

Supporting information

Dissolved oxygen triggers a low concentration of H₂O₂ conversion over carbon-supported nanoscale zero-valent iron for fluoroquinolone degradation

Siyuan Zhang^{1,2}, Lin Niu^{2,3}, Xiaoli Zhao (✉)^{1,2}, Zhi Tang², Guangcan Zhu¹

1 School of Energy and Environment, Southeast University, Nanjing 210096, China

2 State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

3 School of Environment, Tsinghua University, Beijing 100084, China

✉ Corresponding author

E-mail: zhaoxiaoli_zxl@126.com

Table S1. Specific information about the chemical used

Reagent	CAS	Assay	Company
Ferrous acetates	3094-87-9	99.9 %	Sigma
2-aminoterephthalic acid	10312-55-7	99 %	Sigma
Ofloxacin	82419-36-1	99 %	Sigma
Norfloxacin	70458-96-7	97 %	Sigma
Ciprofloxacin	85721-33-1	98 %	Sigma
Hydrogen peroxide	7722-84-1	30 %	Sinopharm Chemical Reagent Co., Ltd
Tert-butanol	75-65-0	98 %	J&K Chemical Co., ltd
1,10-Phenanthroline	66-71-7	98 %	J&K Chemical Co., ltd
Hydroxylamine hydrochloride	5470-11-1	99.9 %	Macklin
L-Histidine	71-00-1	99 %	Sinopharm Chemical Reagent Co., Ltd
1,4-benzoquinone	106-51-4	99.5 %	Aladdin
Sodium acetate	127-09-3	99.5%	Sinopharm Chemical Reagent Co., Ltd
Acetic Acid	64-19-7	99.5%	Sinopharm Chemical Reagent Co., Ltd
Formic acid	64-18-6	HPLC	Thermo Fisher
Acetonitrile	75-05-8	HPLC	Thermo Fisher
Methyl alcohol	67-56-1	HPLC	Thermo Fisher
Sodium hydroxide	1310-73-2	GR	Sinopharm Chemical Reagent Co., Ltd
Hydrochloric acid	7647-01-0	37 %	Sinopharm Chemical Reagent Co., Ltd

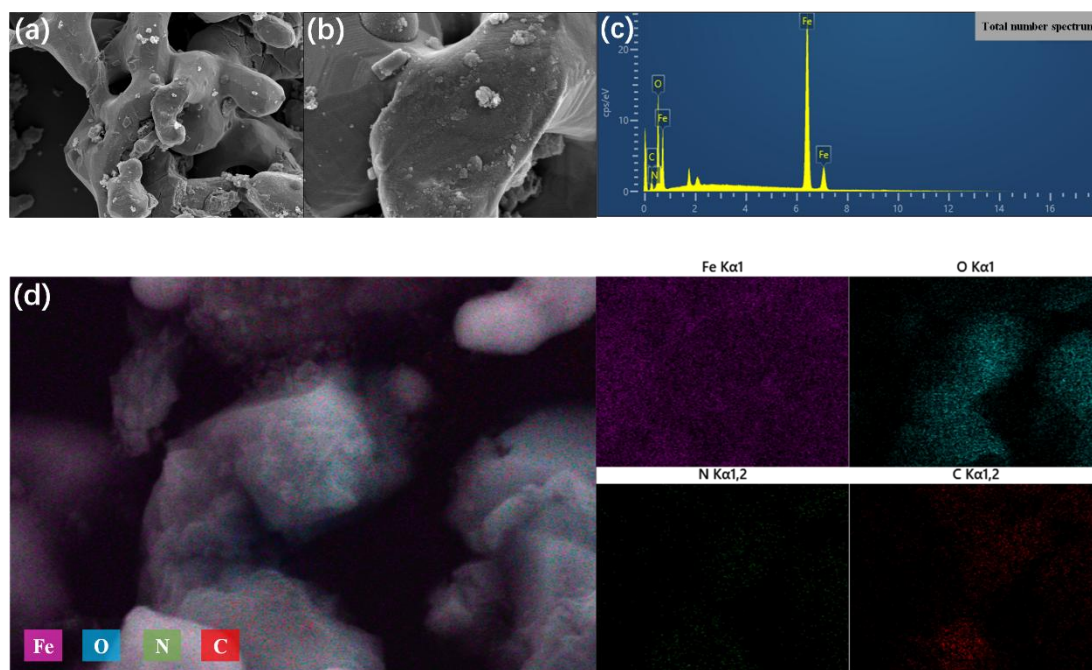


Fig. S1 Surface morphology analysis of nZVI-C-2 by SEM (a-b); quantitative analysis for nZVI-C-2 (c); EDS mapping for the surface element of nZVI-C-2 (d) .

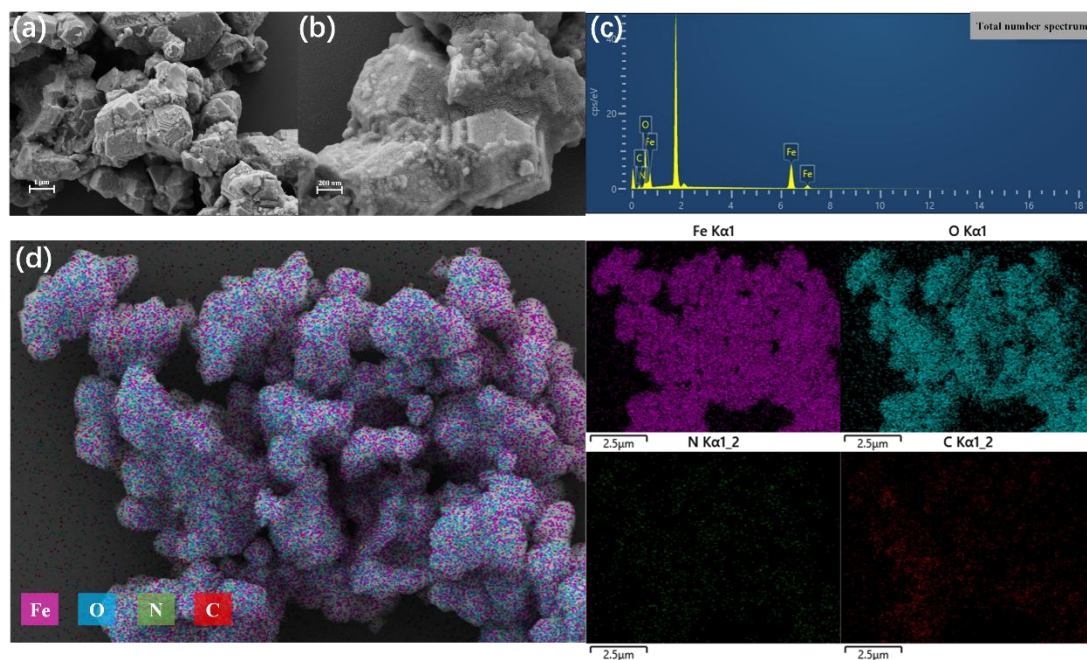


Fig. S2 Surface morphology analysis of nZVI-C-4 by SEM (a–b); EDS quantitative analysis for nZVI-C-4 (c); EDS mapping for the surface element of nZVI-C-4 (d).

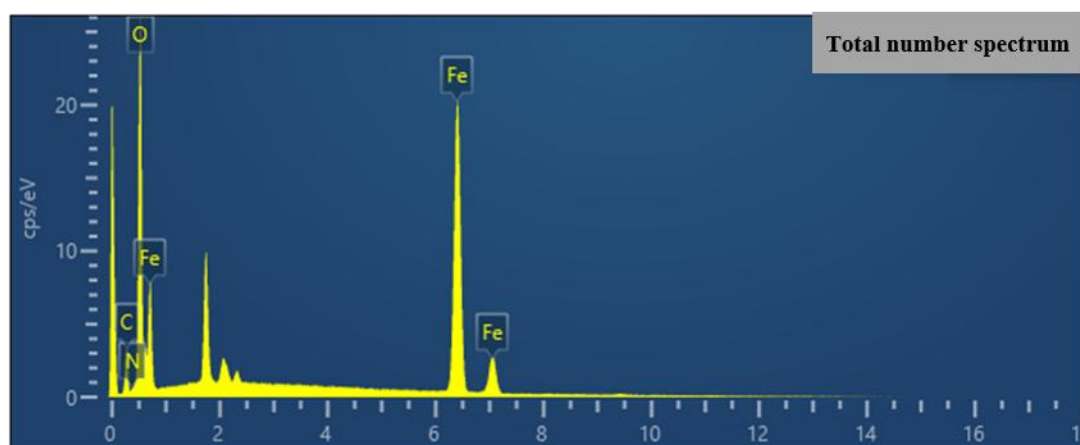


Fig. S3 EDS quantitative analysis for nZVI-C-3.

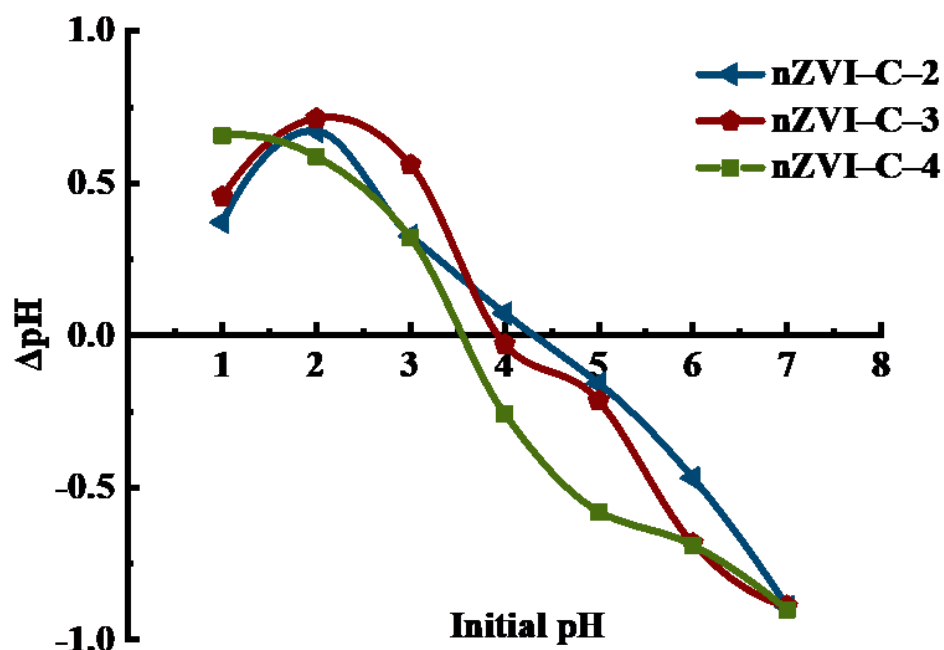


Fig. S4 The point of zero charges of Fe₃O₄@C (The pH_{PZC} of nZVI-C was carried out by the solid addition method. 45 mL of 0.1 mol/L NaCl solution was added in seven 50 mL colorimetric tubes. Then adjusted the pH value to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 by 0.1 mol/L HCl or 1.0 mol/L NaOH. After the initial pH value was adjusted, continued to add 0.1 mol/L NaCl solution to the tick mark (50 mL), and then, 100 mg adsorbent was added. After shaking for 48 h, the ΔpH value of these seven samples was obtained).

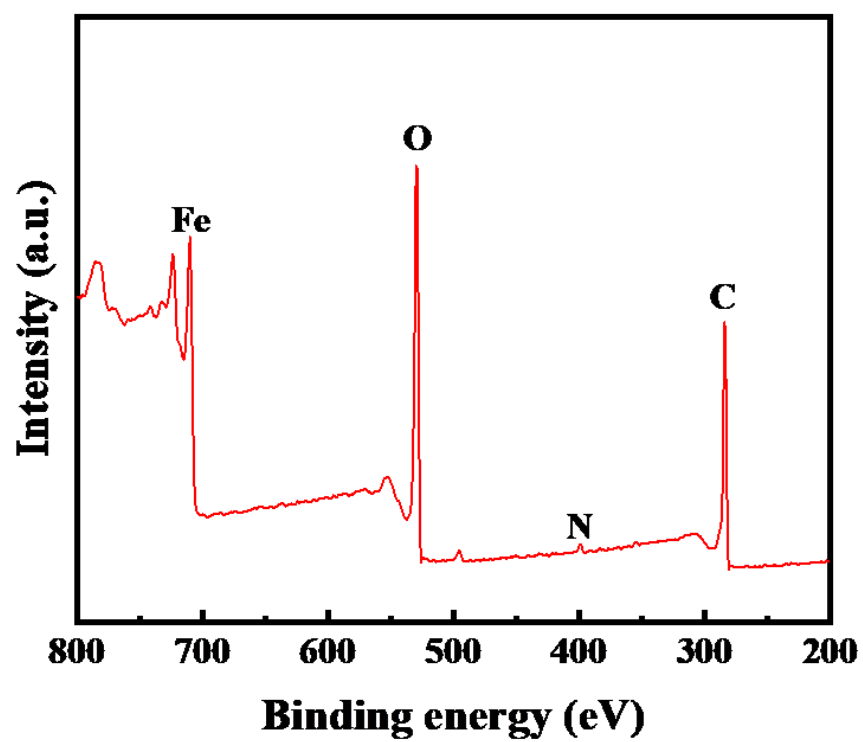


Fig. S5 Element survey for nZVI-C-3.

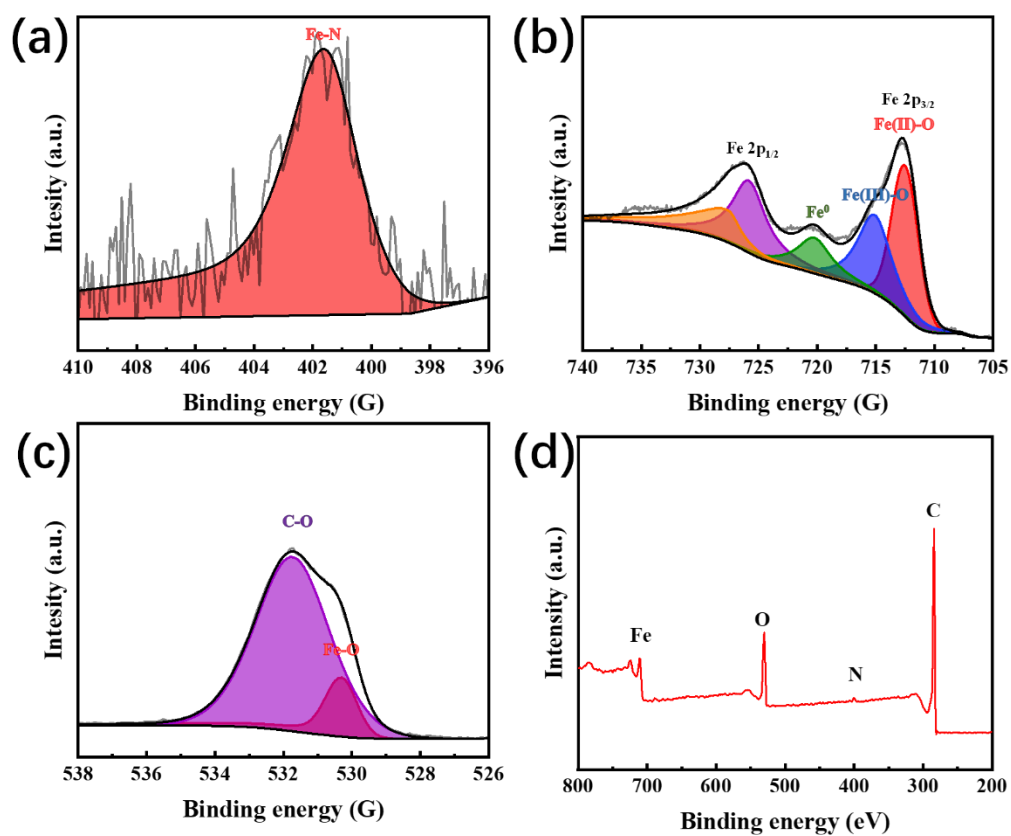


Fig. S6 XPS spectroscopy of nZVI-C-2 including N 1s (a), Fe 2s (b) C 1s (c), and element survey (d).

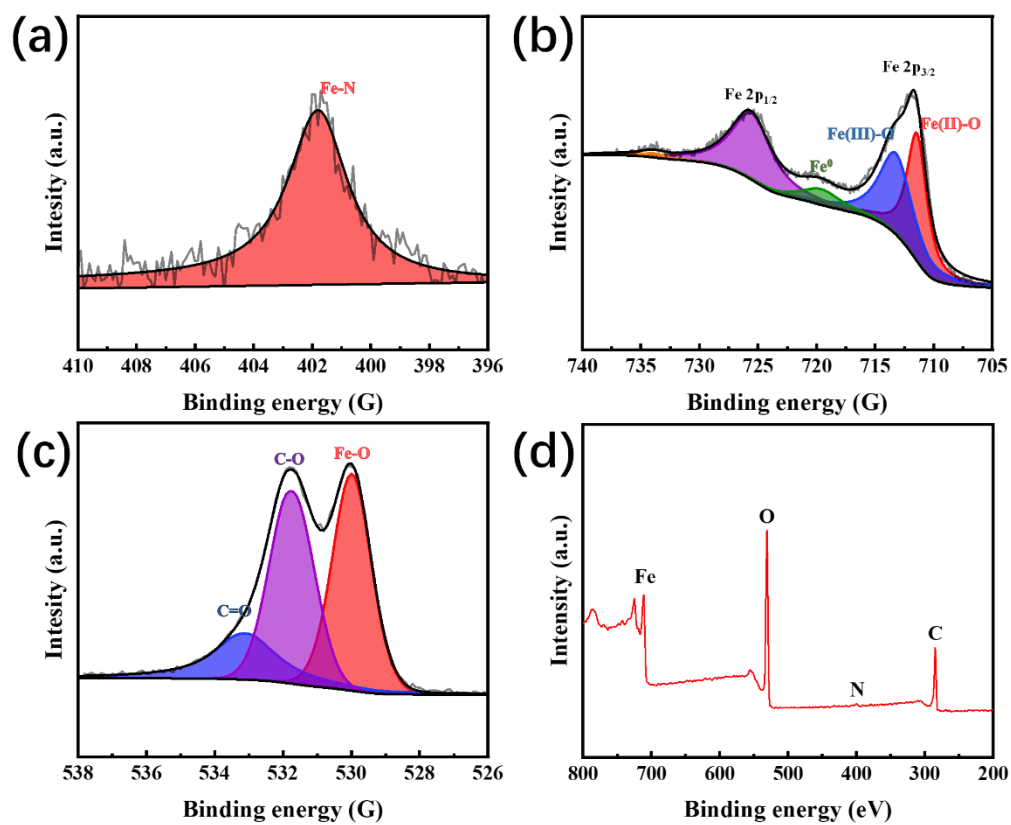


Fig. S7 XPS spectroscopy of nZVI-C-4 including N 1s (a), Fe 2s (b) C 1s (c), and element survey (d).

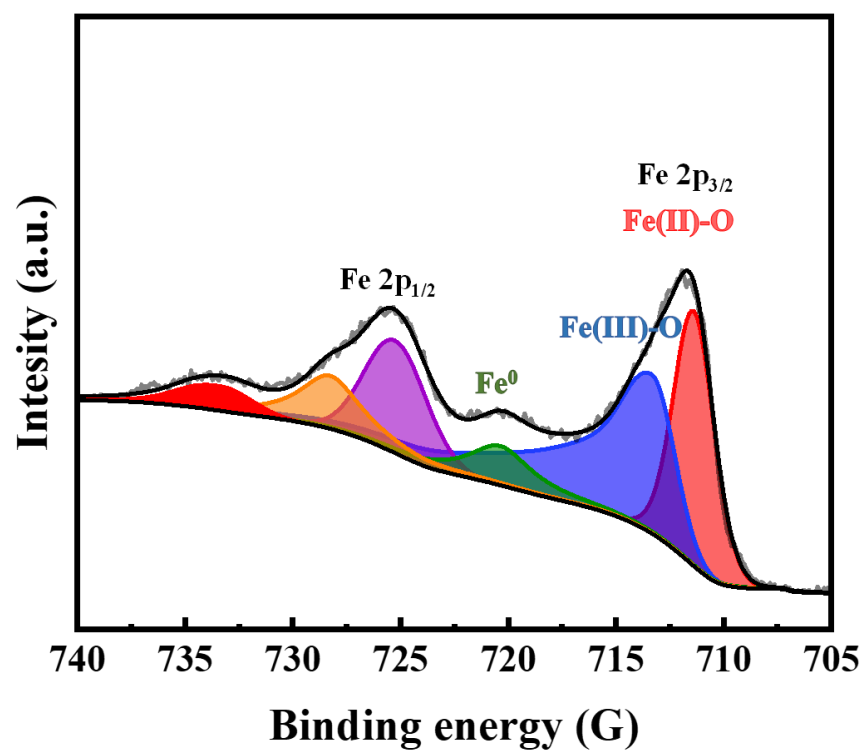


Fig. S8 XPS spectroscopy of Fe 2s for the spent nZVI-C-3.

Table S2. Water quality characteristics of the samples used for applicability evaluation.

Water matrix	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TOC (mg/L)
Lake water	7.8 ± 0.3	492 ± 46	4.9 ± 0.6
Tap water	8.1 ± 0.3	272 ± 13	2.8 ± 0.5
River water	7.7 ± 0.8	921 ± 81	11.3 ± 0.9
Pharmaceutical wastewater	6.7 ± 0.6	3579 ± 288	79.4 ± 6.0

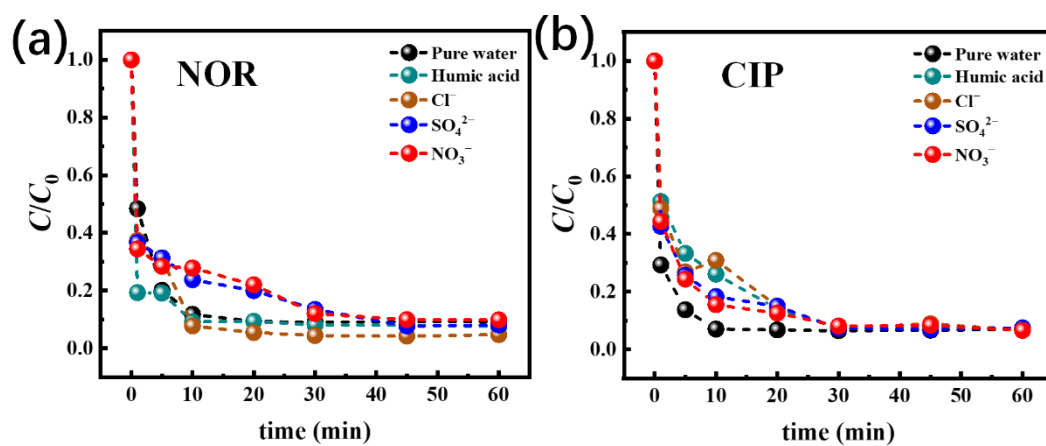


Fig. S9 Degradation dynamics of NOR (a) and CIP (b) in the presence of common substances (Humic acid: 2 mg/L; Cl^- , SO_4^{2-} , and NO_3^- : 20 mmol/L each).

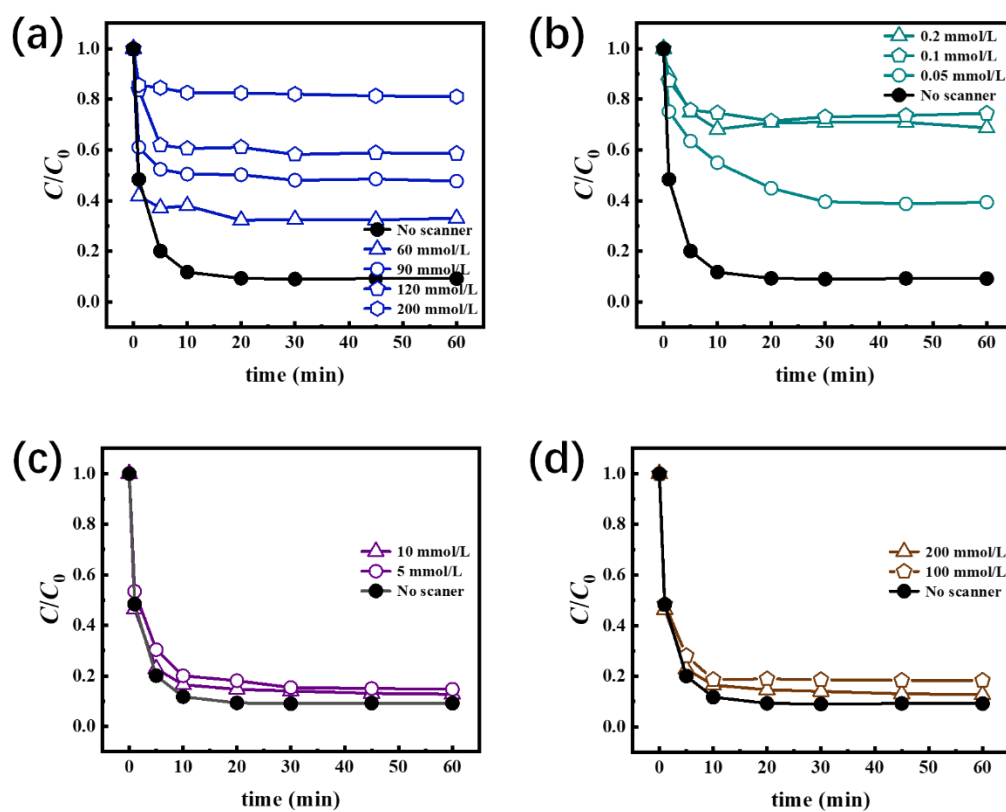


Fig. S10 Quenching experiment for OFL degradation in synergistic activation systems with varying scavenger dosages: TBA (a), pBQ (b), L-histidine (c), and 1,10-Phenanthroline (d).

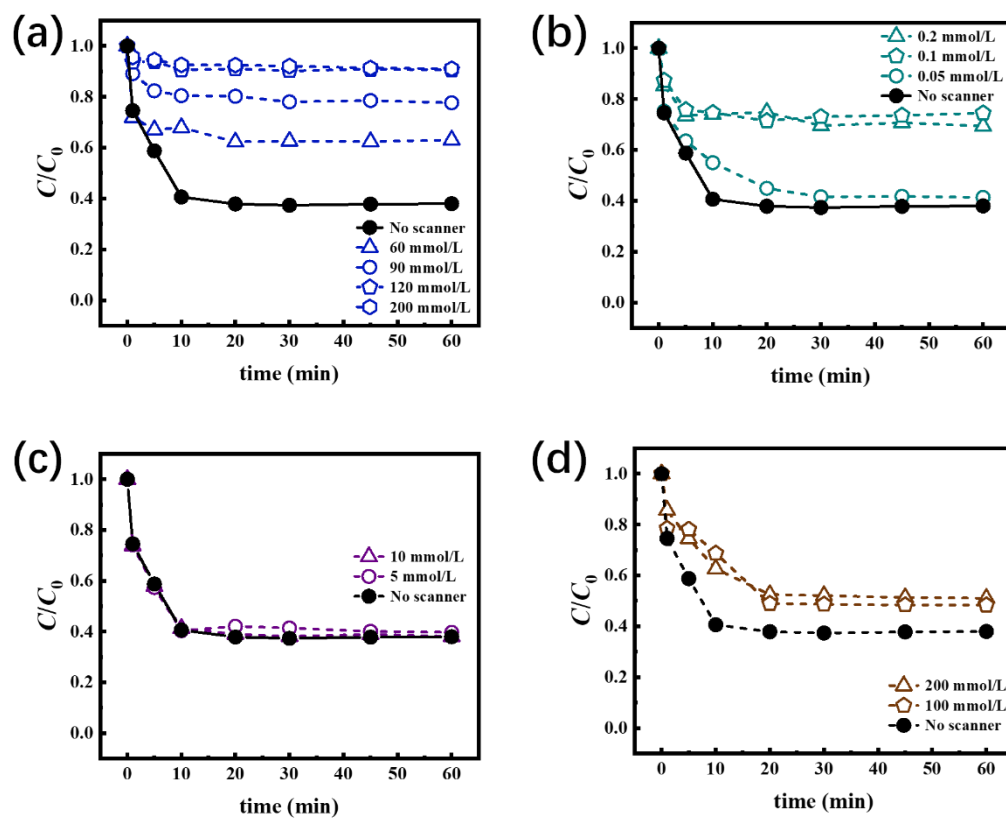


Fig. S11 Quenching experiment for OFL degradation in H_2O_2 activation systems with varying scavenger dosages: TBA (a), pBQ (b), L-histidine (c), and 1,10-Phenanthroline (d).

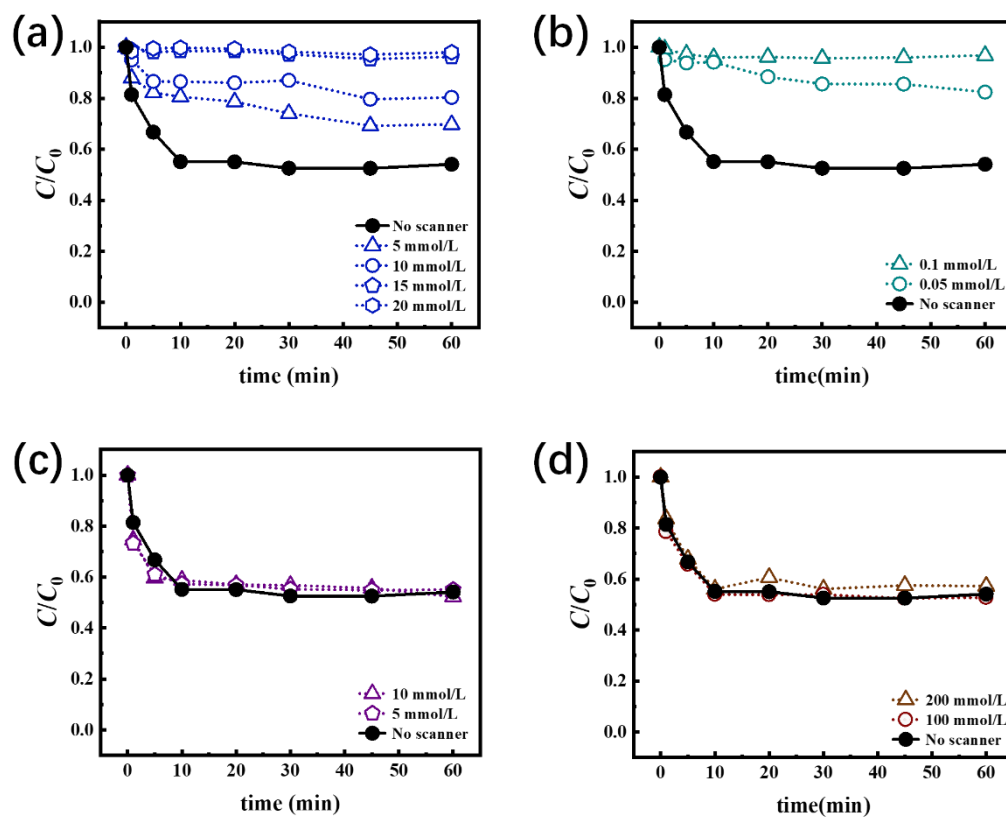


Fig. S12 Quenching experiment for OFL degradation in DO activation systems with varying scavenger dosages: TBA (a), pBQ (b), L-histidine (c), and 1,10-Phenanthroline (d).

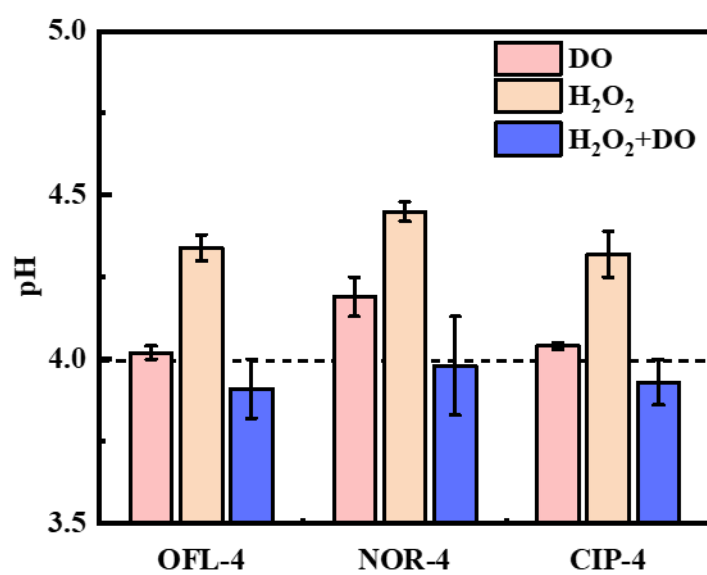


Fig. S13 pH of the solution after a 60-minute reaction under DO Activation, H₂O₂ Activation, and synergistic activation of Both (Initial pH = 4).

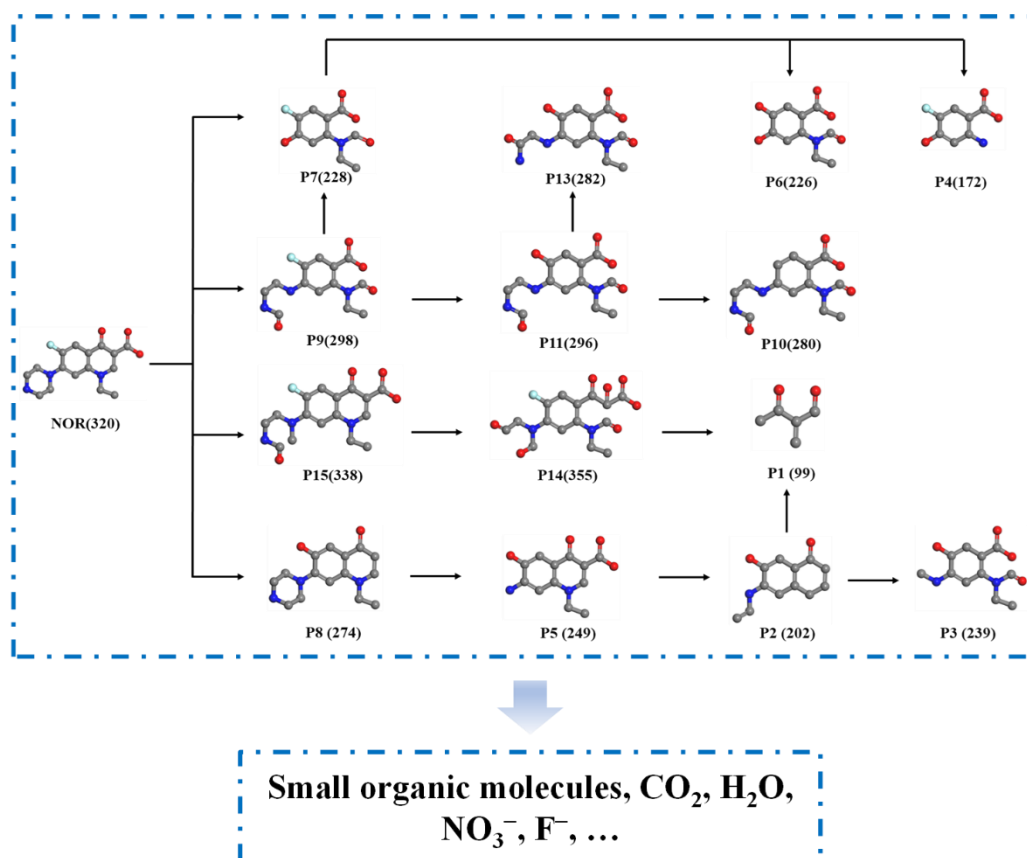


Fig. S14 Possible degradation pathway of NOR.

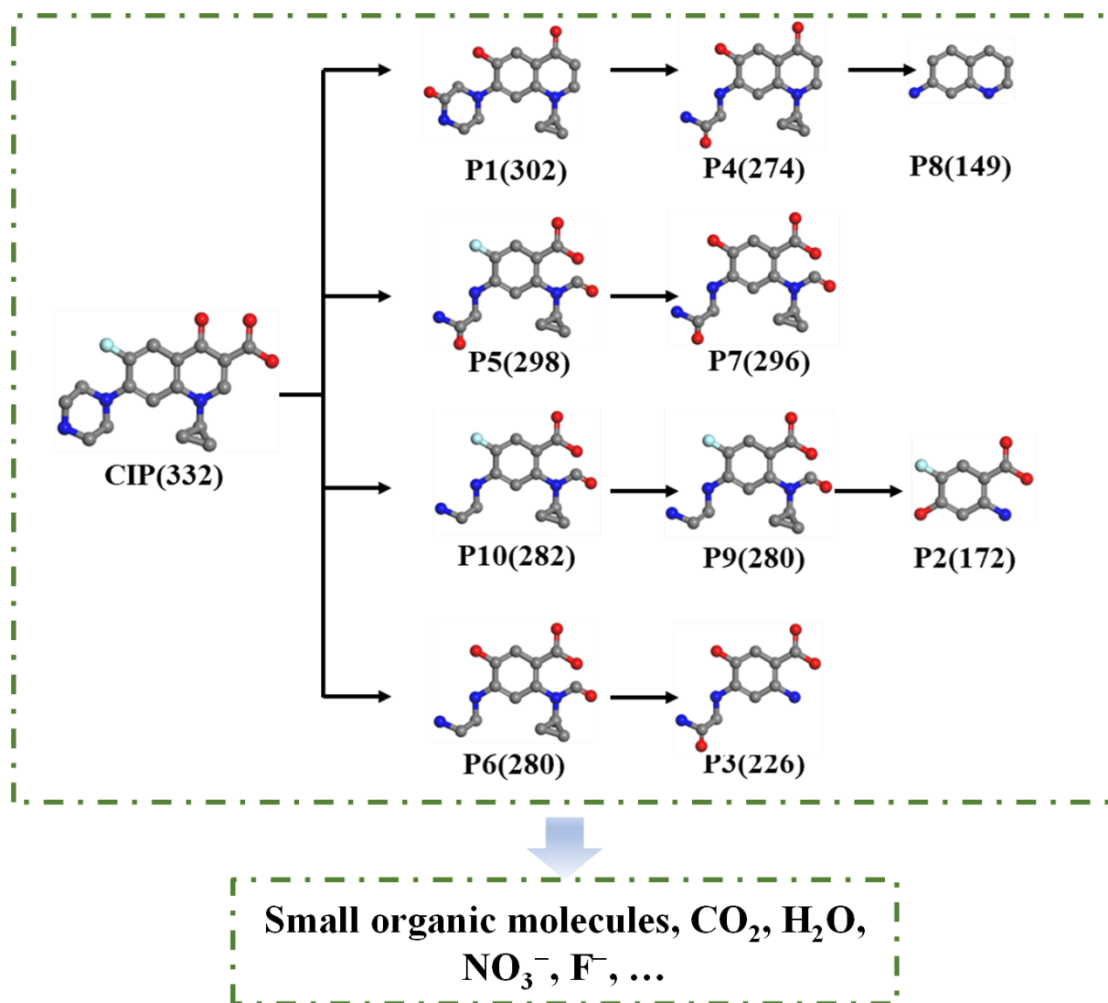


Fig. S15 Possible degradation pathway of CIP.

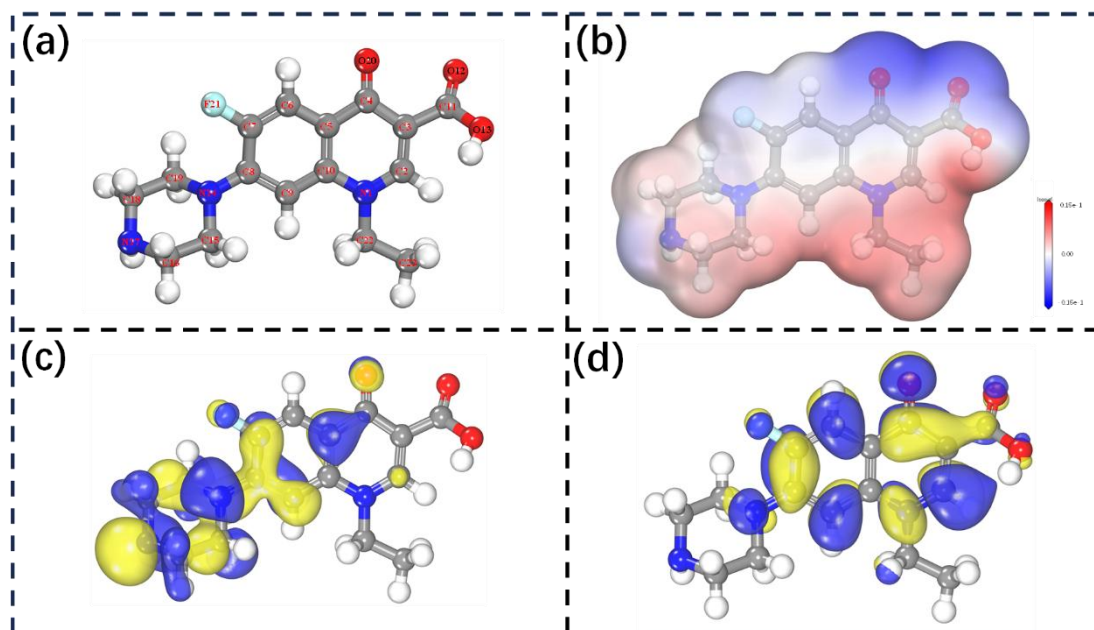


Fig. S16 (a) Optimized structure and atom numbering of NOR, (b) Electrostatic potential mapping. (c,d) HOMO and LUMO of NOR.

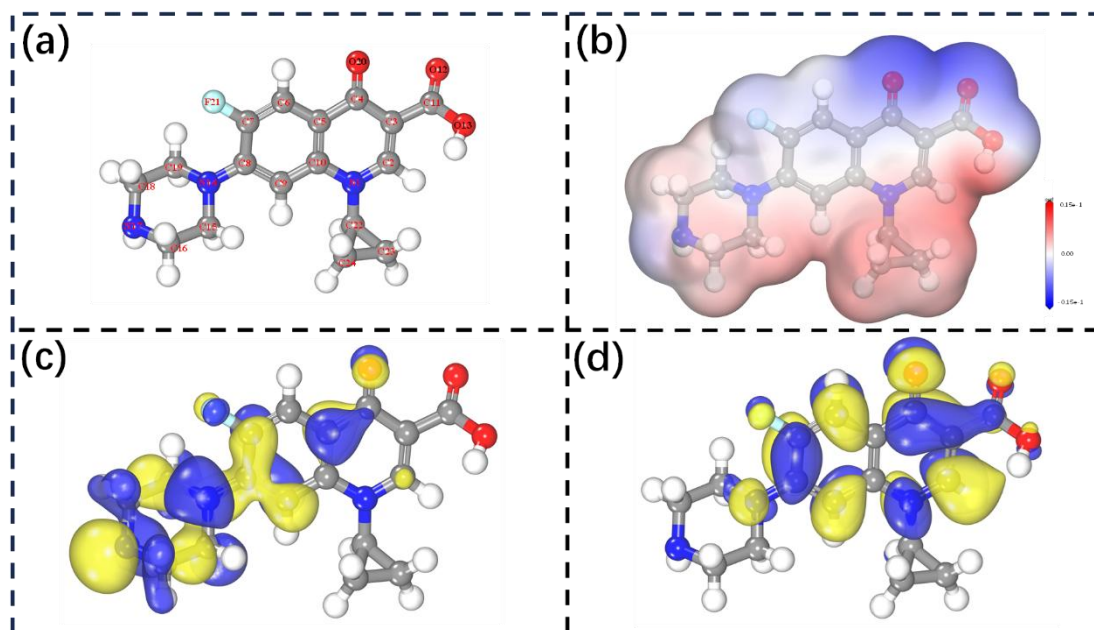


Fig. S17 (a) Optimized structure and atom numbering of CIP, (b) Electrostatic potential mapping. (c,d) HOMO and LUMO of CIP.

Table S3. Fukui function values for atoms in OFL molecule.

Atom number	f^-	f^0
O1	0.03	0.025
C2	-0.006	-0.006
C3	0.004	-0.007
N4	0	0.011
C5	0.026	0.028
C6	0.059	0.059
C7	0.033	0.019
C8	0.015	0.049
C9	0.032	0.034
C10	0.02	0.032
C11	0.015	0.057
C12	0.015	0.016
C13	0.014	0.07
C14	0.009	0.016
O15	0.014	0.023
O16	0.007	0.012
O17	0.03	0.068
N18	0.097	0.054
C19	-0.027	-0.018
C20	-0.018	-0.01
N21	0.056	0.028
C22	-0.017	-0.009
C23	-0.022	-0.015
C24	-0.011	-0.007
C25	-0.003	-0.096
F26	0.017	0.02

Table S4. Fukui function values for atoms in NOR molecule.

Atom number	f^-	f^0
N1	0	0.008
C2	0.013	0.07
C3	0.009	0.015
C4	0.014	0.049
C5	0.033	0.02
C6	0.021	0.051
C7	0.032	0.038
C8	0.011	0.025
C9	0.045	0.056
C10	0.016	0.021
C11	0.006	0.015
O12	0.009	0.021
O13	0.005	0.011
N14	0.08	0.048
C15	-0.022	-0.017
C16	-0.012	-0.007
N17	0.157	0.08
C18	-0.012	-0.006
C19	-0.017	-0.013
O20	0.031	0.062
F21	0.017	0.021
C22	-0.006	-0.01
C23	-0.002	-0.007

Table S5. Fukui function values for atoms in CIP molecule.

Atom number	f^-	f^0
N1	0	0.015
C2	0.012	0.013
C3	0.009	0.022
C4	0.015	0.087
C5	0.033	0.007
C6	0.022	0.076
C7	0.031	0.043
C8	0.011	0.039
C9	0.043	0.061
C10	0.017	0.026
C11	0.006	0.025
O12	0.009	0.035
O13	0.005	0.018
N14	0.08	0.016
C15	-0.022	-0.013
C16	-0.012	-0.002
N17	0.156	0.003
C18	-0.012	-0.001
C19	-0.017	-0.009
O20	0.031	0.096
F21	0.017	0.026
C22	-0.008	-0.018
C23	0.002	0.001
C24	-0.003	0.002

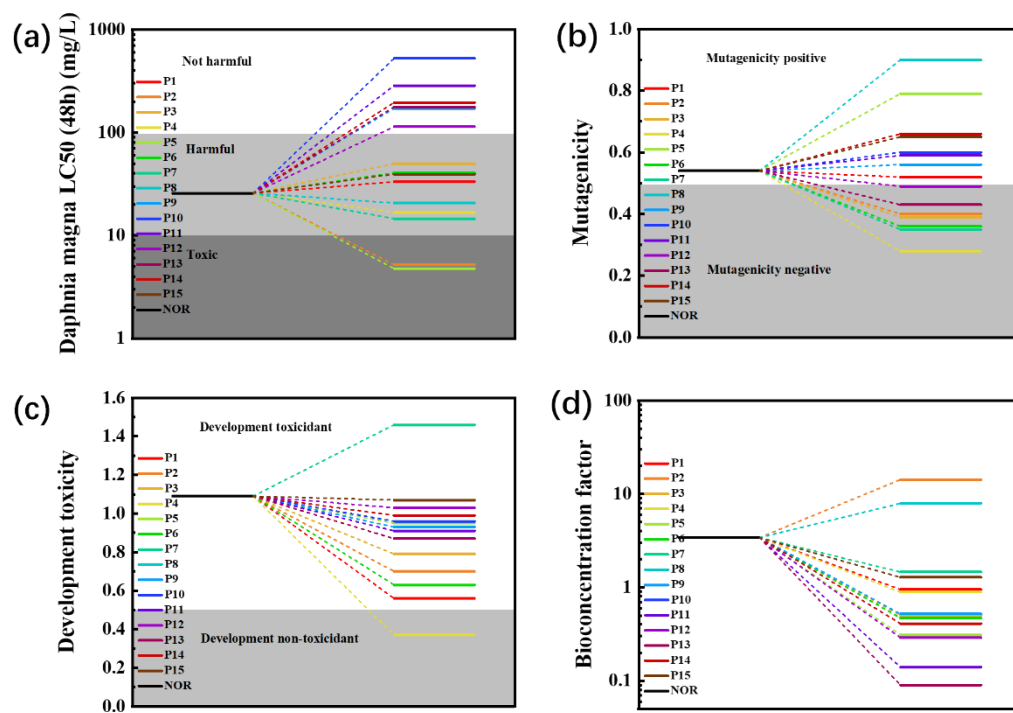


Fig. S18 The toxicity indexes related to by-products of NOR degradation derived from QSAR: daphnia magna LC₅₀-96 h (a), mutagenicity (b), development toxicity (c), and bioconcentration factor (d).

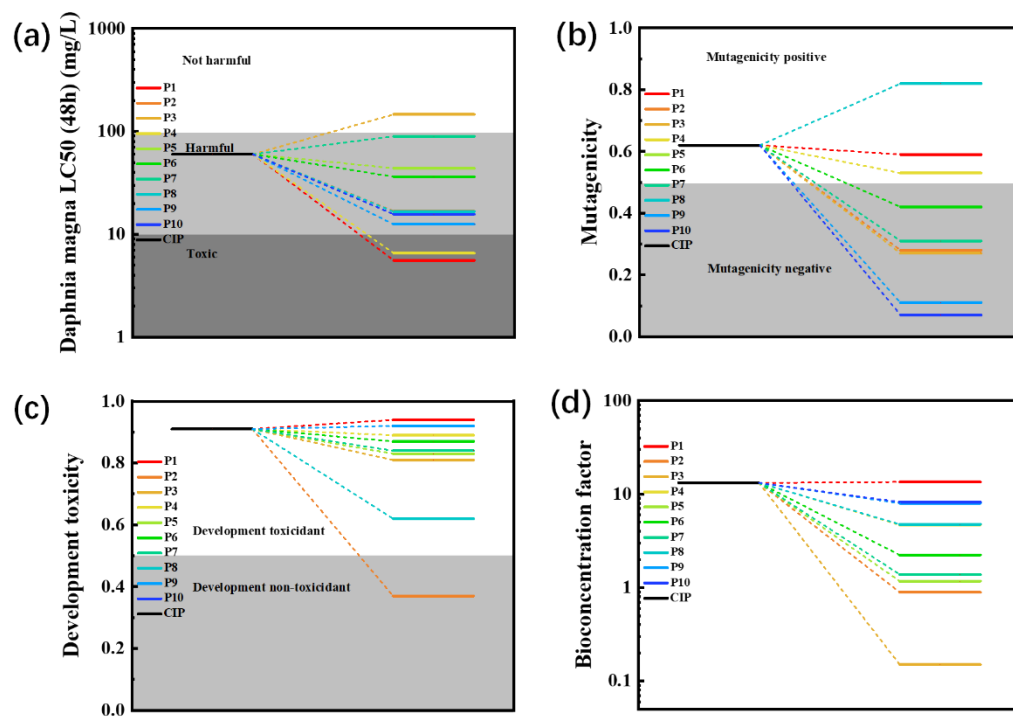


Fig. S19 The toxicity indexes related to by-products of NOR degradation derived from QSAR: daphnia magna LC₅₀-96 h (a), mutagenicity (b), development toxicity (c), and bioconcentration factor (d).