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Research Article

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Posted Date: September 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10637336/v1>

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Additional Declarations: No competing interests reported.

Coupled Homogeneous-Heterogeneous Oxidation of Tetracycline by Natural Pyrite and H₂O₂: The Roles of Fe(II) Release and Sulfur Transformation

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Abstract: Antibiotic wastewater remediation demands catalysts that combine high activity, stability, and ecological safety. Herein, we report natural pyrite (FeS₂) as an exceptionally active and robust heterogeneous Fenton-like catalyst for ultrafast antibiotic degradation, operating efficiently under dark conditions. With an optimized system 90% of tetracycline was removed within 5 min, corresponding to an apparent rate constant (0.334 min⁻¹) approximately an order of magnitude higher than those of conventional iron-based catalysts. Mechanistic investigations unveiled a synergistic homogeneous-heterogeneous pathway, where the continuous release of Fe²⁺ initiates the homogeneous Fenton reaction, while the lattice disulfide (S₂²⁻) acts as an intrinsic electron donor to rapidly regenerate surface Fe²⁺ from Fe³⁺, thereby sustaining a high-speed Fe²⁺/Fe³⁺ redox cycle via sulfur-mediated electron transfer. This unique mechanism facilitates the generation of multiple reactive oxygen species ($\cdot\text{OH}$, $\cdot\text{O}_2^-$, and $^1\text{O}_2$), ensuring high degradation efficiency. Combined DFT calculations and LC-MS identify preferential electrophilic/nucleophilic attack sites and delineate three parallel degradation pathways. Notably, QSAR toxicity assessment reveals a decisive detoxification. Acute toxicity drops by an order of magnitude, and key intermediates lose mutagenicity, confirming ecological safety. The system operates effectively across pH 4.0-9.2, degrades five structurally different antibiotics (>80%), and tolerates

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common water constituents. A simple catalyst replenishment offsets deactivation from sulfur oxidation. This work not only clarifies the intrinsic synergy of iron and sulfur in natural minerals but also establishes pyrite as a sustainable, scalable, and cost-effective platform for practical antibiotic treatment.

Keywords: Pyrite; Tetracycline degradation; Homogeneous-heterogeneous synergy; Efficient and fast; Sulfur species

1. Introduction

The widespread use of antibiotics in human medicine and livestock farming has led to their continuous release into aquatic environments, posing significant threats to ecosystem security and human health due to the potential development of antibiotic resistance genes (P. Li et al. 2022; Samrot et al. 2023; S. Sun et al. 2023). Conventional wastewater treatment strategies, such as membrane separation and adsorption, primarily relocate contaminants rather than eliminating them, while coagulation methods are often costly and prone to inducing secondary pollution (Huo et al. 2024; Ju et al. 2025; Lalmalsawmdawngliani et al. 2024). In contrast, heterogeneous Fenton-like oxidation technology emerges as a robust alternative, capable of generating highly reactive oxygen species (ROS; e.g., $\cdot\text{OH}$, $^1\text{O}_2$, $\cdot\text{O}_2^-$) that non-selectively mineralize a wide spectrum of refractory organic pollutants, thereby offering a potent and streamlined solution for antibiotic remediation (Jiang et al. 2025; C.-C. Lin and Zhong 2023; Sedaghati et al. 2023).

Advancements in this technology hinge critically on the development of efficient, stable, and economically sustainable catalysts. Conventional iron-based solids, including iron oxides and spinel ferrites, frequently exhibit constrained activity, sluggish kinetics, and excessive H_2O_2 demand (Cheng et al. 2023), underscoring the necessity for improved catalytic systems. Transition-metal sulfides have recently emerged as attractive alternatives. Their superior catalytic activity is often attributed to the sulfur component, which can accelerate the critical $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycle by providing electrons through surface sulfur vacancies or oxidation processes, thereby

enhancing radical generation (Yangju Li et al. 2021; Yuqing Sun et al. 2023). Among these materials, pyrite (FeS_2) stands out due to its natural abundance, low cost, and distinctive attributes, such as the sustained release of Fe^{2+} and the creation of localized acidic conditions (Ltaïef et al. 2018; Thiel et al. 2019; H. Wang et al. 2019; X. Wang et al. 2020; Zheng et al. 2025).

To further enhance performance, significant efforts have been devoted to synthesizing pyrite with controlled morphologies or constructing complex composites. Zeng et al. achieved complete pollutant removal within 4 min using hydrothermally synthesized pyrite (Zeng et al. 2019). Similarly, composites like pyrite/g- C_3N_4 and pyrite/ MoS_2 have been designed to improve charge separation and expand the application under visible light (L. Li et al. 2021; P. Yan et al. 2023). Although these synthetic strategies yield impressive activities, they commonly entail intricate, energy-intensive procedures, raising concerns regarding cost-effectiveness and long-term stability in large-scale implementations (Shi et al. 2022). Consequently, natural pyrite, as an inherently available and low-cost mineral, represents a distinctly sustainable and economically viable catalytic platform. Nevertheless, its potential remains underexploited, overshadowed by the prevailing emphasis on synthetic analogues, and a systematic, mechanistic understanding of its intrinsic catalytic behavior is still nascent.

Several interconnected knowledge gaps currently hinder the rational deployment of natural pyrite in antibiotic wastewater treatment. Firstly, although Fe^{2+} leaching is known to initiate homogeneous Fenton reactions, the quantitative contributions and dynamic interplay between homogeneous (solution-phase) and heterogeneous (surface-mediated) pathways throughout the degradation process remain ambiguous. Resolving this balance is essential for system optimization. Secondly, the precise function of inherent sulfur species, particularly the lattice disulfide (S_2^{2-}), in promoting the $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycle via electron transfer lacks direct, unequivocal verification beyond indirect evidence. Clarifying whether S_2^{2-} acts merely as a source of leachable iron or as a dedicated solid-state electron shuttle is critical. Thirdly, the practical stability of

natural pyrite is often compromised. For example, a drastic decline in sulfamethazine degradation efficiency (from 100% to 20%) has been observed after merely five cycles (X. Lin et al. 2024). The root causes of this deactivation, whether dominated by physical mass loss, surface passivation, or irreversible sulfur oxidation, are not thoroughly diagnosed. Finally, mineralization efficiency is frequently unsatisfactory. TOC removal remains around 30% in many systems despite high pollutant degradation (L. Sun et al. 2019; R. Yang et al. 2023), and the underlying reasons for this discrepancy in pyrite systems are not fully understood. Compounding these issues, most prior investigations have concentrated on dye wastewater models (Bi et al. 2024; H. Sun et al. 2021), whereas studies addressing the more complex and structurally diverse antibiotic contaminants remain relatively scarce.

In light of these gaps, this study comprehensively evaluates natural pyrite as a high-performance Fenton-like catalyst using tetracycline as a representative antibiotic probe. We first conduct a detailed physicochemical characterization to correlate the inherent surface composition of pyrite with its catalytic behavior. Systematic optimization of key operational parameters including catalyst dosage, H_2O_2 concentration, and initial pH, is performed to maximize degradation efficiency. Moving beyond conventional performance metrics, we specifically investigate the mineralization capacity and cycling stability of the system, identifying the principal factors governing its gradual deactivation. Most significantly, through an integrated approach combining radical quenching experiments, intermediate analysis, and quantitative ion leaching measurements, we decouple the homogeneous and heterogeneous contributions to tetracycline degradation. This enables us to elucidate a synergistic reaction mechanism centered on sulfur-mediated electron transfer, which sustains the $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycle and facilitates multi-pathway ROS generation. Furthermore, density functional theory (DFT) calculations and liquid chromatography-mass spectrometry (LC-MS) analysis were integrated to systematically predict the reactive sites for radical attack. Consequently, the molecular-level degradation pathways of

tetracycline were comprehensively uncovered. The insights derived from this work not only clarify the fundamental role of natural pyrite's surface chemistry in driving efficient Fenton-like oxidation but also establish a mechanistic foundation for its practical implementation in the treatment of antibiotic-laden wastewaters.

2. Experimental Section

2.1. Materials and reagents

The pyrite used in this study was sourced from Anhui Province, China; its composition is shown in Table S1. It had a purity of roughly 95% and a particle size of about 44 μm (325 mesh). Hydrogen peroxide (H_2O_2 , 30 wt %), tert-butyl alcohol (TBA), isopropanol (IPA), chloroform, L-histidine, ciprofloxacin, tetracycline, oxytetracycline, and sulfamethazine were all purchased from Sinopharm Chemical Reagent Co., Ltd. and were of analytical-reagent grade, requiring no further purification. Norfloxacin was obtained from Shanghai Macklin Biochemical Co., Ltd. and was likewise analytical-reagent grade.

2.2. Catalytic tests

The prepared catalyst (0.01, 0.05, 0.10, or 0.15 g) was added to 200 mL of a 20 $\text{mg}\cdot\text{L}^{-1}$ tetracycline solution in beakers adjusted to various pH values (the native pH of the tetracycline solution was 5.47). The suspensions were magnetically stirred in the dark for 30 min to establish adsorption–desorption equilibrium. Hydrogen peroxide (0.1, 0.5, 1, 5, 10, 20, or 30 mM) was then introduced to initiate the Fenton reaction (If illumination is required, turn on the xenon lamp as the light source). At predetermined intervals, 3 mL aliquots were withdrawn, filtered through a 0.45 μm membrane, and the filtrates were analyzed with a UV-Vis spectrophotometer (TU-1901). The degradation efficiency (η) of the antibiotic solutions was calculated with Formula (1), where A_0 and A_t (or C_0 and C_t) are the absorbance (or concentration) at time 0 and at reaction time, respectively. Tetracycline shows a maximum absorbance at 357 nm; the maxima for ciprofloxacin, oxytetracycline, norfloxacin, and sulfamethazine are 272, 354, 273, and

265 nm, respectively. Kinetic data were fitted with a pseudo-first-order model (Formula (2)), where k_{app} (min^{-1}) is the apparent rate constant. To examine pH effects, the tetracycline solution pH was adjusted with HCl or NaOH before the catalytic tests. For quenching experiments, after the 30 min adsorption stage, the scavenger and then H_2O_2 were sequentially added before the degradation test.

$$\eta = \left(1 - \frac{C_t}{C_0}\right) \times 100\% = \left(1 - \frac{A_t}{A_0}\right) \times 100\% \quad (1)$$

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{app} \cdot t \quad (2)$$

The initial tetracycline solution and the tetracycline solution after the reaction under different conditions were taken, the total organic carbon (TOC) of the solution was measured, and the TOC removal efficiency of the solution after the reaction was calculated (Formula (3)). Among them, TOC_0 and TOC_t represent the total organic carbon concentration of the initial tetracycline solution and the solution at t time, $\text{mg} \cdot \text{L}^{-1}$, respectively.

$$\text{TOC removal efficiency} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100\% \quad (3)$$

2.3. Characterization and analysis

The elemental composition of the pyrite was determined with an X-ray fluorescence spectrometer (XRF-1800, Japan). Crystal structure before and after reaction was examined by X-ray diffraction (XRD, martLab 9kW, Rigaku, Japan), and elemental chemical states were probed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, USA). Micro-morphology was observed with a scanning electron microscope (SEM, ZEISS Sigma 500, Germany). High-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20) was used to detect the lattice fringes of the sample. The phase structure of pyrite samples before and after reaction was characterized using a Raman spectrometer (Horiba LabRAM HR Evolution, Japan). The Brunauer Emmett and Teller (BET, ASAP 2460, USA) was used to measure the specific surface area and pore size. Zeta potentials of pyrite at different pH values were measured using a Zetasizer Nano ZS90 (UK).

Concentrations of major elements in the leachate were quantified by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 7000DV, USA), while sulfur species of various oxidation states were analyzed by ion chromatography (IC, ICS 1100, USA). Reactive radicals in the catalytic system were detected by electron spin resonance (ESR, Bruker A3000, Germany) with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping agent. Intermediates formed during tetracycline degradation were identified using an Ultimate 3000 UHPLC coupled to a Q Exactive quadrupole-orbitrap mass spectrometer (Thermo Scientific, USA) with 0.1% formic acid solution and methanol as the mobile phase.

The degradation intermediates of tetracycline were analyzed using a Thermo Scientific UltiMate 3000 ultra-high-performance liquid chromatography (UHPLC) system coupled with a Q Exactive high-resolution mass spectrometer. Chromatographic separation was achieved on a Thermo Hypersil GOLD C18 column (2.1 mm × 100 mm, 1.9 µm). Mass spectrometry data were acquired using an electrospray ionization (ESI) source operating in the positive ion mode. Based on the elucidated molecular structures of the intermediates, the Toxicity Estimation Software Tool (T.E.S.T.) developed by the United States Environmental Protection Agency (US EPA) was utilized to evaluate the potential ecological and health risks of tetracycline and its degradation products. Quantitative structure-activity relationship (QSAR) methodology was utilized to evaluate several toxicity endpoints, encompassing acute toxicity (represented by the 96 h LC₅₀ for fish and *Daphnia magna*), developmental toxicity, and mutagenicity.

2.4. Density function theory calculations

The three-dimensional structure of tetracycline for density function theory (DFT) calculations was constructed using the Avogadro 2 (Hanwell et al. 2012). Quantum chemical calculations were performed using the ORCA 6.2 (Neese 2003, 2012, 2023, 2025; Neese et al. 2009). The optimization of the molecular geometry and energy calculations of tetracycline are based on density functional theory (DFT), performed at the B3LYP/6-311G(d,p) level (Bykov et al. 2015; Krishnan et al. 1980; Stephens et al.

1994). To accelerate the evaluation of Coulomb and exchange integrals, the RIJCOSX approximation was applied (Helmich-Paris et al. 2021). Default integration grids were utilized for all calculations. The Grimme D3 dispersion correction was introduced to accurately capture weak interactions within the molecule (Grimme et al. 2010, 2011). The simulation utilized the SMD implicit solvent model to characterize the influence of the water environment on molecular conformations (Garcia-Ratés and Neese 2019, 2020). After the geometry optimization was completed, vibrational frequency analysis was performed at the same theoretical level. The results indicated the absence of imaginary frequencies, confirming that the obtained structures represent true energy minima on the potential energy surface. To predict the radical attack sites on tetracycline, we conducted electrostatic potential (ESP) analysis and Fukui function calculations on the optimized tetracycline wavefunction file using Multiwfn 2026.6.2 (T. Lu and Chen 2012; T. Lu 2024; T. Lu and Manzetti 2014; FU Rong 2014; Pino-Rios 2025; Cao et al. 2015; T. Lu and Chen 2022). Visualizations were realized via VMD 1.9.3 For detailed computational principles and methods, see the Supplementary Materials 4.DFT Calculation Method (Humphrey et al. 1996).

3. Results and discussion

3.1. Characterization of pyrite

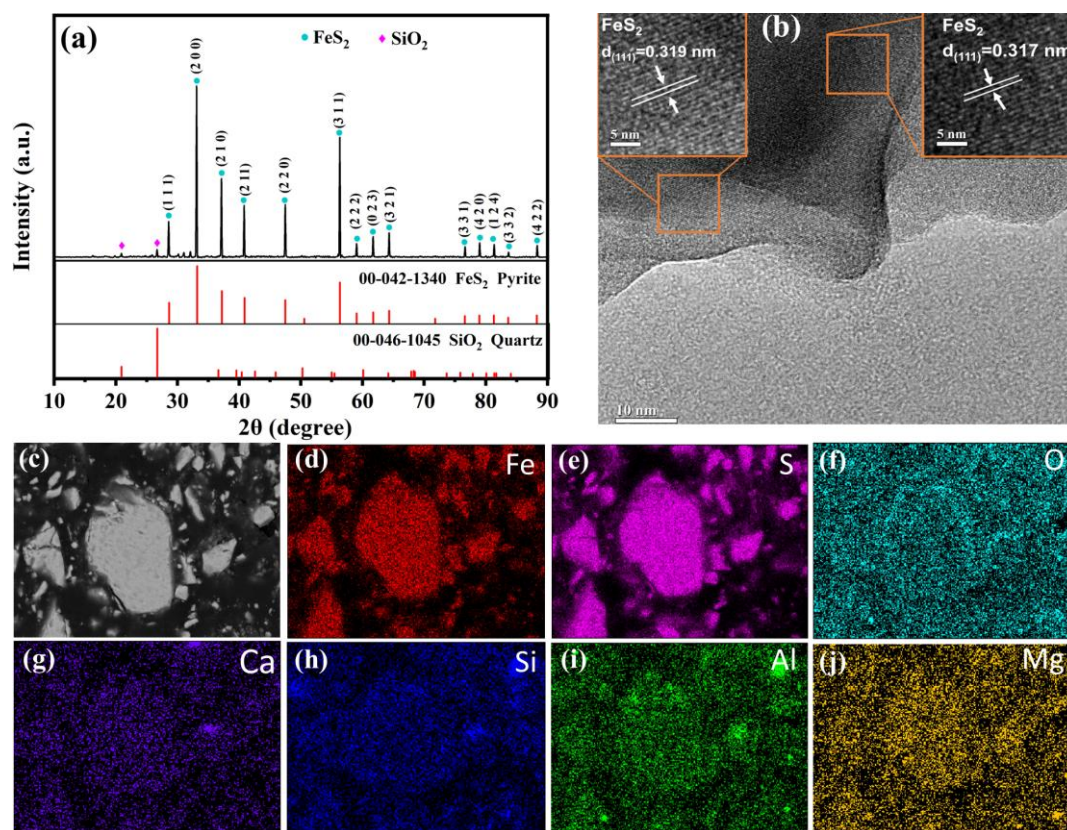


Figure. 1. (a) XRD pattern of the natural pyrite, (b) HRTEM lattice fringe image of pyrite, (c) Back-scattered SEM image, (d-j) EDS elemental maps for Fe, S, O, Ca, Si, Al, and Mg.

Figure. 1a presents the XRD pattern of the natural pyrite. Diffraction peaks located at $2\theta = 28.5^\circ, 33.0^\circ, 37.1^\circ, 40.8^\circ, 47.4^\circ, 56.3^\circ, 59.0^\circ, 61.7^\circ, 64.4^\circ, 76.6^\circ,$ and 79.0° are indexed to the (111), (200), (210), (211), (220), (311), (222), (023), (321), (331), and (420) planes of FeS₂, respectively. Although the pyrite is of relatively high purity, minor associated minerals such as quartz (SiO₂) are still present. Figure. 1b presents the transmission electron microscopy (TEM) characterization results of natural pyrite. In the locally magnified high-resolution TEM region, clear and continuous lattice fringes indicate good crystallinity and regular crystal structure of the sample. The interplanar spacing $d=0.317$ nm and 0.311 nm are characteristic crystal plane parameters of pyrite crystals (1 1 1), corresponding to its typical cubic crystal structure. Figure. 1c shows a back-scattered scanning electron micrograph, revealing irregular polyhedral particles. Figure. 1d-j display EDS elemental maps for Fe, S, O, Si, Al, Ca, and Mg. The nearly identical spatial distributions of Fe and S confirm that the primary phase is FeS₂, while the presence of other elements further illustrates the natural origin of the pyrite.

XPS was used to probe the crystal and surface chemistry of pyrite. In the high-resolution Fe 2p spectrum (Figure. 2a), three peaks at 707.2, 709.8, and 712.1 eV are assigned to $\text{Fe}^{2+}\text{-S}$, $\text{Fe}^{2+}\text{-O}$, and $\text{Fe}^{3+}\text{-O}$, respectively. The $\text{Fe}^{3+}\text{-O}$ signal indicates that part of the pyrite surface has oxidized to form ferric oxides, while the $\text{Fe}^{2+}\text{-O}$ peak suggests ferrous species bonded to oxygen, likely arising from surface hydroxylation. $\text{Fe}^{2+}\text{-S}$ corresponds to the bonding of Fe^{2+} and S in pyrite, which reflects the main structural characteristics of pyrite. The S 2p spectrum (Figure. 2b) reveals sulfur in multiple valence states, including monosulfide (S^{2-}), disulfide (S_2^{2-}), polysulfide or elemental sulfur ($\text{S}_n^{2-}/\text{S}^0$), and sulfate (SO_4^{2-}), most likely generated by natural surface oxidation. The peak at 162.7 eV corresponds to S_2^{2-} , while the signal near 169.1 eV is attributed to SO_4^{2-} . The feature at 164.7 eV arises from S^0 or S_n^{2-} ; because these species typically coexist and their peaks overlap, they are difficult to distinguish. The doublet at 162.2 and 163.4 eV is characteristic of S^{2-} in pyrite (He et al. 2021; Yajie Wang and Dong 2023). The O 1s spectrum (Figure. 2c) exhibits two characteristic peaks: a prominent feature at 531.5 eV corresponding to iron oxides and another in the 533.0 eV region. The latter peak may originate from sulfate species (with characteristic binding energy around 532.5 eV) or adsorbed water molecules (typically observed near 532.9 eV), as these two components exhibit overlapping spectral signatures that are challenging to resolve. These oxygen-containing species likely result from multi-step reactions between the mineral surface and atmospheric $\text{O}_2/\text{H}_2\text{O}$. The pore structure of the sample was characterized by nitrogen adsorption-desorption tests. As shown in Figure. 2d, its adsorption-desorption isotherm exhibits typical type IV isotherm characteristics, which is a characteristic curve of mesoporous materials. Combined with the pore size distribution curve in the inset, it can be seen that the pore size of the sample is mainly concentrated within 20 nm, with an average pore size of approximately 18.20 nm, indicating good uniformity in pore size. This uniform mesoporous structure is conducive to sufficient contact between pollutant molecules and catalyst active sites.

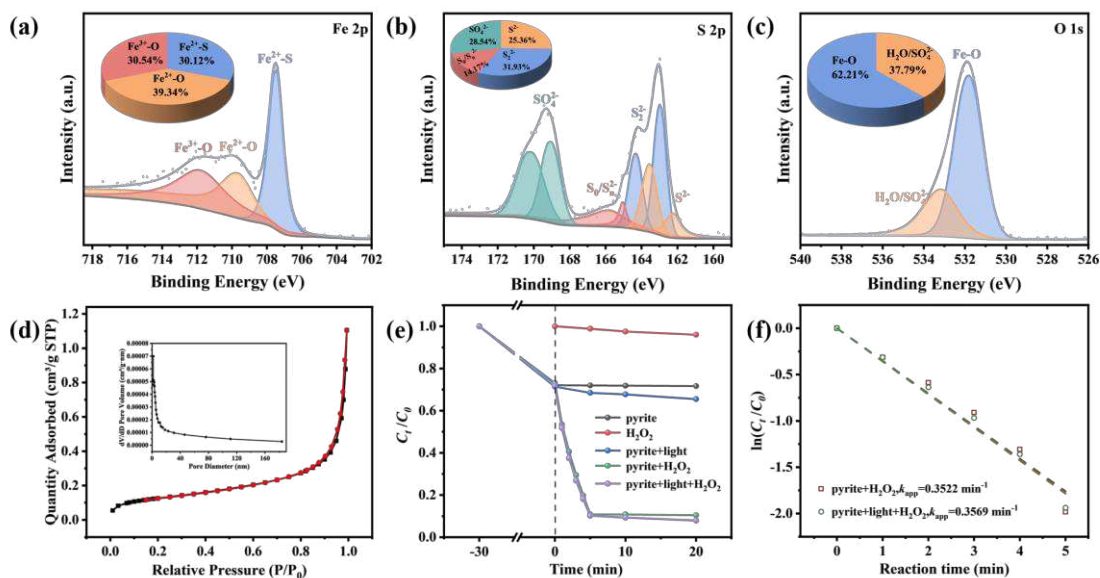


Figure. 2. XPS analysis of natural pyrite, (a) High-resolution Fe 2p, (b) S 2p, (c) O 1s; (d) N₂ adsorption-desorption isotherm (The inset figure represents the pore size distribution curve); (e) Tetracycline degradation curves and (f) Corresponding kinetic plots under different systems (Catalytic test conditions: pyrite = 0.5 g·L⁻¹, H₂O₂ = 20 mM, pH = 5.47, tetracycline = 20 mg·L⁻¹).

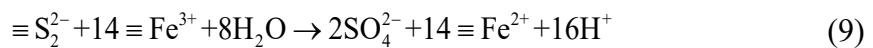
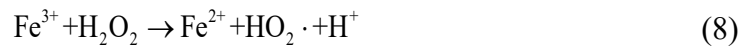
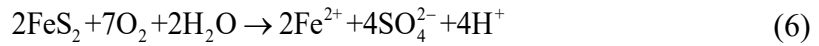
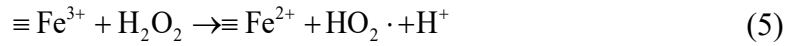
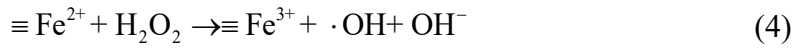
3.2. Optimization of catalytic conditions

3.2.1. Catalytic Performance and the Critical Role of Sulfur Redox Chemistry

As shown in Figure. 2e, the adsorption of tetracycline on pyrite alone reached equilibrium within 30 min, confirming its limited capacity for physical removal. The introduction of light only led to a marginal improvement in efficiency, which can be attributed to the rapid recombination of photogenerated carriers in narrow-bandgap pyrite (≈ 0.95 eV (Ferrer et al. 1990)). In contrast, the addition of H₂O₂ triggered a remarkably rapid degradation, with removal rates reaching $92.1\% \pm 1.6\%$ and $89.2\% \pm 1.2\%$ under light and dark conditions within 20 min, respectively. Most notably, the high efficiency achieved in the dark clearly highlights that the catalytic process is primarily driven by chemistry at the solid-liquid interface, rather than semiconductor photocatalysis.

This exceptional performance in the dark is fundamentally linked to the unique redox properties of pyrite, particularly the involvement of sulfur species. While surface Fe²⁺ (denoted as $\equiv\text{Fe}^{2+}$) sites initiate the Fenton reaction by activating H₂O₂ to generate $\cdot\text{OH}$ radicals (Eqs. (4)-(5)), the key to sustaining the catalytic cycle lies in the

efficient regeneration of active Fe^{2+} . Our XPS analysis (Figure. 2d) confirmed that approximately 70% of the surface iron is in the Fe^{2+} state, but more importantly, it revealed the presence of multiple sulfur species, including disulfide (S_2^{2-}), polysulfide (S_n^{2-}), and sulfate (SO_4^{2-}). The standard redox potentials provide a critical insight, that is, the much lower potential of $E^\theta(\text{S}_2^{2-}/\text{SO}_4^{2-}) \approx 0.146 \text{ V}$ compared to $E^\theta(\text{Fe}^{2+}/\text{Fe}^{3+}) = 0.770 \text{ V}$ and $E^\theta(\text{O}_2/\text{H}_2\text{O}) = 1.229 \text{ V}$, implies that sulfur is thermodynamically favored to be oxidized over iron. This suggests that in aerated solution, dissolved O_2 preferentially oxidizes S_2^{2-} , a process that not only releases additional Fe^{2+} into solution (Eq. (6)) to trigger homogeneous Fenton reactions (Eqs. (7)-(8)), but we propose, more critically serves as the primary electron-transfer pathway to reduce surface-bound $\equiv\text{Fe}^{3+}$ back to $\equiv\text{Fe}^{2+}$ (Eq. (9)).



This S-mediated electron shuttle mechanism (Eq. (9)) bypasses the slow kinetics of the classical surface Fe^{3+} reduction by H_2O_2 (Eq. (5)), thereby maintaining a high concentration of active sites and explaining the steep concentration drop observed within the first 5 min. Consequently, although light provides a minor degradation enhancement and little difference in the apparent rate constants (Figure. 2f), the “pyrite + H_2O_2 ” system operates with high efficiency in the dark, offering a more practical and economical configuration. Therefore, all subsequent experiments were conducted under dark conditions to focus on and elucidate this dominant chemical catalytic mechanism.

3.2.2. Influence of catalytic parameters on tetracycline degradation

The effects of key operating parameters, catalyst dosage, H₂O₂ concentration, and pH on tetracycline removal were investigated. As shown in Figure. 3a, increasing the amount of pyrite boosted adsorption, because more solid was available to bind tetracycline. When the dosage was raised from 0.05 g·L⁻¹ to 0.25 g·L⁻¹, the 5-min degradation efficiency rose from 84.6% to 90.4%. A further increase, however, caused a slight decline. Although additional catalyst accelerates H₂O₂ decomposition and the Fenton-like reaction, an excessive amount can lead to particle agglomeration that masks active site (Yulian Li et al. 2020). Consequently, 0.25 g·L⁻¹ was selected as the optimum dosage for the subsequent tests.

In Figure. 3b, with 0.1-0.5 mM H₂O₂, tetracycline degradation was low, indicating that few reactive species were formed. In the 1-20 mM range, tetracycline degradation exceeded 87%, yet raising the concentration from 1 mM to 20 mM improved efficiency by only ~3%. Above 20 mM, performance declined because excess H₂O₂ both scavenges radicals (Eq. (10)) and competes with tetracycline for active sites, reducing H₂O₂ utilization (Wan and Wang 2017). For cost-effectiveness, 1 mM H₂O₂ was chosen.



In addition, the effect of pH value on catalytic degradation was also discussed, as illustrated in Figure. 3c. Tetracycline degradation remained almost unchanged from pH 4.00 to 9.20, showing that the pyrite system works in either acidic or mildly alkaline media. At pH ≥ 9.72 the reaction was strongly inhibited, this may be because the pH range of complete precipitation of Fe²⁺ in the solution is 8.50-9.50. When the pH is higher than 9.50, most of the Fe²⁺ has been precipitated, resulting in a low concentration of Fe²⁺ in the solution, thereby inhibiting the occurrence of Fenton reaction. Also at high pH value, H₂O₂ is preferentially decomposed into H₂O and O₂. (Eqs. (11)-(12)) (Nie et al. 2022). In addition, it should be noted that the adsorption capacity of pyrite to tetracycline changed greatly at different pH values. This mainly depends on the charge characteristics of the catalyst particles (Zeta potential) and the tetracycline ions formed in the solution. It is reported that the zero charge point (pH_{pzc}) of pyrite is between 3.5 and 7.2, which is related to the concentration of pyrite powder in solution,

the chemical composition of pyrite and the degree of impurities (Mashayekh-Salehi et al. 2021). The pH_{pzc} value of pyrite used in this experiment is about 4.9 (Figure. 3d), when both surfaces and tetracycline are positively charged ($\text{pH} < 3.30$) or both are negative ($\text{pH} > 7.68$), electrostatic repulsion lowers adsorption; otherwise, uptake is higher.

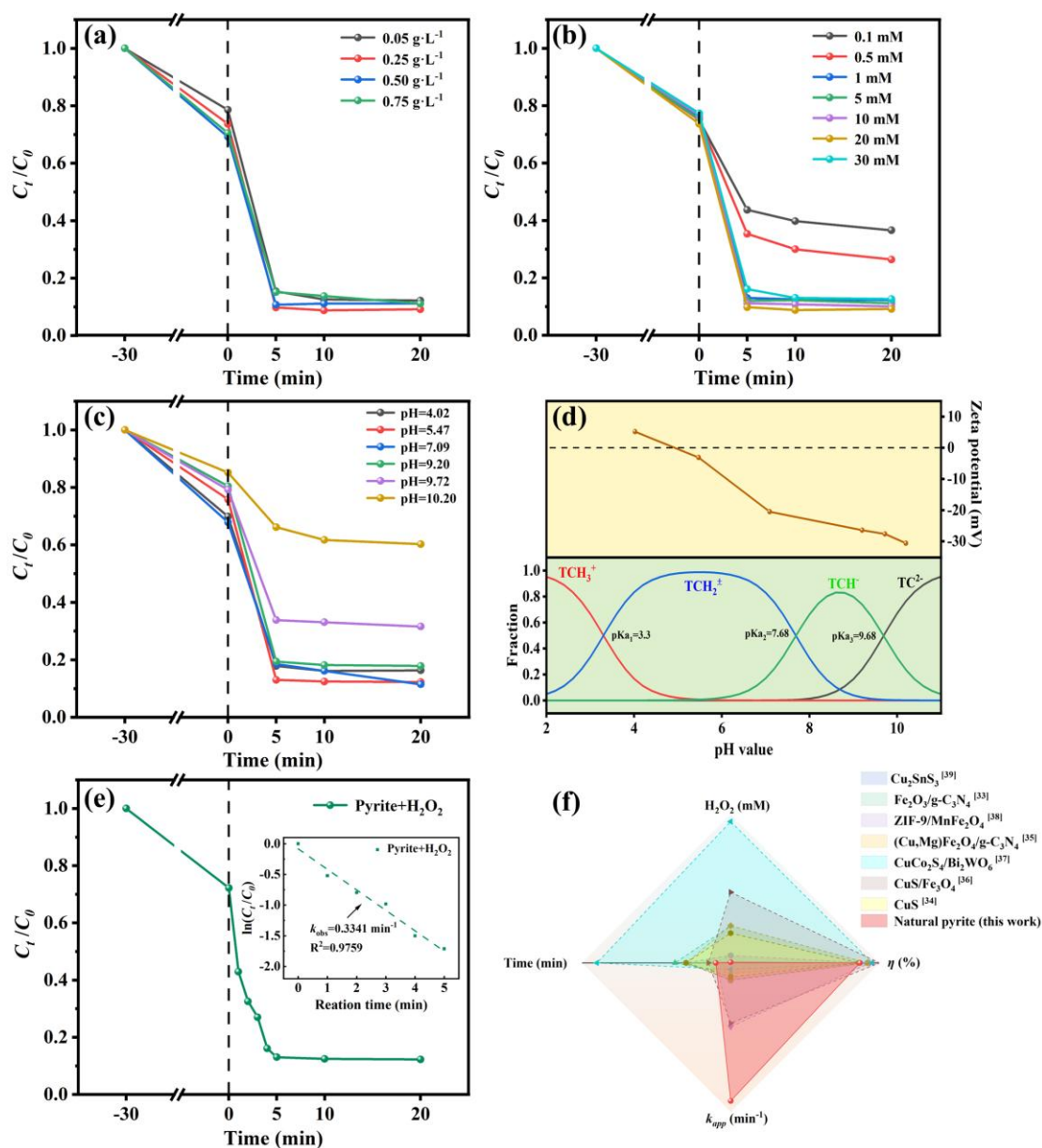


Figure. 3. Effects of catalytic parameters on tetracycline degradation: (a) Catalyst dosage (Fenton conditions: $\text{H}_2\text{O}_2 = 20 \text{ mM}$, $\text{pH} = 5.47$), (b) H_2O_2 concentration (Fenton conditions: pyrite = $0.25 \text{ g} \cdot \text{L}^{-1}$, $\text{pH} = 5.47$), (c) pH value (Fenton conditions: pyrite = $0.25 \text{ g} \cdot \text{L}^{-1}$, $\text{H}_2\text{O}_2 = 1 \text{ mM}$), (d) Zeta

potential of pyrite and tetracycline speciation versus pH value, (e) Degradation profile under optimal conditions with inset kinetic plot (Fenton conditions: pyrite = 0.25 g·L⁻¹, H₂O₂ = 1 mM, pH = 5.47), (f) Comparison with other typical catalysts

To sum up, the best “pyrite + H₂O₂” system therefore uses 0.25 g·L⁻¹ catalyst, 1 mM H₂O₂, and the solution’s native pH of 5.47. Under these conditions, as shown in Figure. 3e, 20 mg·L⁻¹ tetracycline is quickly degraded, reaching 87.0% removal within 5 min. Short-interval sampling and kinetic fitting give an apparent rate constant k_{app} of 0.3341 min⁻¹. As Figure. 3f illustrates, natural pyrite clearly outperforms many common iron oxides, spinel ferrites, and sulfide catalysts (Guo et al. 2019; Huang et al. 2022; G. Lu et al. 2024; Matos et al. 2021; Yingxian Wang et al. 2022; Z. Wang et al. 2020; Q. Yang et al. 2023). By contrast, natural pyrite only requires a dosage of H₂O₂ that is one-tenth or even less than that of some catalysts, while its rate constant can be more than ten times higher than that of the latter. Our natural pyrite can achieve rapid and efficient degradation with only a low dose of H₂O₂.

3.3. Sustainable application of pyrite in water treatment

3.3.1. Mineralization of tetracycline

When evaluating the effectiveness of tetracycline removal, the total organic carbon (TOC) removal efficiency, an index of mineralization, matters as much as the degradation rate itself, because it directly indicates how efficiently organic pollutants are converted into inorganic end-products (e.g., CO₂, H₂O). To obtain a fuller picture, residual H₂O₂ was monitored (standard curve in Figure. S1). Figure. 4a quantifies its evolution over time. At an initial dose of 1 mM, H₂O₂ was completely consumed (100% utilization). At starting doses of 10 mM and 20 mM, utilization fell to 38.7% and 24.8%, respectively. Thus, although the optimized low-dose system uses H₂O₂ efficiently, the small absolute amount of ·OH generated cannot continuously attack the intermediates, limiting mineralization. Only when the system approaches an H₂O₂ “saturation” level can enough reactive species be produced to achieve maximal TOC removal. Under the optimized reaction conditions established in this work, the TOC removal efficiency reached only 33.6% at 20 min, whereas tetracycline concentration dropped far more

rapidly. The gap suggests that tetracycline is first broken down into organic intermediates that still contain carbon, so they continue to be detected as TOC. Increasing H_2O_2 from 1 mM to 20 mM sharply boosted TOC removal. Further raising it to 30 mM, however, produced no additional benefit (Figure. 4a). Excess H_2O_2 undergoes radical-scavenging side reactions, and the surface active sites may become saturated, so radical generation and quenching balance each other.

Here, we propose a new definition, namely the TOC removal efficiency per unit H_2O_2 concentration (under saturation conditions). We represent it with R , and we can see that even at 20 mM, however, the H_2O_2 dosage of natural pyrite is still well below the typical levels used in many iron-based Fenton systems reported in the literature (L. Li et al. 2021; Qiu et al. 2022; Yu Sun et al. 2024; J. Yan et al. 2023) (Figure. 4b).

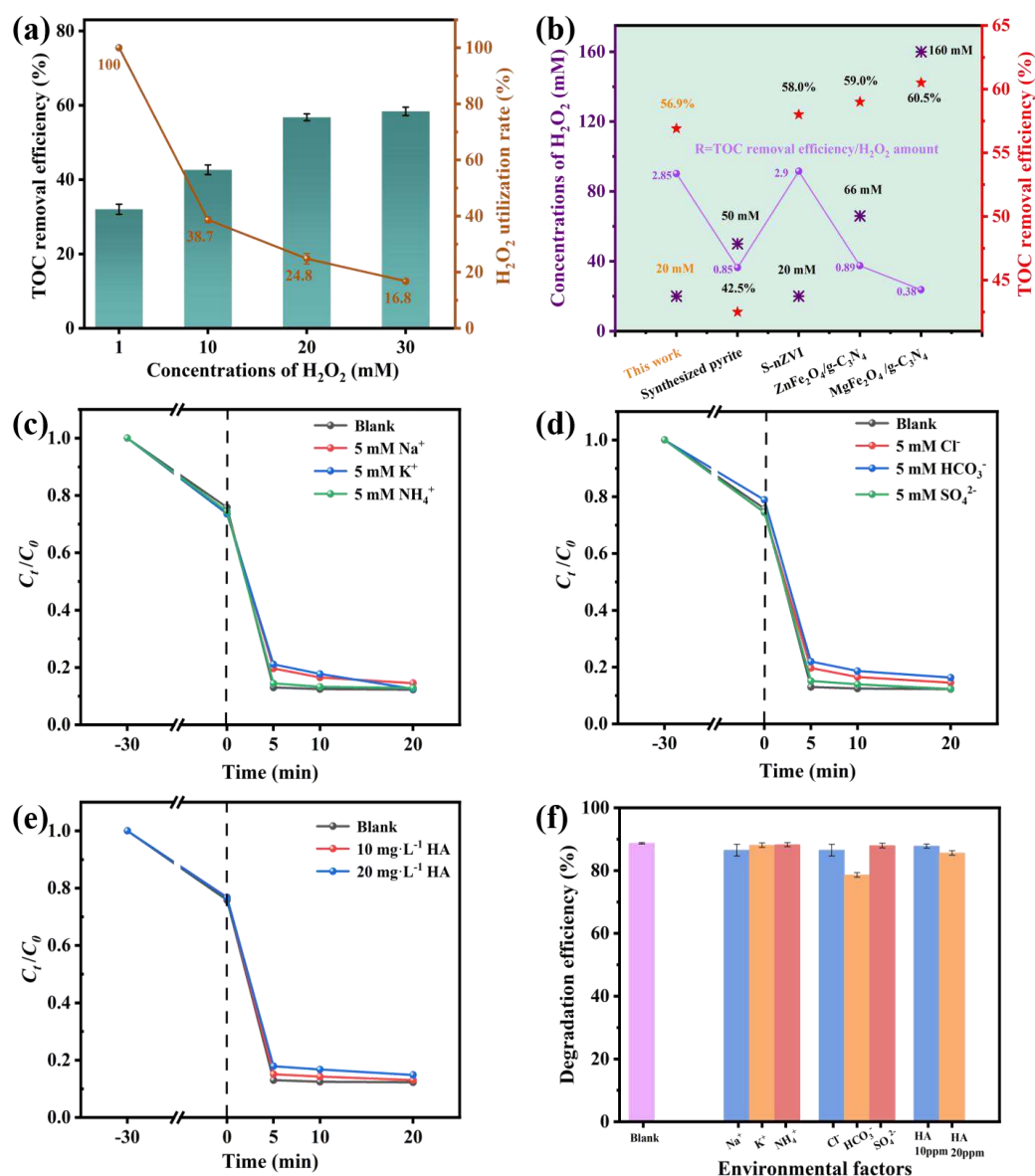
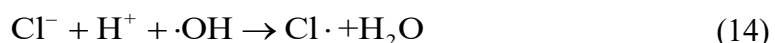
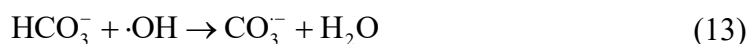


Figure 4. (a) TOC removal efficiency and H_2O_2 utilization rate under different H_2O_2 concentrations, (b) Comparison of the present system with other catalysts; Effects of (c) Different cations, (d) Different anions, and (e) Humic acid on tetracycline degradation, and (f) The influence trend of different environmental factors on the degradation of tetracycline. (Fenton conditions: pyrite = 0.25 g·L⁻¹, H_2O_2 = 1 mM).

3.3.2. Influence of environmental factors on pyrite-catalyzed degradation of tetracycline

To better approximate real-world waters, we introduced representative background constituents into the pyrite/ H_2O_2 system and examined their influence on tetracycline degradation. Selected cations (Na^+ , K^+ , NH_4^+), anions (Cl^- , SO_4^{2-} , HCO_3^-) and natural

organic matter (humic acid, HA) were added individually. As shown in Figure. 4c, the three cations produced only a slight inhibitory effect, which is attributable to their adsorption on the negatively charged pyrite surface and the consequent blockage of active sites. In contrast, HCO_3^- and Cl^- exerted a more pronounced suppression (Figure. 4d), likely because they react competitively with $\cdot\text{OH}$ to generate $\text{CO}_3^{\cdot-}$ and $\text{Cl}\cdot$ (Eqs. (13)-(14)). These secondary radicals have considerably lower redox potentials ($E^0(\text{HCO}_3^-/\text{CO}_3^{\cdot-}) = 1.7 \text{ V}$ and $E^0(\text{Cl}^-/\text{Cl}\cdot) = 2.4 \text{ V}$) than $E^0(\text{OH}^-/\cdot\text{OH}) = 2.8 \text{ V}$, thereby diminishing overall oxidative activity. Humic acid, ubiquitous in natural waters at roughly $0.1\text{-}50 \text{ mg}\cdot\text{L}^{-1}$, caused only a mild decline in removal efficiency as its concentration increased (Figure. 4e). This is ascribed to competition for reactive species but does not substantially hamper tetracycline degradation at environmentally relevant levels (Awfa et al. 2020). Overall, as shown in Figure. 4f, cations and humic acid have little effect on the degradation system, while anions, especially those that can induce quenching reactions such as HCO_3^- ions, have a slightly greater impact on degradation. These observations indicate that pyrite retains considerable potential for treating antibiotic-containing wastewaters under realistic environmental conditions.



3.3.3. Degradation performance of pyrite toward various antibiotics

To verify the suitability of natural pyrite for wastewater treatment, we evaluated its catalytic activity against several structurally distinct antibiotics including the tetracyclines oxytetracycline and tetracycline, the fluoro-quinolones ciprofloxacin hydrochloride and norfloxacin, and the sulfonamide sulfamethazin. As the degradation curves in Figure. 5a presents, pyrite removed oxytetracycline, ciprofloxacin, norfloxacin, and sulfamethazine by 85.4%, 86.1%, 86.4%, and 81.8% within 20 min, respectively. Figure. 5b demonstrates that these antibiotics possess diverse molecular structures, and pyrite is capable of effectively degrading three major categories of antibiotics, underscoring its promise for industrial-scale applications.

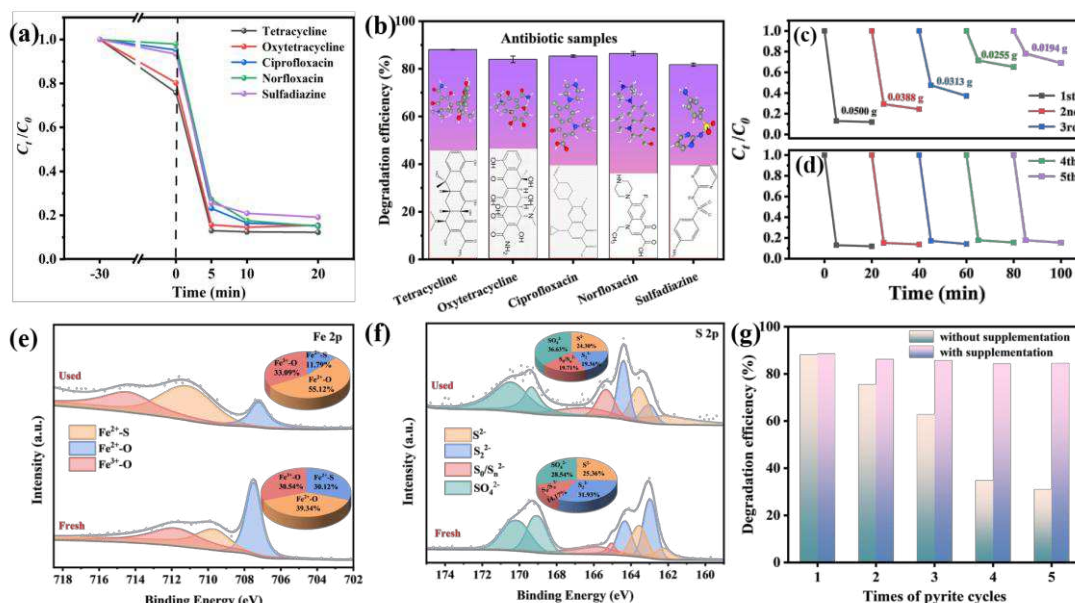


Figure 5. (a) Degradation profiles of different antibiotics catalyzed by natural pyrite; (b) degradation efficiency after 20 min of reaction (Fenton conditions: pyrite = $0.25 \text{ g} \cdot \text{L}^{-1}$, $\text{H}_2\text{O}_2 = 1 \text{ mM}$, each antibiotic = $20 \text{ mg} \cdot \text{L}^{-1}$); (c) Tetracycline -degradation plots over five reuse cycles without supplementation (Fenton conditions: $\text{H}_2\text{O}_2 = 1 \text{ mM}$, $\text{pH} = 5.47$, tetracycline = $20 \text{ mg} \cdot \text{L}^{-1}$); (d) Tetracycline -degradation plots over five reuse cycles with supplementation (Fenton conditions: pyrite = $0.25 \text{ g} \cdot \text{L}^{-1}$, $\text{H}_2\text{O}_2 = 1 \text{ mM}$, $\text{pH} = 5.47$, tetracycline = $20 \text{ mg} \cdot \text{L}^{-1}$); (e) Fe 2p XPS spectra, (f) S 2p XPS spectra of pyrite before and after five degrading cycles; (g) Comparison of Tetracycline Degradation Efficiency in Pyrite-Supplemented vs. Non-Supplemented Systems over 5 Cycles.

3.3.4. Cyclic Stability and Deactivation Mechanism of Pyrite

Cycling stability is a critical metric for evaluating the practical potential of a catalyst. After each degradation run, the spent pyrite was separated by centrifugation, washed alternately with deionized water and ethanol, dried, and reused in the next cycle. As depicted in Figure. 5c,d, the degradation efficiency of tetracycline progressively declined with each reuse cycle, dropping to 62.9% after three cycles and only 31.1% after five cycles. While mass loss due to dissolution (approximately 20% per cycle, Eq. (6)) is a significant factor, our analysis reveals that the deactivation is a more complex process involving the irreversible transformation of surface active sites.

The primary cause of activity loss was identified as the continuous depletion of the catalytically essential $\text{Fe}^{2+}\text{-S}$ and S_2^{2-} species. High-resolution XPS analysis provides direct evidence for this surface evolution (Figure. 5e,f). The Fe 2p spectrum

shows an 18.33% decrease in the Fe^{2+} -S signal, indicating the leaching of structural Fe^{2+} . Concurrently, the formation of a surface passivation layer is evidenced by a 15.78% increase in the Fe^{2+} -O component and a 2.55% rise in Fe^{3+} -O, suggesting the accumulation of iron hydroxides. More critically, the S 2p spectrum (Figure. 5g) reveals a pronounced consumption of the key electron-donor species, that is, the S_2^{2-} peak is significantly attenuated, while the SO_4^{2-} peak is enhanced. This irreversible oxidation of S_2^{2-} to SO_4^{2-} disrupts the S-mediated electron-transfer pathway that is crucial for efficient $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling. The disproportionate loss of sulfur species (a 12.57% decrease in elemental sulfur proportion) compared to the minor change in iron oxidation state underscores that sulfur depletion, not just iron transformation, is the dominant deactivation mechanism. This leads to a gradual passivation of the surface, blocking active sites and hindering the catalytic cycle.

To decouple the effects of physical mass loss from chemical surface deactivation, a catalyst supplementation experiment was performed. As shown in Figure. 5d,g, replenishing the pyrite to its initial mass after each cycle successfully restored the degradation efficiency, maintaining it at approximately 85% over five cycles. This confirms that physical depletion is the primary limiting factor for cyclic stability under these conditions. The XRD patterns (Figure. S2a) show retained crystal structure, and SEM images (Figure. S2b) indicate surface smoothing, both consistent with surface dissolution and oxidation rather than bulk phase change. While mass loss can be mitigated through supplementation, future work aimed at enhancing intrinsic stability should focus on protecting the sulfur lattice from oxidation, for instance, by engineering sulfur-rich surfaces or constructing protective composite structures.

3.4. Pyrite-driven degradation mechanism

3.4.1. Identification of reactive species

To determine which reactive oxygen species (ROS) govern tetracycline removal, four scavengers were applied, such as tert-butanol (TBA), isopropanol (IPA), chloroform, and L-histidine. TBA and IPA selectively quench $\cdot\text{OH}$ (TBA captures both

solution-phase and surface-bound $\cdot\text{OH}$, whereas IPA targets only bulk $\cdot\text{OH}$, chloroform traps superoxide ($\cdot\text{O}_2^-$), and L-histidine scavenges singlet oxygen ($^1\text{O}_2$) (Nie et al. 2022). As shown in Figure. 6a, adding TBA, IPA, L-histidine, and chloroform lowered the tetracycline removal efficiency from 88.1% to 40.7%, 49.8%, 56.8%, and 78.3%, respectively. Through the inhibitory effect, we semi-quantitatively calculated the relative contributions of various free radicals, among which $\cdot\text{OH}$ contributed the most, accounting for 55%. This was followed by $^1\text{O}_2$ and $\cdot\text{O}_2^-$, with contributions of 35% and 10%, respectively. The ESR results in Figure. 6b further confirm the presence of these free radicals.

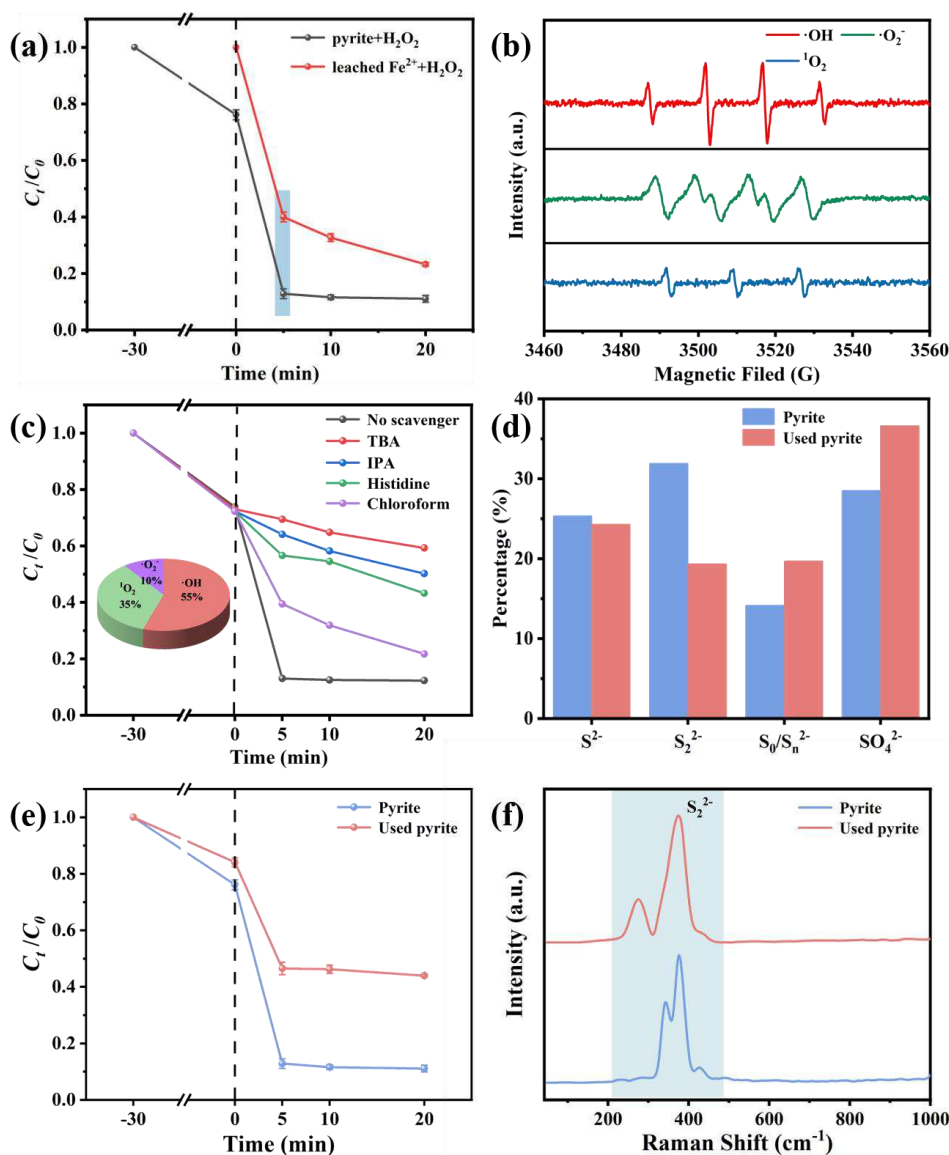


Figure. 6. (a) Effect of different scavengers on tetracycline degradation (Fenton conditions: pyrite = $0.25 \text{ g}\cdot\text{L}^{-1}$, $\text{H}_2\text{O}_2 = 1 \text{ mM}$, $\text{pH} = 5.47$, tetracycline = $20 \text{ mg}\cdot\text{L}^{-1}$), (b) ESR spectra of $\text{DMPO}\cdot\cdot\text{OH}$, $\text{DMPO}\cdot\cdot\text{O}_2^-$, and $\text{TMPO}\cdot\cdot\text{O}_2^-$ adducts: (c) Influence of leached iron on tetracycline degradation in the pyrite/ H_2O_2 system, (d) XPS ratios of various sulfur valence states before the reaction between pyrite and used pyrite, (e) Degradation curves of pyrite and used pyrite (Fenton conditions: catalyst = $0.25 \text{ g}\cdot\text{L}^{-1}$, 325 mesh, $\text{H}_2\text{O}_2 = 1 \text{ mM}$, tetracycline = $20 \text{ mg}\cdot\text{L}^{-1}$); (f) Raman spectra of natural pyrite before and after reaction.

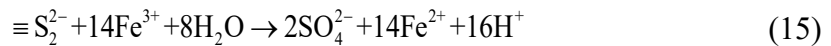
3.4.2. *Quantifying Homogeneous and Heterogeneous Contributions and Elucidating the S_2^{2-} -Mediated Catalytic Mechanism*

The ion leaching data (Figure. S3a) confirms that a significant homogeneous Fenton pathway is operational. After 30 min of adsorption, $1.98 \text{ mg}\cdot\text{L}^{-1}$ of dissolved Fe^{2+} (with no detectable Fe^{3+} , as verified by the potassium-thiocyanate test in Figure. S3b, $5.41 \text{ mg}\cdot\text{L}^{-1}$ of total dissolved sulfur (primarily as sulfite and sulfate) were present. The filtrate experiment (Figure. 6c) demonstrated that this leached Fe^{2+} alone could achieve 59% tetracycline degradation in 5 min, accounting for approximately 68% of the initial degradation in the pyrite/ H_2O_2 system. However, this alone cannot explain the system's sustained activity, as the homogeneous reaction would be self-limiting without a continuous supply of Fe^{2+} . The key to maintaining this supply, we hypothesize, lies in the electron-donating capability of lattice S_2^{2-} , which facilitates the reduction of Fe^{3+} on the pyrite surface.

To verify this hypothesis and emphasize the uniqueness of S_2^{2-} in pyrite, we designed a comparative experiment using pyrite after 5 cycles as a control. Based on Figure. 6d, we can see that the main difference between the two is in the S species rather than the Fe species (the Figure. 5e shows that there is no difference in the ratio of Fe^{2+} and Fe^{3+} before and after the reaction). Under the same reaction conditions ($0.25 \text{ g}\cdot\text{L}^{-1}$, $1 \text{ mM H}_2\text{O}_2$, $\text{pH} 5.47$), natural pyrite (with the highest intrinsic S_2^{2-} content) achieved a tetracycline degradation rate of about 90% within 5 minutes, while the latter only reached about 56% (Figure. 6e). Compare and analyze the crystal structure changes of fresh and reacted pyrite through Raman spectroscopy (Figure. 6f). Fresh pyrite exhibits typical characteristic peaks at 341 , 376 , and 430 cm^{-1} , belonging to the Eg, Ag, and Tg

vibration modes of S_2^{2-} dimer, respectively. After the reaction, the peak shape of pyrite widened, and the peak intensities at 341 and 430 nm decreased. This change indicates that the crystal structure of pyrite has been disrupted during the reaction process, and the local vibration environment of the S_2^{2-} group has been altered for oxidation. These results reveal a key trend. The S_2^{2-} peak is most prominent in pyrite. The positive correlation between the degree of oxidation of S_2^{2-} to SO_4^{2-} and the catalytic degradation rate provides convincing evidence that S_2^{2-} is not a passive bystander, but an active participant in driving the catalytic cycle.

Therefore, we propose a refined mechanistic model (Figure. 7) where S_2^{2-} serves as the electron-transfer hub. (1) In the homogeneous pathway, dissolved O_2 oxidizes pyrite, releasing Fe^{2+} and initiating the Fenton reaction (Eqs. (6)-(7)). Part of the Fe^{3+} formed is reduced back to Fe^{2+} by excess H_2O_2 (Eq. (8)), while another part is reduced on the mineral surface. Lattice disulfide (S_2^{2-}) acts as the main electron donor to convert Fe^{3+} to Fe^{2+} , sustaining the Fe^{2+}/Fe^{3+} redox cycle (Eq. (15)). (2) The heterogeneous pathway is initiated by surface $\equiv Fe^{2+}$ sites reacting with H_2O_2 (Eq. (4)). The key sustaining step, however, is the rapid reduction of the resulting surface $\equiv Fe^{3+}$. This is not primarily achieved by the slow reaction with H_2O_2 (Eq. (5)), but by the efficient electron transfer from the underlying S_2^{2-} lattice (Eq. 9). (3) Dissolved O_2 is activated both in the solution and on the surface to generate $\cdot O_2^-$ and $^1O_2$ (Eqs. (16)-(18)). Thus, the synergy between the homogeneous and heterogeneous pathways is orchestrated by the S_2^{2-} -mediated electron transfer. This mechanism not only explains the high initial efficiency driven by leached Fe^{2+} but also the sustained catalytic activity, underpinning the superior performance of natural pyrite over other iron sulfides.



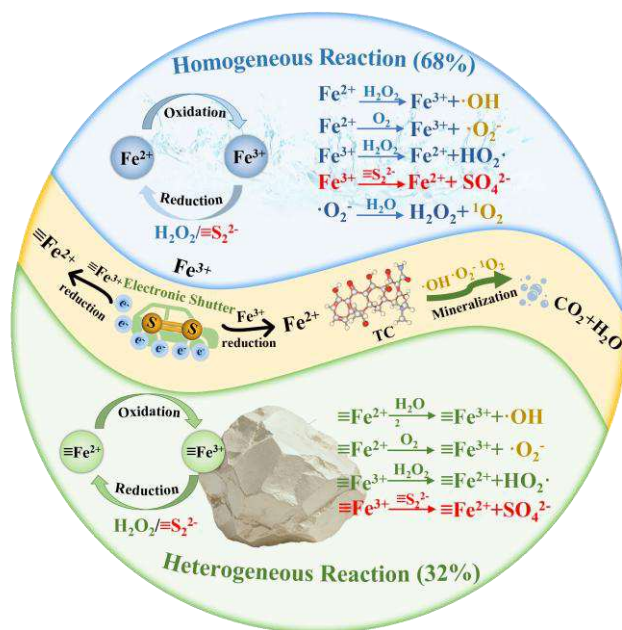


Figure. 7. Schematic diagram of the synergistic reaction mechanism for the degradation of tetracycline in the “pyrite + H₂O₂” system (blue represents homogeneous process, green represents heterogeneous process).

3.4.3. Degradation pathways of tetracycline

To gain deep molecular-level insights into the catalytic degradation mechanism of tetracycline by the “pyrite + H₂O₂” catalytic system, DFT calculations were performed to systematically analyze the electronic structure characteristics of the tetracycline molecule. Due to the high localized electron density of the HOMO (Figure. 8a) and the extremely high electrophilicity index (Table S2), these two functional groups act as electron-rich donors and are highly likely to become the primary targets for electrophilic species such as $\cdot\text{OH}$ and ${}^1\text{O}_2$. Based on the wavefunction distribution of the LUMO (Figure. 8a) and the nucleophilic attack f^+ of tetracycline (Table S2), three carbonyl oxygen atoms (O20, O22, and O23) exhibit strong electrophilicity. Consequently, the strongly nucleophilic superoxide radical $\cdot\text{O}_2^-$ preferentially attacks these carbonyl sites. In addition to the atom-based local reactive site analysis, the calculated bond dual descriptors (BDDs, Figure. 8b) further elucidate the cleavage mechanisms and selectivity of chemical bonds within the tetracycline backbone. The computational results demonstrate that the C16=C17 exhibits the most negative BDD value among all chemical bonds in the tetracycline molecule (reaching -0.117),

signifying its exceptionally strong nucleophilicity. In contrast, the highest positive BDD values (0.045) are observed for the C15–C16 and C2=C3, implying a highly electrophilic character for these two chemical bonds. Combined with the molecular electrostatic potential (ESP) isosurface (Figure. 8c), the C16=C17 and C15-C16 bonds are located in the central region of the molecule, precisely corresponding to the white electrostatically neutral transition zone. Consequently, the C2=C3 bond, which is situated in the electron-deficient region, is more susceptible to attack by $\cdot\text{O}_2^-$.

To confirm the theoretical insights obtained from DFT calculations, liquid chromatography-mass spectrometry (LC-MS) was utilized to identify the reaction intermediates, which revealed 12 possible intermediate species during tetracycline degradation (listed in Table S3), with their proposed structures shown in Figure. 8d. The LC-MS data support three parallel degradation routes:

(I) The parent ion at m/z 445 first loses the N-methyl group on its tertiary amine, giving m/z 431. Subsequent dehydration yields m/z 413. This demethylation process corresponds to the attack of electrophilic $\cdot\text{OH}$ and $^1\text{O}_2$ on the dimethylamino nitrogen atom (N30), which is highly consistent with the previous theoretical analysis. Subsequently, the m/z 431 loses a water molecule, yielding m/z 413. Oxidative deamination by $\cdot\text{OH}$ rapidly converts this species to m/z 371, which undergoes ring-opening to produce m/z 219 and m/z 241. These ring-opened fragments are further mineralised to CO_2 and H_2O (Z. Li et al. 2020). (II) Tetracycline is dehydroxylated to m/z 427; the newly exposed C=C bond is then oxidatively cleaved, forming m/z 392. Additional oxidative demethylation and substitution steps generate m/z 321, which fragments into smaller species such as m/z 165 before complete mineralization to CO_2 and H_2O (W. Wang et al. 2023). Because this pathway initiates with a dehydration reaction, which is a non-redox elimination process. It cannot be effectively predicted by static molecular descriptors such as Fukui functions and ESP. (III) The attack of $\cdot\text{O}_2^-$ on the carbonyl groups and double bonds induced nucleophilic addition and ring-opening rearrangement, this specific attack site is highly consistent with the DFT

predictions. The m/z 433 is obtained after the reaction. Further oxidation and deamination yield m/z 322. As the reaction proceeds, intermediate m/z 175 appears, indicating continued ring scission and terminal oxidation. These low-molecular-weight products eventually degrade fully to CO_2 and H_2O (Xu et al. 2020).

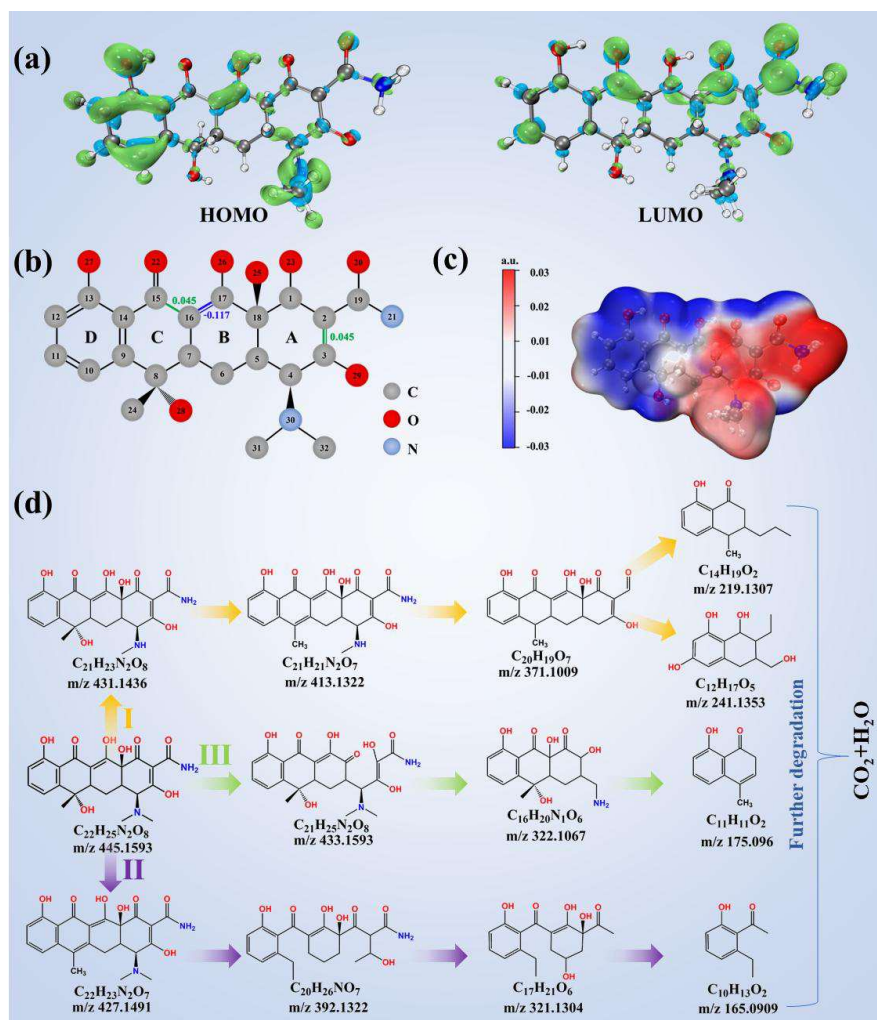


Figure 8. (a) HOMO and LUMO orbitals, (b) bond dual descriptors, and (c) ESP isosurfaces of tetracycline; (d) The possible degradation pathway of tetracycline in the “pyrite + H_2O_2 ” catalytic.

3.4.4. Toxicity evolution assessment of the degradation process

To comprehensively assess the ecological safety and health risks during tetracycline degradation, the acute aquatic toxicity, developmental toxicity, and mutagenicity were systematically evaluated for the parent molecule and its transformation products (TPs) (Figure. 9). Here, the acute toxicity was indexed by the 96 h LC_{50} for fathead minnow and *Daphnia magna*, and the numbers suffixed to the TPs represent their mass-to-charge ratios (m/z) detected via mass spectrometry. To

assess the acute toxicity of the system, the 96 h median lethal concentration (96-h LC₅₀) for fathead minnow and *Daphnia magna* was employed as the biological indicator (Figure. 9a, b). Generally, smaller LC₅₀ values denote greater acute lethal potency of a given compound. Notably, during the initial stage of degradation, certain intermediates (particularly P371 and P427) exhibited higher acute toxicity than the parent tetracycline. Mechanistically, this transient toxicity spike is primarily attributed to the oxidation of the tetracycline polycyclic skeleton into highly bioreactive quinone or ketene structures before complete ring-opening cleavage. Critically, the robust deep oxidation capacity of the “pyrite + H₂O₂” system guarantees that these high-toxicity intermediates are rapidly captured and sequentially transformed into less toxic or completely non-toxic small molecular products. As the reaction proceeded, a substantial reduction of nearly an order of magnitude was observed in the overall acute toxicity of the solution, providing compelling evidence for the effectiveness and eco-safety of this deep oxidation technology.

In the QSAR predictions of developmental toxicity and mutagenicity (Figure. 9c,d), a value of 0.5 typically serves as the safety threshold (prediction index greater than 0.5 denoting developmental toxicity or a positive mutagenic response). The evaluation results revealed that the untreated parent tetracycline was unambiguously classified as both “developmentally toxic” and “mutagenicity-positive.” Following catalytic degradation, although some intermediates still retained a certain degree of developmental toxicity, their quantitative prediction indices exhibited a significant decline compared to the parent compound. More significantly, the mutagenicity assessment revealed a decisive detoxification transition: the indices of as many as four specific mid-to-late stage degradation products (P241, P392, P219, and P175) dropped substantially, leading to their successful reclassification as “mutagenicity-negative”. From the perspective of overall environmental risk control, the generation of transient intermediates with residual toxicity is inevitable along the degradation pathway. However, the “pyrite + H₂O₂” catalytic system ultimately achieves a substantial

containment and remediation of the integrated ecological risk. This outcome fully validates the high reliability of the system for practical applications in antibiotic wastewater treatment.

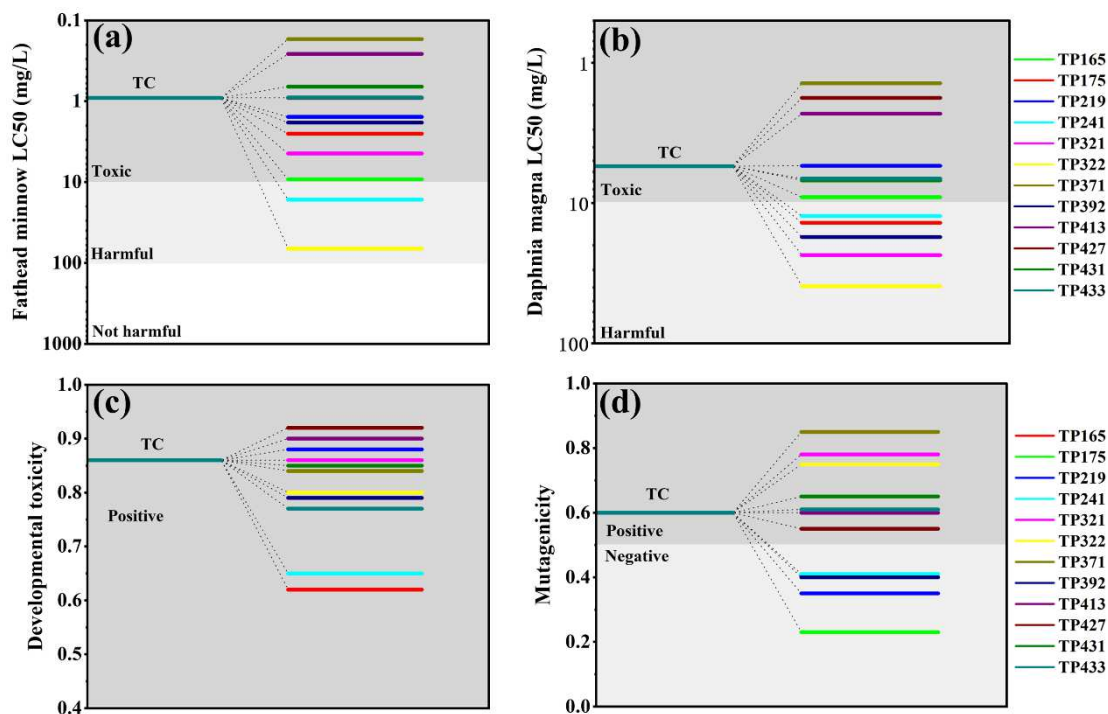


Figure 9. Tetracycline and its degradation intermediates: (a) 96-h LC_{50} for fathead minnow, (b) 96-h LC_{50} for *Daphnia magna*, (c) developmental toxicity, and (d) mutagenicity.

4. Conclusion

This study establishes natural pyrite as a highly efficient, cost-effective, and ecologically safe heterogeneous Fenton-like catalyst, achieving rapid tetracycline degradation (90% within 5 min, $k_{app} = 0.334 \text{ min}^{-1}$) under optimized dark conditions with remarkably low H_2O_2 demand (1 mM). The exceptional catalytic performance is fundamentally attributed to a synergistic mechanism dominated by sulfur-mediated electron transfer, wherein leached Fe^{2+} drives the homogeneous Fenton pathway (contributing ~68% of initial degradation), while lattice disulfide (S_2^{2-}) acts as a potent intrinsic electron donor to sustain surface Fe^{2+}/Fe^{3+} cycling. This mechanism, validated by comparative reactivity and spectroscopic analyses, ensures continuous multi-ROS ($\cdot OH$, $\cdot O_2^-$, $^1O_2$) generation. Integrating DFT calculations with LC-MS identification has precisely mapped the reactive sites and elucidated three parallel degradation

pathways, providing a molecular-level foundation for the observed kinetics. Crucially, beyond mere pollutant abatement, the system demonstrates a profound detoxification capacity. QSAR-based toxicity assessments confirm that although short-lived intermediates may exhibit transient ecotoxicity, the robust oxidative environment ensures their rapid conversion, culminating in a dramatic reduction of overall aquatic toxicity and the elimination of mutagenic potential, a critical criterion often overlooked in conventional catalytic studies. From a practical standpoint, the system exhibits superior operational stability, functioning effectively across a wide pH range (4.0-9.2), degrading multiple antibiotic classes (>80% efficiency), and resisting interference from environmental matrices. While gradual deactivation arises primarily from irreversible sulfur oxidation and mineral dissolution, a simple catalyst supplementation strategy successfully restores sustained performance over multiple cycles. This work not only elucidates the high-efficiency mechanism of natural pyrite but also validates its potential as a sustainable platform for practical antibiotic wastewater remediation, with future research directed toward stabilization strategies such as surface engineering or composite design to enhance long-term durability and enable resource recovery.

CRedit authorship contribution statement

Runchang Su: Writing – original draft, Visualization, Investigation. **Yuhang Liu:** Writing – review & editing, Formal analysis. **Mei Zhang:** Supervision, Project administration. **Min Guo:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China

(No. 52572312, U24A20555).

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