

Supporting Information

Microwave synthesis of Fe-Cu diatomic active center MOF: Synergistically cyclic catalysis of persulfate for degrading norfloxacin

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Text S1. Reagents and materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), terephthalic acid (H_2BDC , $\geq 99\%$), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 98\%$), N, N-dimethylformamide (DMF, 99.8%), methanol (MeOH, 96%), tert butyl alcohol (TBA, $\geq 99.9\%$), furfuryl alcohol (PhOH, $\geq 98\%$), L-histidine (L-HIS, $\geq 98\%$), sodium azide (NaN_3 , $\geq 98\%$) Norfloxacin (NOF, $\geq 99\%$) was provided by Sinopharm Chemical Reagent Co., Ltd. Without special statement, deionized water with the specific resistance of $18.25 \text{ M}\Omega \cdot \text{cm}$ was applied to prepare solutions. The above reagents are commercially available analytical pure reagents, which are directly used without further purification.

Text S2. Evaluation and analytical methods

Experimental procedure: 20 mg of catalyst and 10 mg of PDS were added to a conical flask containing 50 ml of NOF solution (20 mg/L), and then put into a constant temperature water bath shaking box. The reaction temperature was set at 25 ± 0.1 °C and the catalytic process was completed at an oscillation frequency of 150 rpm for 1 h. During the experiment, take 1 mL sample from the reaction solution at a preset time interval, quench it with excessive methanol, and for HPLC analysis. Under the same conditions as above, the recoverability of the catalyst was checked by four repeated degradation experiments. Quenching experiments were carried out by adding different scavengers, which included methanol (MeOH) and tert-Butanol (TBA), L-HIS, sodium azide (SA), furfuryl alcohol (FAH).

Electrochemical measurements: Four types of catalyst powders were attached to the glassy carbon electrode for electrochemical testing of synthetic materials. 10 mg material solids and 40 μ L of nafion were dispersed in 1 mL of a mixture of ethanol and water (1:4) with a vortex. Then, 15 μ L of the resulting dispersion was dropped onto the surface of the working electrodes and dried at room temperature. The electrochemical station (CHI 660E, China) was employed to carry out electrochemical measurements in 0.5 M Na₂SO₄ electrolyte. The Ag/AgCl electrode and Pt sheet were served as reference electrode and counter electrode, respectively. The scan direction for the CV was changed from reduction to oxidation and the scan rate was 50 mV/s and the EIS data were modeled with the ZSimpWin data analysis software.

HPLC analysis operation: The samples were filtered with 0.22 μ m cellulose

acetate syringe membrane filter to determine the NOF concentration via (HPLC, Agilent 1100 series, USA) with an Agilent TC-C18 column (4.6×250 mm, 5 μ m). The mobile phase consisted of phosphoric acid (pH=3, adjusted by triethylamine) and acetonitrile (85:15, v/v%), the flow rate was 1.0 mL/min and 20 μ L, respectively. The detector wavelength was set at 278 nm. The retention time of NOF was 3.8 min.

Liquid chromatography-mass spectrometry: Determination of the degradation intermediates of NOF were carried out on a LC-MS system equipped with a 6460 HPLC (Agilent, USA) and an API 3000 mass analyzer. The HPLC column was a Kromasil C18 column (4.6×100 mm) from Agilent. 0.1% of formic acid aqueous solution and acetonitrile were used as mobile phases A and B, respectively. The eluent flow rate keeps 0.45 mL/min. An injection volume of 10 μ L was used in analysis and column temperature at 302 K (30°C).

PDS concentration determination: Specifically, 0.5 mL sample was added into 4.5 mL KI (92.22 g/L)/NaHCO₃ (4.44 g/L) solution, then mixed well and equilibrated for 30 min, finally detected at 352 nm.

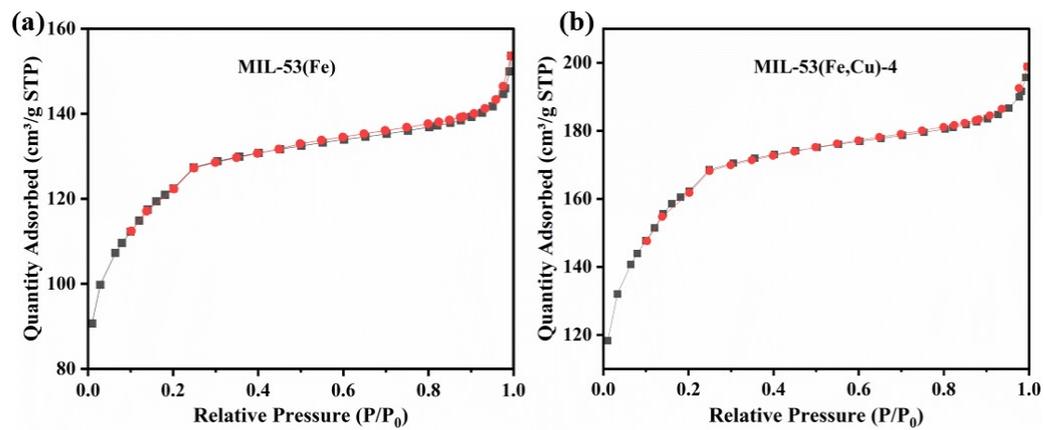


Fig. S1 N_2 adsorption-desorption isotherms of MIL-53(Fe) and MIL-53(Fe, Cu)-4.

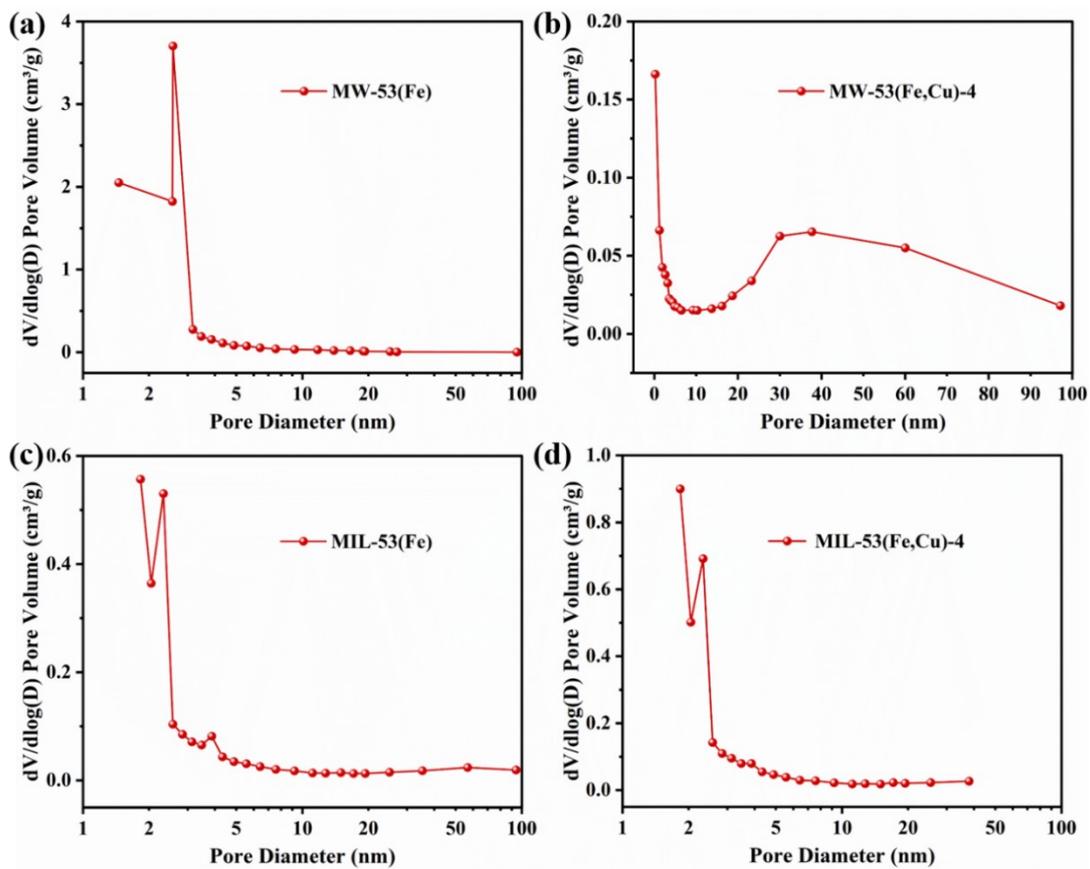


Fig. S2 Pore diameter distribution of various catalysts.

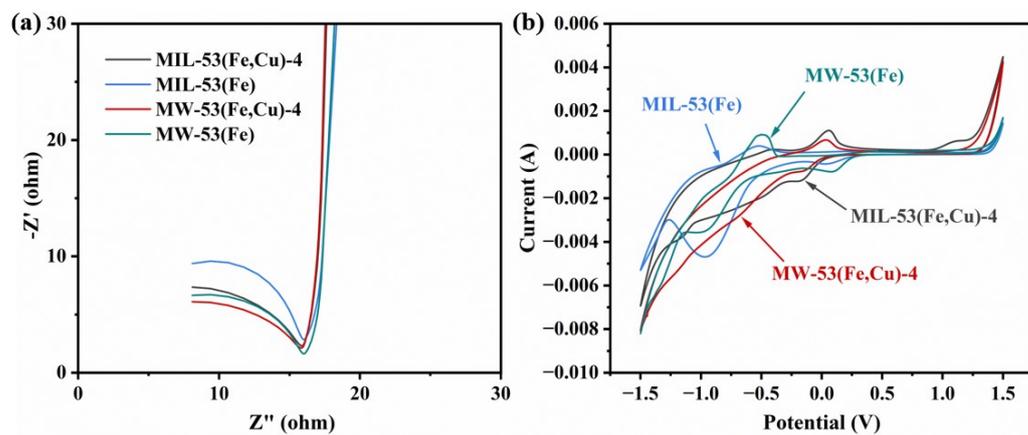


Fig. S3 Cyclic voltammogram (CV) curves (a), and EIS spectra (b) of MIL-53(Fe), MIL-53(Fe, Cu)-4, MW-53(Fe) and MW-53(Fe, Cu)-4 catalysts.

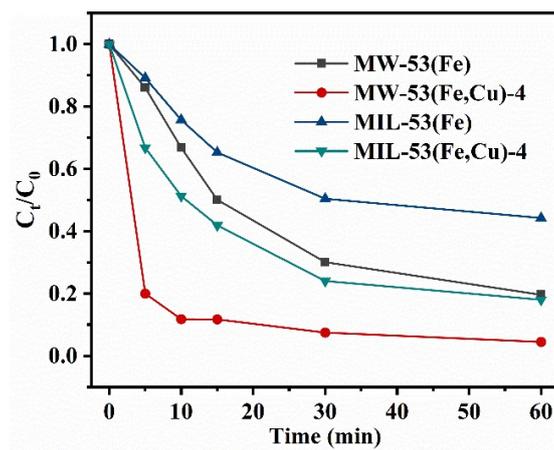


Fig. S4 NOF degradation efficiency in the system with various catalysts. (NOF: 20 mg/L; catalyst: 0.4 g/L; PDS: 0.2 g/L; initial pH = 6.55; T = 298 K)

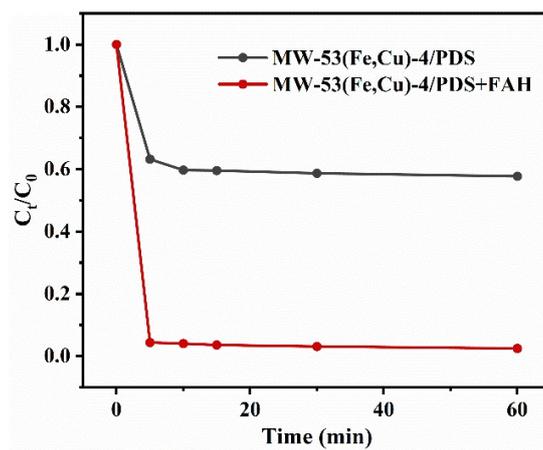


Fig. S5 Consumption of PDS in different systems. (NOF: 20 mg/L; catalyst: 0.4 g/L;

PDS: 0.2 g/L; FAH:10 mM; initial pH = 6.55; T = 298 K)

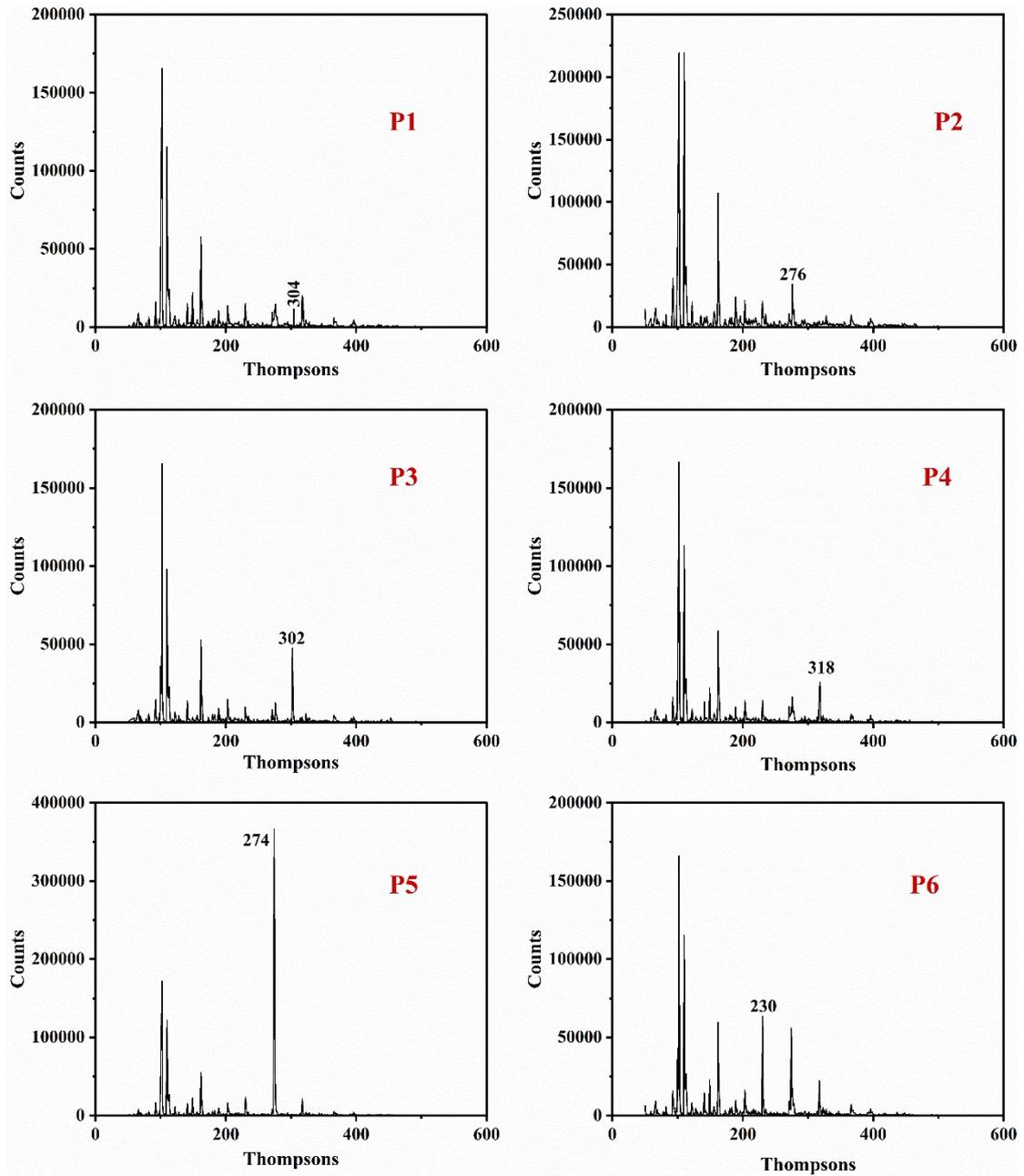


Fig. S6 Mass spectra corresponding to pollutants

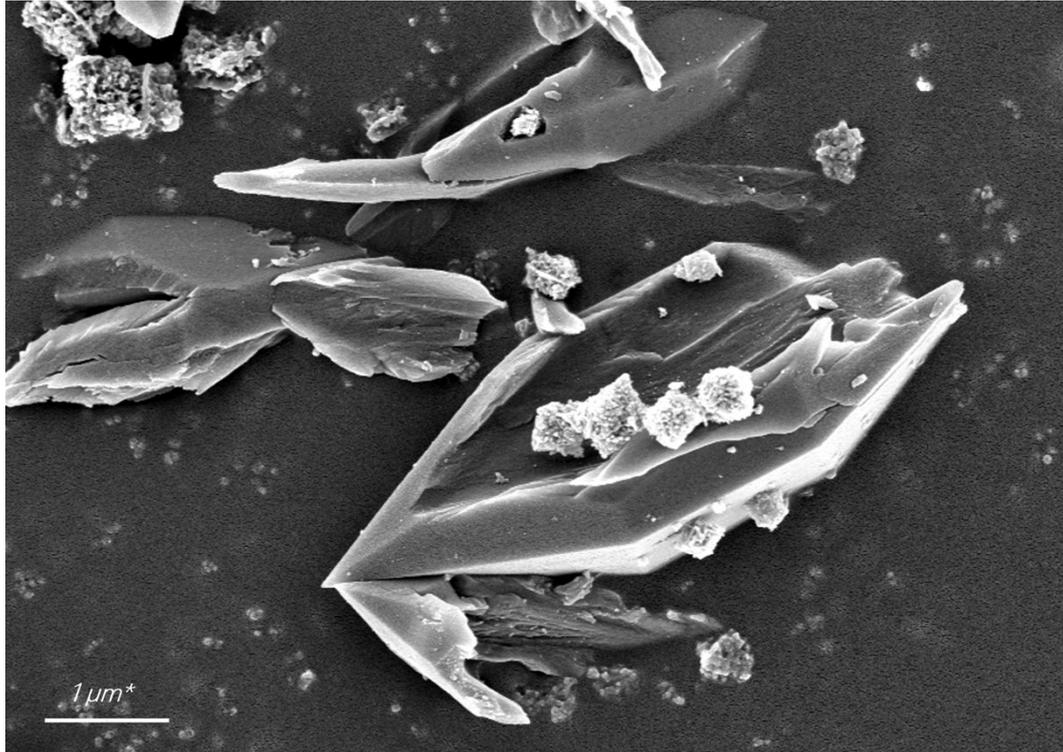


Fig. S7 SEM images of MW-53(Fe, Cu)-4 after reaction

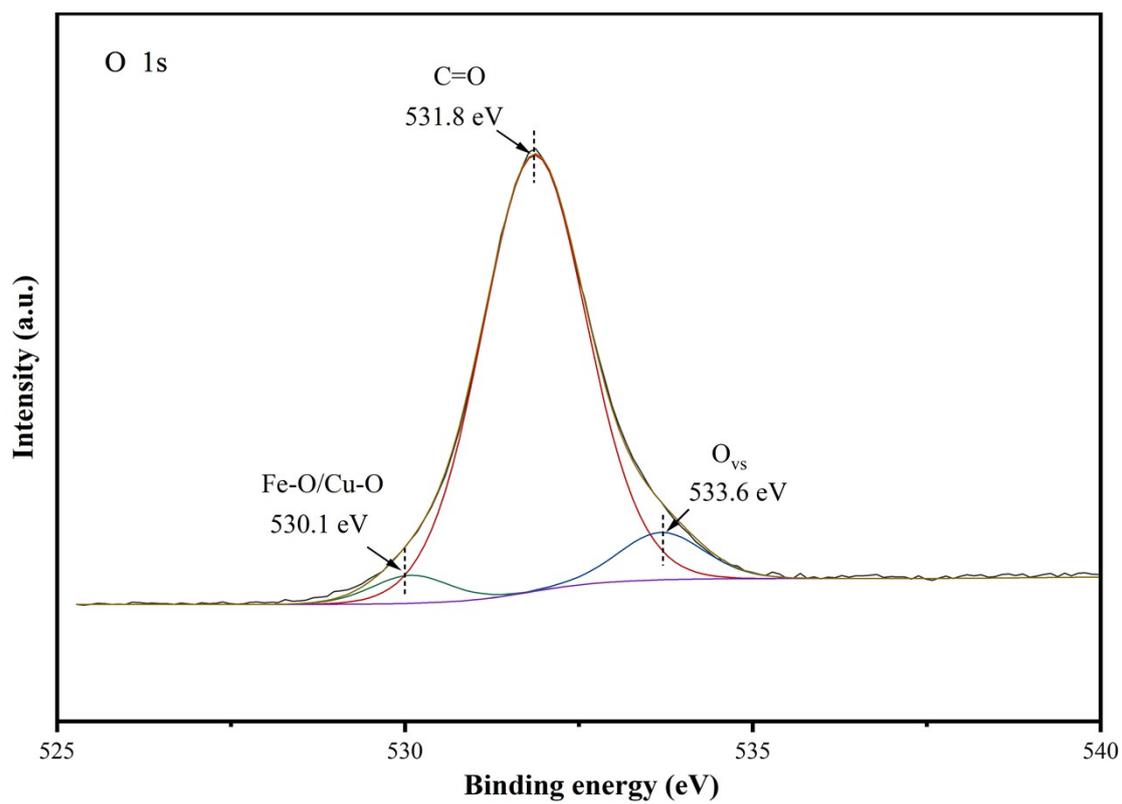


Fig. S8. XPS spectra of O1s (MW-53(Fe, Cu)-4)

Table S1 BET surface area and parameters of the porous structure for MW-53(Fe), MW-53(Fe, Cu)-4, MIL-53(Fe), MIL-53(Fe, Cu)-4.

Samples	BET surface area ^a (m ² g ⁻¹)	Pore size ^b (nm)	V _t ^c (cm ³ g ⁻¹)
MW-53(Fe)	932.77	2.44	0.57
MW-53(Fe, Cu)-4	107.97	5.99	0.09
MIL-53(Fe)	414.89	2.97	0.15
MIL-53(Fe, Cu)-4	551.26	2.63	0.21

Table S2 The elemental percentages of MW-53(Fe, Cu)-4 and MIL-53(Fe, Cu)-4.

Samples	Weight			
	C (%)	O (%)	Fe (%)	Cu (%)
MW-53(Fe, Cu)-4	62.13	22.45	12.67	2.75
MIL-53(Fe, Cu)-4	67.07	25.49	6.36	1.08

Table S3 Comparison of the performance of MW-53(Fe, Cu)-4 and other catalysts.

Target	Catalyzer	Reaction conditions	Synthesis	Performance	Mineralization rate	pH	References
NOF	MW-53(Fe, Cu)-4	Catalyst : 0.4 g/L , PDS : 0.83 mM , NOF : 20 mg/L , T : 25°C , pH : 6.55	Microwave-hydrothermal, 50 min	95.48% , 60 min	58%	3-10	This work
NOF	Fe/Ce-MIL-101-5%	Catalyst : 0.3 g/L , H2O2 : 20 mM , NOF : 10 mg/L , T : 25°C , pH : 7.0	Solvothermal, 20 h	94.8% , 60 min	58%	3-7	1
NOF	CuFe ₂ O ₄	Catalyst : 0.2 g/L , PMS : 0.5 mM , NOF : 8 mg/L , T : 25°C , pH : 7.0	Sol-el combustion, 14 h	90% , 120 min	64% , 12 h	7-9	2
NOF	BC@nZVI/Ni	Catalyst : 0.2 g/L , PS : 0.4 mM , NOF : 10 mg/L , T : 30°C , pH : 3.0	Liquid reduction, 1 h	80.5% , 40 min	-	3-7	3
NOF	CoFe ₂ O ₄ -NC	Catalyst : 0.1 g/L , PS : 0.32 mM , NOF : 10 mg/L , T : 25°C , pH : 6.5	Solvothermal, 12 h	91.2% , 60 min	33% , 3 h	2-9	4
NOF	Fe ₃ O ₄ -CuO	Catalyst : 0.5 g/L , PDS : 6 mM , NOF : 30 mg/L , T : 25°C , pH : 8.5	Calcine, 10 h	94.5% , 180 min	-	7-9	5

Table S4 Intermediates of NOF identified by LC-MS within 60 min

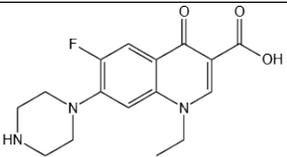
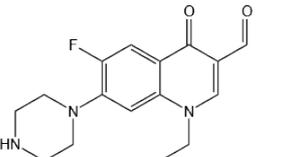
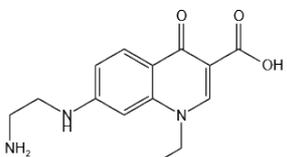
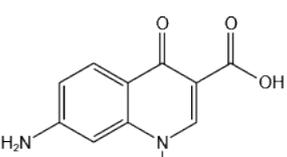
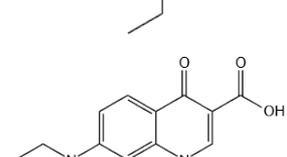
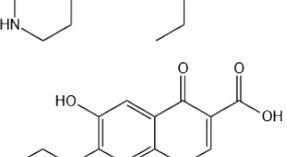
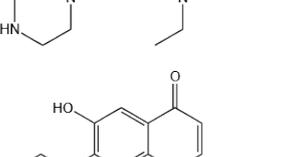
Structure NO.	Molecular Formula	M/Z	Probable Structure
NOF	$C_{16}H_{18}O_3N_3F$	320	
P1	$C_{16}H_{19}O_2N_3F$	304	
P2	$C_{14}H_{17}O_3N_3$	276	
P3	$C_{12}H_{12}O_3N_2$	230	
P4	$C_{16}H_{19}O_3N_3$	302	
P5	$C_{16}H_{19}O_4N_3$	318	
P6	$C_{15}H_{19}O_2N_3$	274	

Table S5 The data on water quality for the actual water bodies.

	DO (mg/L)	pH	NH ₄ -N (mg/L)	TP (mg/L)
XJR	7.39	7.36	0.18	0.08
TZL	5.93	6.31	0.15	1.16
MW	2.54	7.73	14.58	8.35

References

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