.4 g·L$^{-1}$. This could be attributed to the fact that the more CoFe$_2$O$_4$ in the system, the more active sites were provided on the surface that participated in the PMS activation, generating more free radicals to degrade AMX (Fei et al. 2013). However, the removal rate of AMX was only increased by about 3% when the catalyst usage was greater than 0.2 g·L$^{-1}$. This phenomenon might be related to the magnetism of the catalyst itself, which tended to aggregate with each other at high concentrations, and reduced the specific surface area of the catalyst in the system (Fan et al. 2018). These would result in a decrease in the average chance of contact between the catalyst and PMS. Based on the comprehensive consideration of degradation efficiency and catalyst consumption, the catalyst dosage was 0.2 g·L$^{-1}$.
Figure 2 | (a, b) SEM images and (c) EDS diagram of CoFe$_2$O$_4$ nanoparticles.

Figure 3 | Magnetic hysteresis regression line of CoFe$_2$O$_4$ nanoparticles.
PMS usage

In the CoFe₂O₄/PMS system, as the source of SO₄⁻² (Equation (3)), the PMS concentration would directly affect the number of free radicals and the degradation of AMX. Figure S2 illustrated the influence of PMS concentration changes on AMX degradation of the system. Increasing the PMS concentration from 0.25 to 2.0 mmol·L⁻¹, the removal rate of AMX and the reaction rate constant were also further raised from 65.1%, 1.12×10⁻³ min⁻¹ to 87.9%, 2.35×10⁻³ min⁻¹ within 90 min. Ding et al. also found that the increase of PMS concentration could significantly accelerate the degradation of tetra-bromobisphenol A (Ding et al. 2013). It is worth mentioning that when the PMS concentration was greater than 0.5 mmol·L⁻¹, the reaction speed changed little while the concentration was doubled (0.5, 1.0 and 2.0 mmol·L⁻¹), and the removal rate was only increased by about 2.4%. Presumably the reason was that excessive PMS reacts with SO₄⁻² to produce SO₅⁻² which had a weaker oxidizing ability and SO₄⁻² was self-consumed at the same time (Equations (4) and (5)) (Li et al. 2021), both impacted the high-efficiency degradation of AMX. The optimal usage of PMS was 0.5 mmol·L⁻¹.

\[
\begin{align*}
2\text{HSO}_3^- + e^- & \rightarrow \text{SO}_4^{2-} + \text{SO}_3^2^- + \text{H}^+ \quad (3) \\
\text{HSO}_3^- + \text{SO}_4^{2-} & \rightarrow \text{HSO}_4^- + \text{SO}_5^- \quad (4) \\
\text{SO}_4^{2-} + \text{SO}_3^- & \rightarrow 2\text{SO}_2^- \quad (5)
\end{align*}
\]

AMX initial concentration

Under the certain amount conditions of catalyst and oxidant, the amount of SO₄⁻² produced in the system and organic matter that could be degraded were determined. Figure S3 demonstrates the degradation at various initial AMX concentrations (2.5, 5, 10 and 20 mg·L⁻¹). It was obvious that the efficiency of AMX was almost stable (about 86.5%) and the rate constant gradually declined (from 2.39×10⁻² min⁻¹ to 2.15×10⁻² min⁻¹) with a rise of the initial AMX concentration in the range of 2.5–10 mg·L⁻¹. However, as the usage amount went up to 20 mg·L⁻¹, the AMX removing rate dropped to 75.6% instead. During the degradation process, the generation of sulfate radicals was the key reaction (Syaifullah et al. 2012). Excessive adsorption of AMX occupied active sites on the surface of the catalyst, resulting in SO₄⁻² adsorption competition. As a result, the reaction rate and removal rate were reduced. Accordingly, the initial concentration of AMX in the experiment was 10 mg·L⁻¹.

Initial pH

The traditional Fenton process required strict control of the reaction pH = 2–4 conditions (Wang & Wang 2007), while the per-sulfate oxidation process could be performed under a wider pH condition and had a wider application range (Chen et al. 2017). In order to explore the optimal pH of the experiment, the degradations of AMX were carried out at initial pH of 3.0, 5.0, 7.0, 9.0 and 11.0 separately. As described in Figure S4, 62.3% of the AMX was degraded at pH 3.0 during 90 min in the CoFe₂O₄/PMS system. When the pH gradually rose to 7 and then to 9, the removal rate first raised to 84.8%, and further reached 86.6%, but as the pH went up to 11, the AMX removal rate was significantly reduced to 66.0%. The reaction rate also showed a trend of first increasing and then decreasing with the pH rise, reaching the maximum at pH = 9, about 2.24×10⁻² min⁻¹. This result could be accounted for by two main factors. On the one hand, H⁺ in the solution could capture SO₄⁻² and ·OH and deactivated them in low pH (Equations (6)–(8)) (Dong 2019), resulting in poor catalytic activity. When the pH was greater than 9, the HSO₄⁻ would undergo a secondary dissociation reaction to form SO₅⁻² of lower activity (Equation (9)) (Chen & Chu 2016). On the other hand, SO₄⁻² could react with OH⁻ to produce ·OH (Equation (10)) (Li et al. 2021), it was known that the oxidation-reduction potential of ·OH was lower than that of SO₄⁻², which led to a decline in the reaction rate. The CoFe₂O₄/PMS system had higher efficiency under the neutral and weakly alkaline conditions of the initial pH, and the optimal pH was 9.

\[
\begin{align*}
\text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_3^{2-} + \text{OH}^- + \text{H}^+ \quad (6) \\
\cdot \text{OH} + \text{H}^+ + \text{e}^- & \rightarrow \text{H}_2\text{O} \quad (7) \\
\text{SO}_4^{2-} + \text{H}^+ + \text{e}^- & \rightarrow \text{HSO}_4^- \quad (8) \\
\text{HSO}_4^- + \text{SO}_4^{2-} & \rightarrow \text{SO}_5^- + \text{SO}_3^{2-} + \text{H}^+ \quad (9) \\
\text{SO}_4^{2-} + \text{OH}^- & \rightarrow \text{SO}_2^- + \cdot \text{OH} \quad (10)
\end{align*}
\]

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Temperature

The reaction temperature was a key operating parameter in the catalytic reaction, because high temperature would improve the decomposition of persulfate to promote the reaction. The experiment studied the effect of temperature on the AMX removal in the CoFe$_2$O$_4$/PMS system through three different temperatures at 15, 25 and 35 °C. Consistent with the previous description, it could be seen from Figure S5 that the rise of temperature led to the accelerated degradation of AMX. In detail, when the temperature varied from 15 to 35 °C, the degradation of AMX was enhanced (from 71.2 to 88.7%) and the reaction rate constant was improved (from $1.38 \times 10^{-2}$ to $2.42 \times 10^{-2}$ min$^{-1}$). There were two reasons for this result (Liu et al. 2014), the first was from a molecular dynamics point of view, the average kinetic energy of the molecules in the reaction increased with rising temperature, accelerating the activation and decomposition of PMS to form SO$_4$$^-$ (Equation (11)); In addition, temperature raising could enhance the effective collision between reactant molecules and accelerate the reaction. In order to calculate the activation energy (Ea) of CoFe$_2$O$_4$ activated PMS, which was used to measure the difficulty of a chemical reaction. The relationship between AMX degradation rate constant (k) and temperature (T) conformed to the Arrhenius formula (Equation (12)):

$$\ln k = \frac{\ln A - Ea}{RT}$$  \hspace{1cm} (12)

Among them, R is the molar gas constant (8.314 J mol$^{-1}$ K$^{-1}$), T is the temperature (K), A is the former factor, and Ea is the activation energy. The fitting result was displayed in Figure S5(a) inset.

The calculated result of Ea was 20.70 kJ mol$^{-1}$, which was more than the general diffusion-controlled reaction (10–13 kJ mol$^{-1}$), demonstrating that the reaction process was not a simple mass transfer, but a chemistry reaction occurred on the surface of the oxide (Xu & Wang 2012). Contrast with relevant cobalt/iron-based catalysts in the literature that activated persulfate to degrade pollutants (shown in Table S1), the Ea of the CoFe$_2$O$_4$ reaction was significantly lower, which meant that the reaction could be carried out under lower energy conditions, showing a superior catalytic performance.

Coexisting ions

HCO$_3$ and Cl$^-$ are common anions in water, the presence of them has been found to affect the removal of organic pollutants by activated persulfate according to research findings (Rao et al. 2019). In the study, a variety of different concentrations of HCO$_3$ and Cl$^-$ (5.0, 10.0, 25.0 and 50.0 mmol·L$^{-1}$) were added to the reaction solution to reveal the influences of HCO$_3$ and Cl$^-$ on the degradation of AMX. As observed in Figure S6((a)-(b)), with the increase of HCO$_3$ concentration, the removal efficiency of AMX after 90 min reaction went up in the first stage and then went down, when [HCO$_3$]$^-$ = 10 mmol·L$^{-1}$, the removal rate and the degradation rate constant reached the top, which were 88.6% and 2.36 $\times$ $10^{-2}$ min$^{-1}$, separately. This was due to the hydrolysis of HCO$_3$ in the water, changing the pH of water. The CoFe$_2$O$_4$/PMS system had better efficiency for AMX degradation in neutral and weak alkalinity. However, when the concentration of HCO$_3^-$ rose further, too much HCO$_3^-$ would capture SO$_4$$^-$ in the system, and reacted to produce CO$_3$$^-$ and H$^+$, which were less reactive (Equation (13)) (Feng et al. 2017), causing the reaction rate to slow down.

Figure S6((c)-(d)) showed that when the [Cl$^-$] in the solution ranged from 0 to 50 mmol·L$^{-1}$, the 90 min AMX removal rate continuously decreased from 83.53 to 55.2%, and the reaction rate constant also continued to decline first fast and then slowly. Cl$^-$ could significantly inhibit the progress of the catalytic oxidation reaction, because it would react with SO$_4$$^-$ and HSO$_5$ in the CoFe$_2$O$_4$/PMS system (Equations (14)–(17)) to generate Cl· (E$_0$ = 2.41 V), HOCl (E$_0$ = 1.48 V) and Cl$_2$ (E$_0$ = 1.36 V), and so on. (Yuan et al. 2011), which reduced the degradation of AMX. As the concentration of [Cl$^-$] continued to rise, the inhibitory effect tended to stabilize, the reaction formula was as follows:

$$\text{SO}_4^{2-} + \text{HCO}_3^- \rightarrow \text{SO}_4^{2-} + \text{CO}_3^- + \text{H}^+$$  \hspace{1cm} (13)

$$\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}.$$  \hspace{1cm} (14)

$$\text{HSO}_5^- + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{HOCl}$$  \hspace{1cm} (15)
Cl\(^+\) + Cl\(^-\) → Cl\(_2\)^{2-}\hfill(16)

Cl\(_2\)^{2-} + Cl\(_2\)^{2-} → Cl\(_2\) + 2Cl\(^-\)\hfill(17)

**Reuse**

To investigate the stability of CoFe\(_2\)O\(_4\), the experiment carried out 5 cycles of degradation tests on the catalyst. As seen from Figure 4(a), after recycling 5 times, the catalyst also maintained a higher catalytic efficiency, and the removal rate reached 76.5\%, only 9\% lower than the removal rate of the initial reaction. This indicated that CoFe\(_2\)O\(_4\) had good stability, and the catalytic effect was not influenced obviously by the reuse process, which was in accord with the XRD expression of the catalyst after the last reaction Figure 4(b). The causes of the removal rate decreases were as follows: the small molecule intermediate produced in the degradation was enriched in the surface of the catalyst, and the catalyst was agglomerated due to its own magnetic properties during the recovery. Both could result in a reduction in specific surface area of the catalyst, leading to a decline of the AMX removal rate.

**Reaction mechanism**

**Degradation of AMX in different systems**

The experiment investigated the degradation performance of AMX by the three systems of CoFe\(_2\)O\(_4\) alone, PMS alone and CoFe\(_2\)O\(_4\)/PMS. As described in Figure 5, the degradation efficiency of AMX by PMS alone and CoFe\(_2\)O\(_4\) alone for 90 min was 4.0\% and 7.39\%, which was far lower than that of a CoFe\(_2\)O\(_4\)/PMS system under the same conditions (about 85.5\%). Apparently, both the adsorption of the CoFe\(_2\)O\(_4\) nanoparticles and the direct oxidation of PMS could not effectively remove AMX. It was certain that the catalyst promoted the decomposition of PMS and the effective degradation of AMX was mostly referable to the heterogeneous catalytic reaction of CoFe\(_2\)O\(_4\) activated PMS. After full contact between CoFe\(_2\)O\(_4\) and PMS in the system, the surface metal ions successfully activated the PMS to produce a large amount of SO\(_4\)^{2-} with strong oxidization to achieve AMX degradation.

**Active free radical identification**

Two kinds of free radicals are generated in the activation of persulfate by the transition metal catalyst, namely SO\(_4\)^{2-} and ·OH (Matzek & Carter 2016), and SO\(_4\)^{2-} can react with H\(_2\)O or O\(^2-\) to generate ·OH (Equations (6) and (10)), both contribute to the degradation of organic pollutants. According to the literature (Ding et al. 2013), the reaction rates of TBA and EtOH with ·OH and SO\(_4\)^{2-} were displayed in Table S2. Obviously, the reaction rate of EtOH and ·OH was approximately 50 times as much as that of SO\(_4\)^{2-}, the reaction rate of TBA and ·OH was nearly 1,000 times that of SO\(_4\)^{2-}. When two free radicals coexist

*Figure 4 | The influence of cycle runs on the reaction of (a) AMX degradation ([AMX]\(_0\) = 10 mg·L\(^{-1}\), [CoFe\(_2\)O\(_4\)]\(_0\) = 0.2 g·L\(^{-1}\), [PMS]\(_0\) = 0.5 mmol·L\(^{-1}\), T = 25 °C), (b) XRD pattern after recycling 5 times.*
in the solution, TBA could effectively quench ·OH, while EtOH targeted ·OH and SO₄⁻ at the same time (Fei et al. 2013). The contribution of the two free radicals in the system could be judged by comparing the effects of the two quenchers on the degradation of AMX.

As exhibited in Figure 6, the removal efficiency of AMX within 90 min had dropped from 85.5% without quencher to 41.2% and 19.9% after adding TBA and EtOH to the system. This conclusion proved that ·OH and SO₄⁻ coexisted in the system. The two quenchers inhibited the degradation of AMX to different degrees, and the quenching of EtOH inhibited the reaction more obviously. The large amount of capture of ·OH and SO₄⁻ in the solution caused the removal rate of AMX to decrease faster, which indirectly proved that ·OH played the foremost role in the reaction system base (Akbari et al. 2016).

Based on the results of free radical quenching experiments and literature reports (Ma et al. 2020), the degradation mechanism of organic pollutants in the CoFe₂O₄/PMS system was speculated, as displayed in Figure 7. After the catalyst was added to the system, the catalyst first strengthened the contact between PMS and AMX through adsorption. The active sites Co(II) and Fe(III) on the catalyst surface could activate PMS to produce SO₄⁻, and the reaction formulas were shown in Equations (18)–(20). Simultaneously, SO₄⁻ could also react with H₂O to generate ·OH (Equation (6)). These free radicals diffused freely in the solution, and finally attacked the chemical bonds in AMX, causing them to be decomposed and mineralized (Equations (21)–(23)). In addition, CoFe₂O₄ also included the redox reaction between Co and Fe in the heterogeneous catalysis process (Equation (24)). Consequently, the catalyst simultaneously reacted and repaired itself during the degradation process,

Figure 5 | The AMX of degradation in different systems ([AMX]= 10 mg·L⁻¹, [CoFe₂O₄]= 0.2 g·L⁻¹, [PMS]= 0.5 mmol·L⁻¹, T = 25 °C).

Figure 6 | The influence of different quenchers on the degradation of AMX.
resulting in a reduction in its own loss and a prolonged service life, which was of great significance to practical engineering applications.

$$\text{Co}^{\text{II}} + \text{HSO}_5^- \rightarrow \text{SO}_4^{\text{2-}} + \text{Co}^{\text{III}} + \text{OH}^-$$  \hspace{1cm} (18)

$$\text{Fe}^{\text{III}} + \text{H}_2\text{O} \rightarrow \text{Fe}^{\text{II}} + \text{OH} + \text{H}^+$$  \hspace{1cm} (19)

$$\text{Fe}^{\text{II}} + \text{HSO}_5^- \rightarrow \text{SO}_4^{\text{2-}} + \text{Fe}^{\text{III}} + \text{OH}^-$$  \hspace{1cm} (20)

$$\text{SO}_4^{\text{2-}} \text{ (adsorbed)} \rightarrow \text{SO}_4^{\text{2-}} \text{ (free)}$$  \hspace{1cm} (21)

$$\cdot\text{OH} \text{ (adsorbed)} \rightarrow \cdot\text{OH} \text{ (free)}$$  \hspace{1cm} (22)

$$\text{SO}_4^{\text{2-}} + \cdot\text{OH} + \text{AMX (dissolved)} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \ldots$$  \hspace{1cm} (23)

$$\text{Co}^{\text{III}} + \text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{II}} + \text{Fe}^{\text{III}}$$  \hspace{1cm} (24)

**Intermediates and pathways of AMX degradation**

In order to further study the reaction mechanism of AMX degradation, the intermediates of the reaction were detected by HPLC-MS, nine intermediates with mass charge ratio (m/z) of 160, 235, 340, 354, 382, 384, 400, 412 and 428 were present compared with the blank control. Combined with previous studies (Sun et al. 2021), the possible degradation pathways of AMX were speculated to be as shown in Figure S7. The degradation of AMX was a reaction process dominated by the attack of ·OH and SO$_4^{\text{2-}}$. The first pathway was hydroxylation, which might occur in positions containing lone pairs of electrons, such as the nitrogen atom and the benzoic acid ring. AMX molecules could produce intermediate products with m/z = 382, 412, 428 by adding different numbers of hydroxyl groups. The first two were further cracked to produce product with m/z = 235. The other was the destruction of the β-lactam ring to produce penicillic acid (m/z = 384) and its derivatives m/z = 400. Then penicillic acid was decarboxylated to produce an intermediate product (m/z = 340). Methyl oxidation on the thiazolidine ring could produce intermediate product m/z = 354, and the previous derivatives could be cleaved into products with m/z = 160.

**CONCLUSIONS**

Nano-CoFe$_2$O$_4$ was successfully fabricated by hydrothermal method and used to activate PMS to degrade AMX. The degradation efficiency of AMX in the CoFe$_2$O$_4$/PMS system reached 85.5% within 90 min after parameter optimization. After 5 cycles of degradation, the efficiency decreased by 9%, which proved that the catalyst had good recoverability and stability, and further confirmed its practical application potential. Quenching experiments indicated that SO$_4^{\text{2-}}$ and ·OH were the main active species leading to the degradation of AMX, both of them degraded or mineralized AMX through two ways of
hydroxylation and β-lactam ring opening. The oxidation-reduction reaction cycle of Co^{3+}/Co^{2+} and Fe^{3+}/Fe^{2+} on the catalyst surface could realize the self-repair and regeneration of CoFe_2O_4. This study provides theoretical support for the practical engineering application of sulfate-based AOP in antibiotic treatment.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Akbari, S., Ghanbari, F. & Moradi, M. 2016 Bisphenol A degradation in aqueous solutions by electrogenerated ferrous ion activated ozone, hydrogen peroxide and persulfate: applying low current density for oxidation mechanism. Chemical Engineering Journal 294, 298–307.

Anipstakis, G. P. & Dionysiou, D. D. 2003 Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt. Environmental Science & Technology 37, 4790–4797.

Bergamonti, L., Bergonzì, C., Graiff, C., Lottici, P. P., Bettini, R. & Elviri, L. 2019 3D printed chitosan scaffolds: a new TiO_2 support for the photocatalytic degradation of amoxicillin in water. Water Research 163, 114841.

Chen, M. & Chu, W. 2016 H_2O_2 assisted degradation of antibiotic norfloxacin over simulated solar light mediated Bi_2WO_6: kinetics and reaction pathway. Chemical Engineering Journal 296, 310–318.

Chen, Y., Yan, J., Ouyang, D., Qian, L., Han, L. & Chen, M. 2017 Heterogeneously catalyzed persulfate by CuMgFe layered double oxide for the degradation of phenol. Applied Catalysis A: General 538, 19–26.

Chen, G., Yu, Y., Liang, L., Duan, X., Li, R., Lu, X., Yan, B., Li, N. & Wang, S. 2021 Remediation of antibiotic wastewater by coupled photocatalytic and persulfate oxidation system: a critical review. Journal of Hazardous Materials 408, 124461.

Ding, Y., Zhu, L., Wang, N. & Tang, H. 2013 Sulfate radicals induced degradation of tetrabromomobiphenol A with nanoscaled magnetic CuFe_2O_4 as a heterogeneous catalyst of peroxymonosulfate. Applied Catalysis B: Environmental 129, 153–162.

Dong, S. 2019 CoFe_2O_4 and CoFe_2O_4/Graphene Oxide Catalyzed Degradation of Norfloxacin by Persulfate. Master Thesis, Nanjing Agricultural University, Nanjing, PR China.

Fan, J., Gu, L., Wu, D. & Liu, Z. 2018 Mackinawite (FeS) activation of persulfate for the degradation of p-chloroaniline: surface reaction mechanism and sulfur-mediated cycling of iron species. Chemical Engineering Journal 333, 657–664.

Fei, Q., Wei, C. & Bingbing, X. 2013 Catalytic degradation of caffeine in aqueous solutions by cobalt-MCM41 activation of peroxymonosulfate. Applied Catalysis B: Environmental 134–135, 324–332.

Feng, Y., Song, Q., Lv, W. & Liu, G. 2017 Degradation of ketoprofen by sulfate radical-based advanced oxidation processes: kinetics, mechanisms, and effects of natural water matrices. Chemosphere 189, 645–651.

Ghanbari, F. & Moradi, M. 2017 Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: review. Chemical Engineering Journal 310, 41–62.

Ghauch, A., Baalbaki, A., Amasha, M., El Asmar, R. & Tantawi, O. 2017 Contribution of persulfate in UV-254 nm activated systems for complete degradation of chloramphenicol antibiotic in water. Chemical Engineering Journal 317, 1012–1025.

Grzegorz, S., Marta, B., Anna, B., Kinga, S., Piotr, S. & Ksenia, P. 2016 Determination of antibiotic residues in southern Baltic Sea sediments using tandem solid-phase extraction and liquid chromatography coupled with tandem mass spectrometry. Oceanologia 58 (3), 221–234.

Huang, Y., Huang, Y., Huang, C. & Chen, C. 2009 Efficient decolorization of azo dye Reactive Black B involving aromatic fragment degradation in buffered Co^{3+}/PMS oxidative processes with a ppb level dosage of Co^{3+}-catalyst. Journal of Hazardous Materials 170, 1110–1118.

Jung, Y. J., Kim, W. G., Yoon, Y., Kang, J., Hong, Y. M. & Kim, H. W. 2012 Removal of amoxicillin by UV and UV/H_2O_2 processes. Science of the Total Environment 420, 160–167.

Karimrezazhad, H., Navarchian, A. H., Tavakoli Gheinani, T. & Zinadini, S. 2020 Amoxicillin removal by Fe-based nanoparticles immobilized on polyacrylonitrile membrane: effects of input parameters and optimization by response surface methodology. Chemical Engineering and Processing - Process Intensification 147, 107785.

Kerkez-Kuyumcu, Ö., Bayazıt, Ş. S. & Salam, M. A. 2016 Antibiotic amoxicillin removal from aqueous solution using magnetically modified graphene nanoplatelets. Journal of Industrial and Engineering Chemistry 36, 198–205.

Li, L., Zhang, Q., She, Y., Yu, Y. & Hong, J. 2021 High-efficiency degradation of bisphenol A by heterogeneous Mn–Fe layered double oxides through peroxymonosulfate activation: performance and synergetic mechanism. Separation and Purification Technology 270, 118770.

Liu, Y., Jianming, X., Liuyang, H., Li, W., Yongfei, M., Huan, C., Hong, L., Pai, P. & Zulin, Z. 2019 Review on ultrasound assisted persulfate degradation of organic contaminants in wastewater: influences, mechanisms and prospective. Chemical Engineering Journal 378, 122146.
Liu, J., Gong, X., Song, S., Zhang, F. & Lu, C. 2014 Heat-activated persulfate oxidation of chlorinated solvents in sandy soil. *Journal of Spectroscopy* **2014**, 1–5.

Ma, Q., Nengzi, L., Zhang, X., Zhao, Z. & Cheng, X. 2020 Enhanced activation of persulfate by AC@CoFe2O4 nanocomposites for effective removal of lomofloxacin. *Separation and Purification Technology* **233**, 115978.

Manaia, C. M., Rocha, J., Scaccia, N., Marano, R., Radu, E., Biancullio, F., Cerqueira, F., Fortunato, G., Iakovides, I. C., Zammit, I., Kampouris, I., Vaz-Moreira, I. & Nunes, O. C. 2018 Antibiotic resistance in wastewater treatment plants: tackling the black box. *Environment International* **115**, 312–324.

Marco, P., Ahmad, D., Ignasi, S., Mariam, H., Nihal, O. & Mehmet, A. O. 2014 Complete mineralization of the antibiotic amoxicillin by electro-Fenton with a BDD anode. *Journal of Applied Electrochemistry* **44**, 1327–1335.

Matzek, L. W. & Carter, K. E. 2016 Activated persulfate for organic chemical degradation: a review. *Chemosphere* **151**, 178–188.

Minashree, K. & Arun, K. 2020 Human health risk assessment of antibiotics in binary mixtures for finished drinking water. *Chemosphere* **240**, 124864.

Moreira, N., Sousa, J. M., Macedo, G., Ribeiro, A. R., Barreiros, L., Pedrosa, M., Faria, J. L., Pereira, M., Castro-Silva, S., Segundo, M. A., Manaia, C. M., Nunes, O. C. & Silva, A. 2016 Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO2 with LEDs: micropollutants, antibiotic resistance genes and estrogenic activity. *Water Research* **94**, 10–22.

Nuno, F. F. M., José, M. S., Gonçalo, M., Ana, R. R., Luisa, B., Marta, J. P., Joaquim, L. F., Pereira, M. F. R., Sérgio, C., Marcela, A. S., Célia, M. M., Olga, C. N. & Adrián, M. T. S. 2016 Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO2 with LEDs: micropollutants, antibiotic resistance genes and estrogenic activity. *Water Research* **94**, 10–22.

Oh, W., Dong, Z. & Lim, T. 2016 Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: current development, challenges and prospects. *Applied Catalysis B: Environmental* **194**, 169–201.

Rama, P., Roggy, D., Satinder, K. B., Patrick, D., Francois, P., Mausam, V. & Rao, Y. S. 2018 Activation of persulfate by homogeneous and heterogeneous iron catalyst to degrade chlorotetracycline in aqueous solution. *Chemosphere* **207**, 543–551.

Rao, Y., Han, F., Chen, Q., Wang, D., Xue, D., Wang, H. & Pu, S. 2019 Efficient degradation of diclofenac by LaFeO3-Catalyzed peroxymonosulfate oxidation – kinetics and toxicity assessment. *Chemosphere* **218**, 299–307.

Sepyani, F., Darvishi, C. S. R., Jorfi, S., Godini, H. & Safari, M. 2018 Implementation of continuously electro-generated Fe3O4 nanoparticles for activation of persulfate to decompose amoxicillin antibiotic in aquatic media: UV254 and ultrasound intensification. *Journal of Environmental Management* **224**, 315–326.

Shirsath, S. E., Liu, X., Assadi, M., Younis, A., Yasukawa, Y., Karan, S. K., Zhang, J., Kim, J., Wang, D., Morisako, A., Yamauchi, Y. & Li, S. 2019 Au quantum dots engineered room temperature crystallization and magnetic anisotropy in CoFe2O4 thin films. *Nanoscale Horizons* **4**, 434–444.

Song, H. L., Zhang, S., Guo, J., Yang, Y. L., Zhang, L. M., Li, H., Yang, X. L. & Liu, X. 2018 Vertical up-flow constructed wetlands exhibited efficient antibiotic removal but induced antibiotic resistance genes in effluent. *Chemosphere* **203**, 434–441.

Sun, Y., Zhao, J., Zhang, B., Li, J., Shi, Y. & Zhang, Y. 2019 Oxidative degradation of chloroxenol in aqueous solution by thermally activated persulfate: kinetics, mechanisms and toxicities. *Chemical Engineering Journal (Lausanne, Switzerland: 1996)* **568**, 553–563.

Sun, X., Qin, Y. & Zhou, W. 2021 Degradation of amoxicillin from water by ultrasound-zero-valent iron activated sodium persulfate. *Separation and Purification Technology* **275**, 110980.

Syafullah, M., Pradeep, R. S., Moses, O. T. & Shaobin, W. 2012 Heterogeneous activation of peroxymonosulphate by supported ruthenium catalysts for phenol degradation in water. *Journal of Hazardous Materials* **215–216**, 183–190.

Tilli, I., Caria, G., Ouddane, B., Horbel-Abid, I., Ternane, R., Trabelsi-Ayadi, M. & Net, S. 2016 Simultaneous detection of antibiotics and other drug residues in the dissolved and particulate phases of water by an off-line SPE combined with on-line SPE-LC-MS/MS: method development and application. *Science of the Total Environment* **563–564**, 424–433.

Vineet, S., Bhawna, P. & Surindra, S. 2018 Phytotoxicity of amoxicillin to the duckweed *Spirodela polyrhiza*: growth, oxidative stress, biochemical traits and antibiotic degradation. *Chemosphere* **201**, 492–502.

Wan, F., Shi, P., Wang, E. & Xu, S. 2011 Performance of Graphite Oxide load Co3O4/Oxone system for Acid Orange II degradation. *Procedia Environmental Sciences* **10**, 1023–1028.

Wang, J. & Wang, J. 2007 Application of radiation technology to sewage sludge processing: a review. *Journal of Hazardous Materials* **143**, 2–7.

Xiao, R., Luo, Z., Wei, Z., Luo, S., Spinney, R., Yang, W. & Dionysiou, D. 2018 Activation of peroxymonosulfate/persulfate by nanomaterials for sulfate radical-based advanced oxidation technologies. *Current Opinion in Chemical Engineering* **19**, 51–58.

Xin, Z., Zhipeng, L., Wen, L. & Baowei, H. 2020 The magnetic covalent organic framework as a platform for high-performance extraction of Cr (VI) and bisphenol a from aqueous solution. *Journal of Hazardous Materials* **393**, 122535.

Xu, L. & Wang, J. 2012 Magnetic nanoscaled Fe3O4/CeO2 composite as an efficient Fenton-like heterogeneous catalyst for degradation of 4-chlorophenol. *Environmental Science & Technology* **46**, 10145–10153.

Yang, Q., Choi, H., Al-Abed, S. R. & Dionysiou, D. D. 2009 Iron–cobalt mixed oxide nanocatalysts: heterogeneous peroxymonosulfate activation, cobalt leaching, and ferromagnetic properties for environmental applications. *Applied Catalysis B: Environmental* **88**, 462–469.

Yilmaz, H. Ç., Akgeyik, E., Bougarrani, S., El Azzouzi, M. & Erdemoglu, S. 2020 Photocatalytic degradation of amoxicillin using Co-doped TiO2 synthesized by reflux method and monitoring of degradation products by LC-MS/MS. *Journal of Dispersion Science and Technology* **41**, 414–425.
Yin, X., Jia, A. & Hui, Z. 2016 The mechanism of degradation of bisphenol a using the magnetically separable CuFe$_2$O$_4$/peroxymonosulfate heterogeneous oxidation process. *Journal of Hazardous Materials* **309**, 87–96.

Yuan, R., Ramjaun, S. N., Wang, Z. & Liu, J. 2011 Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: implications for formation of chlorinated aromatic compounds. *Journal of Hazardous Materials* **196**, 173–179.

Zhang, T., Zhu, H. & Croué, J. 2013 Production of sulfate radical from peroxymonosulfate induced by a magnetically separable CuFe$_2$O$_4$ spinel in water: efficiency, stability, and mechanism. *Environmental Science & Technology* **47**, 2784–2791.

Zhang, T., Chen, Y. & Leiknes, T. 2016 Oxidation of refractory benzothiazoles with PMS/CuFe$_2$O$_4$: kinetics and transformation intermediates. *Environmental Science & Technology* **50**, 5864–5873.

Zhou, H., Lai, L., Wan, Y., He, Y., Yao, G. Y. & Lai, B. 2020 Molybdenum disulfide (MoS$_2$): a versatile activator of both peroxymonosulfate and persulfate for the degradation of carbamazepine. *Chemical Engineering Journal* **384**, 123264.

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