Degradation of oxytetracycline by magnetic MOFs heterojunction photocatalyst with persulfate: high stability and wide range

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Abstract
Photocatalysis with persulfate (PS) is an effective method for the degradation of degrading organic pollutants. In this study, Fe3O4/MIL-101(Fe), a magnetic heterojunction photocatalyst, was produced using a hydrothermal method. The material coupled with PS exhibited excellent removal efficiency for oxytetracycline (OTC) (87.1%, 1 h). And it has a wide range of applications, with good removal efficiency for OTC concentrations of 30 to 70 mg/L and pH values of 3 to 9. •SO4− and •OH played a major role in the OTC removal reaction and there was an Fe(III)/Fe(II) cycle during the reaction. With excellent stability and recoverability, the OTC removal efficiency decreased by only 4.29% after four cycles, and the Fe leaching did not exceed 0.035 mg/L per cycle. This study provides significant insights into the removal of organic pollutants from water bodies.

Keywords Antibiotics · Magnetism · Metal–organic frameworks (MOFs) · Organic pollutant removal · Persulfate · Photocatalysis

Introduction
Oxytetracycline (OTC) is a broad-spectrum antimicrobial agent of the tetracycline family that is widely used in animal and human medicine. It is mostly released in its original form after metabolizing in the body, with good water solubility and easy storage and accumulation in the environment (Wen et al. 2019; Lin et al. 2015; Wang et al. 2017). These residual OTC in the environment can enter the food chain through drinking water, livestock, and poultry products, leading to the development of corresponding antibiotic resistance in humans (Wang et al. 2021; Yang et al. 2020). Unfortunately, conventional biological treatment, physical adsorption, and chemical degradation have various limitations on the removal of OTC, such as secondary contamination, complex processes, and high costs (Du et al. 2021c; Guo et al. 2021).

Sulfate radical (•SO4−) advanced oxidation technology (SR-AOP) is gradually gaining cognizance owing to its high redox potential, long half-life, and mild generation environment of •SO4− (Chen et al. 2021; Yang et al. 2019). Persulfates (PS) can be activated by light (Yang et al. 2021a), heat (Li et al. 2020), ultrasound (Monteagudo et al. 2018), transition metal ions (Wang and Wang, 2018), and metal oxides (Do et al. 2013) to produce •SO4− (E0 = 2.5–3.1 eV) with a redox potential higher than •OH (E0 = 1.9–2.7 eV).

Metal–organic frameworks (MOFs) are crystalline porous materials that are self-assembled by inorganic metal centers (metal ions or metal clusters) and connected with organic ligands to form a periodic network structure (Cao et al. 2021). Due to their large specific surface area, good pore structure, easily adjustable structure, and good light response effect, they are one of the excellent catalysts for the

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combined photodegradation of organic pollutants in water (Huang et al. 2020). Iron-based MOFs are ideal Fenton catalysts for the degradation of organic pollutants in water. They have high surface area and high density of dispersed Fe sites, providing an abundance of adsorption and catalytic metal sites for persulfate activation (Espinosa et al. 2018).

Material recycling has been one of the main reasons limiting the introduction of photocatalysis into practical applications, and the preparation of magnetic materials is an effective way to address this issue (Du et al. 2021d). In this study, Fe₃O₄ nanospheres were embedded on MIL-101(Fe) nano-octahedral crystals by a hydrothermal method to produce magnetic materials along with the construction of heterojunctions, such that the materials were applied to visible light/PS system to remove OTC in water. The effects of material dosing, pollutant concentration, persulfate dosing, and pH on the removal of OTC were also investigated. The stability, recyclability, and recoverability of the materials were also investigated, and we further explored the mechanism of the Fe₃O₄@MIL-101/PS/vis system for the degradation of OTC.

Materials and methods

Pharmaceuticals

Ferric chloride hexahydrate (FeCl₃•6H₂O), terephthalic acid (H₂BDC), N,N-dimethylformamide (DMF), ethylene glycol (EG), benzoquinone (BQ), isopropyl alcohol (IPA), methanol (MeOH), sodium chloride (NaCl), potassium persulfate (K₂S₂O₈), oxytetracycline (OTC), ammonium acetate (NH₄Ac), sodium sulfate (Na₂SO₄), and anhydrous ethanol were purchased from Sinopharm Group Co. Ltd. (Shanghai, China). All chemicals involved were analytical grade and did not require refining.

Preparation of catalysts

Preparation of MIL-101

MIL-101 powder was synthesized according to a previously reported method (Zhao et al., 2020). In this method, 1.622 g (6 mmol) FeCl₃•6H₂O and 0.997 g (6 mmol) H₂BDC were added to 40 mL of DMF solution and stirred for 15 min to obtain a yellow-clarified solution, then transferred to a 100-mL Teflon-lined autoclave and heated at 110 °C for 20 h. The yellow–brown liquid was then cooled to room temperature and centrifuged to obtain a yellow solid, which was purified using DMF and then washed for 3 h with 100 mL of ethanol at 60 °C. They were then washed several times alternately with distilled water and anhydrous ethanol. Finally, the solid was dried at 60 °C and then ground to obtain a yellow powder.

Preparation of Fe₃O₄

Fe₃O₄ nanospheres obtained using the traditional hydrothermal method (Shao et al., 2012). 3.46 g FeCl₃•6H₂O was dissolved in EG (70 mL) and then 2.66 g NH₄Ac was added under continuous stirring. The solution was subsequently transferred to a Teflon-lined autoclave and heated at 200 °C for 8 h. After cooling to room temperature, the powder was filtered, washed, dried, and ground to obtain a black powder.

Preparation of MIL-101/Fe₃O₄

The MIL-101/Fe₃O₄ heterojunction was prepared by dispersing Fe₃O₄ into DMF solution dissolved in FeCl₃ and H₂BDC, and the subsequent preparation process was identical to that of MIL-101 (Fig. 1). The obtained material was named MF-x depending on the amount of Fe₃O₄ added (x is the mass ratio of FeCl₃ to Fe₃O₄).

Characterization of catalyst

X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo Scientific K-Alpha Microprobe. The X-ray diffraction (XRD) spectra were captured using a Bruker D8 Advance. Scanning electron microscopy (SEM) images were obtained using a Zeiss Sigma300 microscope. UV–vis diffuse diffraction (UV–vis DRS) spectra were measured on a Lambda 750. The electron spin resonance (ESR) spectra were acquired using a LakeShore 7404. Hysteresis line analysis results were obtained using a LakeShore 7404 vibrating sample magnetometer. Electrochemical impedance spectroscopy (EIS) and Mott Schottky tests were performed using an electrochemical workstation (CHI 660E, Chenhua).

Photocatalytic activity tests

A certain amount of catalyst was added to 100 mL of oxytetracycline solution, and the reaction was first performed under dark conditions for 30 min to reach the equilibrium of adsorption and desorption. Subsequently, a quantity of K₂S₂O₈ was added, and the reaction system was transferred to light conditions using a 300-W xenon lamp with a 420-nm filter. The reaction system was maintained at 25 °C throughout the reaction in the presence of circulating water, and stirring was maintained to disperse the material uniformly in the solution. Three milliliters of the suspension was taken at 10-min intervals during the reaction and filtered using
a 0.45-μm filter head to obtain a clear solution. The concentration of oxytetracycline was tested using a UV spectrophotometer. The residual ratio of the TC solution was calculated as \( C/C_0 \), where \( C \) represents the solution concentration at different times and \( C_0 \) represents the initial solution concentration.

**Results and discussion**

**Morphological and structural analysis**

The SEM images of Fe\(_3\)O\(_4\), MIL-101(Fe) and MF-50 are shown in Fig. 2. It is observed that Fe\(_3\)O\(_4\) is a structure consisting of clusters of nanospheres and MIL-101(Fe) showing...
an octahedral structure, which is similar to previous reports (Zhang et al. 2021; Zhao et al., 2020). The MF-50 composite was identified as a roughly octahedral-like structure with a few nanospheres on its surface, demonstrating that the Fe$_3$O$_4$ and MIL-101(Fe) components are combined and in good contact. EDS supports the study of the chemical composition of MF-50. The EDS elemental analysis is shown in Fig. 2e, revealing the co-existence of C, O, and Fe elements in MF-50.

The application of XRD is necessary in order to study the crystal structure and phase composition of the materials. Figure 3a shows the XRD spectra of Fe$_3$O$_4$, MIL-101(Fe), and MF-50. The XRD patterns of Fe$_3$O$_4$ showed diffraction peaks at 18.3°, 30.1°, 35.4°, 37.1°, and 43.1°, which corresponded to the JCPDS 19–0629 standard card for Fe$_3$O$_4$, demonstrating that the preparation of Fe$_3$O$_4$ was satisfactory. The XRD plots of MF-50 show peaks of Fe$_3$O$_4$ and MIL-101, proving that the material has been successfully compounded. When Fe$_3$O$_4$ was introduced, the intensity of the diffraction peaks of MIL-101(Fe) at $2\theta=9.3^°$ and $10.5^°$ decreased, suggesting that the introduction of Fe$_3$O$_4$ particles may inhibit the growth of some planes of MIL-101(Fe) during the synthesis of MIL-101(Fe). Furthermore, no shift in the position of the characteristic peaks of MIL-101(Fe) was observed in the Fe$_3$O$_4$/MIL-101 samples, indicating that the crystal structure was not disrupted by the introduction of Fe$_3$O$_4$ during the synthesis process. Moreover, the compounding of Fe$_3$O$_4$ resulted in an increase in the intensity of the diffraction peak of MF-50 at $2\theta=35.4^°$.

The use of XPS assisted in the analysis of the chemical properties of the materials. The survey of the XPS spectrum (Fig. 3b) shows that the MF-50 material contains the elements C, O, Fe, and Cl. Figure 3c shows the Fe 2p spectra, where the area ratio of the Fe 2p 1/2 peak of Fe$_3$O$_4$
to the Fe 2p 3/2 peak is 2:1, which is consistent with the Fe(III):Fe(II) = 2:1 feature of Fe₃O₄; as for MIL-101, the difference between the Fe 2p 3/2 (711.2 eV) peak and the Fe 2p 1/2 (724.9 eV) peak is 13.7 eV, which is similar to that previously reported (Zhao et al. 2020). The spectrum of MF-50 is very similar to that of MIL-101, but its satellite peaks are shifted, demonstrating an interaction between Fe₃O₄ and MIL-101. As shown in the Fig. 2d, the O 1s spectra of both MIL-101 and MF-50 can be divided into three peaks corresponding to C–O, C=O, and Fe–O bonds (Guo et al. 2020). The Fe–O peak of MIL-101 was lower than that of the C=O bond, while the opposite was observed for MF, indicating that Fe₃O₄ was successfully compounded with MIL-101.

Analysis of photoelectric properties and energy band structure

The employment of the UV–vis DRS allows the exploration of the light absorption characteristics of the material and the derivation of bandgap energy of the material. As shown in the Fig. 4a, MIL-101 exhibits excellent light absorption in the UV–vis region and when compounded with Fe₃O₄, the absorption in the visible region is improved. This can be attributed to the coupling between Fe₃O₄ and MIL-101, which enhances the efficiency of visible light utilization. The Kubelka–Munk function for counting the band gap energy of photocatalysts based on UV–vis DRS spectra is as follows (Yang et al. 2021; Du et al., 2021b)

\[
\alpha h\nu = A(h\nu - E_g)^{n/2}
\]

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the light frequency, \(E_g\) is the band gap energy, \(A\) is a constant, and \(n\) depends on the characteristics of the transition in a semiconductor. Plotting the light energy \((\alpha h\nu)^2\) versus energy \((h\nu)\), the band gap energy of MIL-101 and Fe₃O₄ are calculated to be 2.54 eV and 1.57 eV (Fig. 4b). Analysis of the XPS valence band spectrum can be used to calculate the valence band potential of the materials. According to Fig. 4e, the valence band potentials of Fe₃O₄ and MIL-101 were 0.99 eV and 2.5 eV, respectively. The Mott Schottky test can estimate the flat-band potentials. Based on Fig. 4d, the flat-band potentials of Fe₃O₄ and MIL-101 were −0.45 eV and 0.06 eV, respectively, and both are n-type semiconductors. Typically, the flat-band potentials of n-type semiconductors are slightly higher (0.1–0.2 eV) than the conduction band potential (Yu et al., 2016).

![Fig. 4](image-url)  
\(\text{a} \) UV–vis diffuse reflectance spectra of as-prepared samples. \(\text{b} \) The transformed diffuse reflectance spectra. \(\text{c} \) The EIS of as-prepared samples. \(\text{d} \) The Mott-Schottky plots. \(\text{e} \) The XPS valence band spectra of Fe₃O₄ and MIL-101. \(\text{f} \) Zeta potential of MF-50.
Therefore, the conduction band potentials of Fe$_3$O$_4$ and MIL-101 were $-0.58$ eV and $-0.04$ eV, respectively. The energy band structures of both Fe$_3$O$_4$ and MIL-101 were consistent with previous reports (Li et al. 2019; Wu et al. 2020).

EIS analysis allows the charge transfer capability of the samples to be studied. The EIS surveys of the samples were conducted in Na$_2$SO$_4$ solution (0.20 M) with a frequency range of $10^{-5}$ to 0.01 Hz. The Nyquist diagram consists of two parts: a semicircle and a straight line. The half-circle at high frequencies corresponds to the rate at which charge transfer occurs on the electrode surface, and the diameter of the half-circle is the value of the resistance; the smaller the diameter, the lesser resistance to charge transfer and the more efficient the separation of photogenerated hole electrons, making the reaction between the electrode and the electrolyte faster and conducive to the photocatalytic process (Du et al. 2021a; Yang et al. 2012). As shown in the Fig. 4c, MF-50 has a smaller arc radius at high frequencies than both MIL-101 and Fe$_3$O$_4$, indicating that the heterojunction contributes to the separation of photogenerated hole electron pairs.

### Photodegradation performance

Figure 5a demonstrates the removal efficiency of OTC in the photo-Fenton system for MF with different Fe$_3$O$_4$ compound ratios. The removal efficiency was significantly improved after the Fe$_3$O$_4$ compounding because of the formation of heterojunctions and the increase in Fe sites. The highest removal efficiency (87.1%) was observed for MF-50/light/PS.

To investigate the role of the components of the reaction, a number of control experiments were performed. As shown in Fig. 5b, there was no OTC degradation under visible light alone, indicating its structural stability. In the light/PS system, OTC was only slightly degraded, demonstrating the ineffectiveness of PS activation by visible light. In addition, the removal efficiency of OTC in photocatalytic systems is still relatively low. However, in the Fenton system (MF-50/PS), 61.1% of the OTC was removed, indicating that the sample had a superior activation effect on PS. Notably, in the photo-Fenton system, the synergistic effect of light, MF-50, and PS significantly enhanced the removal efficiency of OTC.
Effect of catalyst dosage

The dosage of the catalyst is an important factor that affects the removal efficiency of OTC. We set up parallel experiments with different MF-50 doses (0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 g/L), and the results are shown in the Fig. 5e. The removal efficiency of OTC by the dark reaction increased with the amount of catalyst, because when more catalyst was provided, the adsorption was more. While in the light reaction, the removal efficiency was well improved when the catalyst dosage was increased from 0.05 to 0.2 g/L, but the removal efficiency was not significantly improved from 0.2 to 0.5 g/L, which may be due to the scattering of light caused by the increase in the amount of catalyst.

Effect of pH

The initial pH value of the solution is an important factor that influences the removal of OTC. Hence, HCl (0.1 M) or NaOH (0.1 M) was used to tune the pH value of the OTC solution to investigate the impact of pH value on OTC removal. Figure 5d shows the removal efficiency of OTC in the MF/vis/PS system at different initial solution pH values. The dark reaction was less effective in an acidic environment. Combined with the results of zeta potential analysis (Fig. 4f), the zero potential point of the MF material was 9.48, while the OTC molecule exhibited electropositivity. However, in strongly alkaline aqueous solutions, the activity of Fe-activated PS was reduced, which decreases the removal efficiency of the material in the photoreactive phase. Meanwhile, excessive adsorption can reduce the utilization of light by the samples (Ye et al. 2019).

Effect of OTC concentration

Investigating the degradation efficiency of MF-50 at different antibiotic concentrations is a major step in testing the suitability of the material. In this study, the removal efficiency of MF-50 coupled with PS was evaluated at OTC concentrations of 30, 40, 50, 60, 70, and 100 mg/L. As shown in Fig. 5e, MF-50/PS/light has a good removal efficiency for OTC from 30 to 70 mg/L. When the concentration of OTC was increased to 100 mg/L, the removal efficiency decreased slightly. This could be attributed to the fact that high concentrations of OTC are more susceptible to light scattering, which reduces the number of photons captured by MF-50. In addition, the increased competition of OTC molecules is a reason for the low removal efficiency of high OTC concentrations (Jiang et al. 2018).

Effect of PS concentration

The addition of PS has a non-negligible effect on the removal of OTC, so it is necessary to investigate the optimum amount of persulfate to be added. As shown in the Fig. 5f, the removal rate of OTC increased when the amount of PS increases from 0.1 to 0.5 g/L. This improvement was caused by the increased concentrations of active species associated with the conversion of more PS molecules into free radicals (Pan et al. 2020). However, when the PS continued to increase from 0.5 to 1.0 g/L, the removal efficiency of OTC did not improve, which may be because excessive oxidant would clean up the generated free radicals, resulting in a lower removal efficiency (Heidarpour et al. 2020).

Recyclability and stability

Recyclability and stability are two important indicators for the practical application of materials. After each use, the material was recovered with magnets, washed, and dried, and then the OTC was removed four times, and the total iron in the water samples at the end of each experiment was measured. As shown in Fig. 6a, after four cycles, the removal efficiency was only reduced by 4.29% and none of the leached iron exceeded 0.035 mg/L. Furthermore, in combination with XPS analysis and SEM of the used material (Fig. 3b), the results showed that the structure of the material remained virtually unchanged, demonstrating the excellent stability of the material. The determination of the hysteresis lines helps to characterize the magnetic properties of the material. According to Fig. 6b, MF-50 is paramagnetic with a saturation magnetic strength of 3.52 emu/g.

Mechanistic analysis

Trapping experiments were carried out to investigate the role of free radicals in the degradation of oxytetracycline. In our work, MeOH (1 mol/L), IPA (1 mol/L), BQ (1 mmol/L), and NaCl (1 mmol/L) were used as scavengers for •SO4−, •OH, •O2−, and h+, respectively. As shown in the Fig. 7a, the addition of IPA significantly reduced the removal efficiency of OTC, indicating that •OH was involved in the removal process of OTC. After the addition of MeOH, the removal efficiency of OTC was further reduced, indicating that •SO4− also played a role in the removal process of OTC. However, the addition of BQ and NaCl had no effect on the removal of OTC. Thus, •SO4− and •OH were the main active substances for OTC degradation. To further verify the reactive oxygen species in the photocatalytic system, ESR spin-trap measurement involved 5,5-dimethyl-1-pyrroline N-oxide (DMPO) in aqueous solution. Experiments were conducted in the dark and irradiated with visible light for 5 min. As shown in Fig. 7b, the DMPO•OH adduct
could observe a four-wire ESR signal under light, while the DMPO–SO₄⁻ could observe a six-wire ESR signal, indicating that MF-50/light could effectively activate the PDS to produce •SO₄⁻ and •OH radicals, resulting in excellent OTC removal efficiency. In contrast, there was no obvious peak during the dark reaction, which also further illustrates the coupling of photocatalysis with persulfate.

The charge transfer paths can be deduced from the analysis of free radicals (Fig. 8). According to the analysis results of the material energy band structure, Fe₃O₄ and MIL-101 combine to form a heterojunction structure with interleaved energy levels, so both photocatalysts may form type II heterojunction and Z-type heterojunction structures. MF-50 can generate electron leaps upon photoexcitation of both Fe₃O₄ and MIL-101. Because the conduction band potential of Fe₃O₄ is lower than that of O₂/•O₂⁻ (−0.33 eV vs. NHE), and •O₂⁻ does not participate in the degradation of OTC according to the trapping experiments, the electrons on Fe₃O₄ are subsequently transferred to the conduction band of MIL-101, which activates persulfate to generate persulfate. At the same time, the h⁺ on the valence band of Fe₃O₄ should migrate to the valence band of MIL-101 and convert H₂O to •OH. This is because the valence band potential of Fe₃O₄ is lower than •OH/H₂O (2.38 eV vs. NHE), and h⁺ is not the main active substance in the active substance analysis. In addition, comparing Fe³⁺/Fe²⁺ (0.77 eV vs. NHE),

![Fig. 6](image-url)  
**Fig. 6** a Recycle experiments of CMG-10 for the degradation of OTC and the Fe leaching. b Magnetization curves of MF-50

![Fig. 7](image-url)  
**Fig. 7** a Trapping experiments of MF-50 for OTC degradation in light/PS system. b ESR spectra of •SO₄⁻ and •OH
the Fe(III) and Fe(II) cycles are present during the reaction. When the catalyst is exposed to light, the free electrons generated will reduce Fe(III) to Fe(II), which can then react with $\text{S}_2\text{O}_8^{2-}$ to form Fe(III) again. This is also evidenced by a new peak at 710.6 eV in the XPS Fe2p pattern of the used material, which corresponds to Fe(II).

**Conclusion**

In summary, magnetic type II heterojunction photocatalyst Fe3O4/MIL-101 was accomplished by a hydrothermal method, which demonstrated excellent degradation performance against OTC in the presence of coupled persulfate. Compounding of Fe$_3$O$_4$ not only provides the material with magnetic properties, but also builds heterojunctions to enhance charge conduction and facilitate the activation of PS. Furthermore, a good adaptability to various operating conditions and environmental fluctuations has been demonstrated. The material has excellent stability, and its structure does not change significantly after four cycles. Furthermore, only a small amount of Fe was leached out during each cycle. The removal efficiency is reduced to a minimum in each cycle, and the material can be recovered using magnets after each cycle. •OH and •SO$_4^-$ are the main active substances attacking the OTC molecules, and the Fe(III)/Fe(II) cycle facilitates charge transfer. Overall, the Fe$_3$O$_4$/MIL-101 photocatalyst coupled with persulfate is an effective method for the degradation of organic pollutants in water bodies.

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Chunyan Du: Conceptualization, Project administration, Funding acquisition.
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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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