The Journal of Green Energy and Environmental Engineering

Research Paper

Study on the Degradation of Tetracycline by Biochar-Supported Nano Zero-Valent Iron Fenton-like Reaction System

Hafida Boussetta [1], Hassan Grimi [1], Sahar Solin [1], Tuuli Bras [2,*]

[1] Chemical Processes and Applied Materials Team, Polydisciplinary Faculty, Sultan Moulay Slimane University, BP 592, Beni Mellal, Morocco
[2] University Grenoble Alpes, CNRS, Grenoble INP, LGP2, Grenoble 38000, France

*Corresponding author: tuuli.bras@grenoble-inp.fr

Abstract. Tetracycline is a widely used antibiotic worldwide, and its residues in aquatic environments can cause persistent pollution, affect the ecological balance, and be harmful to human health. Fenton-like reaction is a commonly used advanced oxidation method for removing refractory organic pollutants, while nano-zero valent iron is a commonly used and efficient catalyst. In this study, biochar-nano zero valent iron (BC-nZVI) composite materials were prepared from food waste and peanut shells by liquid phase reduction method to construct a BC-nZVI+H2O2 Fenton-like system for the degradation of tetracycline in water. The degradation performance of the system, the influence of various experimental conditions, the reaction mechanism, and the catalytic performance and stability of BC-nZVI were investigated. Tetracycline degradation experiments on the prepared materials showed that when the preparation temperature of biochar was 280 °C and Fe:C=1:1, the material had the best performance. The iron loading capacity of the material was 426.5 mg/g, with good physical and chemical stability. After ten uses, BC-nZVI could still remove 79.05% of tetracycline. Characterization by FTIR, SEM, XRD, BET and other methods showed that nano-zero valent iron could be uniformly loaded on biochar, and BC-nZVI materials had a large specific surface area and rich pores. The optimal experimental conditions were determined as follows: initial concentration of tetracycline 30 mg/L, material dosage 0.1 g/L, H2O2 concentration 0.27 g/L, pH=4.0. The reaction orders for the dosage of BC-nZVI material, the initial concentration of hydrogen peroxide, and the initial concentration of tetracycline were 0.8374, 0.5737, and 0.2324, respectively.

Keywords: *Biochar; BC-nZVI; Fenton-like; Tetracycline*

Received on 15 Sep 2024, Accepted on 15 Oct 2024, Published on 15 Dec 2024

1 Introduction

The biochar-supported nanoscale zero-valent iron Fenton-like system entails immobilising nanoscale zero-valent iron (nZVI) onto biochar to yield BC-nZVI composites that serve as H_2O_2 activators, thereby establishing a Fenton-like catalytic regime. This effectively prevents nZVI agglomeration, improves iron utilization, and addresses issues of high catalyst loss and sludge production in traditional Fenton oxidation. nZVI can easily generate Fe^{2+} in acidic aqueous solutions, which then catalyzes H_2O_2 decomposition to produce free radicals, removing organic pollutants from water [1].

Biochar is a dark, porous solid produced via carbonisation of waste biomass or thermolysis of organic matter. Many inexpensive and readily available biomass sources, such as crop straws, kitchen waste, natural wood, fallen leaves, some industrial by-products, and various sludges, can be used to prepare biochar. Biochar preparation typically involves pyrolysis and hydrothermal carbonization. Its final properties (pore structure, specific surface area, surface functional groups, elemental composition, etc.) largely depend on the raw material type and carbonization conditions, such as temperature, heat transfer, residence time, and pressure [2]. Pyrolysis is a method to prepare biochar by reacting biomass at 300–900°C under anaerobic or oxygen-deficient conditions.

The original surface morphology of the biomass raw material remains unchanged during pyrolysis, but a porous structure forms during high-temperature devolatilization. Additionally, the H/C and O/C ratios significantly decrease, generating abundant aromatic bonds. Due to the high pyrolysis temperature, the biomass crystallinity is high, giving the product a distinct graphite structure. Hydrothermal carbonization refers to preparing biochar at lower temperatures (150–300°C). The resulting product has uniform size, stable physicochemical properties, and a surface rich in oxygen-containing functional groups, making it suitable as a catalyst carrier. This method offers high material conversion rates (usually over 90%), low cost, strong adaptability, and good controllability. In practical applications, raw material type, economic feasibility, and operability must be considered. Kitchen waste, comprising carbohydrates, proteins, and lipids, is a high-quality raw material for biochar preparation, while also reducing environmental pressure. Hydrothermal carbonization reactions occur in water. Despite the complex composition of kitchen waste, they undergo steps such as hydrolysis, dehydration, decarboxylation, aromatization, and polycondensation [3]. Owing to its expansive surface area and porosity, biochar finds extensive application in remediating deleterious contaminants across soil, sediment and aqueous matrices. To further augment its functionality, diverse modification strategies—encompassing coating, functionalisation, impregnation, loading, incorporation as support materials or composite fabrication—have been deployed upon pristine biochar, extending its utility as a catalytic scaffold [4]. Nguyen et al. [5] used sunflower seed shells as raw material, successfully prepared biochar via hydrothermal carbonization at 180°C for 6 hours with $ZnCl_2$ impregnation and heating, which showed good adsorption capacity for tetracycline over a wide pH range. Wu et al. [6] prepared a biochar with high adsorption capacity for pesticides by hydrothermal carbonization of rice husk and chicken manure at an appropriate ratio, simultaneously enhancing hydrogen production capacity.

Nanoscale zero-valent iron (nZVI) is extensively employed for eliminating environmental contaminants—spanning heavy metals, organics and inorganics in wastewater—by virtue of its elevated reactivity, potent adsorption-reduction capability and environmental compatibility. However, nZVI particles exhibit pronounced aggregation in aqueous media attributable to high surface energy and strong magnetic forces, potentially diminishing reactivity and compromising target pollutant removal efficiency. Moreover, the inherent chemical instability of nZVI renders it susceptible to oxidation, curtailing its environmental longevity [7]. Consequently, modification strategies are actively pursued to enhance performance. Biochar, functioning as a support matrix, effectively anchors nZVI, mitigates agglomeration and furnishes supplementary reactive sites [8]. The loading of nanoparticles on BC carriers may involve various mechanisms: adsorption, immobilization, coordination, chelation, and bridging. Preparation methods are mainly divided into physical and chemical methods. Physical methods include mechanical ball milling, severe plastic deformation, evaporation-condensation, freeze-drying, and deposition. Chemical methods include electrochemical deposition, pyrolysis, microemulsion, and liquid-phase reduction. Liquid-phase reduction is widely used due to low preparation cost, environmental friendliness, and the ability to maintain an average nZVI particle size below 100 nm. The biochar-nZVI pairing delivers multiple benefits: (1) biochar's substantial specific surface area and abundant porosity afford robust pollutant adsorption while effectively dispersing nZVI particles and shielding them from oxidation; polar surface functionalities (e.g., –COOH, –OH) further enhance composite dispersibility in aqueous media. Furthermore, the expanded surface area supplies additional nucleation sites for precipitate formation, while abundant oxygenated surface groups complex and sequester aqueous ions, thereby safeguarding nZVI against oxidative degradation. (2) Electron transfer is markedly enhanced: quinone and phenolic moieties on biochar engage in redox cycling, mediating electron shuttling. The conjugated aromatic framework and oxygenated functionalities of biochar contribute significantly to electron-donating capacity [9,10]. Ya et al. [11] fabricated phosphate-functionalised biochar-supported nZVI composites; P-BC/nZVI markedly outperformed pristine P-BC and nZVI in Cr(VI) sequestration through a multifaceted mechanism encompassing adsorption, reduction, surface complexation and coprecipitation. At a P-BC:nZVI mass ratio of 3:1, near-quantitative Cr(VI) removal (~97%) was attained within 30 min. Rong et al. [12] synthesised PE-FeNPs@BC by immobilising pear-peel-extract-stabilised iron nanoparticles (PE-FeNPs) onto corn-stalk biochar (BC), achieving uniform dispersion and reduced agglomeration. Under 45 °C and pH 3.7, PE-FeNPs@BC removed 98.97 % of vanadium, surpassing bare BC by 63.9 %.

This experiment utilizes inexpensive and readily available kitchen waste as a raw material for material synthesis, demonstrating good economic efficiency and providing reference value for the development of new environmentally friendly catalytic materials. Through experiments, the influence of various factors in the reaction system on degradation efficiency was determined. Additionally, the stability and reusability of the material were explored, and the mechanism of degradation of tetracycline in the reaction system was analyzed, providing a

theoretical basis for practical tetracycline wastewater treatment and indicating broad application prospects.

2 Materials and Methods

2.1 Tetracycline Degradation and Mechanism Study Experiments

2.1.1 Degradation of Tetracycline by BC-nZVI Fenton-like System

First, the standard curve of tetracycline was plotted. A 30 mg L^{-1} tetracycline stock was prepared; aliquots were transferred to volumetric flasks and brought to mark with deionised water to yield working standards of varying concentrations. The pH was adjusted to 2, 3, 4, 5, 7, and 9, and the absorbance was measured to plot the standard curve of tetracycline under different pH conditions. The degradation performance experiment of different materials was carried out in a 250 mL conical flask. 200 mL of simulated wastewater containing 30 mg/L tetracycline was measured, the initial pH was adjusted to 5.0, H_2O_2 solution was added to achieve an H_2O_2 concentration of 5 mmol/L, and 14 mg of different BC-nZVI materials were added to initiate the heterogeneous Fenton reaction. Aliquots were withdrawn at 0, 5, 10, 20, 40, 70, 130, 250, 370, 610 and 850 min, filtered through 0.45 μm membranes, and absorbance was recorded at 359 nm by UV-Vis spectrophotometry. Based on the obtained data, degradation curves were plotted, and combined with characterization results, materials with better degradation effects were selected for subsequent experiment.

Using the prepared tetracycline-laden wastewater as target, the impact of reaction duration, initial pH, H_2O_2 concentration, catalyst loading and initial tetracycline concentration on degradation efficiency was systematically examined. The tetracycline degradation situation (C/C_0) vs. time (t) curve was plotted to determine the experimental conditions of each influencing factor in the H_2O_2 + BC-nZVI Fenton-like system.

2.1.2 Degradation of Tetracycline by Different Reaction Systems

The degradation effects of different components on tetracycline were studied. Simulated tetracycline wastewater was treated under fixed conditions (pH 4.0, 30 mg L^{-1} initial tetracycline, 0.1 g L^{-1} catalyst, 0.27 g L^{-1} H_2O_2) with H_2O_2, nZVI, BC, BC-nZVI, nZVI/H_2O_2, BC/H_2O_2 or BC-nZVI/H_2O_2 added individually. Samples were withdrawn at intervals, filtered through 0.45 μm membranes, and analysed spectrophotometrically at 359 nm to construct degradation profiles, evaluate component-specific effects on tetracycline removal, and delineate mechanistic contributions.

2.1.3 Free Radical Quenching Experiment

This study explored the primary free radical species responsible for tetracycline degradation by implementing selective quenching experiments. Specifically, tert-butanol and p-benzoquinone were introduced into the BC-nZVI/H_2O_2 system to selectively eliminate hydroxyl radicals and superoxide radicals, respectively, thereby identifying their individual contributions to the antibiotic's breakdown. The removal effect of tetracycline under different conditions was observed. The initial conditions were pH=4.0, initial tetracycline concentration 30 mg/L, material dosage 0.1 g/L, hydrogen peroxide concentration 0.27 g/L.

2.2 BC-ZVI Catalytic Decomposition of H_2O_2 Experiment

To examine the kinetic behavior of hydrogen peroxide decomposition catalyzed by BC-ZVI, temporal monitoring of H_2O_2 concentration was essential for reaction classification. The experimental protocol involved preparing a predetermined concentration of hydrogen peroxide in an Erlenmeyer flask, followed by introduction of accurately quantified BC-ZVI catalyst. The reaction mixture was subsequently subjected to continuous agitation at 180 revolutions per minute while maintaining isothermal conditions at 20°C throughout the experimental duration. Every five minutes, a small amount of solution was taken, filtered, added to a centrifuge tube, mixed with a certain amount of 5% titanium sulfate and concentrated ammonia water, centrifuged to remove the supernatant, dissolved in sulfuric acid, and then subjected to the same operation as the standard curve at 0, 5, 10, 15, 20, 25, and 30 minutes for constant volume colorimetry. The decomposition curve was plotted, and the reaction order was fitted to analyze the kinetic process of the reaction.

2.3 Determination of Tetracycline Degradation Intermediates

To elucidate the degradation pathway of tetracycline within this reaction system, the structural characteristics of intermediate metabolites were identified through liquid chromatography-mass spectrometry analysis. The experimental procedure was conducted under standardized operational parameters: solution acidity maintained at pH 4.0, initial antibiotic concentration set at 30 mg/L, catalyst loading at 0.1 g/L, and oxidant concentration at 0.27 g/L. Temporal sampling was performed at six distinct intervals (0, 15, 30, 60, 120, and 240 minutes), with 100 mL aliquots collected at each time point. These samples underwent membrane filtration (0.45 μm pore size), subsequent analyte preconcentration via solid-phase extraction methodology, and final reconstitution in 5 mL methanolic solvent for instrumental analysis. The instrument used in this experiment was a Waters Xevo G2 Q-TOF liquid chromatography-tandem mass spectrometer. Detection conditions: injection volume: 5 μL; ESI+ mode; voltage: 4000 V; scanning m/z range: 50-500 amu. The ion transmission system and collision chamber used "T-WAVE" technology to reduce cross-contamination and improve sensitivity.

2.4 Repeatability Experiment

To evaluate the reusability performance of both nZVI and BC-nZVI catalysts, consecutive degradation cycles were conducted under fixed operational parameters: aqueous pH maintained at 4.0, initial tetracycline loading at 30 mg/L, catalyst concentration at 0.1 g/L, and hydrogen peroxide dosage at 0.27 g/L. At the end of the experiment, the reacted nZVI and BC-nZVI materials were collected by suction filtration, washed and suction filtered, dried in a vacuum drying oven, and the taken materials were added to the solution under given conditions and continued to be used for degradation experiments. The experimental conditions were the same as the initial conditions, and they were recycled 10 times to obtain the removal effects of tetracycline by the two materials upon reuse for comparative analysis.

3 Results and Discussion

3.1 Single-Factor Experiments

Univariate experimental design was employed to establish optimal reaction conditions, wherein each operational parameter was systematically modified in isolation while maintaining all remaining variables at fixed baseline levels.

3.1.1 Effect of Catalyst Dosage on the Reaction System

Aqueous solutions containing tetracycline at 30 mg/L were formulated in 200 mL portions to simulate antibiotic-laden wastewater. The reaction medium was acidified to pH 5.0, followed by introduction of hydrogen peroxide to attain a molar concentration of 5 mmol/L. Varying quantities of BC-nZVI catalyst were dispensed into individual reaction vessels, which were subsequently incubated in a thermostated orbital shaker operating at 180 rpm. Temporal sampling was executed at predetermined intervals spanning 0 to 850 minutes, with collected specimens filtered through 0.45 μm pore-size membranes. Residual tetracycline levels were quantified via spectrophotometric detection, enabling construction of temporal degradation profiles.

Experimental findings illustrated in Figure 1 demonstrate a positive correlation between catalyst loading and tetracycline elimination efficiency within the range of 0.06 to 0.1 g/L. Specifically, incremental augmentations in BC-nZVI concentration yielded progressive enhancement in antibiotic removal performance, with elimination percentages escalating from 69.92% at the lowest tested dosage (0.06 g/L) to 85.55% at the optimal loading of 0.1 g/L. Intermediate dosages of 0.07, 0.08, and 0.09 g/L corresponded to removal efficiencies of 73.83%, 78.09%, and 81.65%, respectively, indicating a consistent upward trajectory in treatment efficacy with increasing material input up to the saturation threshold. This enhancement is attributed to the increase in active sites available for catalyzing H_2O_2 decomposition, leading to greater •OH radical generation. However, beyond 0.1 g/L (e.g., 0.11 g/L, 85.75% removal), the efficiency plateaued or slightly decreased. This is likely due to excess Fe^{2+} scavenging •OH radicals (forming less reactive •HO_2) and potential consumption of oxidants by the biochar support itself. Therefore, the optimal catalyst dosage was determined to be 0.1 g/L.

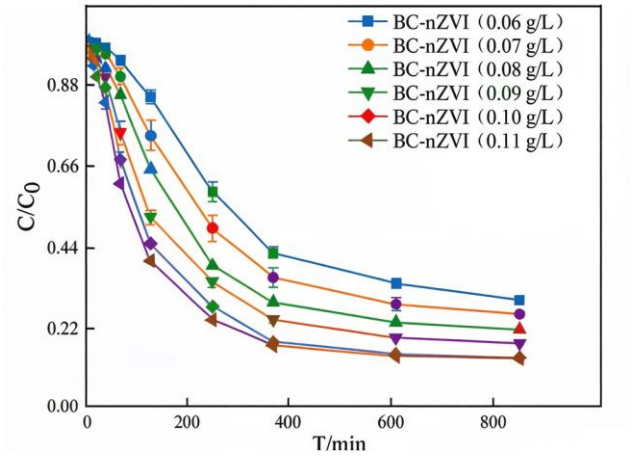

Figure 1 Effect of different material dosages on the degradation efficiency of tetracycline

3.1.2 Effect of Hydrogen Peroxide Concentration on the Reaction System

Experiments were conducted with varying initial H_2O_2 concentrations (0.12, 0.17, 0.22, 0.27, 0.32 g/L) while keeping other parameters constant (TC=30 mg/L, pH=5.0, BC-nZVI=0.1 g/L). The degradation was monitored over time.

As depicted in Figure 2, tetracycline elimination exhibited a concentration-dependent response to oxidant availability, with degradation performance intensifying progressively as H_2O_2 dosage increased from 0.12 to 0.27 g/L. The corresponding removal efficiencies demonstrated steady improvement across this gradient, registering 82.32% at the minimal oxidant level, advancing to 85.55% and 89.26% at intermediate concentrations, and ultimately reaching 94.76% at the optimal hydrogen peroxide loading of 0.27 g/L. Higher H_2O_2 concentrations provide more precursors for •OH radical generation. However, at 0.32 g/L, the efficiency slightly decreased to 94.71%. This is because excess H_2O_2 can scavenge •OH radicals (H_2O_2 + •OH → H_2O + •HO_2), producing hydroperoxyl radicals (•HO_2) and superoxide radicals (•O_2^-), which are less effective oxidants. Thus, 0.27 g/L was selected as the optimal H_2O_2 concentration.

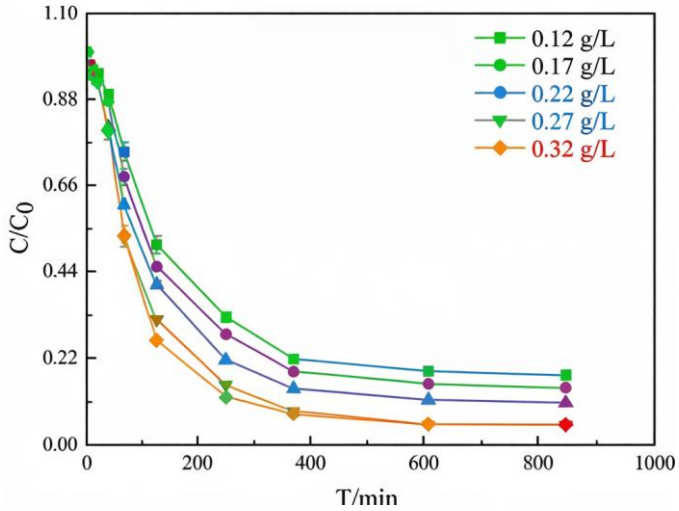

Figure 2 Effect of different hydrogen peroxide concentrations on the degradation efficiency of tetracycline

3.1.3 Effect of Initial Tetracycline Concentration on the Reaction System

The influence of varying initial pollutant loadings on treatment efficacy was systematically evaluated across a concentration spectrum spanning 10 to 50 mg/L. These investigations were performed under previously

established favorable reaction conditions, comprising a catalyst concentration of 0.1 g/L, an oxidant level of 0.27 g/L, and solution acidity maintained at pH 5.0.

Figure 3 shows that the degradation efficiency initially increased with TC concentration, reaching a maximum of 94.76% at 30 mg/L, with rates of 86.01%, 89.19% at 10 and 20 mg/L, respectively. At higher concentrations (40 and 50 mg/L), the efficiency slightly decreased to 93.47% and 93.39%. This trend suggests that at lower concentrations, the active sites and radicals are sufficient for degradation. At very low concentrations, the driving force for adsorption and reaction might be lower. At higher concentrations, the available active sites and radicals become limiting, leading to a slight reduction in efficiency. Therefore, 30 mg/L was chosen for subsequent experiments.

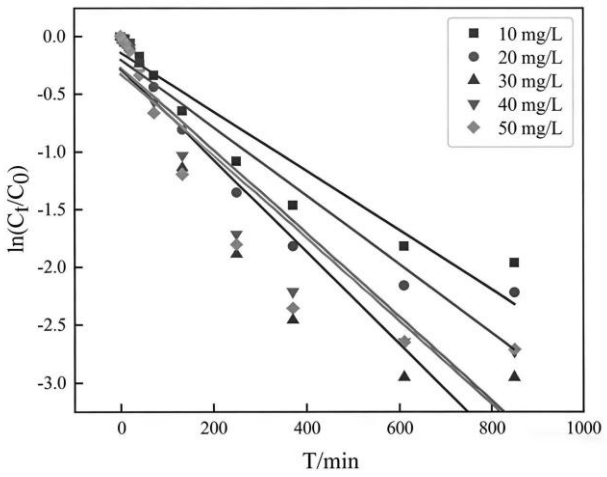

Figure 3 Effect of different initial tetracycline concentrations on the degradation efficiency

3.1.4 Effect of Initial pH on the Reaction System

Aqueous acidity constitutes a governing determinant in Fenton-analogous oxidation processes. Systematic investigations were undertaken to assess pH-dependent behavior across a diversified acidity gradient (2.0–9.0), with experimental parameters standardized as follows: antibiotic substrate concentration of 30 mg/L, nanocomposite catalyst loading of 0.1 g/L, and peroxide oxidant concentration of 0.27 g/L.

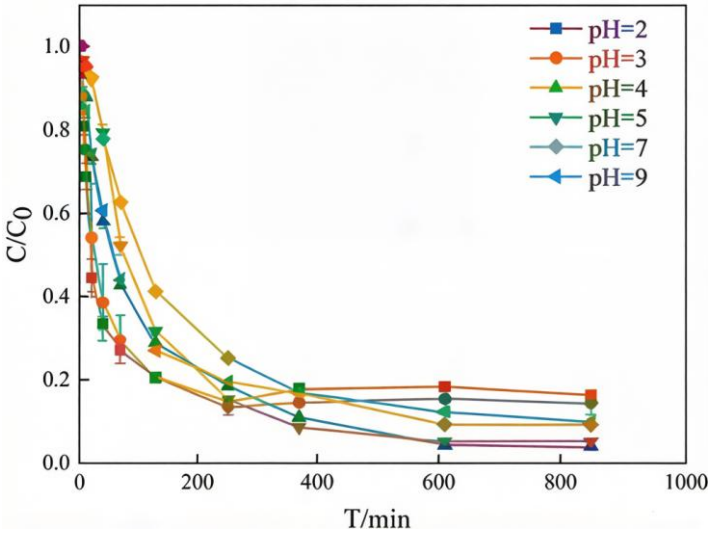

Figure 4 Effect of different initial pH conditions on the degradation efficiency of tetracycline

Experimental outcomes presented in Figure 4 reveal pronounced pH-dependent performance characteristics, with optimal functionality restricted to acidic operational windows. Maximum pollutant elimination (95.92%) was attained at moderately acidic conditions (pH 4.0), whereas diminished efficacy was recorded under strongly acidic environments (pH 2.0–3.0). Marked deterioration in treatment performance occurred upon transitioning toward neutral and alkaline regimes, with substantially reduced removal efficiencies observed at pH 7.0 and 9.0. In strongly acidic conditions (pH 2-3), although Fe^{2+} leaching is high, the predominant species $H_3O_2^+$ can stabilize H_2O_2, reducing its activation. Additionally, high H^+ concentration may favor side reactions. At pH > 5, iron precipitates as hydroxides (e.g., $Fe(OH)_3$), deactivating the catalyst and reducing •OH generation. The BC-nZVI composite showed a relatively wider effective pH range compared to traditional Fenton systems, highlighting the stabilizing effect of the biochar support. The optimal initial pH was determined to be 4.0.

3.2 Kinetic Equation Fitting and Determination of Reaction Order

To gain mechanistic insight into the temporal evolution of substrate depletion, empirical observations were mathematically analyzed through application of two conventional kinetic formalisms: the mono-phasic exponential decay model and the bi-molecular rate expression. The pseudo-first-order model provided a better fit, as indicated by higher correlation coefficients (R^2).

The degradation data for different BC-nZVI dosages were fitted to the pseudo-first-order model. The plots of $\ln(C_t/C_0)$versus time tare shown in Figure 5.

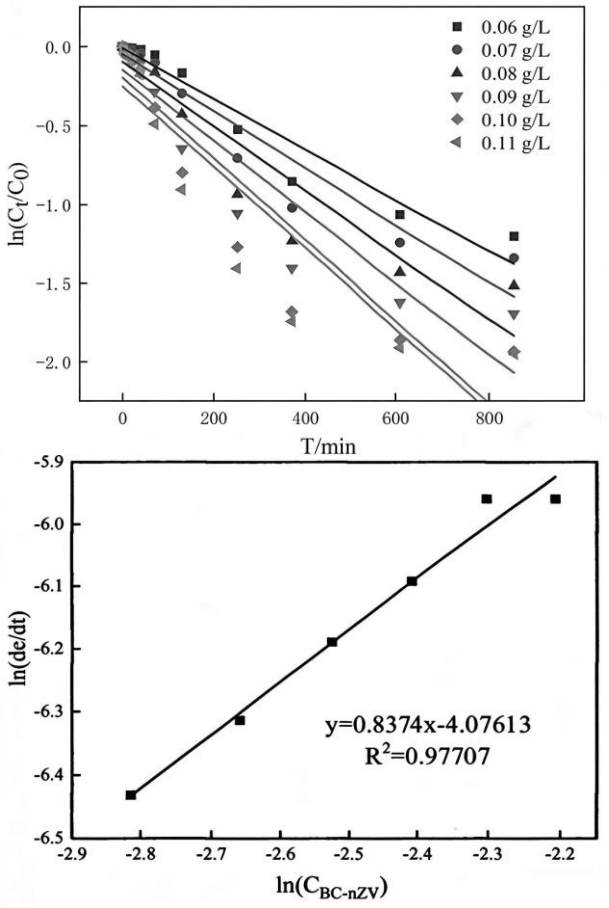

Figure 5 Relationship between ln(Ct/C0) and time under different material addition amounts (a); Reaction order fitting for different material dosages (b)

Comparative evaluation employing the bi-molecular kinetic formalism yielded inferior statistical descriptors, with diminished coefficients of determination substantiating the superior applicability of the mono-exponential

decay framework. This investigation systematically elucidated the modulatory influences of principal operational variables—including catalyst loading, oxidant concentration, initial substrate abundance, and solution acidity—on antibiotic elimination efficiency within the heterogeneous Fenton-analogous system comprising biochar-supported nanoscale zero-valent iron and hydrogen peroxide. Optimized operational specifications were established through systematic parametric evaluation, yielding the following favorable reaction conditions: initial antibiotic loading of 30 mg/L, biochar-supported nanoscale zero-valent iron concentration of 0.1 g/L, hydrogen peroxide availability at 0.27 g/L, and aqueous medium acidity regulated at pH 4.0. Degradation kinetics conformed to first-order behavior, with fractional orders of 0.8374 (BC-nZVI), 0.5737 (H_2O_2), and 0.2324 (tetracycline) determined via parametric analysis. These values indicate that the reaction rate is most sensitive to changes in catalyst concentration, followed by H_2O_2 concentration, and is least sensitive to changes in the initial pollutant concentration under the studied conditions. The results demonstrate the high efficiency and tunability of the BC-nZVI/H_2O_2 system for tetracycline degradation, providing a solid foundation for further mechanistic studies and potential application.

3.3 Study on the Catalytic Performance of BC-nZVI for Hydrogen Peroxide Decomposition

3.3.1 Electron Paramagnetic Resonance (EPR) Detection of Free Radicals

DMPO-assisted EPR spectroscopy was utilized to verify transient oxidizing intermediate formation during the catalytic process. Spectrometric data exhibited the diagnostic 1:2:2:1 quadruplet pattern characteristic of DMPO-OH spin adducts, confirming ·OH production in the BC-nZVI/peroxide system. The intensity of the characteristic peaks gradually increases with reaction time, indicating continuous generation of ·OH radicals (Figure 6).

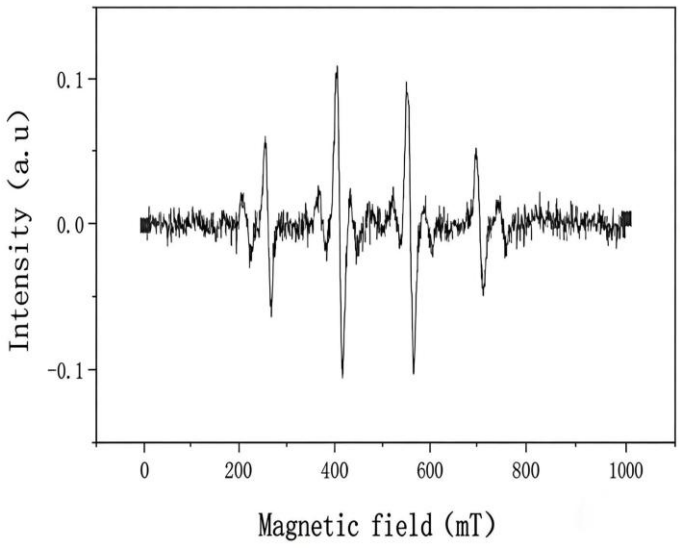

Figure 6 Determination of free radicals produced by decomposition of hydrogen peroxide

3.3.2 Reaction Kinetics of H_2O_2 Catalytic Decomposition

We systematically investigated the kinetic process of H_2O_2 decomposition catalyzed by BC-nZVI. The concentration changes of H_2O_2 were monitored using the titanium sulfate spectrophotometric method, and the results are shown in Table 1.

The reaction order n = 1.0709 indicates that the decomposition is approximately first-order with respect to H_2O_2 concentration. The high degradation efficiency (95% within 30 minutes) demonstrates the excellent catalytic activity of BC-nZVI.

Table 1 Changes in H_2O_2 concentration during the catalytic decomposition process

Time (min)	0	5	10	15	20	25	30
Absorbance	0.869	0.575	0.431	0.255	0.178	0.099	0.047
Concentration (μmol/mL)	2.5	1.65	1.235	0.725	0.505	0.275	0.125

3.3.3 Hydroxyl Radical Generation Kinetics

Using the salicylic acid method, we quantitatively monitored the generation of ·OH radicals. Salicylic acid captures ·OH to form 2,3-dihydroxybenzoic acid, which has a characteristic absorption peak. Empirical observations indicated rapid accumulation of hydroxyl radicals during the initial 20-minute interval, subsequently approaching steady-state levels (Table 2).

Table 2 Changes in hydroxyl radical concentration during the reaction

Time (min)	0	5	10	15	20	25	30
Absorbance	0.000	0.128	0.187	0.239	0.257	0.269	0.272

Results indicates that the ·OH generation rate is closely related to the concentration of intermediate products.

3.4 Degradation Performance of Different Reaction Systems

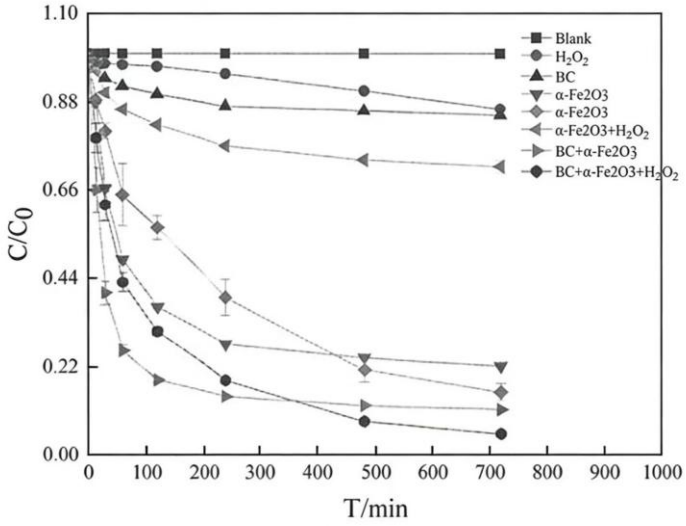

Figure 7 Degradation of tetracycline by Various reaction systems

To distinguish between adsorptive and catalytic contributions of BC-nZVI constituents within the Fenton-analogous system, parallel degradation trials were executed utilizing individual material components and their combinations. Component-specific functionality in antibiotic elimination was systematically evaluated under standardized conditions: 200 mL of synthetic wastewater containing 30 mg/L tetracycline at pH 4.0. (1) No H_2O_2 solution or material was added, serving as a blank control. (2) H_2O_2 solution was added to achieve an H_2O_2 concentration of 0.27 g/L. (3) 20 mg of biochar (BC) was added. (4) 20 mg of nano zero-valent iron (nZVI) was added. (5) 20 mg of BC-nZVI material was added. (6) H_2O_2 solution was added to achieve an H_2O_2 concentration of 0.27 g/L, and 20 mg of biochar was added. (7) H_2O_2 solution was added to achieve an H_2O_2 concentration of 0.27 g/L, and 20 mg of nano zero-valent iron was added. (8) Peroxide was introduced to attain 0.27 g/L, followed by 20 mg BC-nZVI addition. Reactions proceeded at 180 rpm, 20°C, with periodic sampling for C/C_o temporal profiling.

As shown in Figure 7, in the reaction system with only H_2O_2 added, the degradation rate of tetracycline was 13.77% after 720 minutes of reaction. The degradation curve is relatively stable, because the reaction system involves the direct reaction between hydrogen peroxide and tetracycline and the degradation caused by free radicals generated from the natural decomposition of hydrogen peroxide. The reaction process is relatively slow, which is similar to the research results of Ge et al. [13], where tetracycline was almost undegraded in a short time without material addition. In the system with BC added, the final removal rate of tetracycline was 15.35%. Literature demonstrates that biochar surfaces are enriched with oxygenated functional moieties, substantially augmenting their sorptive affinity [14]. Additionally, the extensive specific surface area and porous architecture of biochar facilitate efficient tetracycline sequestration. Prior investigations have delineated the adsorption mechanism into three sequential phases: boundary layer diffusion, progressive surface uptake, and ultimate saturation [15]. The pronounced initial slope reflects film diffusion, wherein antibiotic molecules migrate from bulk solution to the biochar exterior. The subsequent phase exhibits accelerated uptake kinetics, corresponding to intraparticle transport and active site binding. The attenuated terminal slope signifies sorptive equilibrium, where adsorptive and desorptive fluxes equilibrate. This plateau may originate from diminished site availability, electrostatic repulsion between aqueous and surface-bound antibiotic species, or depleted bulk-phase substrate concentrations. After the active sites of biochar are gradually occupied, the adsorption capacity weakens, and the removal rate curve tends to flatten, eventually reaching equilibrium [16]. This is similar to the research results of Wang et al. [104], who prepared biochar from bagasse for adsorbing tetracycline in water and obtained an adsorption curve with three distinct adsorption stages. In the system with only nano zero-valent iron added, the degradation rate of tetracycline at 720 minutes was 77.82%. Nanoscale zero-valent iron exhibits substantial sorptive affinity attributable to its diminutive particle dimensions and expansive surface-to-volume ratio. Concurrently, its elevated reduction potential facilitates facile electron transfer upon interaction with tetracycline molecules. In this process, zero-valent iron itself is oxidized while rapidly reducing tetracycline [17]. In an anaerobic environment, H_2O or H^+ oxidizes zero-valent iron, producing Fe^{2+} and H_2. Besides Fe^0, Fe^{2+} and H_2 may also play a role in reducing tetracycline in this degradation system [106], as shown in as follows:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$$

In the process of tetracycline removal by nZVI, the entire mechanism involves different reactions in different sequences, such as adsorption, reduction, precipitation, and oxidation [18]. In the reaction system with BC-nZVI material added, the removal rate of tetracycline at 720 minutes was 84.22%. In this system, the degradation of tetracycline mainly consists of two parts: biochar adsorption and the reduction by zero-valent iron. Compared to the system with only BC added, the degradation rate of tetracycline in this system is much higher, indicating that the reduction of tetracycline by nano zero-valent iron plays a dominant role in the degradation process. Compared to the system with only nZVI added, the initial reaction rate is slower, but the degradation rate increases with longer reaction time, and the removal effect is better than the nZVI reaction system. This is because nZVI gradually oxidizes during the reaction and tends to agglomerate, leading to reduced catalytic activity and decreased specific surface area [19]. Within the BC-nZVI composite, ferric or ferrous cations coordinate with biochar oxygenated functionalities via bidentate complexation. Additionally, the superficial iron oxide shell surrounding the metallic core establishes stable interfacial linkages with the carbonaceous matrix. This phenomenon reduces the interparticle attraction, thereby decreasing the agglomeration of nZVI and making it more uniformly distributed on the biochar surface [20]. The synergistic effect of BC-nZVI depends on the adsorption capacity of BC and the reducibility of nZVI for pollutant remediation. Biochar can not only transfer electrons through its own functional groups but also promote the redox reaction between zero-valent iron and tetracycline, thereby improving the removal efficiency. In the system with biochar and hydrogen peroxide added, when the reaction proceeded to 720 minutes, the removal rate of tetracycline was 20.07%. The main removal mechanisms are the adsorption by biochar itself and the degradation of tetracycline by free radicals generated from the catalysis of hydrogen peroxide. The extensive surface area and rich functionality of biochar significantly contribute to antibiotic attenuation within the integrated system [21]. Typically, oxygenated surface moieties mediate the sequestration of organic contaminants. BC mainly has two types of oxygen-containing functional groups: (1) acidic groups, such as hydroxyl and carboxyl groups, etc. (2) basic groups, such as the functional groups of chromenes and pyrones obtained after carbonization and pyrolysis [22]. In advanced oxidation systems based on Fenton, the -OH functional groups on BC serve as active sites in the catalytic system

and are also conducive to generating free radicals through a single electron transfer mechanism, as shown in follows:

$R\text{-}OH + H_2O_2 \rightarrow R\text{-}O\bullet + H_2O + OH^-$

$R\text{-}OH + H_2O_2 \rightarrow R^+ + \bullet OH + H_2O_2$

Comparing the system with only BC and H_2O_2 added, the degradation rate of tetracycline is significantly improved, proving that BC has a certain catalytic effect on hydrogen peroxide. Meanwhile, due to limited active sites, which are gradually occupied, the adsorption and catalytic capacity of biochar are reduced, and the system reaction gradually tends to stabilize. In the reaction system with nano zero-valent iron and hydrogen peroxide added, the removal rate of tetracycline at 720 minutes was 88.67%, much higher than the 20.07% of the system with biochar and hydrogen peroxide added. This indicates that nZVI plays a major role in the catalysis of hydrogen peroxide, and this system maintains a high removal rate within the first 240 minutes. This is because nZVI can maintain high catalytic activity for a period during the reaction. In the reaction system using BC-nZVI material as a catalyst, the removal rate of tetracycline at 720 minutes was 94.77%. Compared to using nZVI or BC alone as catalysts, the removal rate is higher, indicating that BC as a carrier aids the catalysis of nZVI. This is because both BC and nZVI can catalyze H_2O_2, generating more active free radicals to degrade tetracycline. Secondly, BC as a carrier allows nZVI to be more uniformly distributed on the surface, preventing agglomeration of nZVI, thereby providing more active sites for catalyzing hydrogen peroxide. Additionally, as the reaction proceeds, H^+ is consumed while OH^- is generated, causing the pH of the reaction system to increase. This leads to the formation of iron hydroxide complexes or iron hydroxide precipitates. These iron precipitates can cover the surface of nZVI, passivating it and causing loss of activity. The presence of BC can accommodate some of the iron precipitates, reducing their impact on zero-valent iron, thus maintaining high catalytic activity [13, 14]. Therefore, this system achieves a high degradation rate for tetracycline

3.5 Free Radical Quenching Experiment

This section investigated the main active free radicals involved in the degradation process of tetracycline by quenching the free radicals generated in the BC-nZVI + H_2O_2 reaction system (adding sufficient tert-butanol (TBA) and p-benzoquinone (BQ) to scavenge hydroxyl radicals and superoxide radicals in the system [15]). The degradation results are shown in Figure 8.

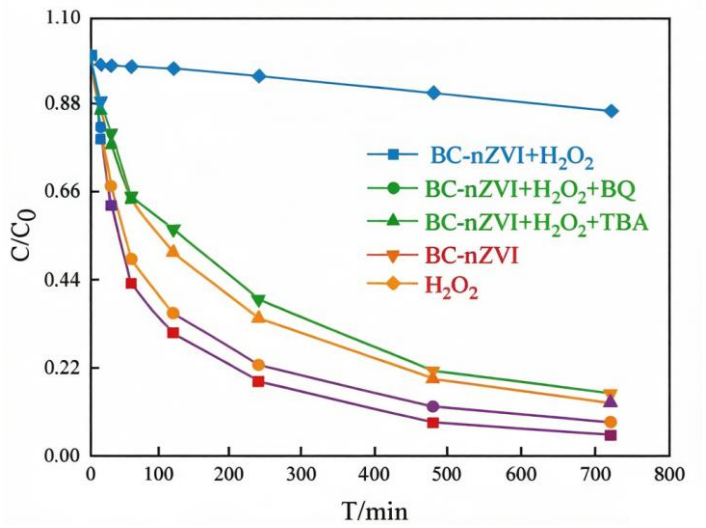

Figure 8 Degradation of tetracycline by Various reaction Systems

After adding TBA, the removal rate was 86.63%, a decrease of 8.14% compared to the BC-nZVI + H_2O_2 system. After adding BQ, the removal rate was 91.56%, a decrease of 3.21%. Tetracycline elimination reached 84.22% with sole BC-nZVI addition. Introduction of radical scavengers partially suppressed removal efficiency, confirming

oxidative pathway involvement. The quenching of hydroxyl radicals (·OH) had a greater impact on the removal rate. After free radical scavenging, the removal of tetracycline mainly relies on the adsorption and reduction by the material itself. These findings demonstrate that hydroxyl radicals constitute the predominant oxidizing species driving tetracycline decomposition, consistent with prior investigations by Chen et al. [24].

3.6 Analysis of Mineralization Ability of Tetracycline by Different Reaction Systems

In advanced oxidation processes, intermediate products generated from incomplete mineralization of refractory organics may have significant toxicity to the environment, potentially causing unpredictable harm. Therefore, TOC was used to represent the final removal capacity of tetracycline by the reaction system, determining the degree of mineralization of tetracycline by the system. Meanwhile, by measuring the changes in TOC during the reaction process, the mechanism of the catalyst and the degradation mechanism of tetracycline by the reaction system were studied. During the removal of tetracycline, the roles of adsorption and degradation were further analyzed. The experimental conditions were: 200 mL of simulated tetracycline wastewater with a concentration of 30 mg/L, initial pH adjusted to 4.0. (1) Addition of 20 mg of nZVI. (2) Addition of 20 mg of BC-nZVI material. (7) Addition of H_2O_2 solution to achieve an H_2O_2 concentration of 0.27 g/L and addition of 20 mg of nZVI. (8) Addition of H_2O_2 solution to achieve an H_2O_2 concentration of 0.27 g/L and addition of 20 mg of BC-nZVI material.

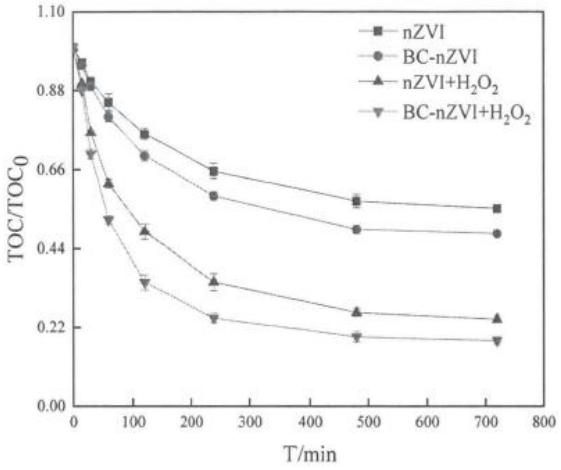

Figure 9 Mineralization degree of tetracycline by diffrent reaction systems

The results are shown in Figure 9. Under the four reaction systems, TOC decreased to varying degrees. For the systems with only nZVI and BC-nZVI added, the TOC removal rates at 480 minutes were 42.78% and 50.68%, respectively. Subsequently, the TOC removal tended to stabilize. At 720 minutes, the TOC removal rates were 44.82% and 51.12%, respectively. Compared to the degradation rate of tetracycline by the systems, the TOC removal rate is lower, indicating limited mineralization ability and incomplete degradation. A large number of intermediates still remain in the system after reaching equilibrium [25]. The degradation mechanisms of tetracycline in these two systems are mainly the reduction by zero-valent iron and the adsorption of the material itself. The reduction by zero-valent iron can degrade tetracycline into small molecular organics but cannot directly reduce TOC. Physical sorption contributes substantially to antibiotic attenuation. Enhanced TOC elimination with BC-nZVI versus nZVI alone stems from the superior porosity and surface area of the carbonaceous support. As a carrier, it can well disperse nano zero-valent iron and prevent agglomeration. During the degradation process, it can maintain high adsorption performance and catalytic activity. Meanwhile, biochar itself has abundant functional groups, which helps adsorb tetracycline [26,27]. When the adsorption of the added material reaches saturation, TOC no longer decreases. Under the nZVI + H_2O_2 and BC-nZVI + H_2O_2 reaction systems, the TOC removal rates at 720 minutes were 75.56% and 81.63%, respectively. At 240 minutes, the TOC removal rates reached 65.39% and 75.34%, respectively, higher than the systems with only material added. This indicates that in the Fenton reaction system, in addition to the physical adsorption mechanism, the chemical oxidation degradation mechanism also plays an important role. This is achieved through the degradation of tetracycline by reactive oxygen species generated by the system, ultimately converting it into CO_2, H_2O, and inorganic ions,

further improving the mineralization degree of tetracycline by the system. The TOC removal rate of the BC-nZVI + H_2O_2 system is higher than that of the nZVI + H_2O_2 system. This is because BC-nZVI has stronger physical adsorption performance and can adsorb more tetracycline when saturated. Meanwhile, as a catalyst, BC-nZVI has more stable catalytic performance, can provide more active sites, and catalyze H_2O_2 to generate more free radicals to degrade tetracycline, resulting in a higher TOC removal rate for the BC-nZVI + H_2O_2 system and a higher degree of mineralization of tetracycline [28]. Comparing the TOC removal curves of the four reaction systems with the degradation curves of tetracycline, it can be found that the degradation rates all follow the rule of gradually decreasing over time. This is caused by the high organic load and free radical content in the initial stage of the reaction. As the reaction continues, the organic load decreases, and some of the generated intermediate products are difficult to degrade. These factors will lead to a decrease in the reaction rate.

3.7 Analysis of Intermediate Products from Tetracycline Degradation

The possible structures of intermediate products were analyzed by LC-MS to explore the degradation pathway of tetracycline by the reaction system. The mass-to-charge ratio situation is shown in Figure 9.

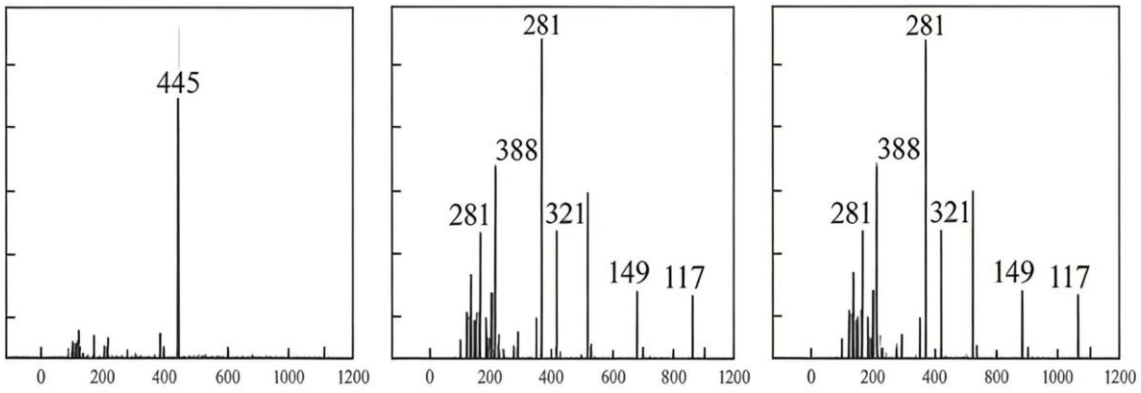

Figure 10 Mass spectrum of intemediate productS from tetracycline degradation

The small molecular substances generated during the degradation process are: 3-phenylpropionic acid ($C_9H_{10}O_2$), 2-(aminomethyl)-4-(methylamino)butane-1,3-diol ($C_6H_{16}N_2O_2$), 3-hydroxypentane-2,4-dione ($C_5H_8O_3$).

3.8 Degradation pathway of tetracycline by reaction system

Based on the m/z of the generated intermediate products, the possible degradation pathway is speculated, as shown in Figure 5.10. First, tetracycline (TC) is attacked by oxygen-containing free radicals and hydroxylated to generate P1 (m/z = 461) [29]. Then, through substitution, re-hydroxylation occurs at C12 to generate P2 (m/z = 463) [30]. Meanwhile, since C3, N4 and the D ring are most vulnerable to attack, P3 (m/z = 388) is generated after demethylation at N4 [21]. Subsequently, the free radicals generated in the system continue to attack the cyclic structure. After the removal of the methylamino group, the product degrades into P3 (m/z = 321) and P4 (m/z = 281). Finally, it is further degraded into small molecule intermediates through oxidation, P5 (m/z = 149), P6 (m/z = 149), P7 (m/z = 117). Most of these small molecule intermediates can be decomposed into CO_2 and H_2O, and have strong biodegradability [22, 23].

Based on the comprehensive experimental data and characterization results presented in the document, the degradation mechanism of tetracycline (TC) by the biochar-supported nanoscale zero-valent iron (BC-nZVI) composite within the Fenton-like system is a complex, synergistic process involving adsorption, chemical reduction, and radical-based catalytic oxidation, all facilitated by the unique structural and chemical properties of the composite material. The mechanism initiates with the rapid adsorption of TC molecules onto the BC-nZVI surface, primarily driven by the large specific surface area (30.78 m^2/g for the optimal composite), the intricate porous structure of the biochar carrier, and interactions such as π-π stacking and hydrogen bonding with surface oxygen-containing functional groups; this preconcentration of pollutants near the active sites significantly

enhances the subsequent degradation efficiency. The core catalytic cycle is driven by the nanoscale zero-valent iron (nZVI) particles, which are uniformly distributed on the biochar surface, preventing their agglomeration. In the acidic aqueous environment (optimal at pH 4.0), the nZVI (Fe^0) corrodes, releasing Fe^{2+} ions ($Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$). These Fe^{2+} ions then catalyze the decomposition of the added H_2O_2 via the classical Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$), generating highly reactive hydroxyl radicals (·OH), the presence of which is directly evidenced by Electron Paramagnetic Resonance (EPR) analysis showing the characteristic 1:2:2:1 quadruplet pattern of DMPO-OH spin adducts. The generated Fe^{3+} can be reduced back to Fe^{2+} either by additional surface-bound Fe^0 or by reaction with hydroperoxyl/superoxide radicals, thus establishing a sustainable catalytic cycle. Concurrently, the nZVI itself can directly reduce certain functional groups of TC through electron transfer. The biochar support plays a multifaceted role beyond mere adsorption: it prevents the agglomeration of nZVI nanoparticles, thereby maintaining a high density of active sites and enhancing material stability and reusability (79.05% removal after 10 cycles). Furthermore, the biochar's functional groups and conductive carbon matrix may facilitate electron transfer and provide additional catalytic sites, as the -OH groups on biochar can also activate H_2O_2 through a single electron transfer mechanism. The generated ·OH radicals, identified as the predominant oxidizing species through quenching experiments (where tert-butanol caused a significant drop in removal efficiency), non-selectively attack the adsorbed TC molecule. As inferred from LC-MS analysis of degradation intermediates, the pathway involves hydroxylation of the aromatic rings (forming P1, m/z=461), further hydroxylation (P2, m/z=463), demethylation at N4 (P3, m/z=388), removal of the methylamino group, and subsequent ring-opening reactions of the naphthacene core structure, ultimately breaking it down into small molecular intermediates like 3-phenylpropionic acid, which are further mineralized into CO_2 and H_2O, as substantiated by the high Total Organic Carbon (TOC) removal rate of 81.63% for the BC-nZVI/H_2O_2 system. The synergy is paramount: biochar efficiently concentrates TC and stabilizes the catalyst, while the dispersed nZVI provides a persistent source of Fe^{2+} for H_2O_2 activation; this combined action of physical adsorption, reduction by nZVI, and radical oxidation leads to the superior performance of the integrated system compared to its individual components, achieving a high degradation rate of 94.77% under optimal conditions. The optimal performance with material prepared at Fe:C=1:1 and 280°C stems from this balance, ensuring sufficient iron loading for catalysis without excessive agglomeration, while the biochar derived from kitchen waste provides a suitable porous structure and surface chemistry for effective support and interaction.

Conclusion

This project used kitchen waste as raw material to prepare biochar by hydrothermal carbonization, and prepared BC-nZVI composite material by liquid phase reduction method. A Fenton-like system was constructed with hydrogen peroxide to degrade tetracycline. The material was characterized and degradation screening was carried out. The optimal preparation conditions of the material were selected. The iron loading stability and reusability of the material were investigated. Systematic investigation encompassed parametric effects on treatment performance, identification of dominant radical intermediates, material functionality elucidation, antibiotic transformation pathways, and ultimate mineralization extent. The following conclusions are drawn:

(1) The material prepared with Fe:C=1:1 at 280°C has a high removal rate for tetracycline and good iron loading stability. The iron loading capacity is 426.5 mg/g. The residual iron loading in the physical and chemical stability experiments were 93.92% and 64.19%, respectively. After 10 cycles of use, the removal rate of tetracycline can still reach 79.05%, proving that the material has good reusability. From the characterization results, FTIR proved the successful preparation of biochar and the appearance of Fe^0 indicating the successful loading of iron. XRD diffraction confirmed Fe^0 presence, verifying iron incorporation. SEM visualization revealed nanoscale zero-valent iron particles dispersed across the porous carbon matrix, with optimal uniformity and density achieved at Fe:C ratio of 1:1. BET analysis revealed substantial surface area (30.78 m^2/g), well-developed porosity, mean pore diameter of 1.49 nm, and total pore volume of 0.05 cm^3/g.

(2) The influence of various influencing factors on the BC-nZVI Fenton-like reaction system was determined through single-factor experiments. The removal rate gradually increased as the material dosage increased from 0.06 g/L to 0.1 g/L. Further increase after reaching 0.1 g/L had little effect on the degradation effect. The reason is that excess Fe^{2+} will consume part of ·OH, and biochar may also consume a certain amount of oxidant in the solution. When the H_2O_2 concentration exceeded 0.27 g/L, the degradation effect deteriorated. This is because

excess H_2O_2 quenches ·OH, generating less active intermediates, such as $\cdot O_2^-$, $\cdot HO_2$, and H_2O. In addition, the initial concentration of tetracycline should also be maintained within a certain range. When it exceeds 30 mg/L, the active sites of the material are insufficient to maintain high catalytic efficiency, and the degradation effect decreases. Meanwhile, pH has a great influence on the degradation effect of the Fenton system. If the pH is too high, it will lead to the hydrolysis of Fe^{2+}/Fe^{3+} to form iron hydroxide complexes or iron hydroxides, which passivate the catalyst surface and reduce the catalytic activity. OH^- will consume part of H_2O_2, reducing the concentration of ·OH. Excessive acidity promotes $H_3O_2^+$ formation, stabilizing hydrogen peroxide and impeding hydroxyl radical generation, thereby diminishing degradation efficiency. From the results, the successful modification of the material broadens the usage conditions of the catalyst. Kinetic fitting was performed on the experimental data, and the reaction orders with respect to BC-nZVI material dosage, initial hydrogen peroxide concentration, and initial tetracycline concentration were determined to be 0.8374, 0.5737, and 0.2324, respectively.

(3) Electron paramagnetic resonance (EPR) shows that the BC-nZVI + H_2O_2 Fenton-like system produces a distinct 1:2:2:1 characteristic peak. DMPO-OH is the reason for this peak, proving the successful generation of hydroxyl radicals, which are also important active species for degrading tetracycline. The results of the hydrogen peroxide catalytic decomposition experiment and hydroxyl radical determination show that the material has high catalytic efficiency. The reaction order n for hydrogen peroxide catalytic decomposition is 1.0709, the reaction rate constant k = 0.1243 min^{-1}. Hydroxyl radical formation exhibited 1.1939-order kinetics with a rate constant of 0.0008 min^{-1}. Component-specific degradation trials demonstrated superior performance of the integrated BC-nZVI/H_2O_2 system, with TOC data confirming extensive mineralization. This benefits from the synergistic effect of physical adsorption, reduction, and catalytic effects maximized by the presence of biochar and nZVI. Through the determination of intermediate products by LC-MS, the degradation pathway of tetracycline is inferred as follows: oxygenation hydroxylation under the action of free radicals, followed by the removal of methyl and methylamino groups, degradation and ring opening, and finally further oxidation into small molecule intermediates until decomposition into CO_2 and H_2O.

References

[1] GIRALDO-AGUIRRE A L, SERNA-GALVIS E A, ERAZO-ERAZO E D, et al. Removal of beta-lactam antibiotics from pharmaceutical wastewaters using photo-Fenton process at near-neutral pH[J]. Environ Sci Pollut Res Int, 2018, 25(21): 20293-303.

[2] PACHECO-ALVAREZ M, PICOS BENITEZ R, RODRIGUEZ-NARVAEZ O M, et al. A critical review on paracetamol removal from different aqueous matrices by Fenton and Fenton-based processes, and their combined methods[J]. Chemosphere, 2022, 303(Pt 1): 134883.

[3] XU H-Y, XU Y, ZHANG S-Q, DAI L-Y, et al. Fabricating a Fe3O4@HNTs nanoreactor to expedite heterogeneous Fenton-like reactions[J]. Materials Letters, 2023, 337: 133985.

[4] LI J, YOU J, WANG Z, et al. Application of a-Fe2O3-based heterogeneous photo-Fenton catalyst in wastewater treatment: A review of recent advances[J]. Journal of Environmental Chemical Engineering, 2022, 10(5): 108329.

[5] QIN H, CHENG H, LI H, et al. Degradation of ofloxacin, amoxicillin and tetracycline antibiotics using magnetic core-shell MnFe2O4@C-NH2 as a heterogeneous Fenton catalyst[J]. Chemical Engineering Journal, 2020, 396: 125304.

[6] HE Z, XU X, WANG B, et al. Evaluation of iron-loaded granular activated carbon used as heterogeneous fenton catalyst for degradation of tetracycline[J]. Journal of Environmental Management, 2022, 322: 116077.

[7] KAZEMI SHARIAT PANAHI H, DEHHAGHI M, OK Y S, et al. A comprehensive review of engineered biochar: Production, characteristics, and environmental applications[J]. Journal of Cleaner Production, 2020, 270: 122462.

[8] PAN X, GU Z, CHEN W, et al. Preparation of biochar and biochar composites and their application in a Fenton-like process for wastewater decontamination: A review[J]. Sci Total Environ, 2021, 754: 142104.

[9] YAASHIKAA P R, KUMAR P S, VARJANI S, et al. A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy[J]. Biotechnology Reports, 2020, 28: e00570.

[10] LI Y, JIN Y, LI J, et al. Current Situation and Development of Kitchen Waste Treatment in China[J]. Procedia Environmental Sciences, 2016, 31: 40-9.
[11] KHOO C G, LAM M K, MOHAMED A R, et al. Hydrochar production from high-ash low-lipid microalgal biomass via hydrothermal carbonization: Effects of operational parameters and products characterization[J]. Environ Res, 2020, 188: 109828.
[12] GUPTA A D, SINGH H, VARJANI S, et al. A critical review on biochar-based catalysts for the abatement of toxic pollutants from water via advanced oxidation processes (AOPs)[J]. Sci Total Environ, 2022, 849: 157831.
[13] NGUYEN T B, NGUYEN T K, CHEN W H, et al. Hydrothermal and pyrolytic conversion of sunflower seed husk into novel porous biochar for efficient adsorption of tetracycline[J]. Bioresour Technol, 2023: 128711.
[14] WU Y, CHEN Y, SHAABAN M, et al. Evaluation of microbial inoculants pretreatment in straw and manure co-composting process enhancement[J]. Journal of Cleaner Production, 2019, 239: 118078.
[15] STEFANIUK M, OLESZCZUK P, OK Y S. Review on nano zerovalent iron (nZVI): From synthesis to environmental applications[J]. Chemical Engineering Journal, 2016, 287: 618-32.
[16] KEN D S, SINHA A. Recent developments in surface modification of nano zero-valent iron (nZVI): Remediation, toxicity and environmental impacts[J]. Environmental Nanotechnology, Monitoring & Management, 2020, 14: 100344.
[17] YAN J, QIAN L, GAO W, et al. Enhanced Fenton-like Degradation of Trichloroethylene by Hydrogen Peroxide Activated with Nanoscale Zero Valent Iron Loaded on Biochar[J]. Sci Rep, 2017, 7: 43051.
[18] SUN P, WANG Z, AN S, et al. Biochar-supported nZVI for the removal of Cr(VI) from soil and water: Advances in experimental research and engineering applications[J]. J Environ Manage, 2022, 316: 115211.
[19] YI Y, WANG X, ZHANG Y, et al. Formation and mechanism of nanoscale zerovalent iron supported by phosphoric acid modified biochar for highly efficient removal of Cr(VI)[J]. Advanced Powder Technology, 2023, 34(2): 103826.
[20] RONG K, LI X, YANG Q, et al. Removal of aqueous vanadium(V) by green synthesized iron nanoparticles supported on corn straw biochar[J]. Journal of Industrial and Engineering Chemistry, 2023, 120: 170-181.
[21] LU C, WAN J, CHEN X, et al. Removal of decabromodiphenyl ethane (DBDPE) by BC/nZVI in the soil: Kinetics, pathways and mechanisms[J]. Journal of Environmental Chemical Engineering, 2022, 10(1): 107004.
[22] LI X, JIA Y, ZHANG J, et al. Efficient removal of tetracycline by H2O2 activated with iron-doped biochar: Performance, mechanism, and degradation pathways[J]. Chinese Chemical Letters, 2022, 33(4): 2105-10.
[23] MAO Q, ZHOU Y, YANG Y, et al. Experimental and theoretical aspects of biochar-supported nanoscale zero-valent iron activating H2O2 for ciprofloxacin removal from aqueous solution[J]. J Hazard Mater, 2019, 380: 120848.
[24] DENG J, DONG H, ZHANG C, et al. Nanoscale zero-valent iron/biochar composite as an activator for Fenton-like removal of sulfamethazine[J]. Separation and Purification Technology, 2018, 202: 130-7.
[25] GAN Q, HOU H, LIANG S, et al. Sludge-derived biochar with multivalent iron as an efficient Fenton catalyst for degradation of 4-Chlorophenol[J]. Sci Total Environ, 2020, 725: 138299.
[26] CHEN X-L, LI F, CHEN H, et al. Fe2O3/TiO2 functionalized biochar as a heterogeneous catalyst for dyes degradation in water under Fenton processes[J]. Journal of Environmental Chemical Engineering, 2020, 8(4): 103905.
[27] XIE E, ZHENG L, DING A, et al. Mechanisms and pathways of ethidium bromide Fenton-like degradation by reusable magnetic nanocatalysts[J]. Chemosphere, 2021, 262: 127852.
[28] PARK J-H, WANG J J, XIAO R, et al. Degradation of Orange G by Fenton-like reaction with Fe-impregnated biochar catalyst[J]. Bioresource Technology, 2018, 249: 368-76.
[29] FALSAFI S R, ROSTAMABADI H, ASSADPOUR E, et al. Morphology and microstructural analysis of bioactive-loaded micro/nanocarriers via microscopy techniques; CLSM/SEM/TEM/AFM[J]. Adv Colloid Interface Sci, 2020, 280: 102166.
[30] PETIT T, PUSKAR L. FTIR spectroscopy of nanodiamonds: Methods and interpretation[J]. Diamond and Related Materials, 2018, 89: 52-66.