Peroxymonosulfate activation by Co-doped magnetic Mn$_3$O$_4$ for degradation of oxytetracycline in water

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Abstract
Co-doped magnetic Mn$_3$O$_4$ was synthesized by the solvothermal method and adopted as an effective catalyst for the degradation of oxytetracycline (OTC) in water. Synergistic interactions between Co-Mn$_3$O$_4$ and Fe$_3$O$_4$ not only resulted in the enhanced catalytic activity through the activation of peroxymonosulfate (PMS) to degrade OTC but also made Fe$_3$O$_4$/Co-Mn$_3$O$_4$ easy to be separated and recovered from aqueous solution. 94.2% of OTC could be degraded within 60 min at an initial OTC concentration of 10 mg L$^{-1}$, catalyst dosage of 0.2 g L$^{-1}$, and PMS concentration of 10 mM. The high efficiency of OTC removal was achieved in a wider pH range of 3.0–10.0. Co (II), Co (III), Fe (II), Fe (III), Mn (II), Mn (III), and Mn (IV) on Fe$_3$O$_4$/Co-Mn$_3$O$_4$ were identified as catalytic sites based on XPS analysis. The free radical quenching experiments showed that $\text{O}_2$•− radicals and $^1\text{O}_2$ played the main role in the degradation process and the catalytic degradation of OTC involved both free radical and non-free radical reactions. Eventually, the intermediates of OTC degradation were examined, and the possible decomposition pathways were proposed. The excellent catalytic performances of Fe$_3$O$_4$/Co-Mn$_3$O$_4$ came from the fact that the large specific surface area could provide abundant active sites for the activation of PMS and the redistribution of inter-atomic charges accelerated the redox reactions of metal ions. The high degradation efficiency and rate constant of OTC in actual water samples indicated that Fe$_3$O$_4$/Co-Mn$_3$O$_4$ had a good practical application potential.

Keywords Fe$_3$O$_4$/Co-Mn$_3$O$_4$ · OTC · Catalytic degradation · PPCPs · Wastewater treatment

Introduction
With people’s increasing attention to environmental sustainability and public health, pharmaceutical and personal care products (PPCPs) are widely used in medicines for preventing and treating human and animal diseases and as personal care in daily life (Zhang et al. 2015; Hutchings et al. 2019), resulting in a large amount of wastewater containing PPCPs and their metabolites being discharged into the environment. PPCPs have been considered as one of the emerging pollutants and one of the biggest culprits affecting the water environment (Shao et al. 2018b; Xie et al. 2015; Wang et al. 2020a). Therefore, there is increasing concern about the harmful impacts of PPCPs and their metabolites on microorganisms (Ferrari et al. 2004; Hagedorn and Alpers 1977), plants (Martins et al. 2012), animals (Isidori et al. 2005), and human beings (Persaud et al. 2015; Zimmermann and Curtis 2019; Chen et al. 2018).

As a semi-synthetic antibiotic, oxytetracycline (OTC) is widely used as an antibacterial agent because of its good compatibility and low price. However, OTC will eventually enter into the natural water bodies in various ways because it is difficult to be absorbed by the digestive tract (Hu et al. 2021). The OTC exposure to the water environment will have an impact on the flora, fauna, and even the ecosystem. The long-term exposure to OTC not only altered the intestinal microbiome of zebrafish but also changed the steady state of thyroid hormone and serotonin in zebrafish (Li et al. 2020). Moreover, OTC had photoinduced toxicity to Daphnia magna (Crustacea, Cladocera) and microalgae Raphidocelis subcapitata (Chlorophyceae) under ultraviolet or
visible short-wave radiation (Peroti et al. 2021). Therefore, it is imperative to explore economical and effective technologies for the removal of OTC in water. In recent years, there have been many reports on the various methods of removing OTC in water bodies, including physical adsorption (Li et al. 2021a), Fenton-like oxidation (Li et al. 2021b), electrochemical catalytic oxidation (Ma et al. 2021), photocatalysis (Wang et al. 2020b), biochemical catalysis (Blair-González et al. 2021), biodegradation (Wang et al. 2019b), and advanced oxidation of persulfate (Liu et al. 2021b).

As an innovative technology for the treatment of wastewater, sulfate radical-based advanced oxidation processes (SR-AOPs) are widely used for oxidizing and degrading recalcitrant pollutants (Lai et al. 2020). SR-AOPs can produce highly reactive substances, which can directly react with pollutants and oxidize them into less toxic compounds, even harmless small molecular compounds such as CO₂ and H₂O. The sulfate radical (SO₄•−) and hydroxyl radical (•OH) produced by SR-AOPs exhibit excellent oxidation capacity in wastewater treatment owing to their higher oxidation potential (2.5–3.1 V and 1.8–2.7 V vs NHE, respectively) (Oh et al. 2016; Kohantorabi et al. 2020), high selectivity, and wide pH response range. Generally, SO₄•− radical is produced via peroxymonosulfate (PMS) activation with various activation methods, such as heat (Nie et al. 2014), UV (Karimian et al. 2020; Chen et al. 2020b), electro-activation (Lin et al. 2014), transition metal (Zhao et al. 2021; Jaafari-Zadeh et al. 2017), and ultrasound (Cai et al. 2015). The transition metal activation is usually used because of its simple equipment, convenient operation, low cost, and more flexibility.

Zero-valent transition metals and their ions (Co²⁺, Cu²⁺, Mn²⁺, Ni²⁺, Fe²⁺, Fe³⁺, etc.) are often used for the activation of PMS to oxidize pollutants. Recently, Mn₃O₄ attracts much more attention and acts as an efficient catalyst for the degradation of organic pollutants in water owing to its high reactivity, low toxicity, abundance of natural resources, environmental compatibility, and multiple valence states (Saputra et al. 2013; Chen et al. 2020a). The rapid redox transformation between Mn²⁺, Mn³⁺, and Mn⁴⁺ plays a key role in the activation of the Mn₃O₄-PMS system (Wang et al. 2021; Shokoohi et al. 2020). However, there are still limits such as the difficulties in the regeneration of actives sites and the separation of catalyst on its aggressive catalytic capacity and application performances, which restrict their further application to some extent. At present, the optimization methods include carbon-encapsulated (Liu et al. 2020), incorporating with metal–organic skeleton (Li et al. 2019), doping more active metal ions (Guo et al. 2021), etc. Among them, doping metal ions such as Co, Ni, Zn, Cu, Fe, and Cr are more feasible due to their high catalytic activity and wide availability. Co has been considered as the most effective PMS activator, in which Co²⁺ can be transformed to Co³⁺ and then converted to Co²⁺ for regeneration (Chen et al. 2008; Hu and Long 2016). Ren et al. (2015) found that CoFe₂O₄ exhibited the highest catalytic ability to activate PMS for the degradation of dibutyl phthalate (DBP), which was higher than that of CuFe₂O₄, MnFe₂O₄, and ZnFe₂O₄. However, the separation and recovery of highly effective catalysts are very important. Although the carbon coating and metal–organic framework used in the above-mentioned literature promoted the catalytic efficiency of PMS, they did not solve the difficult problems of separation and recovery from aqueous solution. The best way to address this issue is to introduce magnetic particles to endow catalyst with a good magnetic response. Compared with other magnetic nanoparticles, nano-Fe₃O₄ with a larger specific surface area can provide more contact area and active sites for PMS activation, thereby exhibiting a higher effect for the removal of pollutants (Zhang et al. 2021b; Li et al. 2016). More importantly, Fe₃O₄ can be prepared by rapid chemical precipitation and its synthesis is simple and more cost-effective.

In this study, a Co-doped Mn₃O₄ magnetic nanocatalyst with rapid magnetic separation and excellent PMS activation performance was synthesized by a solvothermal method. The remarkable advantage of this material was that the addition of highly active Co could change the charge distribution and the electron density, thus significantly improving the catalytic performance of the resulting catalyst and reducing secondary pollution. Meanwhile, magnetic Fe₃O₄ nanoparticles were loaded on the material, which not only increased the active sites and contact area but also was beneficial to the rapid separation and recovery of the catalyst from an aqueous solution. OTC, a common spectral antibiotic, was selected as the target pollutant, and the effects of catalyst dosage, solution pH values, initial OTC concentration, and salt concentration on the removal efficiency of the target pollutant were studied. The free radical quenching experiments were conducted to identify the reactive substances during the catalytic process. To further analyze the degradation mechanisms and pathways, the OTC conversion products were analyzed by high-resolution mass spectrometry. Finally, the reusability and stability of Fe₃O₄/Co-Mn₃O₄ and its potential application in actual water samples were discussed.

Experimental section

Materials

Iron trichloride (FeCl₃·6H₂O), ferrous chloride (FeCl₂·4H₂O), cobalt chloride (CoCl₂·6H₂O), and ethyl alcohol (C₂H₅OH ≥ 99%) were purchased from Damao Chemical Reagent Factory (Tianjin, China). Manganese acetate (Mn(CH₃COO)₂·nH₂O ≥ 98%) was supplied by Kaixin Chemical Industry Co. Ltd. (Tianjin, China).
Synthesis of Fe₃O₄/Co-Mn₃O₄ nanocomposites

Fe₃O₄ nanoparticles were synthesized by the traditional chemical precipitation process as follows: Firstly, 5.4059 g FeCl₃·6H₂O was dissolved in 25 mL of water and injected with nitrogen. After stirring for 30 min, a 25 mL aqueous solution of FeCl₂·4H₂O (1.9881 g) was added to the above solution and stirred for another 30 min. Following, 25 mL of 10 M NaOH was dripped slowly and kept stirring for 1 h. Finally, the mixture was heated to 90 ℃ and lasted for 2 h. The product was separated using a magnet and washed with deionized water until the pH was neutral. The final precipitate was dried at 60 ℃.

The synthetic process of Fe₃O₄/Co-Mn₃O₄ was conducted according to the literature with some modification (Hong et al. 2020): Firstly, 0.1401 g of Fe₃O₄ was added into 50 mL ethanol aqueous solution (the volume ratio of water: ethanol = 1:24) and stirred. Then, 0.9804 g of Mn(CH₃COO)₂ and 0.0327 g of CoCl₂·6H₂O were added under continuous rapid stirring. Finally, 5 mL of NaOH solution (10 mM) was dropped into the solution and stirred vigorously for 10 min. The mixed solution was transferred to a Teflon stainless steel autoclave and maintained at 175 ℃ for 60 min. The products were cooled to room temperature, washed once with acetone, washed three times with a mixture of methanol and acetone (v: v = 10:75), and finally dried at 60 ℃. The synthesizing process of Fe₃O₄/Co-Mn₃O₄ was displayed in Scheme 1.

Characterization of catalysts

The morphology features of Fe₃O₄ and Fe₃O₄/Co-Mn₃O₄ were characterized by scanning electron microscope (SEM, JSM-5600LV) and their morphology structure and dimensions used transmission electron microscope (TEM, TECNANAI G2 TF 20). A specific surface area and pore size distribution analyzer (Micromeritic Chemisorb 2750) was used to acquire the N₂ absorption–desorption curves. X-ray diffraction (XRD) patterns and crystal structure changes before and after catalysis of the prepared materials were obtained via X-ray diffractometer (XRD, Rigaku D/MAX-2400 X-ray diffractometer). Fourier transform infrared spectroscopy (FTIR, Nicolet NEXUS 670) was applied to obtain the absorption spectra of Fe₃O₄ and Fe₃O₄/Co-Mn₃O₄ before and after OTC catalysis in the range from 400 to 4000 cm⁻¹. The changes in the binding energy of the material before and after the catalysis of OTC were analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5702). The magnetic properties of the Fe₃O₄ and Fe₃O₄/Co-Mn₃O₄ were calculated using a vibrating sample magnetometer (VSM, LAKESHORE-7304). The leaching rate of metal ions (Fe, Co, Mn) after the reaction was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Plasma Quant PQ9000). The mineralization of OTC was obtained by measuring the removal rate of total organic carbon (TOC, Multi TOC 2100S, Germany).

The transformation products of OTC degradation were identified by high-performance liquid chromatography-electrospray ionization-tandem mass spectrometry (LC–MS (LTQ-Orbitrap-ETD, ThermoScientificTM, MAUSA)). The column was C₁₈ (100 × 2.1 mm id, 3 μm particles, Thermo, USA). The mobile phase consisted of 0.1% acetic acid in water and acetonitrile (20:80, v/v). MS data of intermediates were analyzed using positive mode electrospray ionization (ESI⁺) using a full-scan mass technique in the range of 100 to 500 m/z, with column temperature maintained at 26.01 ℃, flow rate of 9 µL min⁻¹, and sample volume of 3–4 µL.

Catalytic activity of Fe₃O₄/Co-Mn₃O₄

Batch experiments were conducted to study the activation of PMS by Fe₃O₄/Co-Mn₃O₄, where OTC was selected as the target organic pollutant. The catalytic activity was investigated by adding 0.2 g L⁻¹ catalyst and 10 mM PMS into 100 mL, 10 mg L⁻¹ OTC solution at its natural pH value, and the reaction lasted for 60 min. All experiments were carried out in a thermostatic oscillator at 180 rpm and 20 ℃. To ensure the high efficiency of the catalyst and the effective utilization of active sites, the dosage of the
catalyst was adjusted from 0.01 to 0.03 g. The initial pH value of the OTC solutions was adjusted from 3.0 to 10.0 to explore the influence of pH on the catalytic activity. The initial pH values of the solutions were adjusted with 0.1 mol L⁻¹ of NaOH or HCl solution. The influence of initial OTC concentrations ranging from 10 to 100 mg L⁻¹ was investigated. The effect of salt was studied by adding NaCl, NaHCO₃, and NaNO₃ into OTC solution with the concentration of 0.1 M, respectively. Moreover, the concentration of sodium humate (NaHA) in the OTC solution was set at 0.1 g L⁻¹.

In order to further identify the reactive species in the process of OTC degradation, free radical quenching experiments were carried out. The •OH and SO₄•⁻ radicals were cleared with methyl alcohol (MeOH, 10 mM). The •OH, superoxide anion radical (O₂•⁻), and singlet oxygen (¹O₂) in the reaction system were eliminated by adding 10 mM of isopropanol (i-PrOH), 1, 4-Benzoquinone (BQ), and furfuryl alcohol (FFA), respectively.

We used a UV–vis spectrophotometer (CAM UV300) to determine the residual concentration of OTC at 350 nm. The removal efficiency (%) of OTC by Fe₃O₄/Co-Mn₃O₄ was measured based on the following equation:

\[
RE(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

where \(C_0\) (mg L⁻¹) and \(C_t\) (mg L⁻¹) are the concentrations of OTC at initial and \(t\) min in solution, respectively.

In this study, the pseudo-first-order model was used to describe the catalytic rate of OTC by Fe₃O₄/Co-Mn₃O₄. The kinetic equation was expressed as follows (Chen et al. 2020a):

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

where \(k_{\text{obs}}\) is the catalytic rate constant (min⁻¹).

**Results and discussion**

**Characterization of as-prepared samples**

The microstructure characteristics of the as-prepared samples were well displayed by SEM (Fig. 1a–d) and TEM (Fig. 1e–h). The SEM results showed that the surfaces of Fe₃O₄ and Fe₃O₄/Co-Mn₃O₄ were rough, and Fe₃O₄ was closely bonded with Co-Mn₃O₄. As presented in Fig. 1c and d, pure Mn₃O₄ had both cubic and spherical structures, and

Fig. 1 The SEM images of Fe₃O₄ (a) and Fe₃O₄/Co-Mn₃O₄ (b); SEM images of Mn₃O₄ (c) and Co-Mn₃O₄ (d); TEM images of Fe₃O₄ (e) and Fe₃O₄/Co-Mn₃O₄ (f); and the elemental mapping (Fe, Co, and Mn elements) of Fe₃O₄/Co-Mn₃O₄ (i–l)
the surface tended to be smooth after doping Co. It could be seen from the TEM pictures that the particle size of Fe$_3$O$_4$ was about 5–20 nm and the particle size of Fe$_3$O$_4$/Co-Mn$_3$O$_4$ was about 10–25 nm. In addition, the HRTEM lattice fringes 0.247 nm and 0.309 nm of Fig. 1g and h corresponded to (211) and (112) crystal planes in Mn$_3$O$_4$, respectively. The distribution of elements on the surface of the resulting catalyst was detected, and the results in Fig. 1i–l showed that Fe, Co and Mn elements were evenly distributed on the Fe$_3$O$_4$/Co-Mn$_3$O$_4$ surface.

The N$_2$ adsorption and desorption curves were shown in Fig. 2a. It was obvious that the adsorption-desorption curves of Mn$_3$O$_4$, Co-Mn$_3$O$_4$, Fe$_3$O$_4$, and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ presented hysteresis, and their hysteresis loop appeared to be an H4-type, which indicated that Mn$_3$O$_4$, Co-Mn$_3$O$_4$, Fe$_3$O$_4$, and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ were mesoporous solid mediums. As shown in Table 1, the specific surface area, pore size, and pore volume of pure Fe$_3$O$_4$ were 128.6 m$^2$ g$^{-1}$, 11.10 nm, and 0.36 cm$^3$ g$^{-1}$, respectively, and these values further decreased to 93.49 m$^2$ g$^{-1}$, 10.53 nm, and 0.25 cm$^3$ g$^{-1}$ after the introduction of Co-Mn$_3$O$_4$, which might be due to that the Co-Mn$_3$O$_4$ occupied part of surfaces and channels of the material. These results suggested that the Fe$_3$O$_4$/Co-Mn$_3$O$_4$ possessed high-specific surface area and interpenetrating channels, which would provide more active sites and facilitate the diffusion of the target molecules into the interior of the as-prepared catalyst.

XRD was used to identify the phase information of Fe$_3$O$_4$ and Fe$_3$O$_4$/Co-Mn$_3$O$_4$. As shown in Fig. 2b, Fe$_3$O$_4$ at 30.0°, 35.6°, 43.2°, 57.2°, and 62.3°, respectively, corresponded to its (220), (311), (400), (511), and (440) crystal faces (based on PDF#19–0629) (He et al. 2021). The characteristic diffraction peaks of Mn$_3$O$_4$ were completely consistent with the standard card (based on PDF#24–0734). Among them, the peaks at 18.0°, 28.9°, 31.0°, 32.3°, 36.1°, 37.9°, 44.4°, 50.7°, 58.5°, 59.8°, and 64.7° represented the crystal faces of (101), (112), (200), (103), (211), (004), (220), (321), (224), and (400), respectively (Hong et al. 2020). The illustration in Fig. 2b expressed a slight decrease in the intensity of the characteristic peaks of Mn$_3$O$_4$ after Co was

![Figure 2](image_url)

**Table 1** The specific surface area and pore size distribution of Fe$_3$O$_4$, Mn$_3$O$_4$, Co-Mn$_3$O$_4$, and Fe$_3$O$_4$/Co-Mn$_3$O$_4$

| Materials          | BET surface area (m$^2$ g$^{-1}$) | BJH desorption cumulative volume of pores (cm$^3$ g$^{-1}$) | BJH desorption average pore width (4 V A$^{-1}$) (nm) |
|--------------------|-----------------------------------|--------------------------------------------------------|-----------------------------------------------------|
| Fe$_3$O$_4$        | 128.16                            | 0.36                                                   | 11.10                                               |
| Mn$_3$O$_4$        | 84.29                             | 0.14                                                   | 6.62                                                |
| Co-Mn$_3$O$_4$     | 91.14                             | 0.16                                                   | 6.99                                                |
| Fe$_3$O$_4$/Co-Mn$_3$O$_4$ | 93.49                            | 0.25                                                   | 10.53                                               |
introduced, and the XRD diffraction peaks of Mn$_3$O$_4$ had a shift of 0.1–0.2° after Co doping, which revealed that Co was doped into Mn$_3$O$_4$. After magnetic Fe$_3$O$_4$ nanoparticles were loaded, the intensity of diffraction peaks corresponding to Fe$_3$O$_4$ and Mn$_3$O$_4$ were still obvious, indicating that Fe$_3$O$_4$/Co-Mn$_3$O$_4$ had been successfully obtained.

The functional groups on Fe$_3$O$_4$ and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ surfaces were identified by FTIR (Fig. 2c). There was a broad absorption band from 3200 to 3600 cm$^{-1}$, which represented the stretching vibration of surface adsorbed water. The characteristic peak at 1627 cm$^{-1}$ could be assigned to the H–O–H stretching vibration of water adsorption on Fe$_3$O$_4$. Fe$_3$O$_4$ sample exhibited a peak at around 580 cm$^{-1}$, attributing to the stretching vibration of the Fe–O bond (Peng et al. 2016). The peaks located at around 623.5 cm$^{-1}$ and 435 cm$^{-1}$ were the characteristic absorption peaks of Mn$_3$O$_4$, representing the stretching vibration of tetrahedral sites for Mn–O bonds and the Mn–O stretching vibration modes of Mn$^{3+}$ in tetrahedral, respectively (Li et al. 2017). In addition, the characteristic band at 1435.2 cm$^{-1}$ could be ascribed to the bending vibration of the combination of hydroxyl groups and Mn atoms (Zhao et al. 2017).

The magnetic properties of Fe$_3$O$_4$ and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ were displayed in Fig. 2d. The Fe$_3$O$_4$ and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ exhibited obvious superparamagnetic and ferromagnetic properties. The magnetic saturation intensities of Fe$_3$O$_4$ and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ were 45.5 emu g$^{-1}$ and 40.5 emu g$^{-1}$, respectively. Although the magnetic saturation strength of Fe$_3$O$_4$/Co-Mn$_3$O$_4$ decreased slightly, it did not affect the rapid separation of the material, which would greatly reduce operating costs and improve separation efficiency.

**Catalytic studies**

**Catalytic performances of as-prepared samples**

The removal efficiencies of OTC under different conditions (PMS alone, Fe$_3$O$_4$ + PMS, Fe$_3$O$_4$/Mn$_3$O$_4$ + PMS, Co-Mn$_3$O$_4$ + PMS, Mn$_3$O$_4$ + PMS, Fe$_3$O$_4$/Co-Mn$_3$O$_4$ alone, and Fe$_3$O$_4$/Co-Mn$_3$O$_4$ + PMS) were exhibited in Fig. 3a. It was seen that the adsorption of OTC by individual Fe$_3$O$_4$/Co-Mn$_3$O$_4$ was sufficiently visible and the OTC molecules attached to the surface of the material would facilitate the subsequent degradation. PMS alone, Fe$_3$O$_4$ + PMS, Mn$_3$O$_4$ + PMS, and Fe$_3$O$_4$/Mn$_3$O$_4$ + PMS could degrade OTC, and the removal rates achieved 45.5%, 67.9%, 81.6%, and 68.0% after 60 min of reaction time, respectively. Co-Mn$_3$O$_4$ exhibited the highest catalytic capability to activate PMS and resulted in 96.0% degradation of OTC and 0.1609 min$^{-1}$ of rate constant, which were slightly higher than those of Fe$_3$O$_4$/Co-Mn$_3$O$_4$ (94.2% and 0.1371 min$^{-1}$, respectively). As shown in Fig. 1, the TEM results showed that the addition of Fe$_3$O$_4$ would cover some active sites on the Co-Mn$_3$O$_4$ surface, resulting in a slight decline in catalytic performance. However, after the addition of Fe$_3$O$_4$, Fe$_3$O$_4$/Co-Mn$_3$O$_4$ could provide multiple catalytic sites (Fe,
Mn, and Co) to activate PMS for OTC degradation. Furthermore, the greater advantage of Fe₃O₄/Co-Mn₃O₄ was that it could be quickly separated and recovered from aqueous solutions with the help of an external magnetic field.

The catalytic performances of Fe₃O₄/Co-Mn₃O₄ with different Fe₃O₄ and Co contents were further compared, and the results were presented in Fig. 3c,d and Fig. 4a,b. When the content of Fe₃O₄ increased from 20 to 60%, the degradation efficiency and rate constant of OTC firstly increased and then decreased. When the Co content was in the range of 15–25%, the degradation efficiency of OTC was not affected significantly. Therefore, Fe₃O₄/Co-Mn₃O₄ with 30% of Fe₃O₄ content and 20% of Co content was eventually selected for follow-up experiments.

The dosage of Fe₃O₄/Co-Mn₃O₄

As displayed in Fig. 4c and d, when the dosage of Fe₃O₄/Co-Mn₃O₄ was increased from 0.01 to 0.02 g (experimental conditions: 100 mL, 10 mg L⁻¹ of OTC solution at natural pH value; 10 mM PMS; oscillating condition: 180 rpm, 20°C), the degradation efficiency and rate constant of OTC were significantly enhanced. The increase in catalyst dosage meant more active sites for the activation of PMS, which resulted in higher efficiency of OTC removal. However, the dosage of catalyst higher than 0.02 g did not further increase the degradation efficiency and rate constant of OTC due to a fixed PMS concentration. Considering the degradation efficiency and operation cost, 0.02 g was finally adopted as the best dosage and used in subsequent experiments.

The impact of pH

The catalytic degradation of OTC was performed at different pH values, and the results were demonstrated in Fig. 5a and b. The degradation efficiency of OTC was 87.6% at pH 3.0 with a rate constant of 0.2046 min⁻¹, and the maximum OTC degradation (90.6% removal) took place at pH 7.0 with a high rate constant of 0.2280 min⁻¹; subsequently, it declined to 82.4% at pH 8.0 with a low rate constant of 0.1723 min⁻¹. These results indicated that OTC could be effectively removed in acidic and near-neutral conditions and significantly reduced in alkaline solutions. The pKₐ₁ and pKₐ₂ of PMS were < 0 and 9.4, respectively, indicating that PMS existed mainly as HSO₅⁻ in the acidic/neutral solutions and SO₅²⁻ in basic solutions (Wang et al. 2019a; Chen et al. 2020c). The pKₐ₁ and pKₐ₂ values of OTC were 3.3 and 7.7, respectively; thereby, OTC could exist in the form of cationic species at pH < 3.3, zwitterionic species at pH 3.3–7.7, and anionic species at pH > 7.7 (Jawad et al. 2020). At acidic solution (pH 3.0), OTC was mainly present in cationic form, which brought them into contact with PMS and then attacked by the reactive radicals produced by Fe₃O₄/Co-Mn₃O₄ for the activation of PMS. The removal efficiency of OTC was slightly reduced under an alkaline environment (pH = 8.0 and 10.0). This result could be

![Fig. 4](https://example.com/fig4.png)
ascribed to the fact that HSO₄⁻ could be converted into less reactive SO₅²⁻ under alkaline conditions, which suppressed the generation of reactive radicals. In addition, OTC existed in the form of anionic forms, which were not beneficial to be adsorbed on the negative charge of the as-prepared catalyst surface (pHpzc = 3.1 in Supplementary Fig. S1) and consequently decreased the OTC degradation. These results suggested that Fe₃O₄/Co-Mn₃O₄ could effectively activate PMS to degrade OTC in a wider pH range from near-neutral to acidic conditions.

The effect of initial pollutant concentration and salts

As shown in Fig. 5c and d, with the increasing of initial pollutant concentration from 10 to 100 mg L⁻¹, both the degradation efficiency and rate constant of OTC decreased. Therefore, the combination of Fe₃O₄/Co-Mn₃O₄ and PMS was favorable for the catalytic degradation of OTC at low concentrations. Salts such as NaCl, NaHCO₃, NaNO₃, and NaHA were used to investigate the influence of background electrolytes. It could be concluded from Fig. 6a that all of them promoted the degradation of OTC except NaNO₃ and NaNO₃ significantly inhibited the degradation of OTC.

In traditional AOPs free radical reaction, Cl⁻ was identified as a scavenger for SO₄•⁻/•OH because Cl⁻ could react with SO₄•⁻ and •OH (kCl⁻ + SO₄•⁻ = 3.1 × 10⁸ M⁻¹ s⁻¹, kCl⁻ + •OH = 4.3 × 10⁹ M⁻¹ s⁻¹) to form weak-reactive chloride radicals (Cl⁺, Cl₂•⁻, and ClOH⁺) (Eqs. (3)–(8)) (Deng et al. 2017; Li et al. 2021c; Luo et al. 2020). However, the addition of NaCl did not inhibit but promoted the degradation of OTC, which may be caused by the formation of reactive chlorine substances such as Cl₂ and HOCl with higher oxidation ability. And similar results were observed in the degradation of tetracycline by CoN/N–C@SiO₂ (Zhang et al. 2020c) and atrazine by α-MnO₂ nanowires (Zeng et al. 2020).

The (Ct/C₀)-t curves of different pH values (a) and their rate constant kₜ_{obs} (b); the (Ct/C₀)-t curves of initial OTC concentration (c) and their kinetic fitting (d)
The degradation degree of OTC was significantly inhibited when NO$_3^-$ was present in the solution. NO$_3^-$ could react with SO$_4$$^•$− and •OH to decrease the availability of reactive radicals for OTC degradation (Eqs. (11)–(12)), thereby resulting in a decrease in catalytic performance (Sun et al. 2020). In addition, it was found that the potential of OTC aqueous solution after the addition of 0.1 M NaN$_3$, NaCl, NaHCO$_3$, and NaHA was calculated as 14.8 mV, −7.6 mV, −20.6 mV, and −39.3 mV, respectively. The noticeable potential change made part of PMS inaccessible to the active sites on the Fe$_3$O$_4$/Co-Mn$_3$O$_4$ surface, thereby inhibiting the generation of reactive species and decreasing the degradation efficiency of OTC. While the enhanced degradation of NaHA might be that phenols and quinones in NaHA could stimulate the decomposition of PMS into reactive radicals (Guan et al. 2013).

$$SO_4^{2−} + NO_3^- \rightarrow SO_4^{2−} + NO_2 \quad (11)$$

$$\cdot OH + NO_3^- \rightarrow OH^- + \cdot NO_2 \quad (12)$$

**UV–vis spectroscopic analysis**

Figure 6b showed the UV–vis spectra of Fe$_3$O$_4$/Co-Mn$_3$O$_4$ after catalytic degradation of OTC in the presence of PMS. It could be seen that the maximum absorption peak of OTC expressed a significant decrease in the first 10 min, indicating that the as-prepared catalyst had excellent catalytic activity. However, the absorption spectrum in the UV–vis region did not completely disappear. After the reaction, the characteristic absorption peak of OTC shifted by 48 units, which suggested that OTC molecules were not completely mineralized by Fe$_3$O$_4$/Co-Mn$_3$O$_4$. Therefore, the catalytic reaction of OTC produced intermediate products which needed to be detected and analyzed by mass spectrometry.

**Identification of reactive oxygen species**

To explore the reactive species of Fe$_3$O$_4$/Co-Mn$_3$O$_4$ during PMS activation, free radical scavenging experiments were carried out, and the results were demonstrated in Fig. 6c and d. The MeOH was often used as a scavenger of SO$_4^{•−}$ ($k_{SO_4^{•−}} = 1.6–7.7 \times 10^7$ M$^{-1}$ s$^{-1}$) and •OH ($k_{•OH} = 1.2–2.8 \times 10^9$ M$^{-1}$ s$^{-1}$) radicals because it contained α-H which could react with these two free radicals (Liu et al. 2021b). The i-PrOH was used to scavenge •OH radical ($k_{•OH} = 1.9 \times 10^9$ M$^{-1}$ s$^{-1}$) (Liu et al. 2016), and BQ was used to scavenge O$_2^{•−}$ radical (He and O’Shea, 2020a). The addition of MeOH and i-PrOH inhibited the catalytic reaction slightly, while the
addition of BQ strongly inhibited the catalytic degradation. When MeOH and i-PrOH were added, the \( k_{\text{obs}} \) value of OTC was 0.1071 min\(^{-1}\) and 0.0993 min\(^{-1}\), respectively, which were 4–5 times higher than that of BQ. This indicated that \( \cdot \text{OH} \) and \( \text{O}_2^* \) radicals participated in the catalytic degradation of OTC, while \( \text{O}_2^* \) radicals were the dominant reactive species in Fe\(_3\)O\(_4\)/Co-Mn\(_3\)O\(_4\)/PMS system. To further identify the \( ^1\text{O}_2 \) species in the catalytic process, FFA (\( k_{\text{FFA}+{1^1\text{O}_2}} = 1.2 \times 10^8 \text{M}^{-1} \text{s}^{-1} \)) (He and O'Shea, 2020a) was added into the Fe\(_3\)O\(_4\)/Co-Mn\(_3\)O\(_4\)/PMS system as a typical \( ^1\text{O}_2 \) scavenger. The ultimate results revealed that the catalytic activity was significantly inhibited after FFA was added, which indicated that \( ^1\text{O}_2 \) was another reactive species that contributed to the high efficiency of OTC degradation. These results demonstrated that radicals and nonradicals were all involved in the degradation process of OTC, where \( \text{O}_2^* \) and \( ^1\text{O}_2 \) played a major role in the catalytic reaction.

### Analysis of intermediates and possible degradation mechanisms

XPS was employed to give insights into the chemical states and changes of the binding energy of elements before and after degradation of OTC by Fe\(_3\)O\(_4\)/Co-Mn\(_3\)O\(_4\) in activating PMS (Fig. 7). The peaks at 638.1 eV, 639.1 eV, 640.2 eV, and 641.8 eV corresponded to Mn\(^{2+}\), Mn\(^{3+}\), Mn\(^{4+}\), and satellite peaks, respectively (Fig. 7b) (Wang et al. 2021). After the catalytic reaction, the content of Mn\(^{3+}\) decreased by 12.4%, while the content of Mn\(^{2+}\) and Mn\(^{4+}\) slightly increased. Besides, the changes of the binding energy of Mn\(^{2+}\) (+0.88 eV), Mn\(^{3+}\) (+0.58 eV), and Mn\(^{4+}\) (−0.42 eV) were also observed, which indicated that Mn as the active sites participated in the catalytic reaction. The peaks of Co\(^{2+}\) appeared at 777.9 eV and 793.3 eV, while the peaks of Co\(^{3+}\) appeared at 783.1 eV and 770.3 eV (Fig. 7c) (Jiang et al. 2020). After catalysis, the content of Co\(^{2+}\) decreased from 57.5 to 39.1%, while that of Co\(^{3+}\) increased from 42.5 to 60.9%. The decrease of Co\(^{2+}\) content fully indicated that part of Co\(^{2+}\) was converted into Co\(^{3+}\), suggesting the occurrence of electron transfer within the Co species. At the same time, the binding energy of both Co\(^{2+}\) (+1.32 eV) and Co\(^{3+}\) (+1.29–1.5 eV) increased after the reaction. As shown in Fig. 7d, the element Fe\(_2\)p was divided into four peaks. Among them, the peaks of 707.4 eV and 721.0 eV were attributed to Fe\(^{2+}\), while the peaks of 709.2 eV and 723.3 eV were assigned to Fe\(^{3+}\). Besides, the peaks at 716.1 eV and 730.5 eV corresponded to the satellite peaks (Li et al. 2019). After the catalytic degradation of OTC, the binding energy of Fe\(^{3+}\) increased by 0.35 eV and the content of Fe\(^{3+}\) decreased by 5.6%. These results suggested that redox reactions took place between the metals of different valence states and provided continuously catalytic sites to activate PMS for the generation of reactive species, thereby leading to high catalytic activity (Jiang et al. 2020; Liu et al. 2021a).

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**Fig. 7** XPS total spectra before and after catalysis (a) and XPS spectra of Mn (b), Co (c), and Fe (d) element before and after catalysis.
The removal efficiency and mineralization degree of OTC under different contact times were shown in Fig. 8a. Obviously, with the extension of reaction time, the removal rates of TOC and OTC increased. However, the removal rate of TOC was merely 62.7%, which was lower than that of OTC, revealing that part of OTC molecules was not completely degraded into CO₂ and H₂O but converted into other intermediate products. According to the free radical quenching experiments, the degradation process of OTC included free radical degradation and non-free radical degradation. Among them, free radical degradation meant that OTC molecules were first adsorbed on the surface of Fe₃O₄/Co-Mn₃O₄ and then degraded by SO₄•⁻, •OH, O₂•⁻ free radicals. Through the non-free radical route, the generated ¹O₂ as the reactive species was responsible for OTC degradation.

Based on the above analysis and previous studies, a possible degradation mechanism of OTC by Fe₃O₄/Co-Mn₃O₄ was proposed, as shown in Fig. 9, and the corresponding
equations were supplied in Supplementary information. First, M(II) (M = Mn, Co, and Fe) could react with PMS to produce $\text{SO}_4^{\cdot-}$ radicals and M(III); subsequently, M(III) was further reacted with PMS to regenerate M(II). Then, the generated $\text{SO}_4^{\cdot-}$ reacted with H$_2$O for the formation of $\cdot\text{OH}$ radicals. Moreover, the hydroxyl species such as Mn (III)-OH$^-\text{−}$ and M(II)-OH$^-\text{−}$ on the hydration surface of catalyst could promote the generation of $\text{SO}_4^{\cdot-}$ species through the formation and decomposition of Mn (III)-O–O–SO$_3$$^-\text{−}$ and M(II)-O–O–SO$_3$$^-\text{−}$ intermediates (Wang et al. 2019a; Xu et al. 2016). It was also seen from Fig. 2c that the FTIR band of the -OH groups were found to decrease from 3421 to 3396 cm$^{-1}$ after the catalytic degradation of OTC, which confirmed that the metal-surface hydroxyl groups on Fe$_3$O$_4$/Co-Mn$_3$O$_4$ were participated in the activation of PMS. Besides, metal-surface hydroxyl groups complex such as Mn(IV)-OH$^-\text{−}$ and M(III)-OH$^-\text{−}$ could react with PMS on catalyst surface to form the metastable intermediates (Mn(IV)-O–O–SO$_3$$^-\text{−}$ and M(III)-O–O–SO$_3$$^-\text{−}$), then the coordination bonds of Mn(IV)-O–O–SO$_3$$^-\text{−}$ and M(III)-O–O–SO$_3$$^-\text{−}$ were broken to generate $\text{O}_2^{\cdot+}$ species and consequently resulting in the generation of $^1\text{O}_2$ species through direct oxidation of $\text{O}_2^{\cdot+}$ or recombination of two $^1\text{O}_2$ radicals (Jawad et al. 2020; Zeng et al. 2020). Additionally, the nucleophilic PMS (as the electron donor) could release the electrons to electrophilic C=O groups (as the electron acceptor), which resulted in the generation of $\text{SO}_5^{\cdot-}$ (Shao et al. 2018a). The standard reduction potential of Fe(III)/Fe(II) (0.77 V) was lower than those of Co(III)/Co(II), Mn(IV)/Mn(III), Mn(III)/Mn(II) (1.92, 0.95, and 1.51, respectively) (Xu et al. 2016; Deng et al. 2017); thereby, the redox reactions of metals with different valence states were thermodynamically favorable. The catalytic sites could be regenerated continuously to activate PMS for the production of radical and nonradical species, thus resulting in high efficiency of OTC removal.

The intermediate products of OTC degradation were further authenticated by high-resolution mass spectrometry. According to the mass spectrum of OTC degradation, four possible degradation pathways were deduced (Scheme 2).

Round 1: The intermediate P1 (m/z 279.16) came from OTC degradation, which was caused by the loss of carbonyl, hydroxyl, methyl, and amino groups (Yang et al. 2020). Afterward, $^1\text{O}_2$ species could be derived from the self-reaction of two $\text{SO}_5^{\cdot-}$ radicals, the reaction of $\text{O}_2^{\cdot+}$ and $\cdot\text{OH}$ radicals, and/or the decomposition of PMS (Shao et al. 2018a; Chen et al. 2020a; Zeng et al. 2020). Additionally, the nucleophilic PMS (as the electron donor) could release the electrons to electrophilic C=O groups (as the electron acceptor), which resulted in the generation of $\text{SO}_5^{\cdot-}$ (Shao et al. 2018a). The standard reduction potential of Fe(III)/Fe(II) (0.77 V) was lower than those of Co(III)/Co(II), Mn(IV)/Mn(III), Mn(III)/Mn(II) (1.92, 0.95, and 1.51, respectively) (Xu et al. 2016; Deng et al. 2017); thereby, the redox reactions of metals with different valence states were thermodynamically favorable. The catalytic sites could be regenerated continuously to activate PMS for the production of radical and nonradical species, thus resulting in high efficiency of OTC removal.

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et al. 2020). P4 lost some functional groups and was oxidized and hydrogenated to form P1. Round 4: OTC was oxidized first, losing part of the functional group to form P5 (m/z 355.07). P5 then degraded to produce P1.

Reusability and stability of Fe₃O₄/Co-Mn₃O₄

The Fe₃O₄/Co-Mn₃O₄ could be quickly recovered from an aqueous solution by a permanent magnet after each recycling, washed with the deionized water, dried at 60°C and then dispersed into the freshly prepared OTC solutions to evaluate the reusability and stability of the resulting catalyst. It could be seen from Fig. 8b that the removal rate of OTC by the fresh Fe₃O₄/Co-Mn₃O₄ reached 94.2% within 60 min, while it decreased to 78.1% within 90 min after the second use. Subsequently, in the third, fourth, and fifth runs, the removal efficiencies were 73.8%, 75.4%, and 72.7% when the reaction time was extended to 120 min, respectively. Meanwhile, the value of $k_{obs}$ dropped from 0.1371 to 0.0317 min⁻¹ as the number of cycles increased. This might be attributed to the metal ions leaching from the Fe₃O₄/Co-Mn₃O₄ surface during the catalytic process. The leaching amounts of Mn, Co, and Fe were calculated as 0.5174 mg L⁻¹, 0.9645 mg L⁻¹, and 0.0207 mg L⁻¹, respectively, after the degradation of OTC. Therefore, the loss of active sites on Fe₃O₄/Co-Mn₃O₄ surface resulted in the reduction in removal efficiency and the catalytic performance of Fe₃O₄/Co-Mn₃O₄ decreased as the cycle increased. In addition, the accumulation of intermediates on the surface of the catalyst may reduce the availability of active sites to the PMS. Moreover, the stability of the as-prepared catalyst was further characterized by XRD analysis and the XRD pattern after the reaction had not been significantly affected (Fig. 2b), indicating that the structure of the catalyst had good stability.

Practical application of Fe₃O₄/Co-Mn₃O₄

To further explore the potential of Fe₃O₄/Co-Mn₃O₄ in practical application, the degradation of OTC in actual water samples was conducted. The Yellow River in China, located in Zhongshan Bridge in Gansu Province, was collected as actual water samples. It was observed from Fig. 8c that the characteristic peak of OTC in actual water samples dropped rapidly in the initial 1 min and shifted by 42 units after the reaction. The catalytic performances of Fe₃O₄/Co-Mn₃O₄ in actual water samples were also conducted at
different catalyst dosages and initial OTC concentrations. The higher catalytic efficiency (about 98.8%) and rate constant (0.3264 min⁻¹) of OTC in actual water samples were achieved at a low catalyst dosage of 15 mg, which were higher than those of OTC in deionized water (91.2% and 0.0730 min⁻¹, respectively) (Fig. 8d). At the same time, the removal efficiency was reached up to 76.1% even when the OTC concentration increased to 50 mg L⁻¹ (Fig. 8e). This may be due to the higher ionic strength in actual water samples promoted the catalytic degradation of OTC. These results fully proved that Fe₃O₄/Co-Mn₃O₄ still exhibited excellent catalytic ability for the degradation of OTC in actual water samples and had a great practical application potential.

**Conclusion**

Co-doped magnetic Mn₃O₄ (Fe₃O₄/Co-Mn₃O₄) was successfully prepared, characterized, and applied to activate PMS for the degradation of OTC in an aqueous solution. Fe₃O₄/Co-Mn₃O₄ expressed excellent catalytic ability and removed OTC in a wider pH range of 3.0–10.0, and the removal rate of OTC was as high as 94.2% under studied conditions. Moreover, the addition of NaCl, NaHCO₃, and NaHA effectively promoted the degradation of OTC. The degradation process was analyzed from the aspects of environmental control, rate constant calculation, free radical identification, and product detection. The free radical quenching experiments showed that O₂•⁻ and ¹O₂ played the main role in the degradation process of OTC, while SO₄•⁻ and •OH played a minor role, which revealed that the degradation of OTC included free radical and non-free radical mechanisms. In the catalytic process, Co (II), Co (III), Fe (II), Fe (III), Mn (II), Mn (III), and Mn (IV) synergistically activated PMS to generate different kinds of free radicals, thus triggering the degradation of OTC. Besides, there was also a redox reaction between metals, and this internal metal circulation was beneficial to the regeneration of active metal ions and promoted the catalytic effect. The intermediate products were inferred by high-resolution mass spectrometry, and the possible degradation mechanisms and pathways were proposed. The Fe₃O₄/Co-Mn₃O₄ had good stability and reusability. Finally, the highly efficient degradation of OTC in actual water samples suggested that Fe₃O₄/Co-Mn₃O₄ had a good application prospect in wastewater treatment.

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**Data Availability** Extra data are available from the authors (lixiaoli@lzu.edu.cn) upon reasonable request.

**Declarations**

**Ethics approval** No animal studies are presented in this manuscript. No human studies are presented in this manuscript. No potentially identifiable human images or data are presented in this study.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Conflict of interest** The authors declare no competing interests.

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