Supporting information

Enhanced Bi/nZVI activated molecular oxygen process for degradation of sulfonamides antibiotics in a citrate buffering system

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1. Materials and method

1.1. Chemicals and materials

All chemicals were of analytical grade unless otherwise stated. Sulfamethazine, sulfadiazine, sulfamethoxazole, 1,10-Phenanthroline, dimethyl pyridine N-oxide (DMPO) were obtained from Aladdin (Shanghai, China). Methanol and acetonitrile were of HPLC grade, and purchased from Fisher Scientific (Shanghai, China). Other reagents were supplied by Sinopharm Chemicals Reagent Co., Ltd. (Shanghai, China) All chemicals were used without further purification and solutions were prepared using Milli-Q water (Resistivity > 18 MΩ).

nZVI and Bi/nZVI were synthesized following a previously reported method. Typically, 1 g $FeSO_4 \cdot 7H_2O$ and 0.069 g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 100 mL water under stirring, and the mixed solution was purged with N_2 for at least 15 min to maintain an anaerobic environment. 0.16 g $NaBH_4$ was dissolved in 5 mL water, and then dropped into the mixed solution. The suspension produced by the reaction are collected and washed with absolute ethanol for at least 3 times, followed by drying in a vacuum drying oven at 65 °C for 12 h. nZVI was synthesized in the same way without $Bi(NO_3)_3 \cdot 5H_2O$. The dried particles were finally stored in a vacuum dryer for subsequent use.

1.2. Degradation experiments

The oxidative degradation experiments of SAs in different systems were carried out, and SAs used in this experiment included SM2 (0.2 mM), SD (0.1 mM), SMX (0.2

mM) and their mixed solution (containing 0.2 mM SM2, 0.1 mM SD and 0.2 mM SMX). 50 mg dried particles (1 mg/L), a certain amount of CA (0.1 mM) and NaCA (0.1 mM) were added into the brown vials containing 50 mL of contaminant solution without adjusting the initial pH. Then the vials were transferred to a roller mixer at room temperature (25 ± 2°C), and covered with a black cloth to create a dark environment. Samples were withdrawn at regular intervals using a syringe with a 0.22 μm polyether sulfone (PES) filter. At the end of the reaction in Bi/nZVI-CA/NaCA system, air was continuously injected into the mixed solution for 10 minutes, then the reaction continued for 1 h, and samples were taken at regular intervals. To further explore the role of dissolved oxygen (DO) in Bi/nZVI-CA/NaCA system, the anaerobic and aerobic degradation of the initial mixed solution were conducted by injecting N_2 and O_2 gas respectively for 15 min, and the next steps were the same as the oxidative degradation experiments. The cyclic experiments were conducted after the degradation of SAs by Bi/nZVI-CA/NaCA system, and the solids in the suspension were precipitated from the liquid with magnets. Then 50 mL of contaminant solution containing CA (0.1 mM) and NaCA (0.1 mM) was added to the vial to start the next reaction. Each group of cyclic experiments was cycled three times in total.

1.3. Analytic methods

Quantitative analysis of SAs were done by high performance liquid chromatography (HPLC, 1260 Infinity II, Agilent, USA) equipped with a C18 column (150 mm×4.6 mm, 5 μm) maintained at 30℃, and coupled with a UV detector (SPD-

10AV) selected at wavelength of 260 nm. The mobile phase of SM2 (20:80, v/v), SD (20:80, v/v) and SMX (30:70, v/v) were acetonitrile and 0.1% acetic acid at a flow rate of 0.8 mL/min. The intermediate products of SAs degradation were identified by an ultra performance liquid chromatography connected to a high-resolution mass spectrometry (HR-LC-MS, UltiMate 3000/Q-Exactive Orbitrap, Thermo Fisher Scientific, USA) equipped with a Hypersil GOLD Column (100 mm×2.1 mm, 1.9 μm) maintained at 25℃. The intermediate products were separated by gradient elution at a flow rate of 0.25 mL/min with a spray voltage of 3200 V in positive and negative electrospray ionization (ESI) mode. The mobile phase was a mixture of acetonitrile and water both containing 0.1% formic acid, and the wavelength that detected intermediate products of SAs degradation was 270 nm.

Zeta potential was measured by Zeta potential analyzer (Zetasizer Nano Zs90, Malvern, UK). 1 g/L particles were suspended in 50 mL deionized water at pH=4, 5, 6, 7, and 8 (adjusted with 0.1 mol/L HCl and NaOH). Total organic carbon (TOC) was analyzed with a TOC analyzer (Multi NC 3100, Analytica Jena, Germany) to determine the mineralization of SAs.. pH value and dissolved oxygen (DO) content were measured by pH/DO Meter (MP 525, Sanxin, China). The generated ·OH and $\cdot O_2^-$were captured by DMPO in water and methanol, respectively, and detected by electron paramagnetic resonance spectroscopy (EPR, A200, Bruker, USA).

The concentration of H_2O_2 was measured using a potassium titanium oxalate method with a UV visible spectrophotometer at a wavelength of 400 nm. The release

of ferrous ion (Fe[II]) and total iron ion (Fe[total]) were measured by 1,10-phenanthroline method with the UV-Visible spectrophotometer (UV-Vis, UV-722, Yoke, China) at 510 nm. Heteroatoms (N and S) in SM2, SD and SMX molecules were released as inorganic ions (NH_4^+, NO_3^- and SO_4^{2-}) during oxidative degradation. NH_4^+ concentration was measured by salicylic acid method using an UV-Vis spectrophotometer at 697 nm, while NO_3^- and SO_4^{2-} concentrations were quantified by a Dionex ion chromatograph (IC, ICS-1100, Thermo Fisher Scientific, USA) with a mixture of Na_2CO_3 (3.5 mM) and $NaHCO_3$ (1 mM) as mobile phases at a flow rate of 1 mL/min.

The morphologies of several iron materials were characterized by scanning electron microscope (SEM, QUANTN FEG 450, FEI, USA) equipped with an energy dispersive X-Ray spectroscopy (EDX). X-ray diffraction (XRD, XRD-7000, Shimadzu, Japan) with radiation of a Cu Ka target (λ=0.154 nm) was conducted to identify the crystal phases of iron materials in the range of 2θ between 10º and 80º. The surface chemistry was investigated by the X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, USA). Fourier transform infrared spectroscopy (FT-IR, Nicolet-iS10, Thermo Fisher Scientific, USA) was recorded to determine the functional groups.

Electrochemical impedance spectroscopy (EIS) and Tafel scans were performed in a solution of 100 mM $NaSO_4$ to determine the oxidation and corrosion of iron materials using a electrochemical workstation (CHI 660E, Chenhua Instrument, China)

with a three-electrode system including F-doped Tin Oxide electrode coated with iron material as working electrode, a calomel reference electrode and Platinum electrode (2 cm×2 cm) as reference and counter electrode respectively.

2. Supplementary Figures and Tables

The degradation efficiencies of Bi/nZVI with different Bi concentrations (Bi/Fe atomic ratio of 0%, 3%, 4%, 5%) on SM2 in the presence of CA and NaCA were investigated (Fig. S1). Noticeably, it was found that SM2 exhibited the best degradation efficiency (74%) in 4% Bi/nZVI-CA/NaCA system within 2 h, which was significantly higher than that (52%) of nZVI-CA/NaCA system. Bi^0 wrapped on the surface of nZVI, reducing the activation energy of the reaction system and promoting the removal of pollutants. The kinetic analysis of the SM2 degradation followed pseudo first-order reaction rate.

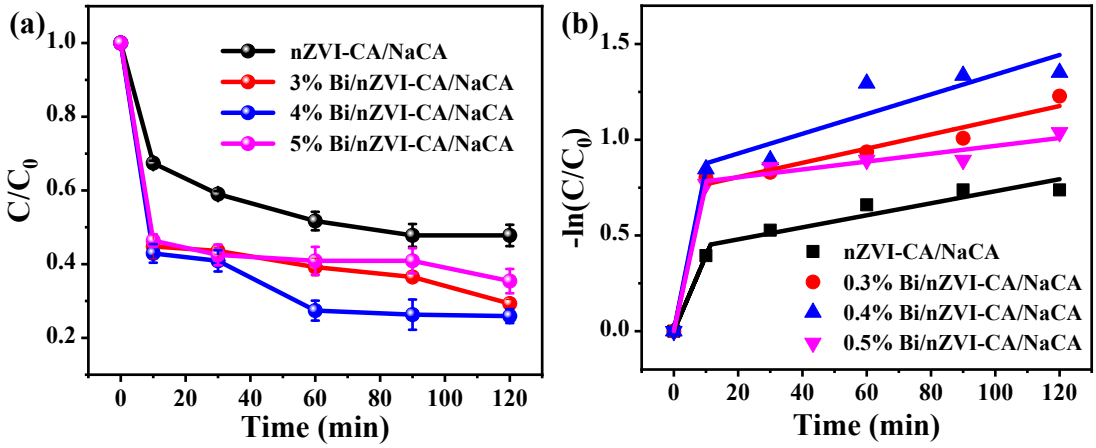


Fig. S1 (a) Degradation efficiency of SM2 in Bi/nZVI-CA/NaCA system with different molar ratios of Bi/Fe; (b) Plots of $\ln(C/C_0)$ versus time for the SAs degradation in different systems

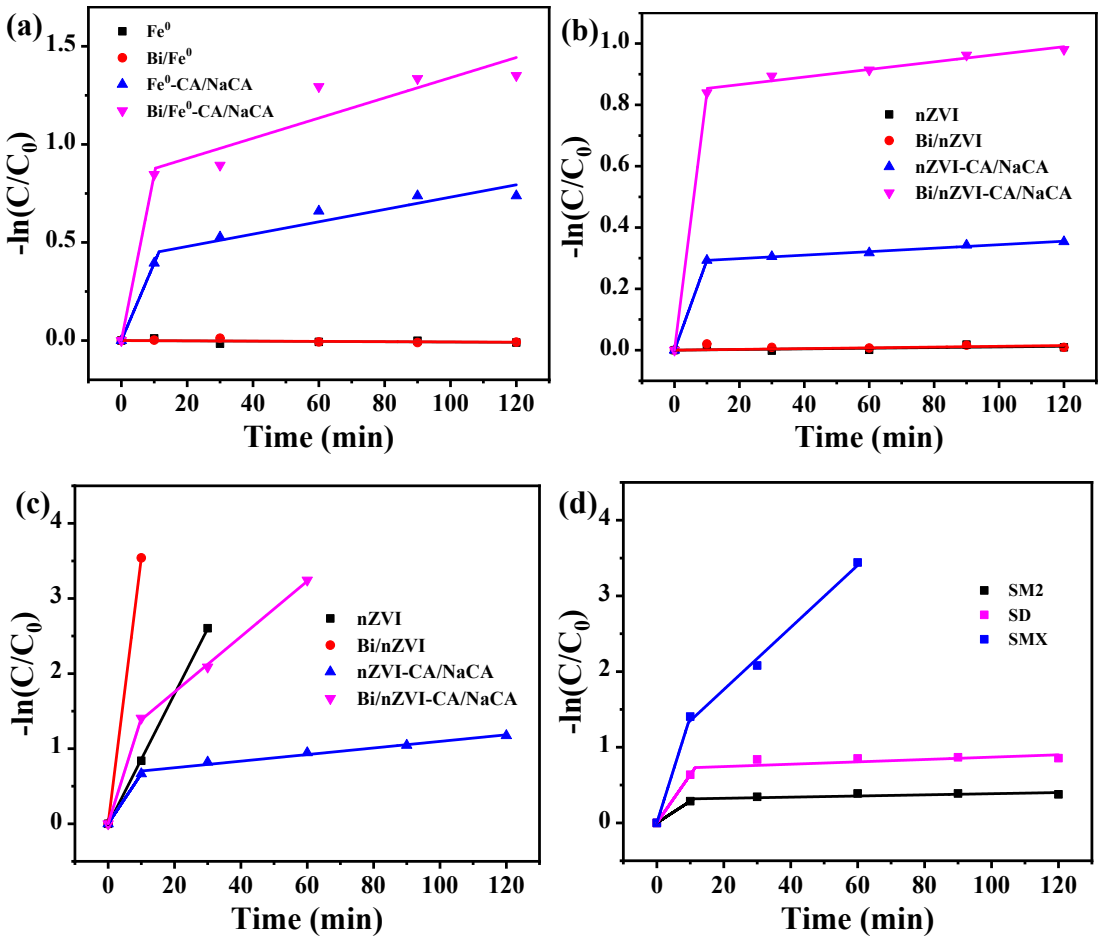


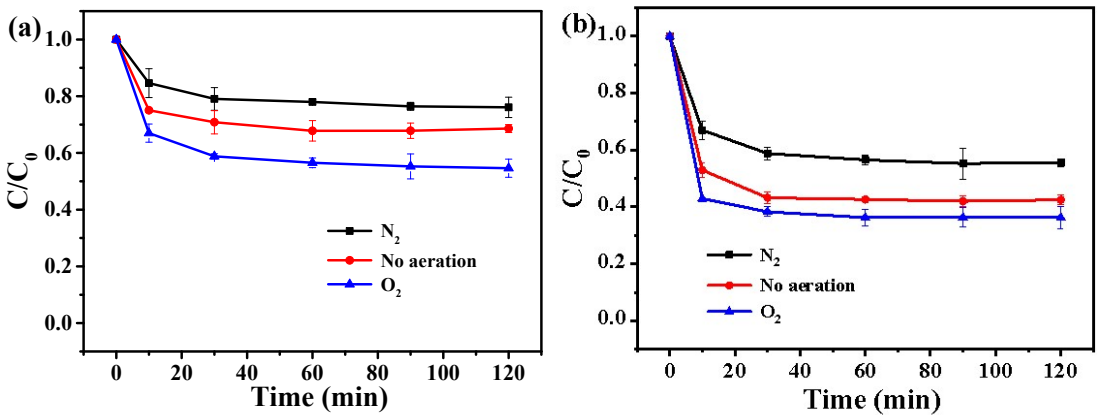
Fig. S2 Plots of $\ln(C/C_0)$ versus time for (a) SM2, (b) SD and (c) SMX degradation in different systems; (d) Plots of $\ln(C/C_0)$ versus time for the SAs degradation in Bi/nZVI-CA/NaCA system

Some advanced methods for sulfonamide antibiotic degradation have been listed. For example, a study reported 89.34% oxidative degradation for SMX after 40 min when using ozone-based advanced oxidation process[1]. Meanwhile, another study reported that the removal rates of SDZ, SMZ, and SMX obtained by recombinant strain 6#P at 60 hours were around 92.0%, 89.0%, and 88.0%, respectively[2]. These treatment processes show more outstanding treatment effects on SDZ or SMZ, but the Bi/nZVI-CA/NaCA system exhibits superior performance towards SMX compared to

other methods. In addition, the Bi/nZVI-CA/NaCA system is more economical to some extent because it does not require additional oxidants and energy consumption.

Table S1 Element content of different samples

No.	Methods	Antibiotics	Removal rates	Reference
1	ozone-based advanced oxidation process	Sulfamethoxazole	89	[1]
2	Biodegradation (Recombinant strain 6#P)	Sulfadiazine Sulfamethazine Sulfamethoxazole	92 89 88	[2]
3	Biological aerated filter	Sulfonamides	> 90	[3]
4	Phosphogypsum modified biochar composite	sulfadiazine sulfamethazine	> 50	[4]
5	Cobalt-doped sulfur-containing biochar from sludge	Sulfamethoxazole Sulfadiazine	92 91	[5]



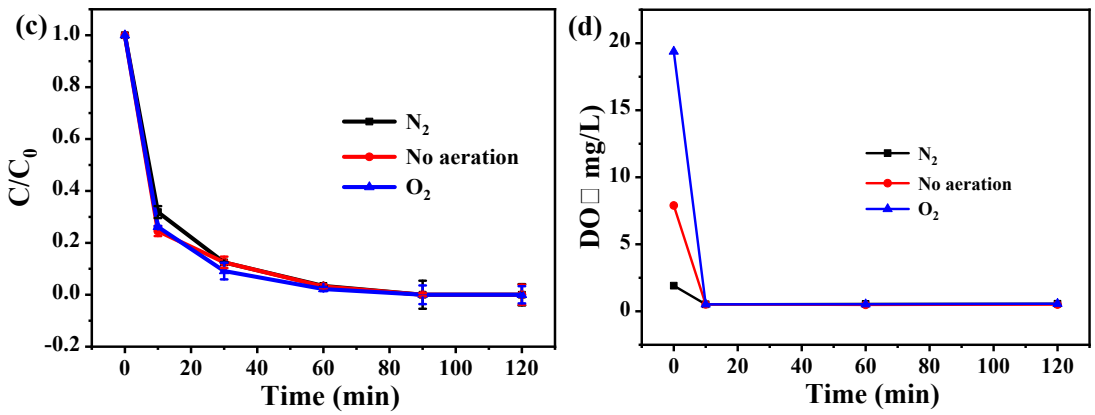


Fig. S3 Degradation of (a) SM2 (b) SMX and (c) SD in the mixed liquid with different initial DO concentrations by Bi/nZVI-CA/NaCA system; (d) DO variation of the mixed liquid with different initial DO concentrations degraded by Bi/nZVI-CA/NaCA system

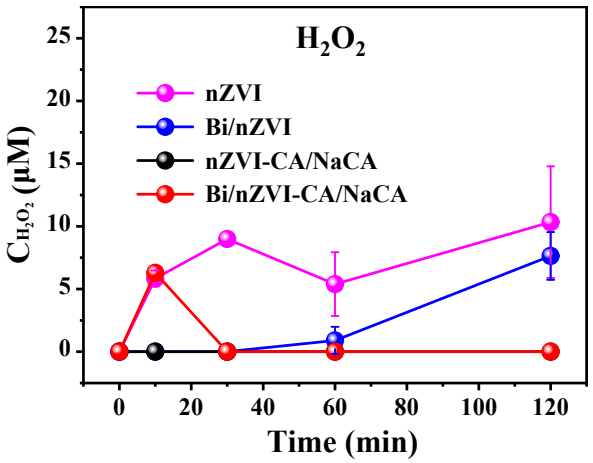


Fig. S4 The concentration of H_2O_2 in different systems.

As shown in Figs. S5a~c, the initial pH values of SM2, SD and SMX solutions in the absence of CA and NaCA were 6.84, 6.35 and 5.62 , respectively. A part of hydrogen ions were consumed in nZVI and Bi/nZVI systems, resulting in a slight increase in pH (pH = 6~7). The addition of CA and NaCA lowered the pH of the SM2, SD and SMX solutions to 4.7, 4.58 and 4.38, respectively, which promoted the acidic environment of solutions. Then the pH value of each solution gradually became stable,

and finally maintained at slightly alkaline (8~9). As shown in Fig. S5d, the pH value of the mixed solution increased to 8.26 within 6 min, then gradually decreased, and finally maintained at slightly alkaline in Bi/nZVI-CA/NaCA system.

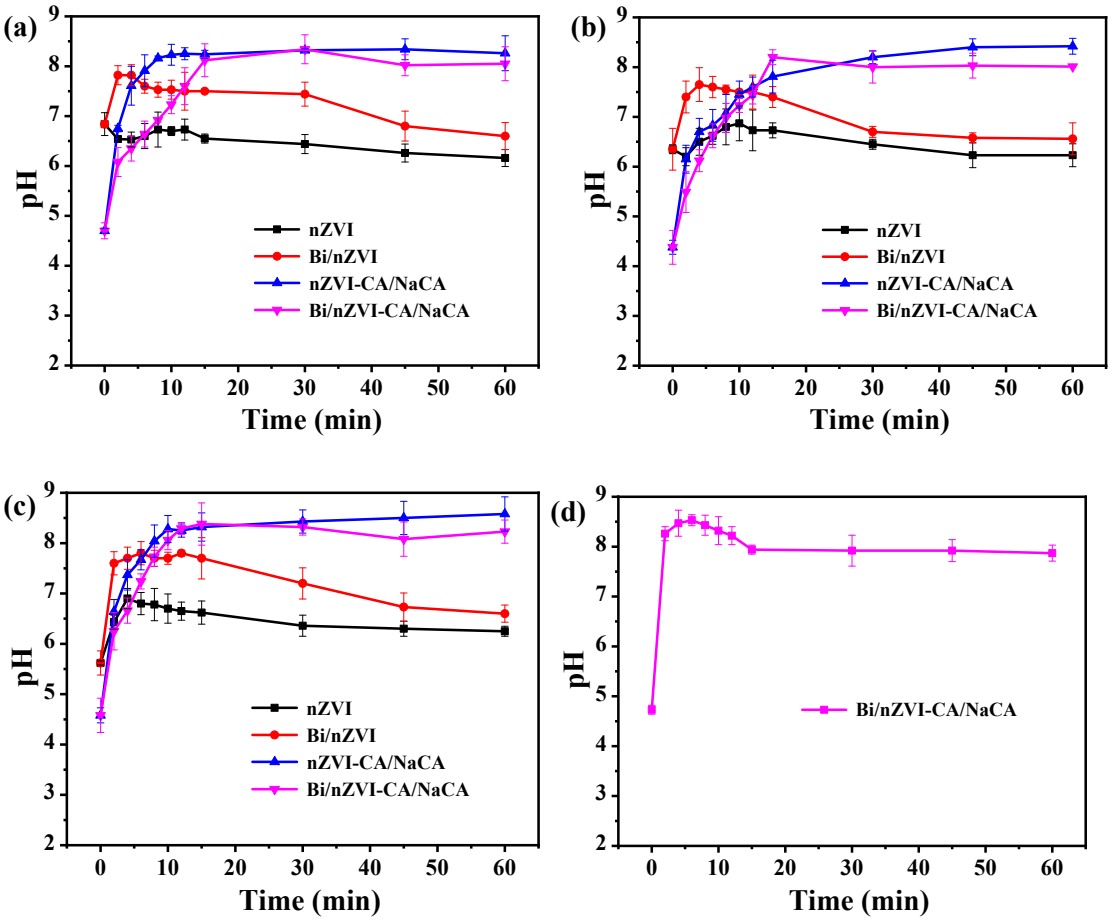


Fig. S5 pH variation of (a) SM2, (b) SD and (c) SMX in different systems; (d) pH variation of the mixed liquid in Bi/nZVI-CA/NaCA system (The mixed liquid is composed of SM2, SD and SMX)

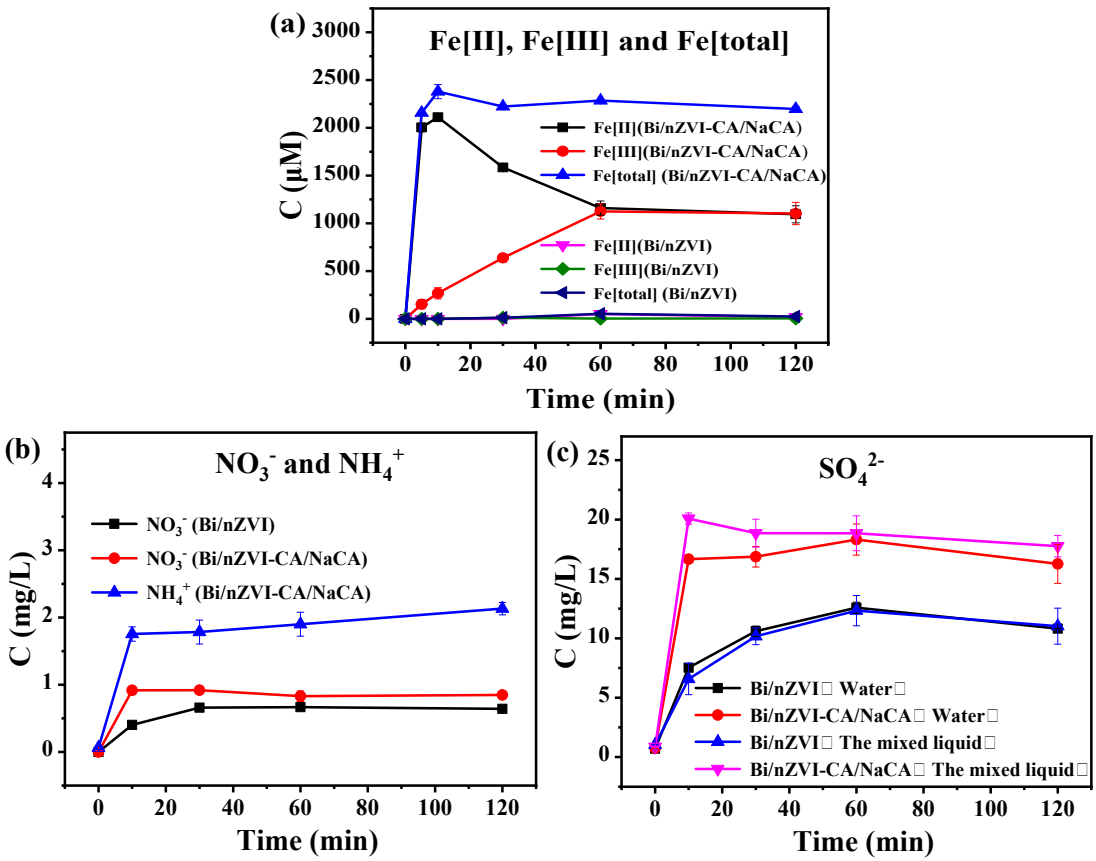
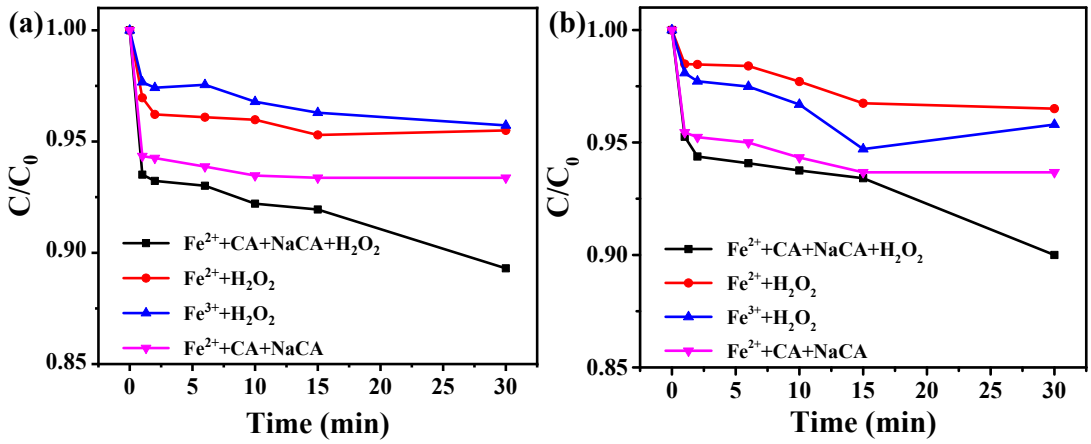


Fig. S6 The concentration of (a) iron ion dissolution and (b) NO_3^-/NH_4^+ in the mixed liquid by different systems; (c) The concentration of SO_4^{2-} in the deionized water and mixed liquid by different systems



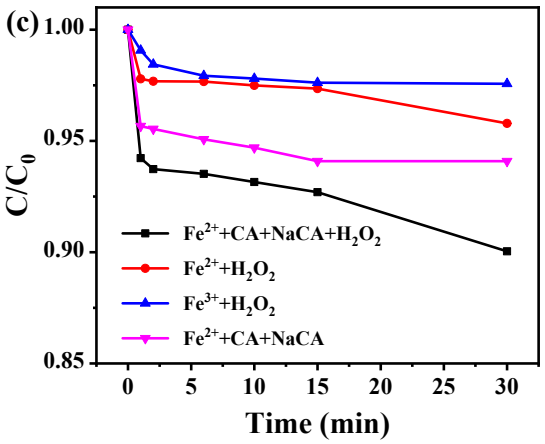


Fig. S7 The degradation effects of different systems on (a) SM2, (b) SMX, and (c) SD in the mixed liquid (initial concentrations of Fe^{2+} and Fe^{3+} are both 2 mmol/L, initial concentrations of CA and NaCA are both 1 mmol/L, the initial concentration of H_2O_2 is 400 μmol/L, and the quencher is tert butanol)

Table S2 Element content of different samples

Element	Weight (%)			Atomic (%)		
	nZVI	Bi/nZVI	3rd Bi/nZVI	nZVI	Bi/nZVI	3rd Bi/nZVI
Fe K	76.07	83.07	80.70	47.67	74.07	64.31
O K	23.93	7.62	12.30	52.33	23.71	34.20
Bi M	0.00	9.31	7.01	0.00	2.22	1.49

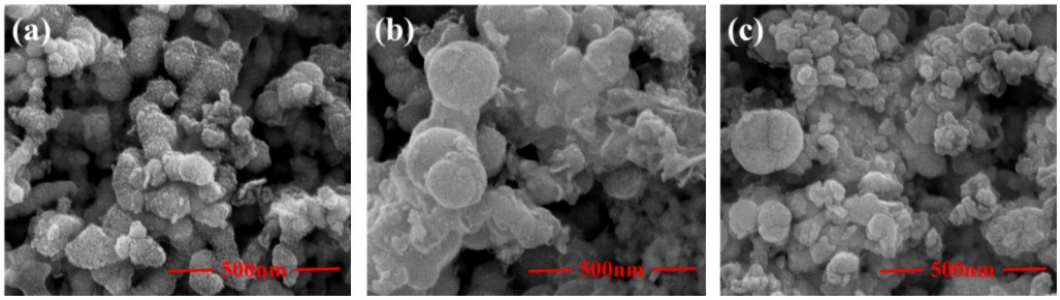


Fig. S8 The SEM of (a) nZVI, (b) Bi/nZVI and (c) 3rd Bi/nZVI

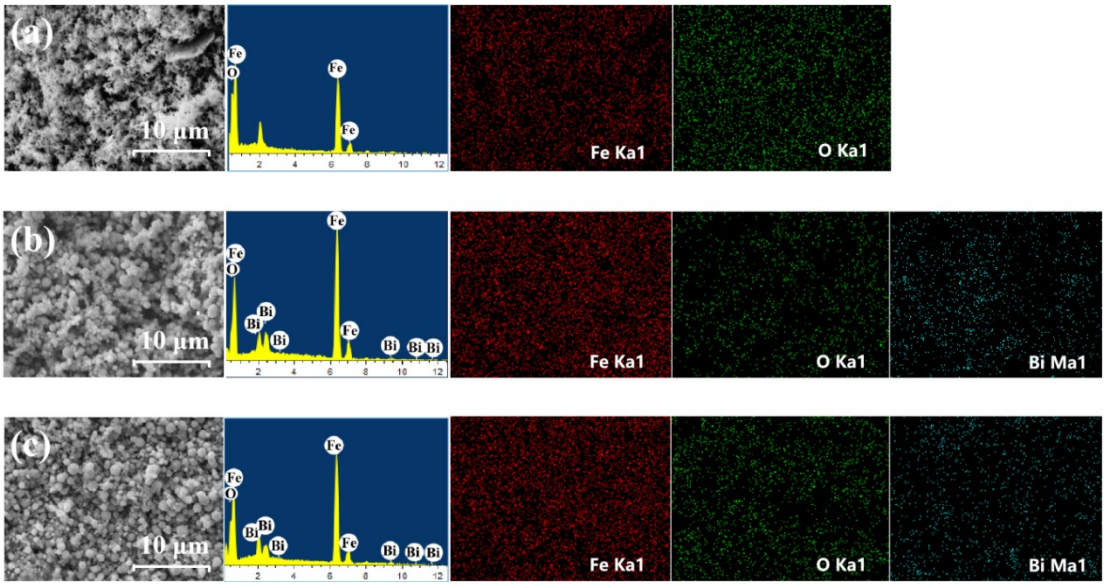


Fig. S9 SEM-EDS elemental mapping of (a) nZVI (b) Bi/nZVI and (c) 3rd Bi/nZVI

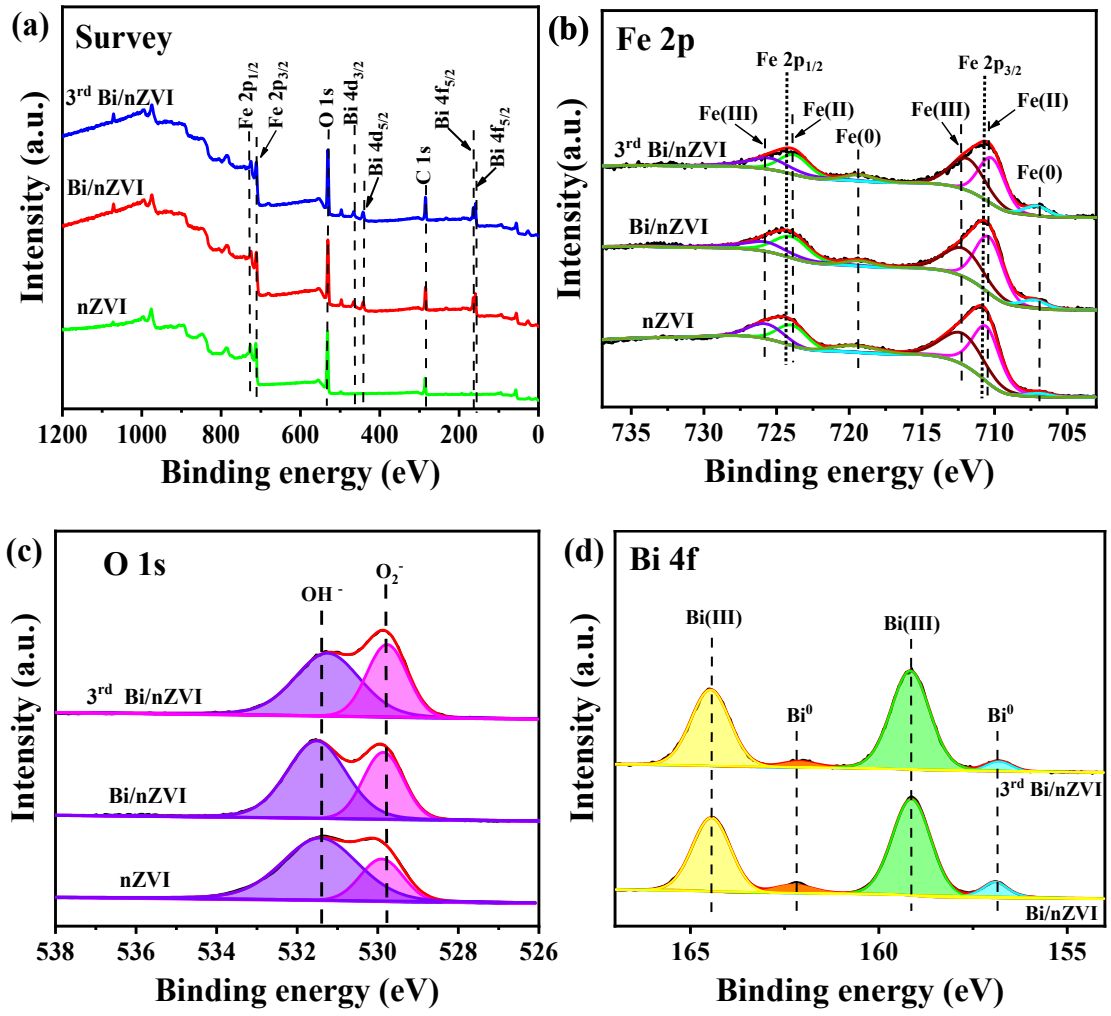


Fig. S10 XPS of (a) survey, (b) Fe 2p, (c) O 1s and (d) Bi 4f of different samples

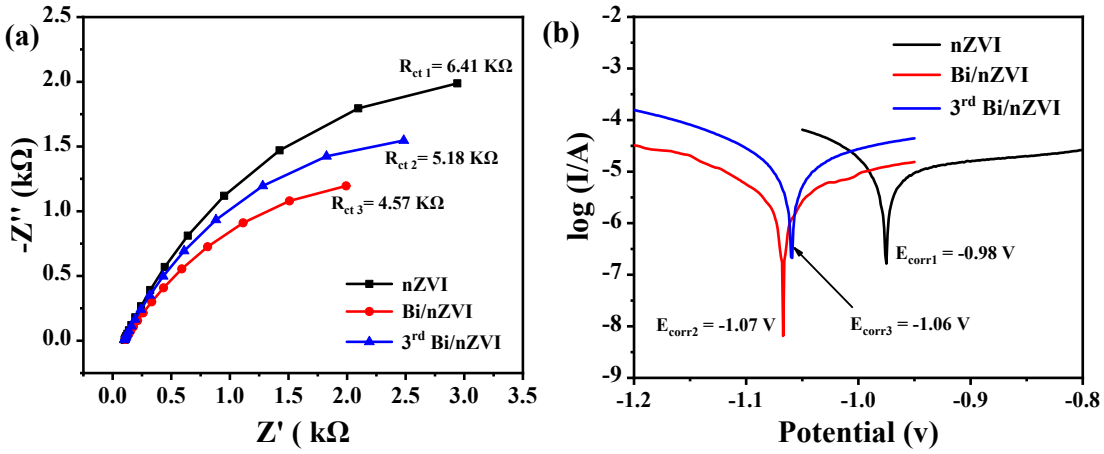
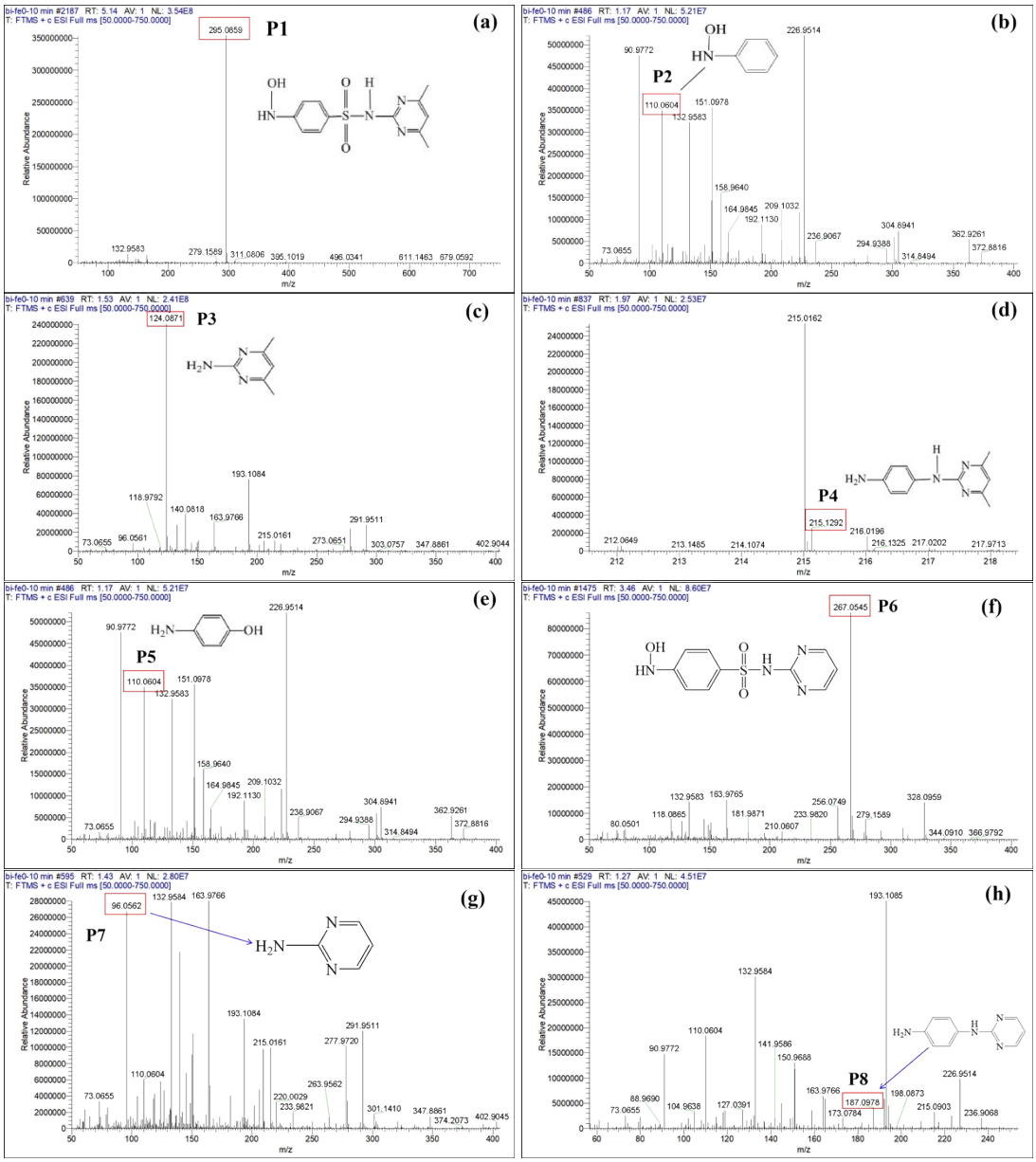


Fig. S11 (a) EIS and (b) Tafel curves of different samples



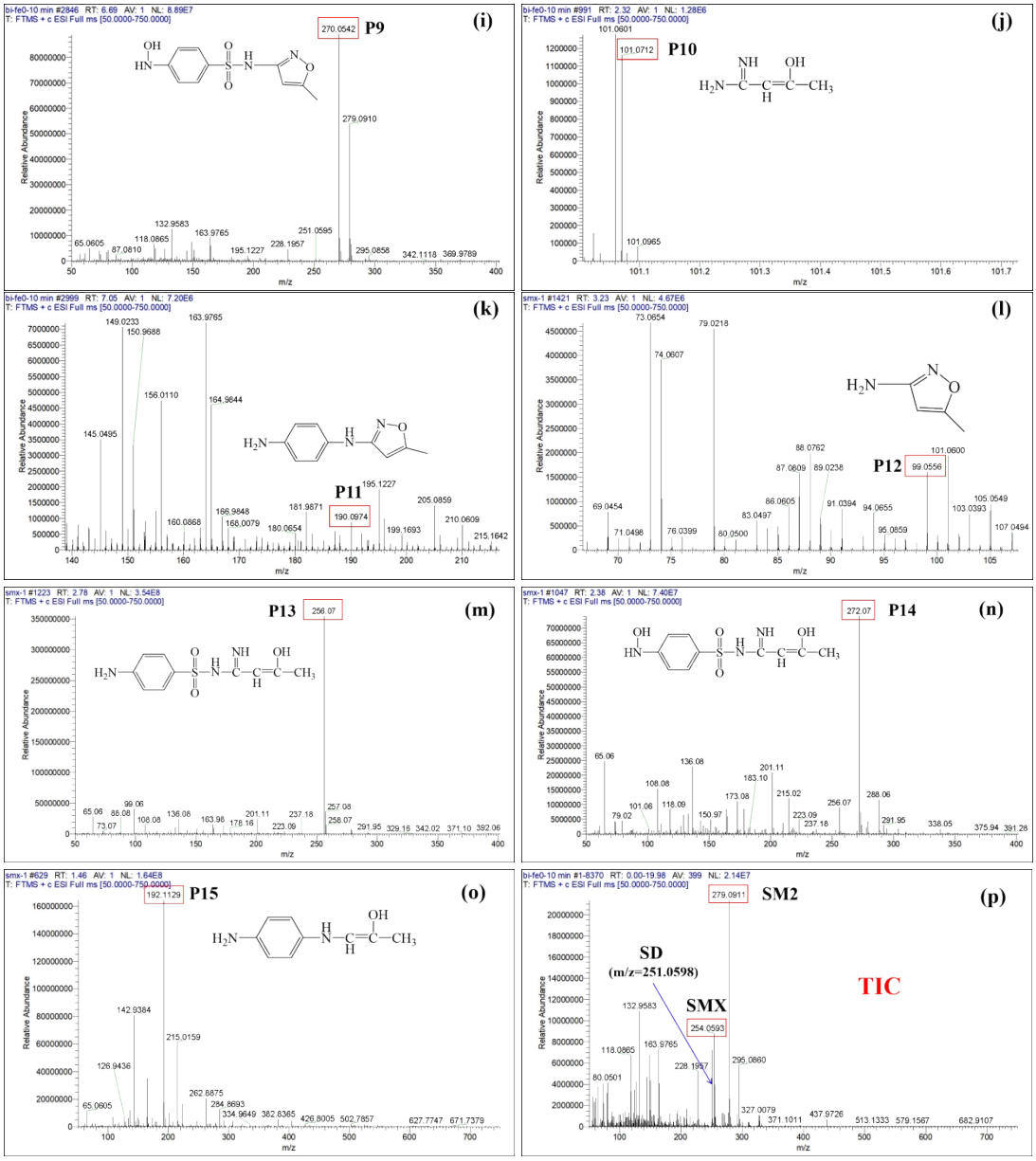
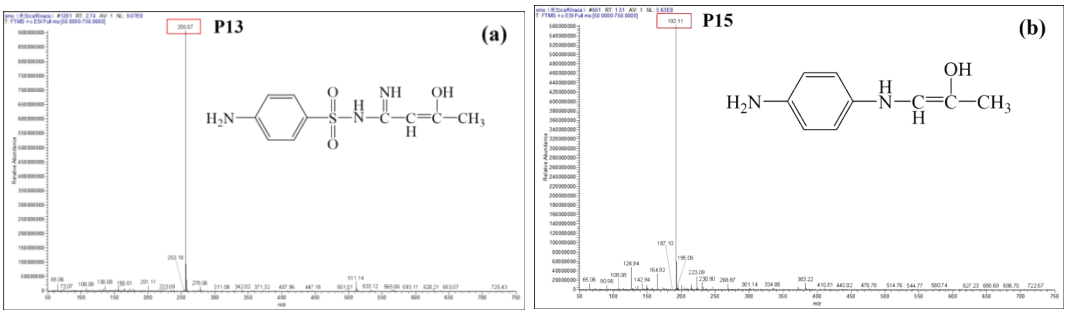


Fig. S12 Mass spectrum of intermediate products produced by the degradation of SAs in Bi/nZVI-CA/NaCA system



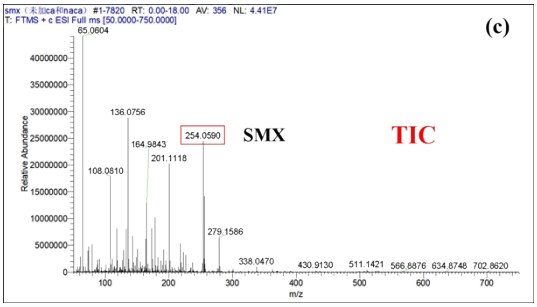


Fig. S13 Mass spectrum of intermediate products produced by the degradation of SMX in Bi/nZVI system

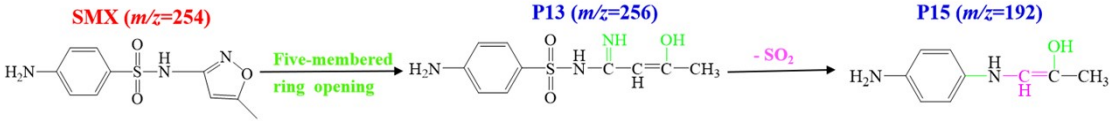


Fig. S14 The pathway of SMX in Bi/nZVI system

References

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