Supplementary Materials

Dual-Functional Ag-Fe@Biochar Systems: Simultaneous Adsorption and Radical-Mediated Oxidation of Antibiotics in Fenton-like Reactions

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Text S1. Chemicals and Reagents

Silver nitrate ($AgNO_3$), analytically pure, produced by Shanghai Fine Chemical Materials Research Institute; ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), levofloxacin (LVF98%), p-benzoquinone (BQ), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium nitrate ($NaNO_3$), sodium borohydride $NaBH_4$, hydrogen peroxide(H_2O_2), analytically pure, were purchased from Aladdin (Shanghai, China). Disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), specification of analytical purity, produced by Shanghai Richjoint Chemical Reagents Co., Ltd. Tert-butanol (TBA), specification of analytical purity, produced by Tianjin Bodhi Chemical Co., Ltd. Anhydrous ethanol, specification of analytical purity, produced by Wuxi Jingke Chemical Co., Ltd. High purity nitrogen (98%), supplied by Wuxi XinXiYi Technology Co., Ltd. All chemical reagents could be used directly without further purification. The water used in the experiments was ultrapure water.

Text S2. Experimental Procedures

S2.1 LVF removal experiment

1 g of analytically pure levofloxacin (LVF) was weighed in a 1 L volumetric flask, a certain amount of ultrapure water was added, and then the solution was condensed. The concentration of the standard solution was 1 g/L. 2 mL of the standard solution was diluted to 100 mL, and the pH value of the initial solution was 3, the concentration of LVF was 20 mg/L, the reaction solution was 100 mL, and the speed of the rotary oscillator was set at 220 rpm. Samples were taken at 0, 5, 10, 20, 40 and 60 min, and then filtered through a 0.45 μm filter head to determine the concentration of levofloxacin. LVF concentration was measured using UV spectrophotometry.

S2.2 Influence factors exploration experiment

The effects of different materials, doping ratios, dosage, H_2O_2 concentration, pH value, initial concentration of LVF and coexisting anions on the removal efficiency were investigated. The pH of the reaction system was adjusted with 1 M NaOH and 1 M HCl. The concentrations of anions (Cl^-, NO_3^-, HCO_3^-, $H_2PO_4^-$and SO_4^{2-}) were set at 5 mM, 10 mM, and 20 mM. Unless otherwise specified, the required pH for the experiment was 3, the initial concentration of the pollutant was 20 mg/L, and the concentration of H_2O_2 was 1 mmol/L.

S2.3 Free radical trapping experiment

The free radical species generated during the degradation process were detected by free radical trapping experiments. First, 0.05 mol/L benzoquinone (BQ) solution (·OH scavenger) and 0.1 mol/L tert-butanol (TBA) solution ($\cdot O_2^-$ scavenger) were prepared. Firstly, 2 mL of tert-butanol and 2 mL of benzoquinone solution was added to 100 mL of a 20 mg/L levofloxacin solution respectively. After the reaction was completed, the absorbance of the post-reaction solution was measured, and the respective removal rates were calculated.

S2.4 Recurring experiment

After the removal experiment, the reacted materials were separated and collected by suction filtration. The removal materials were first rinsed three times with ethanol, and then the same steps were repeated with deionized water to remove the remaining pollutants. After that, the materials were placed in a vacuum drying oven and dried overnight. Subsequently, this material was used to remove levofloxacin again, and the above steps were repeated to examine the stability of the composite material in removing levofloxacin.

Text S3. Characterization

The morphological characteristics of the synthesized materials were analyzed using a scanning electron microscope (Hitachi Regulus 8100, Japan). The samples were directly adhered to the conductive adhesive and sputtered with gold for 45 seconds. EDS was used to analyze the types and distribution of elements in the samples. Based on the above SEM operation, a mapping test was subsequently carried out at a voltage of 20 kV. The structure and crystal form of the materials were analyzed using an X-ray diffractometer (Bruker Milton, Germany). The fine powder samples were filled into the circular holes on the sample holder and placed on the sample stage for scanning. The X-ray source was a sealed 2.2 kW copper tube with a tube voltage of 40 kV and a tube current of 25 mA. The detector was a peltier-cooling solid-state Si(Li) device with an effective energy range of 1 to 60 KeV. The scanning range was from 2° to 90° with a step size of 0.02° per step. The functional groups in the materials were analyzed using a Fourier transform infrared spectrometer (Perkin-Elmer Spectrum GX, USA). The specific operation for tablet pressing was as follows: KBr and the sample were fully ground and uniformly mixed in a mortar at a ratio of 100:1, and then tablet pressing was carried out. The test range was 4000 to 400 cm^{-1}. The elemental composition and chemical states of the materials were analyzed using an X-ray photoelectron spectrometer (Thermo Scientific K Alpha, USA). The Al Kα microfocus monochromatic source had a continuously adjustable spot size ranging from 30 to 400 μm with a step size of 5 μm. For the full spectrum scan: the pass energy was 100 eV and the step size was 1 eV; for the narrow spectrum scan: the pass energy was 30 to 50 eV and the step size was 0.05 to 0.1 eV. The specific surface area and pore size distribution of the materials were determined using a fully automatic specific surface area analyzer (Micromeritics APSP 2460, USA). An electron paramagnetic resonance spectrometer (Bruke EMX PLUS, Germany) was used in the experiment to detect the active species generated during the degradation process, and the degradation mechanism of the antibiotic was speculated based on the results of the free radical trapping experiment. The test procedure was as follows: 30 μL of the sample was taken, 30 μL of DMPO was added, and after thorough mixing, a certain amount of the mixed solution was sucked up with a capillary tube. After putting it into a quartz tube, it was placed in the EPR sample cavity for the test of hydroxyl radicals/superoxide radicals. The test time points were 1 min and 3 min. A liquid chromatography-mass spectrometry (LC-MS) instrument (Agilent 1260, China) was used in the experiment to detect the intermediate products during the degradation of LVF. The possible structures of the intermediate products were speculated based on their mass-to-charge ratios, so as to infer the degradation pathway of LVF. The resolution was < 0.7 amu; the mobile phase was 0.1% formic acid: acetonitrile = 30:70, and the scanning range of the mass-to-charge ratio was 50 to 500.

Table S1 Comparison of degradation performance of LVF by different photocatalytic materials.

Photocatalyst	Conditions	Reaction time	Degradation efficiency	Ref.
Fe^0-PG	C_0=20 mg/L $C_{catalyst}$=0.5 g/L pH=6.5	3 h	78.00%	(Idrees et al., 2022)
$CaTiO_3$@Ag@ZnO	C_0=10 mg/L $C_{catalyst}$=0.2 g/L pH=6.2	60 min	87.00%	(Gu et al., 2025)
Sm_6WO_{12}/g-C_3N_4	C_0=10 mg/L $C_{catalyst}$=0.5 g/L pH=3	70 min	90.80%	(Prabavathi et al., 2021)
Ag/AgCl/Bi_2O_3/$BiFeO_3$@Zeolite	C_0=18 mg/L $C_{catalyst}$=1.2 g/L pH=3	1.5 h	73.55%	(Li et al., 2023)
$MgFe_2O_4$/BC	C_0=10 mg/L $C_{catalyst}$=0.8 g/L pH=5	2 h	87.87%	(Yao et al., 2022)
MRBC/PDS	C_0=10 mg/L $C_{catalyst}$=1.6 g/L pH=5	0.5 h	88.59%	(Yang et al., 2023)
Ag-nZVI/BC	C_0=20 mg/L $C_{catalyst}$=0.3 g/L pH=3	1 h	91.20%	This work

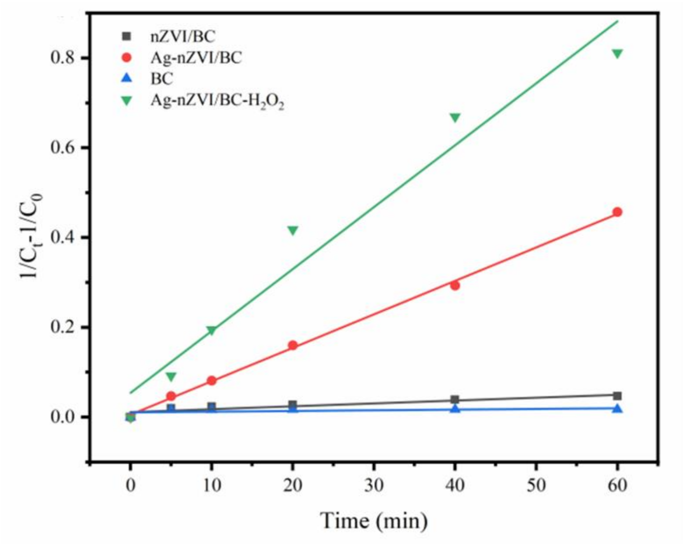

Fig. S1 The first-order kinetic results of Ag-nZVI/BC on LVF removal in different systems

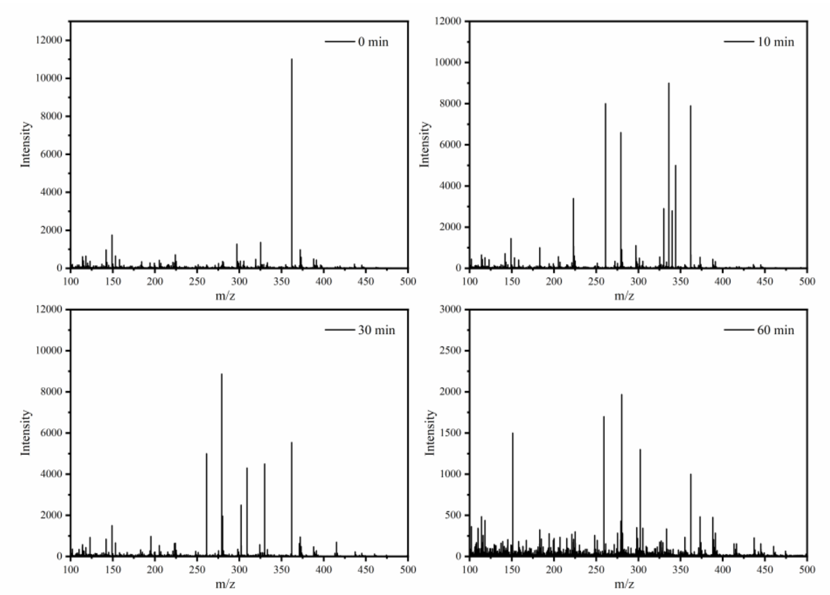

Fig. S2 Degradation mass spectra of LVF at different time periods.

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