Supplementary Material

Activation of Peracetic Acid by $CoFe_2O_4$ for Efficient Degradation of Ofloxacin: Reactive Species and Mechanism

Rong Li, Xing Lu, Jinxiang Gao, Yifan Chen, Shunlong Pan *

School of Environmental Science and Engineering, Nanjing Tech University, Nanjing 211816, China; 202161202058@njtech.edu.cn (R.L.); 202161102009@njtech.edu.cn (X.L.); 202261202027@njtech.edu.cn (J.G.); 202261202055@njtech.edu.cn (Y.C.)

* Correspondence: shunlongpan@njtech.edu.cn

Test S1. Pseudo-first-order kinetic equation

The apparent rate constant (k_{obs}) was calculated by fitting the degradation kinetics of OFX with a pseudo-first-order model:

$$-\ln\left(\frac{C_t}{C_0}\right) = k_{obs}\, t \qquad \text{(S1)}$$

Where, C_0 and C_t represent the concentration of OFX at the initial and a certain reaction time respectively, and t represents the reaction time.

Table S1. An overview of research on the removal of OFX by ferrites.

Catalyst	OFX	Operation conditions	Removal Efficiency	Ref
$Ag_3PO_4/CoFe_2O_4$ (0.5 g/L)	20 mg/L	under visible light; 150 min	95.9%	[1]
$MSm_xFe_{2-x}O_4$ (M = Ni, Co; x = 0, 0.02, 0.06, 0.1) (0.5 g/L)	15 mg/L	$[H_2O_2]$ = 9.8 mM; pH = 2.5; 60 min; under visible light	57%-86%	[2]
$CuFe_2O_4$-Mt (0.4 g/L)	40 mg/L	[PMS] = 2.0 mM; pH = 6.8; 60 min	85.2%	[3]
$CoFe_2O_4@Bi_2O_3/NiO$ (0.3 g/L)	10 mg/L	under visible light; 90 min	95.2%	[4]
Cellulose/PANI/$NiFe_2O_4$ (0.5 g/L)	0.05 mM	$[H_2O_2]$ = 8.8 uM; pH = 2.5; 30 min under visible light	87.44%	[5]
$CoFe_2O_4$/WS (1.0 g/L)	20 mg/L	[PMS] = 1.0 g/L; 30 min	92.8%	[6]
$MnFe_2O_4@C\text{-}NH_2$ (1.0 g/L)	30 mg/L	$[H_2O_2]$ = 29.4 mM; pH = 3; 180 min	97.4%	[7]

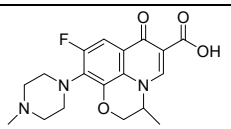
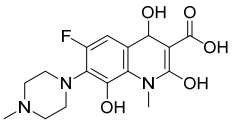
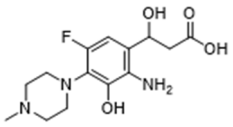
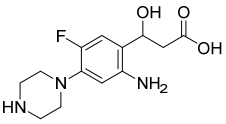
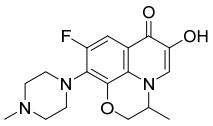
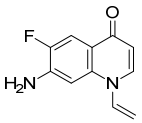
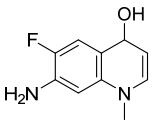
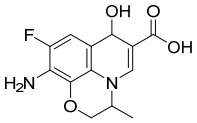
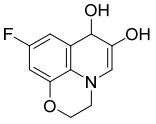
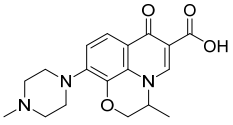
Table S2. Quality of tap water and surface water.

Category	TOC (mg/L)	COD (mg/L)	TN (mg/L)
Tap water	0.79	2.31	1.56
Surface water	12.59	39.03	2.31

Table S3. Change of valence state of elements in $CoFe_2O_4$ before and after reaction by XPS analysis.

Elements		Before	After
Co	Co(II)	46.58%	50.44%
	Co(III)	53.42%	49.56%
Fe	Fe(II)	58.68 %	55.88%
	Fe(III)	41.32%	44.12%
O	Lattice O	75.75%	70.83%
	Surface OH	19.50%	21.39%
	H_2O	4.75%	7.78%

Table S4. Intermediates of OFX degradation in $CoFe_2O_4$/PAA system.

Product ID	Molecular weight [M + H^+]	Molecular formula	Proposed structure
OFX	362	$C_{18}H_{20}O_4N_3F$	
P1	354	$C_{16}H_{20}O_5N_3F$	
P2	314	$C_{14}H_{20}O_4N_3F$	
P3	283	$C_{13}H_{18}O_3N_3F$	
P4	334	$C_{17}H_{20}O_3N_3F$	
P5	205	$C_{11}H_9ON_2F$	
P6	194	$C_{10}H_{11}ON_2F$	
P7	280	$C_{13}H_{13}O_4N_2F$	
P8	224	$C_{11}H_{10}O_3NF$	
P9	344	$C_{18}H_{21}O_4N_3$	

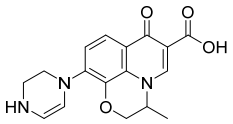
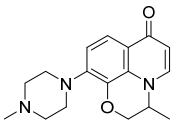
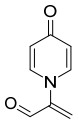
P10	327	$C_{17}H_{17}O_4N_3$	
P11	300	$C_{17}H_{21}O_2N_3$	
P12	149	$C_8H_7O_2N$	

Table S5. CAS Registry Number of chemicals.

Chemicals	CAS	Chemicals	CAS
OFX	82419-36-1	DPD	93-05-0
NOR	70458-96-7	HA	1415-93-6
CIP	85721-33-1	*p*CBA	74-11-3
ENR	93106-60-6	NAP	22204-53-1
TBA	75-65-0	PMSO	1193-82-4
MeOH	67-56-1	$PMSO_2$	3112-85-4
$CHCl_3$	67-66-3	CH_3CN	75-05-8
FFA	98-00-0	HCOOH	64-18-6

Table S6. Details of the detection conditions in HPLC for organic compounds.

Chemicals	Flow rate (mL/min)	Mobile phase	Wavelength (nm)
Ofloxacin (OFX)	1.0	Acetonitrile: 0.1% formic acid (15:85)	288
Norfloxacin (NOR)	1.0	Acetonitrile: 0.1% formic acid (30:70)	275
Ciprofloxacin (CIP)	1.0	Acetonitrile: 0.1% formic acid (30:70)	275
Enrofloxacin (ENR)	1.0	Acetonitrile: 0.1% formic acid (20:80)	278
p-chlorobenzoic acid (*p*CBA)	1.0	Acetonitrile: 0.1% formic acid (40:60)	236
Naproxen (NAP)	1.0	Acetonitrile: 0.1% formic acid (60:40)	231
Methyl phenyl sulfoxide (PMSO)	1.0	Acetonitrile: 0.1% formic acid (25:75)	230
Methyl phenyl sulfone ($PMSO_2$)	1.0	Acetonitrile: 0.1% formic acid (25:75)	215

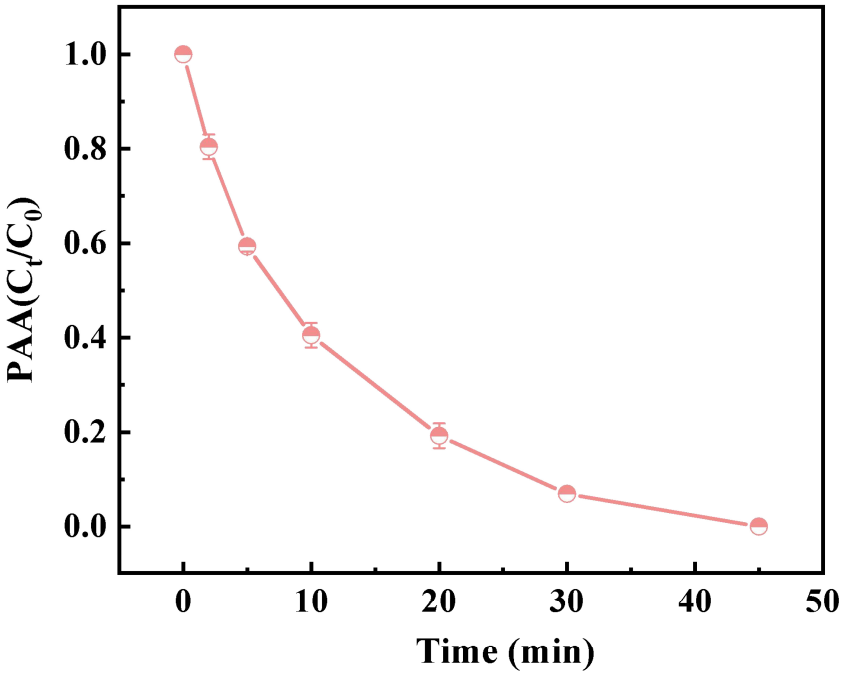


Figure S1. Decomposition of PAA during the reaction. Experimental conditions: [OFX] = 20 μM, $[PAA]_0$ = 0.4 mM, $CoFe_2O_4$ = 0.10 g/L, pH = 7.0, T = 25 ℃.

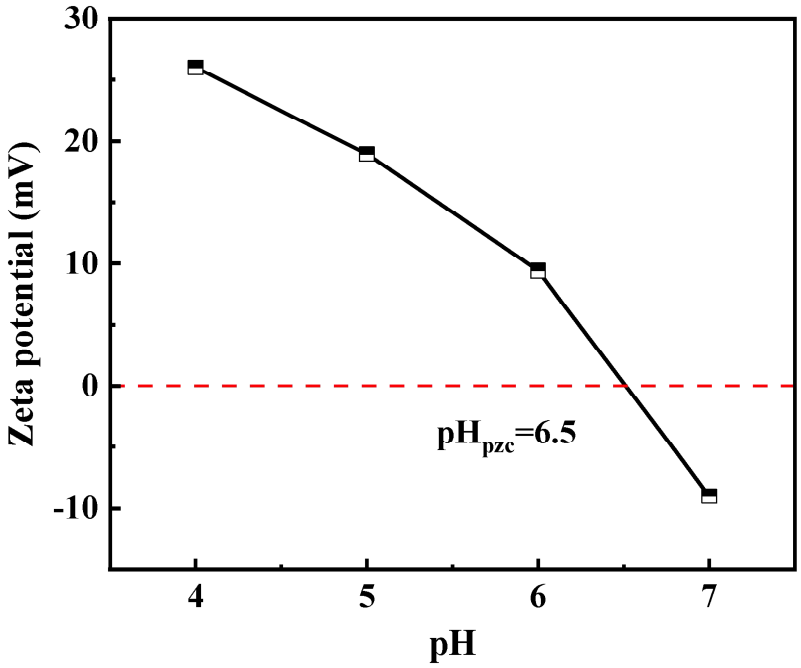


Figure S2. The zeta potential of $CoFe_2O_4$.

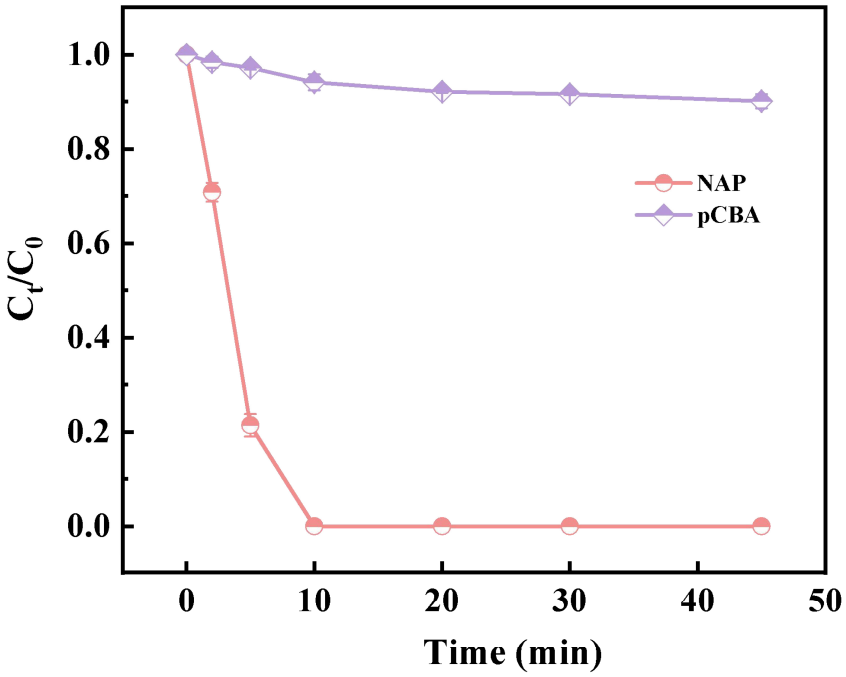


Figure S3. Degradation of NAP and *p*CBA in $CoFe_2O_4$/PAA system. Experimental conditions: [NAP] = [*p*CBA] = 20 μM, $[PAA]_0$ = 0.4 mM, $CoFe_2O_4$ = 0.10 g/L, pH = 7.0, T = 25 ℃.

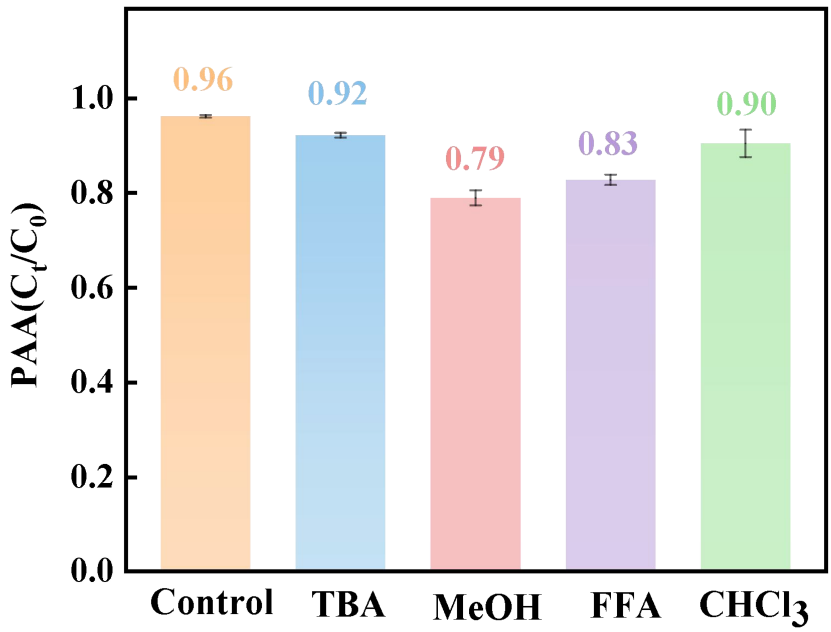


Figure S4. Effects of quenchers on the decomposition of PAA. Experimental conditions: $[PAA]_0 = 0.4$ mM, [TBA] = [MeOH] = 100 mM, [FFA] = $[CHCl_3]$ = 10 mM, pH = 7.0, T = 25 ℃.

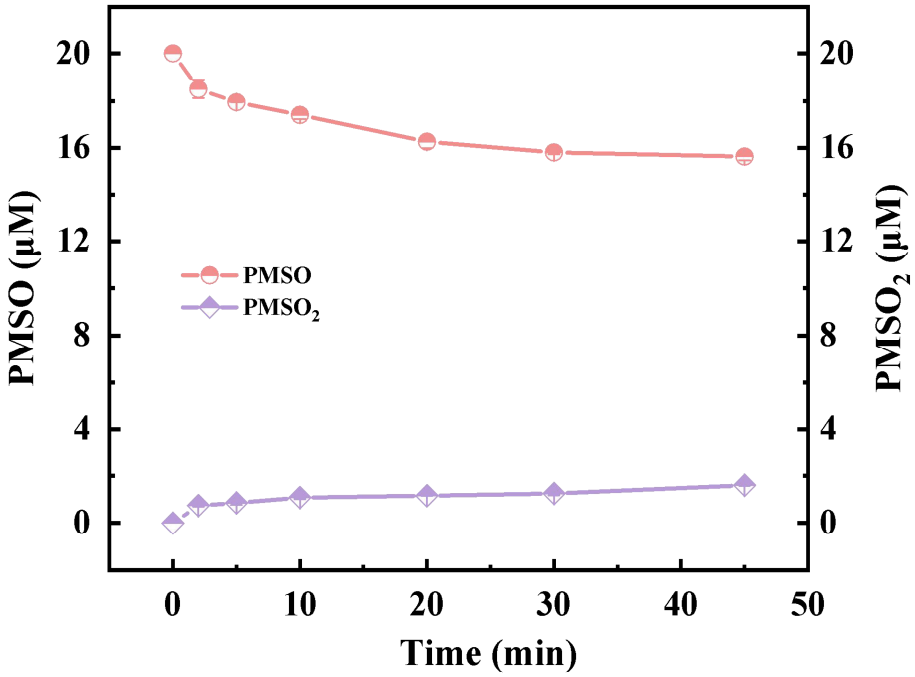


Figure S5. Degradation of PMSO and production of $PMSO_2$ in $CoFe_2O_4$/PAA system. Experimental conditions: [PMSO] = 20 μM, $[PAA]_0$ = 0.4 mM, $CoFe_2O_4$ = 0.10 g/L, pH = 7.0, T = 25 ℃.

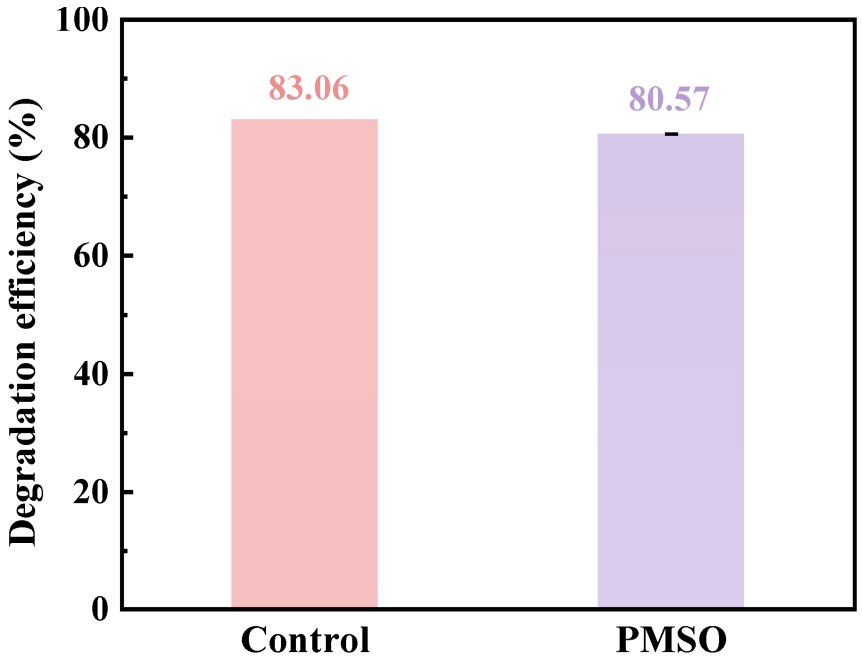
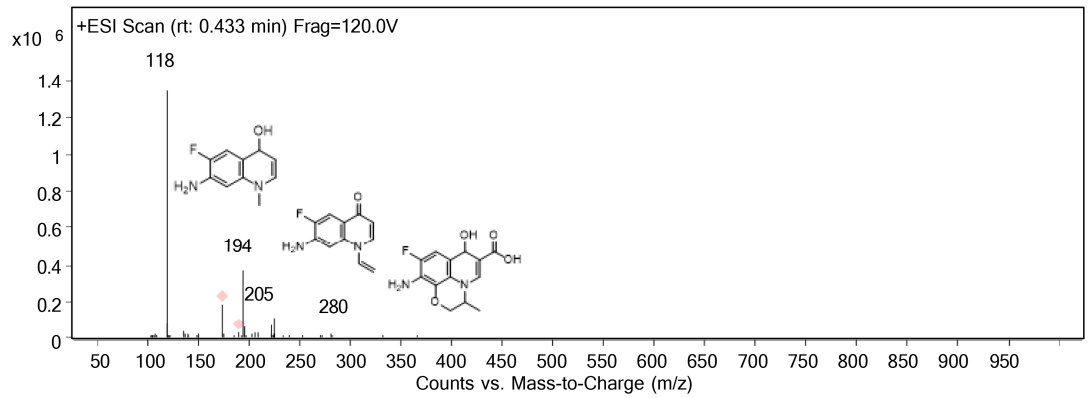
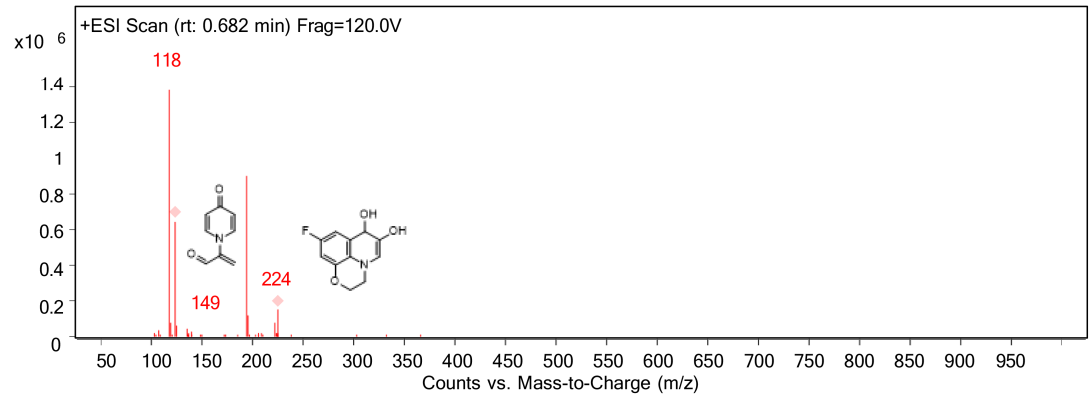
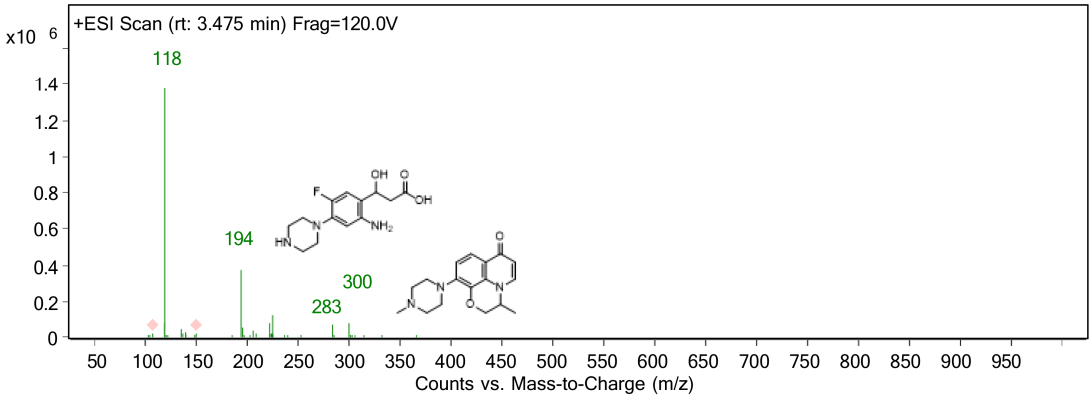
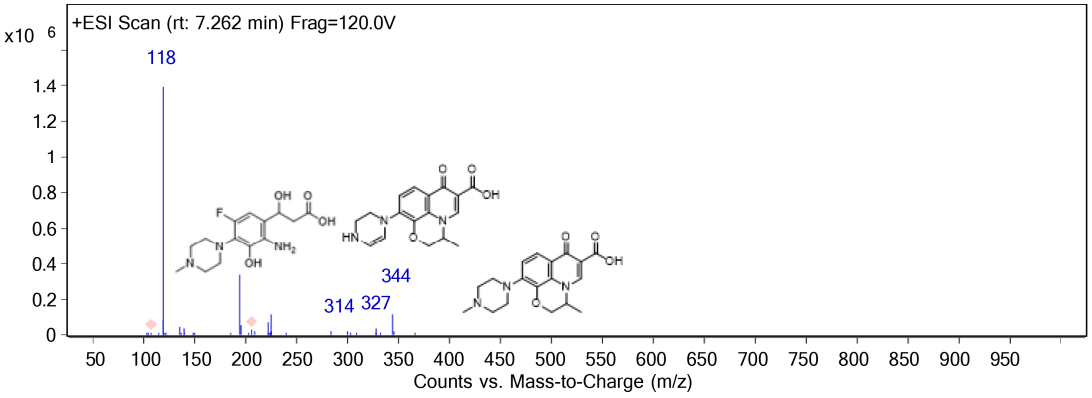


Figure S6. Effect of PMSO on the degradation of OFX. Experimental conditions: [OFX] = 20 μM, [PMSO] = 100 μM, $[PAA]_0$ = 0.4 mM, $CoFe_2O_4$ = 0.10 g/L, pH = 7.0, T = 25 ℃.


+ESI Scan (rt: 0.433 min) Frag=120.0V
x10 6
118
194
205
280
Counts vs. Mass-to-Charge (m/z)


+ESI Scan (rt: 0.682 min) Frag=120.0V
x10 6
118
149
224
Counts vs. Mass-to-Charge (m/z)


+ESI Scan (rt: 3.475 min) Frag=120.0V
x10 6
118
194
283
300
Counts vs. Mass-to-Charge (m/z)


+ESI Scan (rt: 7.262 min) Frag=120.0V
x10 6
118
314
327
344
Counts vs. Mass-to-Charge (m/z)

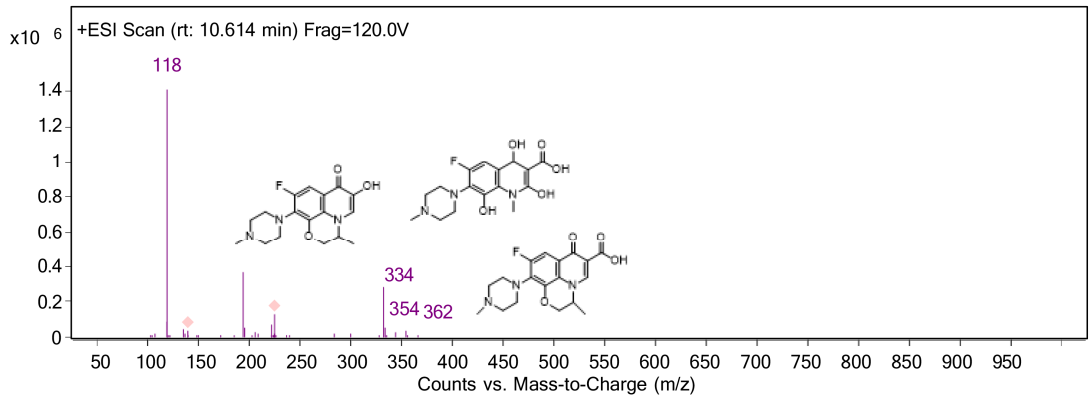


Figure S7. LC-TOF-MS chromatograms of OFX and the intermediates in $CoFe_2O_4$/PAA system.

References

1. Ye, H.; Xia, L.; Wang, Y.; Zhou, H.; Xie, X.; Zuo, G.; Wu, K. Magnetic $Ag_3PO_4/CoFe_2O_4$ Z-scheme heterojunction material for photocatalytic decomposition of ofloxacin. *J. Mater. Sci. Mater. Electron.* **2023**, *34*, 2090.

2. Singh, S.; Kaur, P.; Kumar, V.; Tikoo, K.B.; Singhal, S. Traversing the advantageous role of samarium doped spinel nanoferrites for photocatalytic removal of organic pollutants. *J. Rare Earths.* **2021,** *39*, 781-789.

3. Cao, X.Q.; Xiao, F.; Lyu, Z.W.; Xie, X.Y.; Zhang, Z.X.; Dong, X.; Wang, J.X.; Lyu, X.J.; Zhang, Y.Z.; Liang, Y. $CuFe_2O_4$ supported on montmorillonite to activate peroxymonosulfate for efficient ofloxacin degradation. *J. Water Process. Eng.* **2021**, *44*, 102359.

4. Dhiman, P.; Sharma, G.; Alodhayb, A.N.; Kumar, A.; Rana, G.; Sithole, T.; Alothman, Z.A. Constructing a visible-active $CoFe_2O_4@Bi_2O_3/NiO$ nanoheterojunction as magnetically recoverable photocatalyst with boosted ofloxacin degradation efficiency. *Molecules.* **2022**, *27*, 8234.

5. Nitansh; Kaur, P.; Garg, T.; Renu; Deepeka; Kumar, V.; Tikoo, K.; Kaushik, A.; Singhal, S. A fluorescent biomass derived cellulose/PANI/$NiFe_2O_4$ composite for the mitigation of toxic pollutants and Cr(VI) sensing from aqueous environment. *J. Ind. Eng. Chem.* **2023**.

6. Zheng, C.; Wu, J.Y.; Zhang, Y.J.; Yang, Q.; Yang, Y.C. Walnut shell loaded with cobalt ferrite as efficient peroxymonosulfate activator to degrade ofloxacin. *Water Air Soil Pollut.* **2023**, *234*, 305.

7. Qin, H.; Cheng, H.; Li, H.; Wang, Y. Degradation of ofloxacin, amoxicillin and tetracycline antibiotics using magnetic core–shell $MnFe_2O_4@C\text{-}NH_2$ as a heterogeneous fenton catalyst. *Chem. Eng. J.* **2020**, *396*, 125304.