

Supplementary materials

Effective Heterogeneous Fenton-Like Degradation of Antibiotics by Ferroferric Oxide Nanoparticle Coated Reduced Iron Powder with Accelerated Fe(II)/Fe(III) Redox Cycling

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Text S1

Preparation of FONP@RIP

Firstly, RIP with a diameter of approximately 100 μm , which was utilized as the iron core for FONP@RIP, was vacuum-dried at 378 K for 24 h. Then, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.9 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.4 g) were dissolved in a beaker with 450 mL ultrapure water at 70 $^\circ\text{C}$, following with an addition of RIP (1.18 g) into the solution, then NaOH (50 mL) solution was injected (concentration: 5M; velocity: 10 mL/min) into the mixture. The suspension was kept mechanical stirring for 1 h and then maturing for 2 h. After separation, the collected particles were washed several times with deionized water until the pH of washing solution became neutral. At last, the particles were dried by freeze-drying.

Text S2

Analysis of TC and Intermediates

The residual concentration of TC was quantified by high-performance liquid chromatography (HPLC, 1200 Infinity, Agilent, USA) equipped with a Zorbax Eclipse XDB-C18 column (4.6 mm \times 150 mm, 5 μm , Agilent, USA). The mixed solvent of sodium dihydrogen phosphate solution (0.01 mol/L) and acetonitrile (65:35, v/v) was used as the mobile phase. The column temperature was maintained at 25 $^\circ\text{C}$ and the flow rate of the mobile phase was kept at 1 mL/min. The injection volume of samples was 10 μL and the wavelength for detection was 360 nm.

The intermediates of TC were identified by UPLC-MS (1290 UPLC/Q-TOF 6550, Agilent, USA) by using a mixture of formic acid solution (0.1%, m/m) and acetonitrile (90:10, v/v) as the mobile phase. The column temperature was set at 40 $^\circ\text{C}$ and the injection volume was 5 μL . The flow rate of the mobile phase was kept at 0.3 mL/min. TC and intermediates were estimated using ESI in positive ion mode.

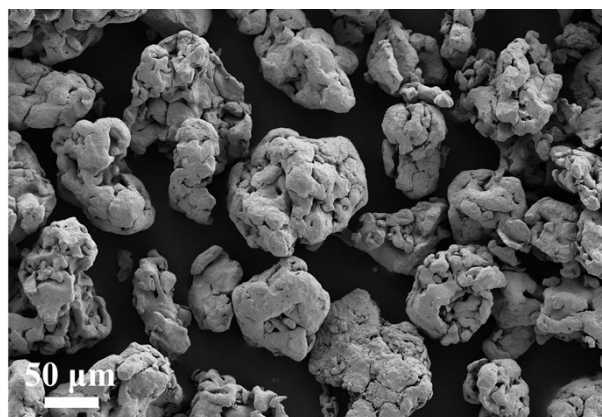


Fig. S1. SEM image of RIP.

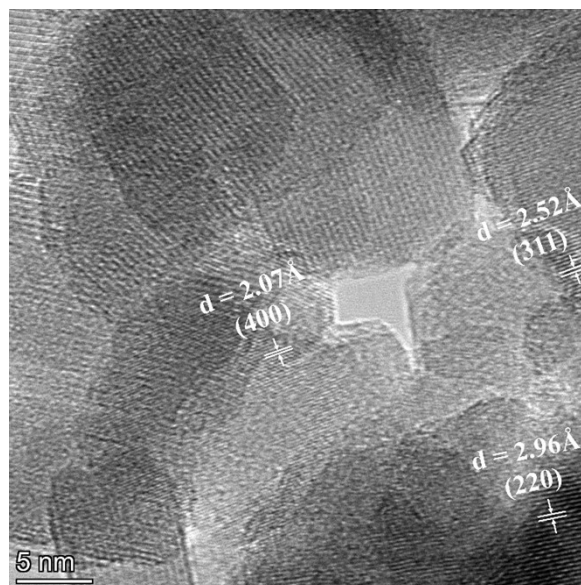


Fig. S2. HRTEM image of FONP@RIP.

Table S1. Relative atomic percentages of Fe 2p on RIP, FONP, and FONP@RIP.

Sample	Fe ⁰ (Fe 2p _{3/2})	Fe (II) (Fe 2p _{3/2})	Fe (III) (Fe 2p _{3/2})	Fe (III) (Fe 2p _{3/2} satellite)	Fe ⁰ (Fe 2p _{1/2})	Fe (III) (Fe 2p _{1/2})
RIP	1.4%	67.1%	n.d.	n.d.	1.7%	29.8%
FONP	n.d.	15.9%	51.6%	4.0%	n.d.	28.5%
FONP@RIP	n.d.	16.3%	49.5%	6.7%	n.d.	27.5%

n.d.: not detected.

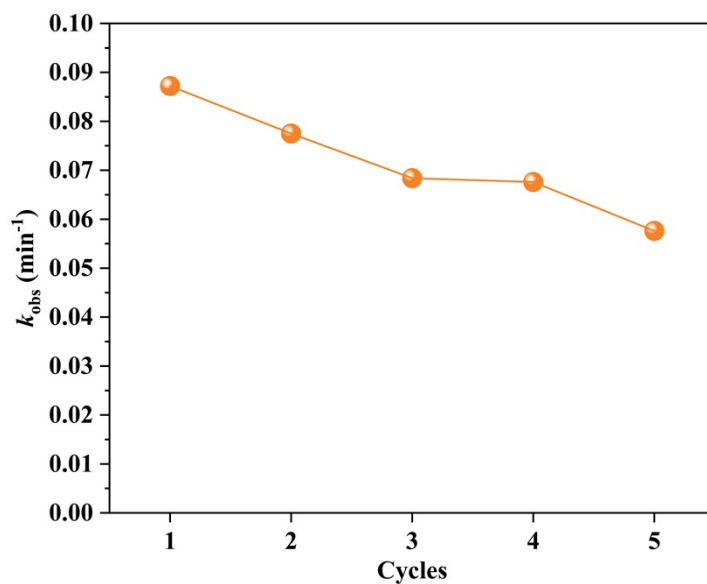


Fig. S3. The analysis of pseudo-first-order kinetics in the FONP@RIP/H₂O₂ system. ($[\text{TC}]_0 = 150$ ppm, FONP@RIP dosage = 0.5 g/L, $[\text{H}_2\text{O}_2]_0 = 5$ mM, and initial pH = 3).

Table S2. The kinetic parameters of TC degradation in the FONP@RIP/H₂O₂ system.

Cycle	k_{obs} (min^{-1})	R^2
1	0.0872	0.9329
2	0.0775	0.9863
3	0.0684	0.9966
4	0.0676	0.9953
5	0.0576	0.9941

Table S3. Relative atomic percentages of Fe 2p on FONP@RIP after H₂O₂ activation.

Retention time	Fe (II) (Fe 2p _{3/2})	Fe (III) (Fe 2p _{3/2})	Fe (III) (Fe 2p _{3/2} satellite)	Fe (III) (Fe 2p _{1/2})
10 min	15.0%	53.4%	4.4%	27.2%
20 min	21.1%	48.2%	3.2%	27.5%
30 min	24.8%	42.7%	3.8%	28.7%

Table S4. Relative atomic percentages of O 1s on FONP@RIP after H₂O₂ activation.

Retention time	Lattice oxygen	Oxygen vacancies	C-O
10 min	47.5%	36.1%	16.4%
20 min	32.6%	55.6%	11.8%
30 min	27.5%	64.1%	8.4%

Table S5. Relative atomic percentages of N 1s on FONP@RIP after TC adsorption (FONP@RIP-TC) and after H₂O₂ activation (FONP@RIP/H₂O₂-TC).

Sample	-NH ₂	Graphitic N	Oxidized N
FONP@RIP-TC	13.1%	86.9%	n.d.
FONP@RIP/H ₂ O ₂ -TC	71.7%	n.d.	28.3%

n.d.: not detected.

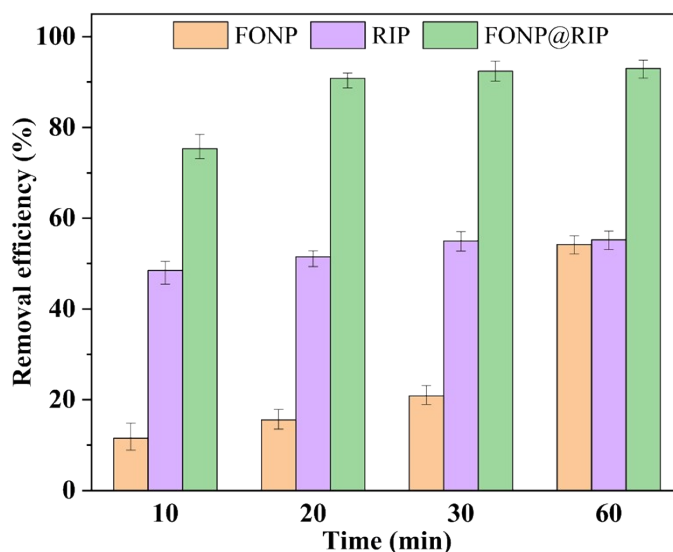
**Fig. S4.** Comparison of degradation efficiency of TC in FONP/H₂O₂, RIP/H₂O₂, and FONP@RIP/H₂O₂ system. ([TC]₀ = 150 ppm, FONP@RIP dosage = 0.5 g/L, [H₂O₂]₀ = 5 mM, and initial pH = 3).

Table S6. Toxicity estimates of intermediates by the ECOSAR program. Red boxes, very toxic (< 1 mg/L); blue boxes, toxic (1-10 mg/L); orange boxes, harmful (10-100 mg/L); green boxes, not harmful (> 100 mg/L).

Compound	m/z	Acute toxicity (mg/L)			Chronic toxicity (ChV, mg/L)			Hazard category
		Fish (LC ₅₀)	Daphnid (LC ₅₀)	Green Algae (EC ₅₀)	Fish	Daphnid	Green Algae	
TC	445	61.44	4.49	10.24	0.96	1.04	2.52	Toxic
ATC	427	20.92	2.14	2.26	0.27	0.45	0.79	Toxic
1	461	34.21	2.30	5.21	0.29	0.49	0.85	Toxic
2	417	90.58	5.72	18.27	1.54	1.38	3.84	Toxic
3	410	16.14	2.21	2.53	0.24	0.47	0.86	Toxic
4	509	388.36	1293.00	19.01	97.44	24.15	5.00	Harmful
5	477	6.26	1.09	1.33	0.08	0.21	0.25	Toxic
6	444	59.42	3.84	13.38	0.68	0.87	1.96	Toxic
7	426	4.62	0.89	1.02	0.06	0.17	0.20	Toxic
8	480	181.56	535.53	10.09	23.60	8.01	2.88	Harmful
9	341	10.06	1.21	0.88	0.12	0.25	0.37	Toxic
10	339	9.71	1.18	0.83	0.12	0.24	0.35	Toxic
11	316	0.61	20.78	1.38	0.04	2.96	1.37	Toxic
12	314	3.17	2.55	0.18	0.42	0.26	1.14	Toxic
13	312	2.93	2.38	0.17	0.39	0.25	1.09	Toxic
14	276	7.91	22.23	0.68	3.73	1.54	4.89	Toxic
15	359	6.95	0.98	0.53	0.08	0.19	0.25	Toxic
16	525	98.57	117.25	7.09	18.69	9.65	32.04	Toxic
17	342	2.32	1.95	0.15	0.32	0.21	0.97	Toxic
18	298	2.26×10 ⁶	4.28×10 ⁵	4.68×10 ⁴	2.61×10 ⁴	2.11×10 ⁴	1.01×10 ⁴	Not Harmful
19	183	349.63	137.36	30.53	33.88	14.48	61.55	Harmful
20	426	9.28	1.83	1.63	0.16	0.38	0.62	Toxic
21	367	1.79×10 ⁵	4.56×10 ⁴	6196.09	1.20×10 ⁴	2810.79	2.18×10 ⁴	Not Harmful
22	496	1153.85	4657.02	239.55	2911.17	1351.56	2221.50	Not Harmful
23	333	145.58	3.71	15.79	0.86	0.87	2.21	Toxic
24	260	6.34	17.32	0.51	2.44	1.08	3.59	Toxic
25	175	3.39	2.56	0.31	0.38	0.35	0.89	Toxic
26	357	13.06	1.30	2.28	0.13	0.26	0.40	Toxic
27	253	2.32×10 ⁷	7.83×10 ⁶	6.82×10 ⁵	1.23×10 ⁶	1.80×10 ⁵	5.62×10 ⁴	Not Harmful
28	308	1.47	1.66	0.14	0.18	0.26	0.49	Toxic
29	351	2.11×10 ⁴	6702.04	1077.80	1625.22	490.10	4065.73	Not Harmful
30	256	11.96	36.59	1.26	10.42	3.54	9.65	Toxic
31	146	1.50×10 ⁴	6887.14	2102.55	1140.55	368.46	340.56	Not Harmful
32	116	5.33×10 ⁴	2.53×10 ⁴	8964.33	4216.20	1496.17	1573.47	Not Harmful
33	100	2.10	1.19×10 ⁴	3592.18	0.17	607.51	315.94	Toxic
34	85	0.19	10.18	1.84	0.02	1.72	0.59	Toxic
35	90	1.68×10 ⁵	6.75×10 ⁴	1.21×10 ⁴	1.09×10 ⁴	2519.06	1466.06	Not Harmful
36	61	556.80	49.33	73.20	80.07	3.04	19.62	Harmful
37	61	1.52×10 ⁵	6.02×10 ⁴	1.02×10 ⁴	9714.58	2167.92	1205.14	Not Harmful

Table S7. Comparison of the TC degradation performance in the FONP@RIP/H₂O₂ system with those of other reported heterogeneous catalysts.

Catalyst	pH	TC initial conc. (ppm)	Conc. of catalyst and H ₂ O ₂	Removal of TC and HRT	Degradation rate ^a (mmol.g ⁻¹ .min ⁻¹)	Ref.
Ca _{0.9} FeO _{3-δ}	3	50	0.1 g/L, 20 mM	88.3%, 150 min	2.4×10 ⁻³	1
Fe-MPC	4.3	40	0.02 g/L, 1 mM	83.0%, 10 min	1.7×10 ⁻³	2
Cu _{2.5} Ni _{0.5} Co-LDH/GO	10.2	20	0.06 g/L, 10 mM	96.5%, 40 min	1.4×10 ⁻³	3
CuFeO ₂ /BC	6.27	20	0.6 g/L, 57.6 mM	89.1%, 300 min	1.8×10 ⁻³	4
14Fe ₃ O ₄ -Cs beads	3	48	0.5 g/L, 10 mM	96.2%, 120 min	1.7×10 ⁻³	5
FeNi ₃ @SiO ₂	7	20	0.1 g/L, 200 mM	73.1%, 180 min	1.8×10 ⁻³	6
FONP@RIP	4	150	0.5 g/L, 5 mM	94.5%, 60 min	1.1×10 ⁻²	This study

^a TC degradation rate = $\frac{M_{TC_0} - M_{TC_t}}{C.t}$, where M_{TC_0} is the initial molar concentration (mM) of TC; M_{TC_t} is the molar concentration (mM) of TC at time t (min); C is the concentration of catalyst (g/L); t is the reaction time (min).

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