

Supplementary Information for

“Activation of peroxymonosulfate by novel red mud based $\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3\text{-Co}_2\text{AlO}_4$ composite for effective degradation of lomefloxacin hydrochloride”

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¹ *The two authors have the same contribution to this study*

Text S1. Materials

The RM used in the study was collected from Guangxi Aluminum Corporation, China. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), aluminum nitrate hexahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3), sodium chloride (NaCl), sodium nitrate (NaNO_3), *p*-benzoquinone (BQ) and methanol (MeOH) were obtained from Guanghua Technology Co., Ltd. PMS ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$) was purchased by Aladdin Biochemical Technology Co., Ltd. LOMH, furfural alcohol (FFA), Tert-butyl alcohol (TBA), $\text{K}_2\text{Cr}_2\text{O}_7$ and disodium ethylenediamine tetraacetate (EDTA-2Na) were obtained from Macklin Biochemical Co., Ltd. In this work, all chemical reagents were analytical grade.

Text S2. Characterization

The phase structure of Co-Fe/RM was characterized with X-ray diffraction (XRD, Rigaku SmartLab SE, Japan). The investigation of functional groups of Co-Fe/RM composite were studied with Fourier transform infrared spectra (FT-IR, Thermo Scientific Nicolet iS5, United States of America). The surface morphologies of the samples were obtained with Scanning electron microscopy (SEM, TESCAN MIRA LMS, Czech Republic). The pore structure of Co-Fe/RM and Brunauer-Emmett-Teller (BET) surface area were determined with N_2 adsorption-desorption method

(Micromeritics ASAP 2460, United States of America). X-ray photoelectron spectro (XPS) of the Co-Fe/RM before and after use werhermo Scientific Nicolet iS50 spectrophotometere characterized by the Thermo Scientific K-Alpha. The LOMH degradation intermediates were tested with a liquid chromatography-mass spectrometry (LC-MS, Agilent 1290, Germany). The concentration of leached Co ion was measured using an inductively coupled plasma optical emission spectrometry analyzer (ICP-OES, Thermo Fisher iCAP PRO, USA). The removal ratio of the total organic carbon (TOC) of the treated LOMH solution was analyzed by a Multi N/C 2100 TOC analyzer (Shimadu TOC-L, Japan).

Text S3. Zero point charge determination method

NaCl solution (0.01 mol/L, 50 mL) was added into a series of iodine measuring flasks. The pH values of each systems were measured and adjusted to 2-10, recording as pH_i ($i = 2-10$). 0.2 g/L of Co-Fe/RM existed in each systems. Then all the iodine measuring flasks were placed in a hydrothermal shaker at a constant temperature of 30 °C and shaken at 160 rpm for 48 hours. After this step, the pH values of each systems were measured again, recording as pH_j ($j = 2-10$). The zero point charge (pH_{zpc}) of Co-Fe/RM was obtained by pH_i and pH_j .

Text S4. Computational methods

For the LOMH molecule, both geometry optimization and frequency calculation were analyzed by the B3LYP/6-31+G (d, p) level. Fukui function has been widely used to predict the regioselectivity (i.e., electrophilic, nucleophilic, and radical attack) ¹. In the condensed version of Fukui function, atomic population number is used to represent the amount of electron density distribution around an atom. The condensed Fukui function (f) can be calculated as following (Eqs. (S1)~(S3)):

$$\text{Electrophilic attack: } f_{\text{A}}^{-} = q_{\text{N}-1}^{\text{A}} - q_{\text{N}}^{\text{A}} \quad (\text{S1})$$

$$\text{Nucleophilic attack: } f_{\text{A}}^{+} = q_{\text{N}}^{\text{A}} - q_{\text{N}+1}^{\text{A}} \quad (\text{S2})$$

$$\text{Radical attack: } f_A^0 = (q_{N-1}^A - q_{N+1}^A) / 2 \quad (\text{S3})$$

where q^A is the atom charge of atom A at corresponding state.

Text S5. Biological toxic experiment

Toxicity Estimation Software Tool (TEST) (Version 5.1.2, 2022) was downloaded from the US EPA website. Chemicals can be found by SMILES code or chemical structure map, and the different toxicity of chemicals are predicted by different prediction software. Six Quantitative Structure-Activity Relationship (QSAR) methods (hierarchical, FDA, single model, group contribution, nearest neighbor, and consistent ²) are provided for the prediction of acute toxicity LC₅₀ and mutagenicity, and consistent method was chosen in our works. Random forest method is used for the prediction of bioaccumulation factor and developmental toxicity by the platform ³.

For the biological toxic experiment, *Chlorella pyrenoidosa* (*C. pyrenoidosa*) was selected as an ecological indicator due to the easy culture and high sensitivity to the contaminant. For the experimental group, a test sample (187.5 mL) with initial *C. pyrenoidosa* cell density of approximately 3.28×10^6 cells/mL was prepared by mixing the LOMH solution (initial or treated solution) with the growth medium and inoculum culture of *C. pyrenoidosa* in a volume ratio of 1:2.75. For the control group, it should be noted that the preparation method of the control sample was almost the same as that of the test sample, except that the deionized water was used instead of the LOMH solution. The cell densities of *C. pyrenoidosa* in test and control samples were measured daily with a VIS-722 spectrometer at 683 nm, respectively ⁴. According to the literature ⁵, the growth inhibition ratio was calculated through the following formula: $\lambda (\%) = (1 - N_t / M_t) \times 100\%$, where t is the time, λ represents the inhibition ratio on day t , N_t and M_t mean the algae cell densities in the experimental group on day t and in the control group on day t , respectively.

Text S6. Adsorption-desorption tests

A certain amount of Co-Fe/RM was added into the LOMH solution to carry out the adsorption-desorption tests without the addition of PMS. The other experiment conditions were as the same of the optimal catalytic degradation experiment.

Text S7. Mineralization assessment

With the use of dichromate method, the removal ratio of chemical oxygen demand (COD_{Cr} , mg/L) of LOMH solution was measured. The COD_{Cr} ($\eta(COD_{Cr}),\%$) was evaluated by Formula (S4):

$$\eta(COD_{Cr}) = \frac{COD_{Cr0} - COD_{Cr t}}{COD_{Cr0}} \times 100\% \quad (S4)$$

Herein, COD_{Cr0} means the chemical oxygen demand of the untreated LOMH solution, and $COD_{Cr t}$ is the chemical oxygen demand of LOMH solution at treatment time t.

The TOC removal ratio of the LOMH solution was obtained by the differential subtraction method on a Multi N/C 2100 TOC analyzer.

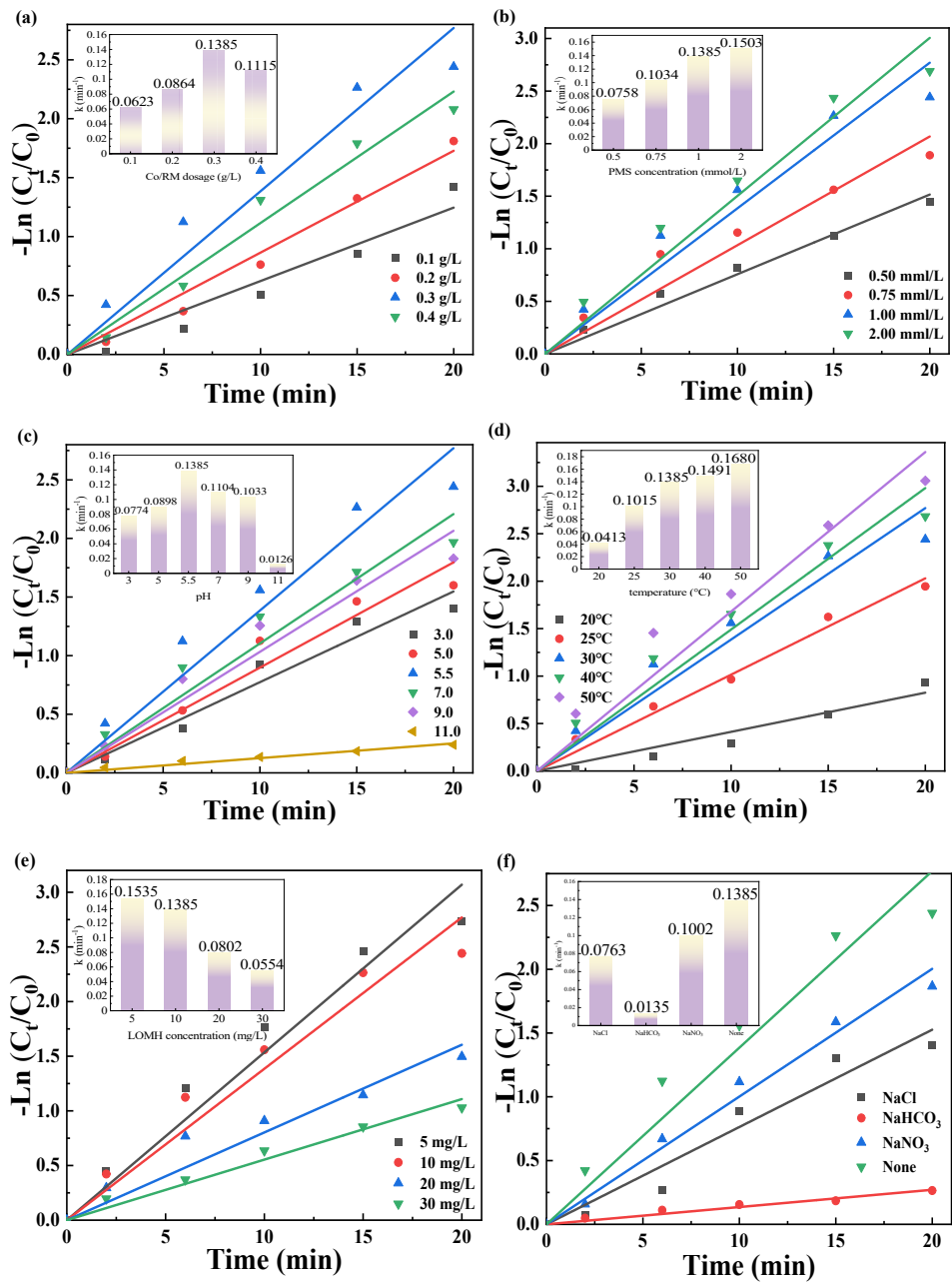


Fig. S1. The value of k under different reaction conditions: Co-Fe/RM dosage (a), PMS concentration (b), initial pH (c), reaction temperature (d), LOMH concentration (e) and inorganic ions (f) on the degradation of LOMH in Co-Fe/RM/PMS system.

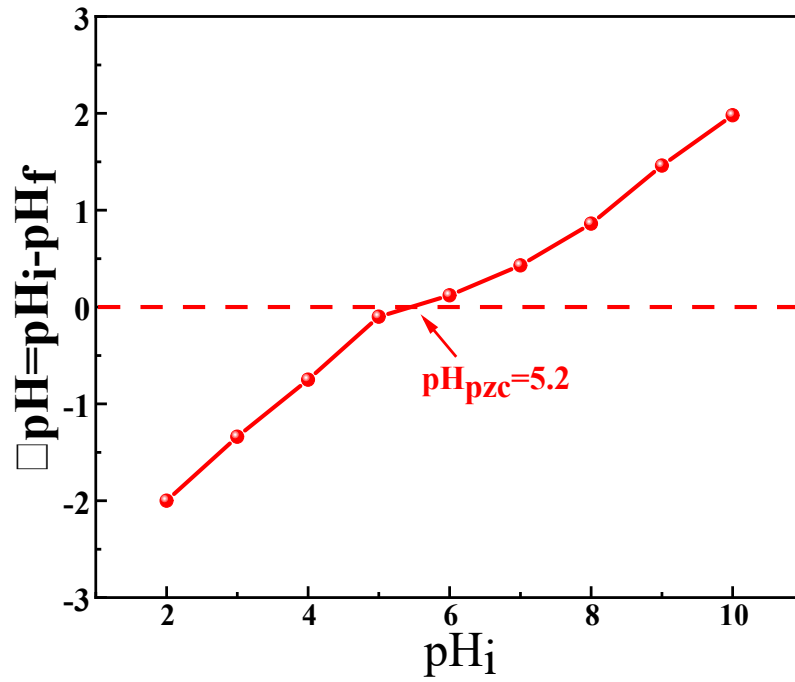
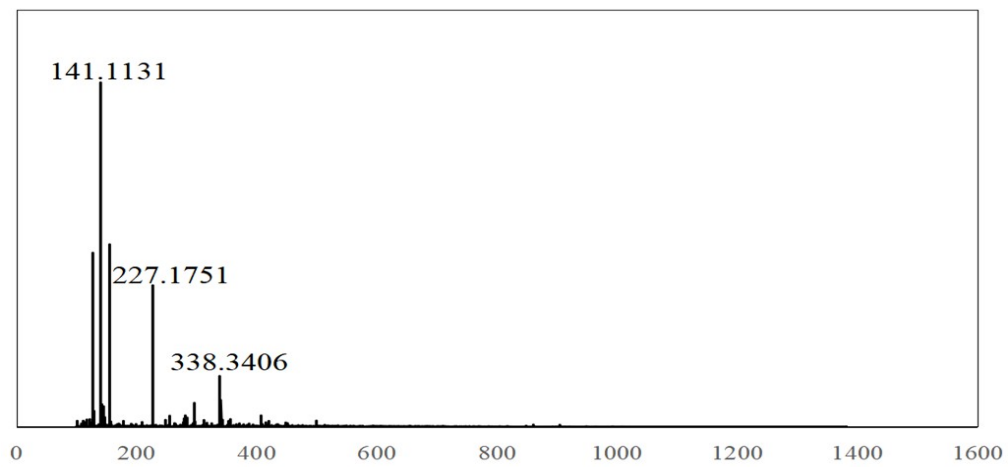
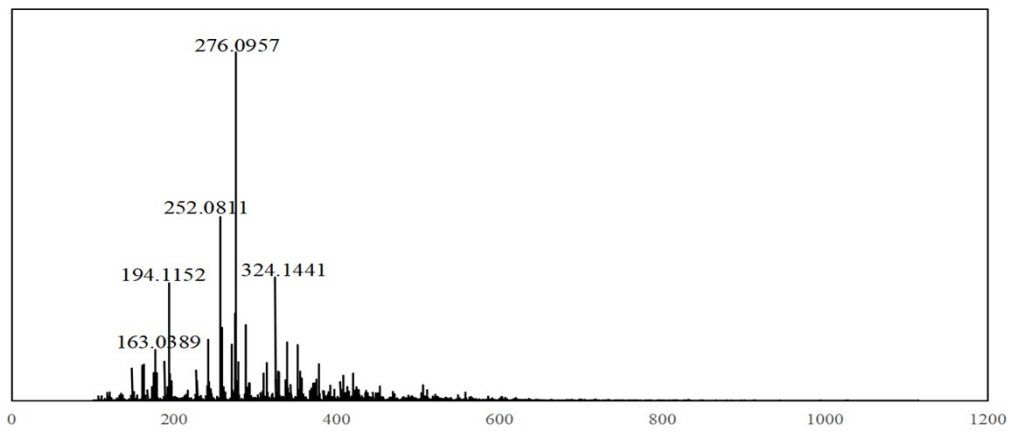


Fig. S2. Plot of point of zero charge for Co-Fe/RM in the Co-Fe/RM/PMS system.



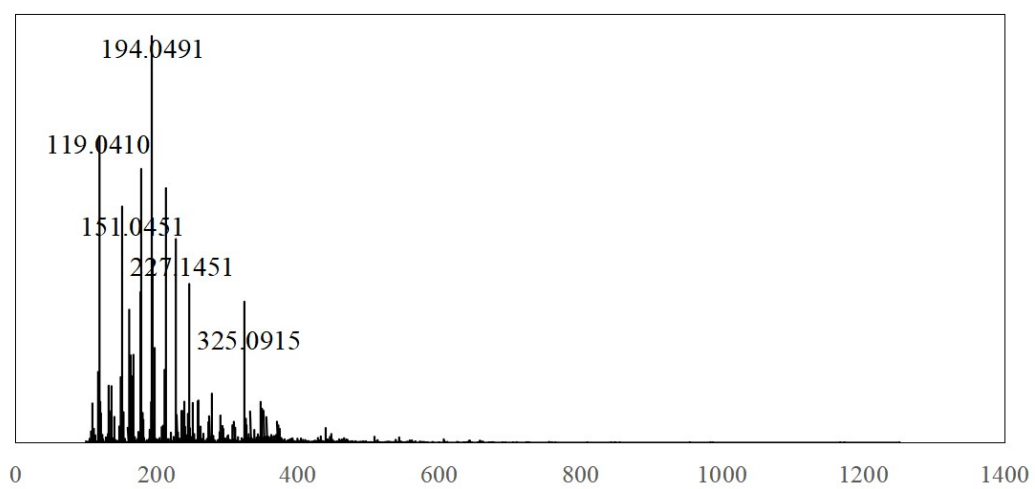
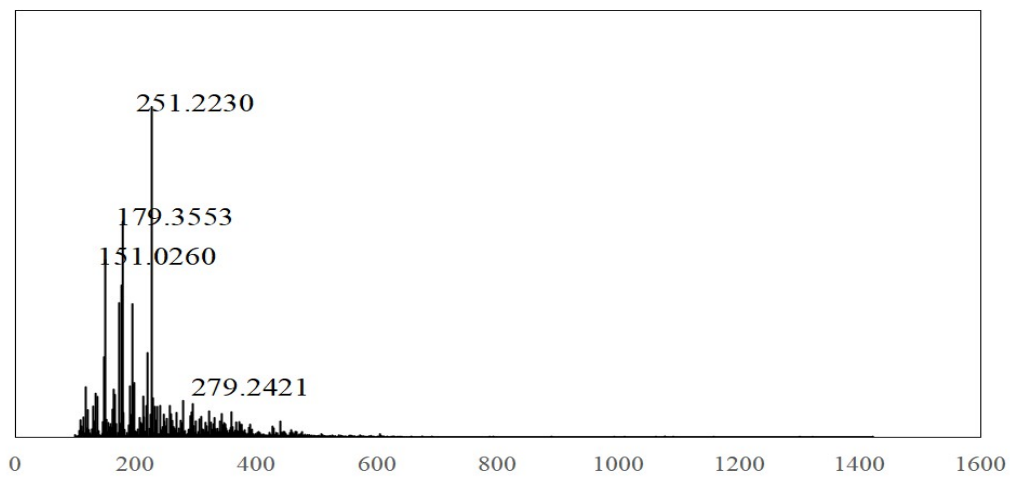


Fig. S3. LC-MS spectra of the intermediates of LOMH degradation.

Table S1. Comparison of the degradation efficiency, mineralization degree and the reaction rate constant of various treatment methods toward LOMH degradation.

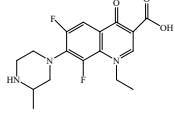
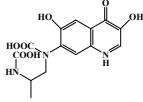
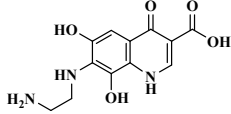
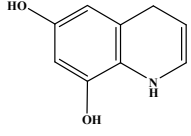
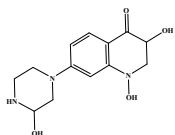
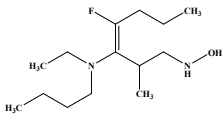
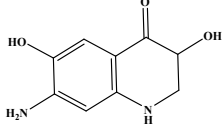
Treatment method	Experimental conditions	LOMH degradation (%)	TOC removal ratio (%)	Kinetic rate (min^{-1})	References
NiFe ₂ O ₄ /CuS + PMS + Visible light	[NiFe ₂ O ₄ /CuS]: 0.6 g/L [PMS]: 2.6 mmol/L [pH]: 5.8 [LOMH] ₀ : 10 mg/L [Time]: 40 min [reaction temperature]:25 °C	88.1	-	0.0368	6
MBC/CoFe ₂ O ₄ + PMS	[MBC/CoFe ₂ O ₄]: 0.6 g/L [PMS]: 0.6 mmol/L [pH]: 5.5 [LOMH] ₀ : 10 mg/L [Time]: 20 min [reaction temperature]:25 °C	86.9	-	0.0426	7
P-CuFe ₂ O ₄ + O ₃ + Visible light	[P-CuFe ₂ O ₄]: 0.05 g/L [PMS]: 0.6 mmol/L	99.0	20.2	0.1318	8

	[pH]: -				
	[LOMH] ₀ : 10 mg/L				
	[Time]: 90 min				
	[reaction temperature]: -				

Co ₃ O ₄ (GCO-	[GCO-500]: 0.1 g/L	93.6	-	0.0156	9
500) + PMS	[PMS]: 0.1 mmol/L				
	[pH]: 7.0				
	[LOMH] ₀ : 5.3 mg/L				
	[Time]: 15 min				
	[reaction temperature]: 25 °C				

Co-Fe/RM +	[Co-Fe/RM]: 0.3 g/L	89.3	81.9	0.1385	This study
PMS	[PMS]: 1.0 mmol/L				
	[pH]: 5.5				
	[LOMH] ₀ : 10 mg/L				
	[Time]: 20 min				
	[reaction temperature]: 30 °C				

Table S2. The structural information of the possible intermediate products.

Intermediates	Molecular Formula	m/z	Molecular structure
LOM	$C_{17}H_{19}F_2N_3O_3$	352	
P1	$C_{14}H_{15}N_3O_7$	338	
P2	$C_{12}H_{13}N_3O_5$	279	
P3	$C_9H_9NO_2$	163	
P4	$C_{13}H_{14}FN_2O_3$	276	
P5	$C_{12}H_9N_3O_2$	251	
P6	$C_9H_{10}N_2O_3$	194	

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