Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information

The performance and mechanism of persulfate activated by CuFe-LDHs for ofloxacin degradation in water

Xue Zhang [a,1], *Kang Zhang* [a,1], *Ting Li* [a, b], *Yujiao Wang* [a, b], *Yin Xu* [a, b,*]

[a] Department of Environment, College of Environment and Resources, Xiangtan University, Xiangtan, Hunan 411105, P. R. China

[b] Hunan Key Lab for Environmental Behavior of New Pollutants and Control Principle, Hunan 411105, P. R. China

[1] Both authors contributed equally to the manuscript

* Authors to whom correspondence should be addressed:

Dr. Yin Xu, Tel: +86 (731)5829-2231; E-mail: xuyin@xtu.edu.cn

Text S1 Chemicals

The reagents used in this study were analytically pure. Ofloxacin (OFL), NaCl, $Cu(NO_3)_2 \cdot 3H_2O$, 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) and humic acid (HA) were purchased from Shanghai Macklin Biochemical Co., Ltd. $Fe(NO_3)_3 \cdot 9H_2O$ and NaOH were purchased from Xilong Scientific Co., Ltd. $Na_2S_2O_8$, Na_2SO_4, NaH_2PO_4 and $NaNO_3$ purchased from Sinopharm Chemical Reagent Co., Ltd. Na_2CO_3 was purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. $NaHCO_3$, methanol (MeOH), tert-butanol (TBA) were purchased from Tianjin Kemiou Chemical Reagents Co., Ltd. p-benzoquinone (p-BQ) was purchased from Tianjin Hengxing Chemical Reagent Co., Ltd.

Text S2 The related calculation formulas of free radical contribution ratio.

$$R_{HO\cdot} = \frac{\eta_0 - \eta_{TBA}}{\eta_0} \times 100\% \quad (1)$$

$$R_{SO_4^{\cdot -}} = \frac{\eta_0 - \eta_{MeOH}}{\eta_0} \times 100\% - R_{HO\cdot} \quad (2)$$

$$R_{O_2^{\cdot -}} = \frac{\eta_0 - \eta_{BQ}}{\eta_0} \times 100\% - R_{HO\cdot} \quad (3)$$

Where $R_{HO\cdot}$,$R_{SO4\cdot-}$, and $R_{O2\cdot-}$ were the contribution ratio of $HO\cdot$, $SO_4^{\cdot -}$, $O_2^{\cdot -}$ (%); η_0 was the degradation rate of OFL at 120 min with no quencher, η_{TBA}, η_{MeOH}, and η_{BQ} were the degradation rate of OFL at 120 min under different quenchers (%).

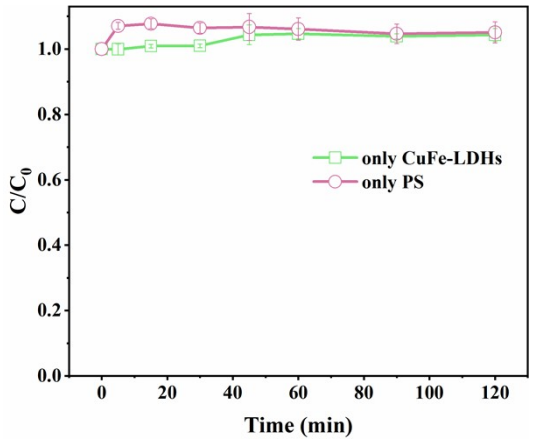

Fig. S1 The OFL degradation efficiency when only CuFe-LDHs or PS was existed.

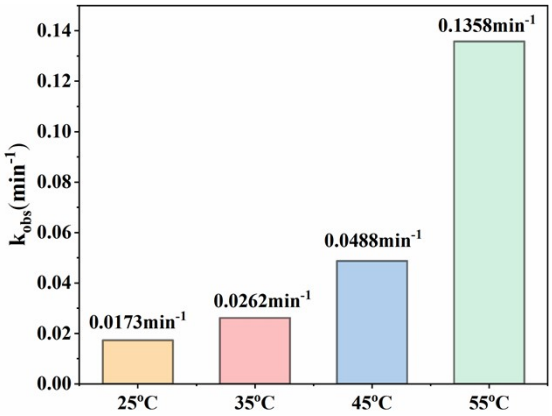

Fig. S2 The k_{obs} values of OFL degradation with the variation of temperature.

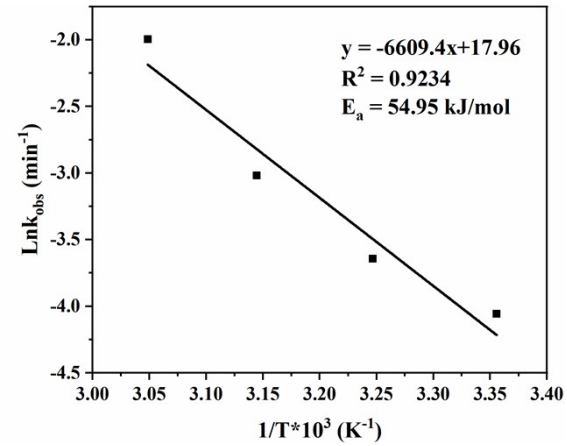

Fig. S3 The relationship between lnk_{obs} and 1/T.

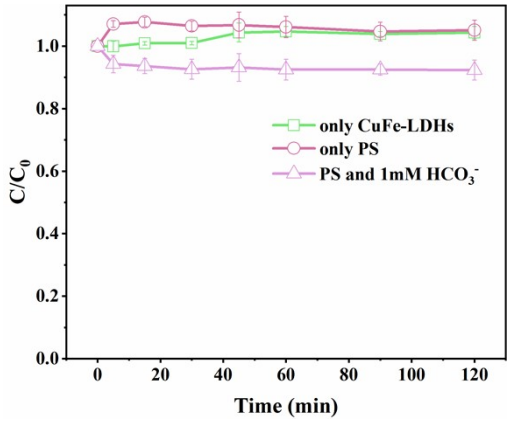

Fig. S4 The OFL degradation performance in the presence of PS and 1 mM HCO_3^-.

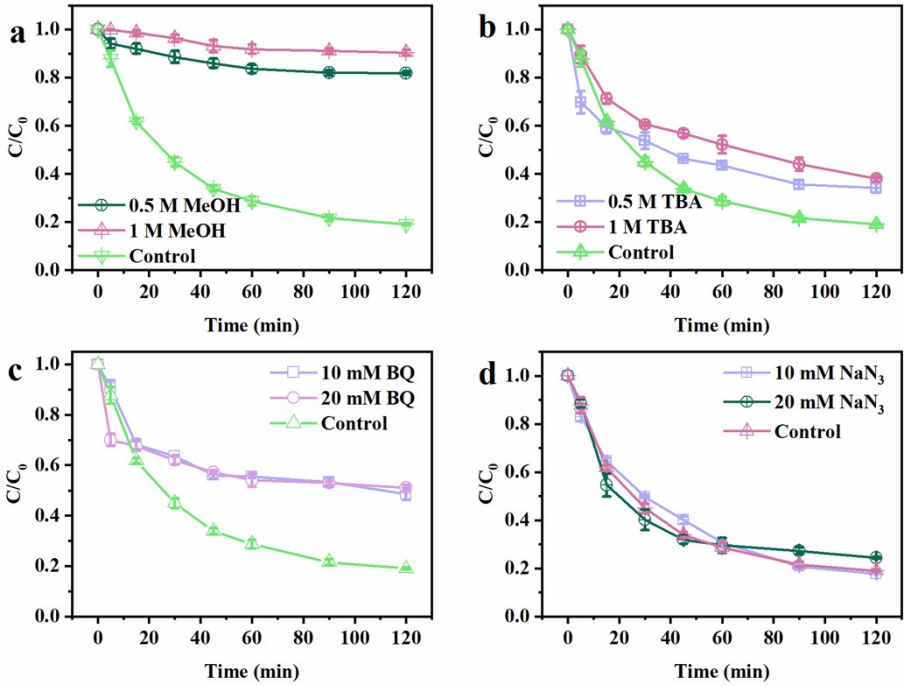

Fig. S5 The experiment of radical scavenger concentration gradients: (a) MeOH, (b) TBA, (c) BQ, (d) NaN_3 (Condition: [CuFe-LDHs]=0.5 g/L, [PS]=0.2 mM. initial pH=5.9±0.1, T=25°C).

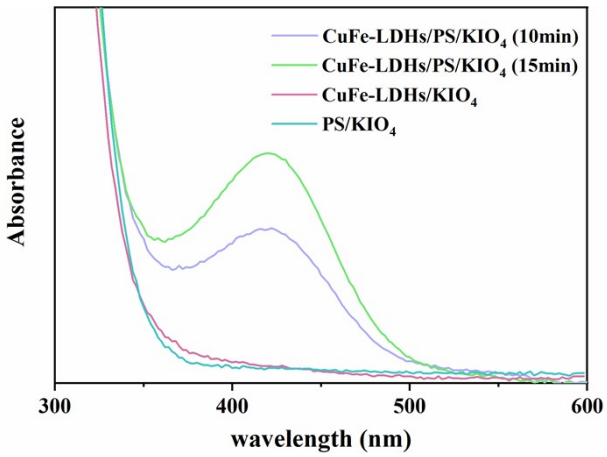

Fig. S6 The ultraviolet-visible absorption spectra of periodate-Cu(III) complex.

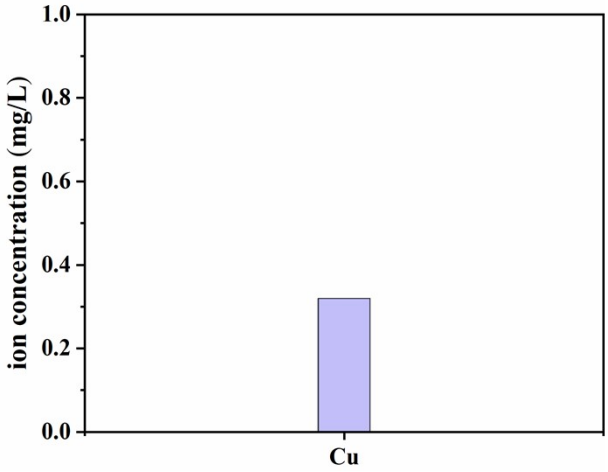

Fig. S7 The dissolution of Cu ion in the CuFe-LDHs/PS/OFL system after five cycles.

Table S1 The BET data of CuFe-LDHs.

Specific surface area (m^2/g)	Pore volume (cm^3/g)	Aperture (nm)
207.88	0.304	29.22

Table S2 The conditions of OFL degradation by different catalysts for activating PS.

Catalysts	OFL concentration (mg/L)	Dosage (g/L)	PS concentration (mM)	Time (min)	Degradation efficiency (%)	pH range	Ref
FeCu-gC_3N_4	10	0.3	1.3	120	91	3.1-9.0	1
Cu-Fe oxide	10	0.5	15	30	96.2	6-10	2
$MnCeO_X$	20	0.8	1	120	83	5-9	3
Mn-CuO	10	0.5	1	20	98	6-10	4
$BaTiO_3/WS_2$	20	1	10	75	90	2-6.5	5
CuFe-LDHs	10	0.5	0.2	120	81	3-11	This work

Table S3 The E_a values for PS activation in various catalytic systems.

Catalytic systems	E_a (kJ/mol)	References
FeCo-LDHs/PS	59.71	6
$CoFe_2O_4$/TNTs/PS	70.56	7
Fe_2O_3/PS	69.225	7
Heat/PS	107.4	8
Heat/PS	102.64	9
Heat/NZVC/PS	67.40	10
VIS/5H-M-101(Fe)/PS	67.63	11
CuFe-LDHs/PS	54.95	This work

Table S4 The anions concentration in rain water.

anion	SO_4^{2-}	Cl^-	NO_3^-
Concentration (mg/L)	0.6504	0.0929	0.7414

References

1. Y. Y. Tian, Q. Li, M. Zhang, Y. L. Nie, X. K. Tian, C. Yang and Y. Li, pH-dependent oxidation mechanisms over FeCu doped g-C_3N_4 for ofloxacin degradation via the efficient peroxymonosulfate activation, *Journal of Cleaner Production*, 2021, **315,** 128207.
2. Q. Wang, B. B. Wang, Y. Ma and S. T. Xing, Enhanced superoxide radical production for ofloxacin removal via persulfate activation with Cu-Fe oxide, *Chem. Eng. J.*, 2018, **354**, 473-480.
3. L. J. Niu, G. Xian, Z. Q. Long, G. M. Zhang, J. Zhu and J. W. Li, $MnCeO_x$ with high efficiency and stability for activating persulfate to degrade AO7 and ofloxacin, *Ecotoxicol. Environ. Saf.*, 2020, **191,** 110228.
4. B. Liu, Y. M. Li, Y. S. Wu and S. T. Xing, Enhanced degradation of ofloxacin by persulfate activation with Mn doped CuO: Synergetic effect between adsorption and non-radical activation, *Chem. Eng. J.*, 2021, **417,** 127972.
5. A. Fazli, F. Zakeri, A. Khataee and Y. Orooji, A $BaTiO_3/WS_2$ composite for piezo-photocatalytic persulfate activation and ofloxacin degradation, *Communications Chemistry*, 2022, **5,** 95.
6. C. Gong, F. Chen, Q. Yang, K. Luo, F. B. Yao, S. N. Wang, X. L. Wang, J. W. Wu, X. M. Li, D. B. Wang and G. M. Zeng, Heterogeneous activation of peroxymonosulfate by Fe-Co layered doubled hydroxide for efficient catalytic degradation of Rhoadmine B, *Chem. Eng. J.*, 2017, **321**, 222-232.
7. Y. C. Du, W. J. Ma, P. X. Liu, B. H. Zou and J. Ma, Magnetic $CoFe_2O_4$ nanoparticles supported on titanate nanotubes ($CoFe_2O_4$/TNTs) as a novel heterogeneous catalyst for peroxymonosulfate activation and degradation of organic pollutants, *J. Hazard. Mater.*, 2016, **308**, 58-66.
8. C. S. Ding, Z. Y. Cai, C. K. Hu, J. Lei, L. Wang, Q. S. Li, X. Y. Li and J. Deng, Degradation of antiviral drug acyclovir by thermal activated persulfate process: Kinetics study and modeling, *Chemosphere*, 2023, **323**, 138247.
9. T. T. Li, S. Lu, W. W. Lin, H. J. Ren and R. Zhou, Heat-activated persulfate oxidative degradation of ofloxacin: Kinetics, mechanisms, and toxicity assessment, *Chem. Eng. J.*, 2022, **433**, 133801.
10. J. Deng, M. Y. Xu, Y. J. Chen, J. Li, C. E. Qiu, X. Y. Li and S. Q. Zhou, Highly-efficient removal of norfloxacin with nanoscale zero-valent copper activated persulfate at mild temperature, *Chem. Eng. J.*, 2019, **366**, 491-503.

11. G. Y. Cheng, C. Yuan, W. S. Ruan, B. Ma, X. Y. Zhang, X. J. Yuan, Z. H. Li, D. Wang and F. Teng, Visible light enhanced persulfate activation for degradation of tetracycline boosting adsorption of persulfate by ligand-deficient MIL-101 (Fe) icosahedron, *Chemosphere*, 2023, **317**, 137857.