

# Enhanced Orange II Removal Using Fe/Mn/Mg<sub>2</sub>-LDH Activated Peroxymonosulfate: Synergistic Radical Oxidation and Adsorption

*Yajie Wang*<sup>1</sup>, *Cui Qiu*<sup>1</sup>, *Peng Cheng*<sup>2,3\*</sup>, *Yuqing Li*<sup>1</sup>, *Yunlong Ma*<sup>1</sup>, *Xiuzhen Tao*<sup>1</sup>, *Bo Weng*<sup>4,5\*</sup> and *Gilles Mailhot*<sup>2</sup>

<sup>1</sup> School of Eco-Environmental Engineering, Guizhou Minzu University, Guiyang 550025, China;

<sup>2</sup> Institut de Chimie de Clermont Ferrand (ICCF) UMR 6296, Université Clermont Auvergne, CNRS, Clermont Auvergne INP, BP 80026, F-63171 Clermont-Ferrand, France;

<sup>3</sup> Hubei Key Lab of Biomass Resource Chemistry and Environmental Biotechnology, School of Resources and Environmental Science, Wuhan University, Wuhan 430079, China

<sup>4</sup> CAS Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment Chinese Academy of Sciences, 1799 Jimei Road, Xiamen 361021, China;

<sup>5</sup> University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China;

\* Correspondence: peng.cheng@uca.fr (Peng CHENG), bweng@iue.ac.cn (Bo WENG)

Supporting Information Pages: 22

Number of Texts: 2

Number of Tables: 3

Number of Figures: 13

**Text S1** Analysis of FTIR spectra of fresh and used Fe/Mn/Mg<sub>2</sub>-LDH

FTIR spectra of different LDHs are depicted in Figure A2. A broad band around 3400 cm<sup>-1</sup> was assigned to the stretching vibration of -OH groups, either from the interlayer water or structural -OH groups. The band observed at 1640 cm<sup>-1</sup> corresponded to the bending vibration of -OH groups in the adsorbed water molecules [1]. A weak band at 1380 cm<sup>-1</sup> was attributed to the asymmetric stretching of CO<sub>3</sub><sup>2-</sup> in the interlayer [2]. The strong band around 590 cm<sup>-1</sup> is derived from the lattice vibrations, such as M-O, M-OH, and M-O-M groups (where M = Mg, Fe, and Mn). It's noteworthy that the intensity of the band at 3400 cm<sup>-1</sup> significantly decreased, suggesting the involvement of the surface-OH groups in the reaction.

**Text S2** Preparation of other LDHs used in this study

**Fe/Mn/Mg-LDH preparation.** Initially,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  were dissolved in oxygen-free water with a molar ratio of  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$  of 1:1:1 and a total metal concentration of approximately  $2.0 \text{ mol L}^{-1}$ . Subsequently, the mixed metal solution was added into a homemade reactor at a flow rate of  $0.5 \text{ ml min}^{-1}$ , while  $3.0 \text{ mol L}^{-1}$  NaOH was added at a variable flow rate to maintain the reaction pH at  $10.0 \pm 0.1$ . The mixed solution was stirred at  $25.0 \text{ }^\circ\text{C}$  under an  $\text{N}_2$  atmosphere for 1 hour. After the preparation process, the mixed solution was allowed to age for 24 hours at ambient temperature. Then the solution was centrifuged and filtered, yielding the catalyst. The obtained catalyst was then washed with Milli-Q water three times and freeze-dried for 96 hours.

**Fe/Mn-LDH preparation.** Initially,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1 mmol) and  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (1 mmol) were dispersed into 100 mL of de-ionized water and stirred at a constant speed for 30 min to form solution A. Simultaneously, solution B was formed by dissolving NaOH (0.035 mol) and  $\text{Na}_2\text{CO}_3$  (0.015 mol) in 100 mL of deionized water. Then, solution B was dripped slowly into solution A and the pH value of resulting suspension was strictly adjusted to 10.4–10.7. The mixture was ultrasonic processed at room temperature for 30 min and then stirred in water bath at  $65 \text{ }^\circ\text{C}$  for 4 h. Lastly, the products MnFe-LDH were acquired by centrifuging (5000 r/min for 5 min), washing and drying in a vacuum oven at  $60 \text{ }^\circ\text{C}$  for 24 h.

**Fe/Mn<sub>2</sub>-LDH preparation.** Initially,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1 mmol) and  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (2 mmol) were dispersed into 100 mL of de-ionized water and stirred at a constant speed for 30 min to form solution A. Simultaneously, solution B was formed by dissolving NaOH (0.035 mol) and  $\text{Na}_2\text{CO}_3$  (0.015 mol) in 100 mL of deionized water. Then, solution B was dripped slowly into solution A and the pH value of resulting suspension was strictly adjusted to 10.4–10.7. The mixture was ultrasonic processed at room temperature for 30 min and then stirred in water bath at  $65 \text{ }^\circ\text{C}$  for 4 h. Lastly, the products MnFe-LDH were acquired by centrifuging (5000 r/min for 5 min), washing and drying in a vacuum oven at  $60 \text{ }^\circ\text{C}$  for 24 h.

**Fe/Mn<sub>5</sub>-LDH preparation.** Initially,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1 mmol) and  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (5 mmol) were dispersed into 100 mL of de-ionized water and stirred at a constant speed for 30 min to form solution A. Simultaneously, solution B was formed by dissolving NaOH (0.035 mol) and

$\text{Na}_2\text{CO}_3$  (0.015 mol) in 100 mL of deionized water. Then, solution B was dripped slowly into solution A and the pH value of resulting suspension was strictly adjusted to 10.4–10.7. The mixture was ultrasonic processed at room temperature for 30 min and then stirred in water bath at 65 °C for 4 h. Lastly, the products MnFe-LDH were acquired by centrifuging (5000 r/min for 5 min), washing and drying in a vacuum oven at 60 °C for 24 h.

**Fe/Mn<sub>8</sub>-LDH preparation.** Initially,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1 mmol) and  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (8 mmol) were dispersed into 100 mL of de-ionized water and stirred at a constant speed for 30 min to form solution A. Simultaneously, solution B was formed by dissolving NaOH (0.035 mol) and  $\text{Na}_2\text{CO}_3$  (0.015 mol) in 100 mL of deionized water. Then, solution B was dripped slowly into solution A and the pH value of resulting suspension was strictly adjusted to 10.4–10.7. The mixture was ultrasonic processed at room temperature for 30 min and then stirred in water bath at 65 °C for 4 h. Lastly, the products MnFe-LDH were acquired by centrifuging (5000 r/min for 5 min), washing and drying in a vacuum oven at 60 °C for 24 h.

**Table S1.** Lattice parameters of samples of Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction.

LDH	Peak position	FWHM	D (nm)	Microstrain ( $\epsilon$ )	Microstrain ( $\epsilon$ )
	$2\theta$ ( $^\circ$ )	$\beta$ ( $^\circ$ )	$\frac{K\lambda}{\beta\cos\theta}$	$\frac{\beta}{4\tan\theta}$	$\times 10^{-3}$
Fe/Mn/Mg <sub>2</sub> -LDH (Before reaction)	11.040	0.763	10.93	3.44E-02	34.45
	19.061	0.707	11.90	1.84 E-02	18.37
	22.079	0.776	10.89	1.74E-02	17.36
	33.686	0.881	9.84	1.27E-02	12.70
	38.360	0.836	10.51	1.05E-02	10.49
	59.298	0.703	13.58	5.39E-03	5.39
Fe/Mn/Mg <sub>2</sub> -LDH (After reaction)	11.657	0.793	10.52	3.39E-02	33.90
	19.161	0.823	10.22	2.13E-02	21.28
	22.901	0.652	12.98	1.40E-02	14.05
	34.506	0.75	11.58	1.05E-02	10.54
	38.762	0.61	14.42	7.57E-03	7.57
	60.042	0.751	12.76	5.67E-03	5.67

Table S2  $k_{\text{obs(overall)}}$ ,  $k_{\text{obs(ads)}}$ , and  $k_{\text{obs(ox)}}$  of Orange II removal in LDHs/PMS systems at its optimal conditions (Experimental conditions: bimetallic materials system :[bimetallic materials] = 0.20 g L<sup>-1</sup>, [PMS] = 0.5 mmol L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, pH 6.0; trimetallic materials system: [trimetallic materials] = 0.16 g L<sup>-1</sup>, [PMS] = 0.5 mmol L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, pH 7.0)

Material	$k_{\text{obs(Overall)}} (\text{min}^{-1})$	$k_{\text{obs(ads)}} (\text{min}^{-1})$	$k_{\text{obs(ox)}} (\text{min}^{-1})$
Mn/Fe-LDH	0.1035	$2 \times 10^{-4}$	0.1032
Mn/Fe <sub>2</sub> -LDH	0.0217	$2 \times 10^{-4}$	0.0215
Mn/Fe <sub>5</sub> -LDH	0.0150	$2 \times 10^{-4}$	0.0148
Mn/Fe <sub>8</sub> -LDH	0.0024	$1 \times 10^{-5}$	0.0024
Mn/Fe/Mg-LDH	0.1151	0.0274	0.0877
Mn/Fe/Mg <sub>2</sub> -LDH	0.1645	0.0348	0.1297

Table S3. Rate constants of ROSs and quenchers

Rate constants for reactions (L mol <sup>-1</sup> s <sup>-1</sup> )					
	SO <sub>4</sub> <sup>•-</sup>	HO•	<sup>1</sup> O <sub>2</sub>	O <sub>2</sub> <sup>•-</sup>	high-valent metals
MeOH [3]	1.0 × 10 <sup>7</sup>	9.7 × 10 <sup>8</sup>			
TBA [4]	8.4 × 10 <sup>5</sup>	6.0 × 10 <sup>8</sup>			
FFA [3, 5]	4.1 × 10 <sup>9</sup>	1.5 × 10 <sup>10</sup>	5 × 10 <sup>8</sup>		1.5 × 10 <sup>3</sup>
SOD [6]				2 × 10 <sup>9</sup>	
phenol [7]	8.8 × 10 <sup>9</sup>	6.6 × 10 <sup>9</sup>	1.2 × 10 <sup>4</sup>		
DMSO [8]	2.7 × 10 <sup>9</sup>	5.8 × 10 <sup>10</sup>			1.2 × 10 <sup>5</sup>

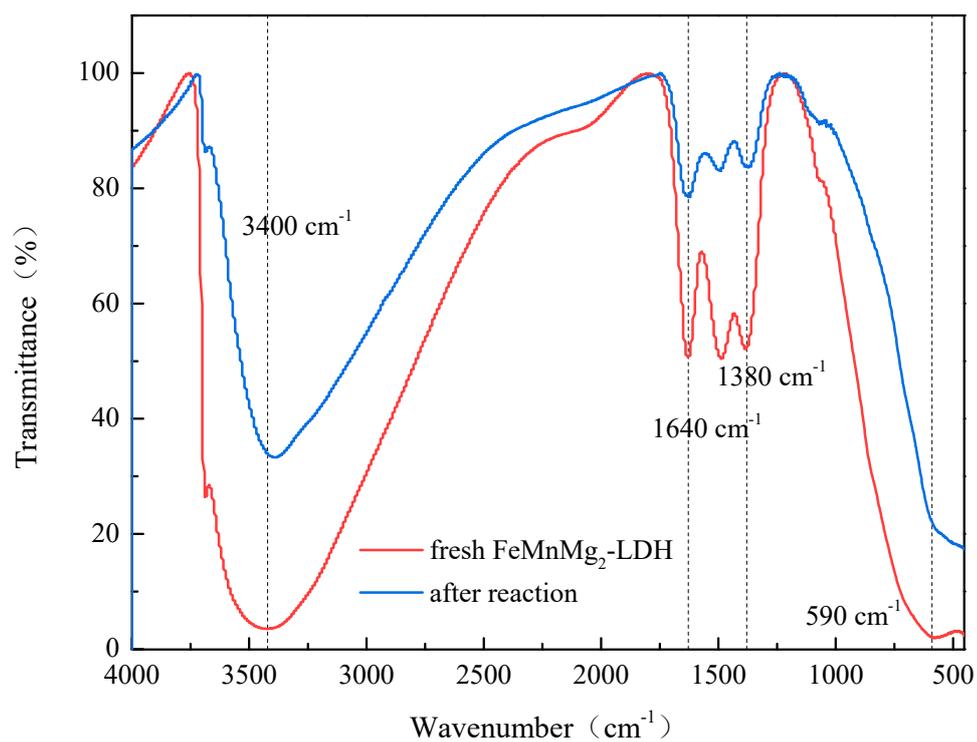


Figure S1. FTIR spectra of Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction

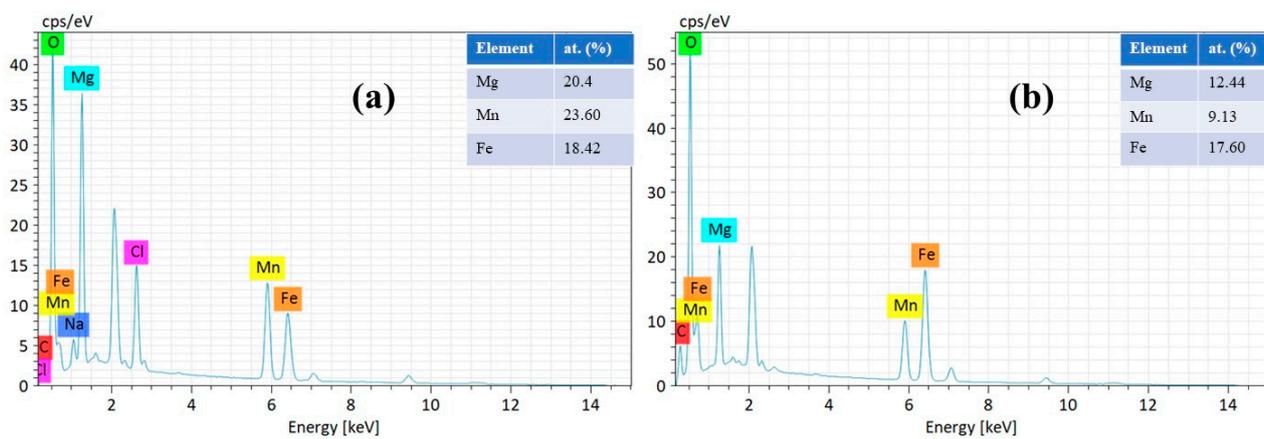


Figure S2. EDS spectra of the Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction

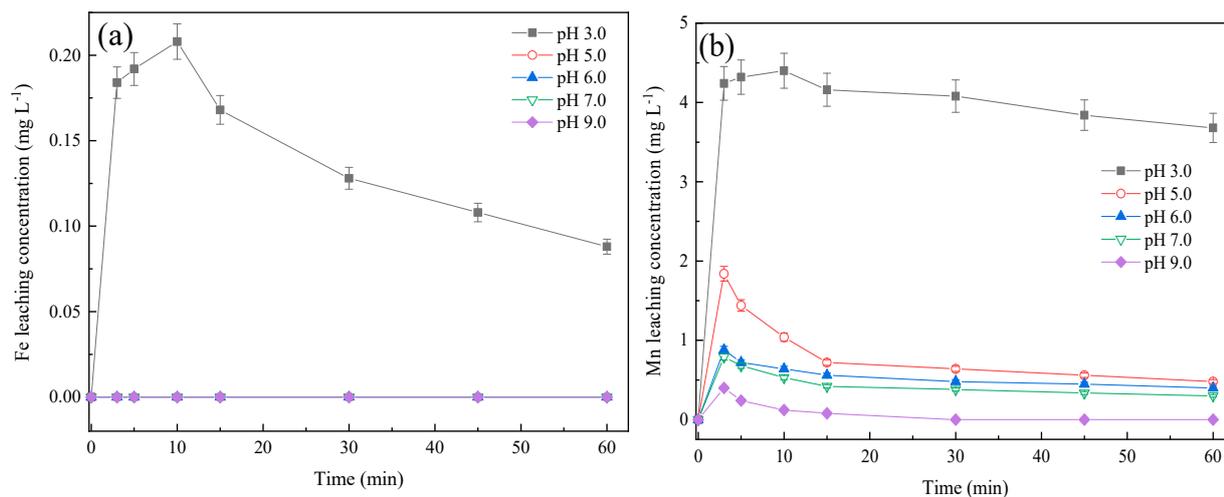


Figure S3. Leaching of Fe (a) and Mn (b) from Fe/Mn/Mg<sub>2</sub>-LDH during reactions at different initial pH conditions (Experimental conditions: [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [PMS] = 1.0 mmol L<sup>-1</sup>)

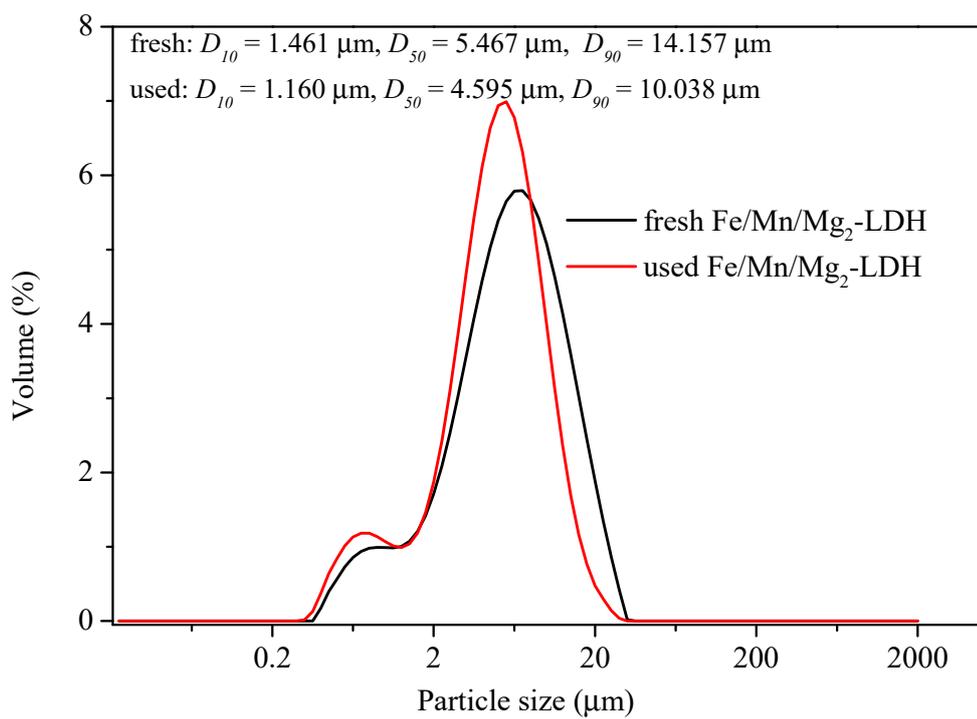


Figure S4. The particle size distribution of the Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction

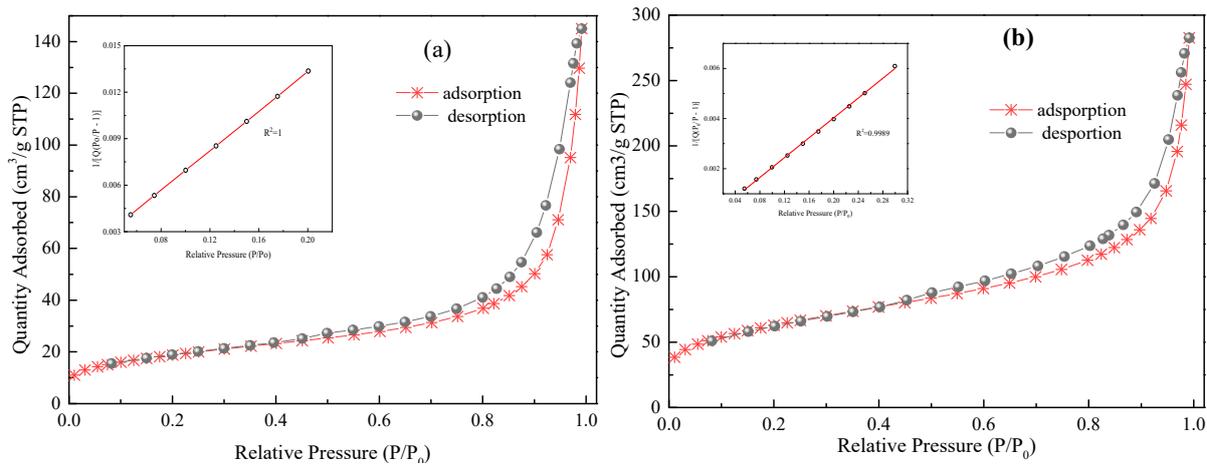


Figure S5. The N<sub>2</sub> adsorption-desorption isotherm and fitting curve of the BET surface area of the Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction

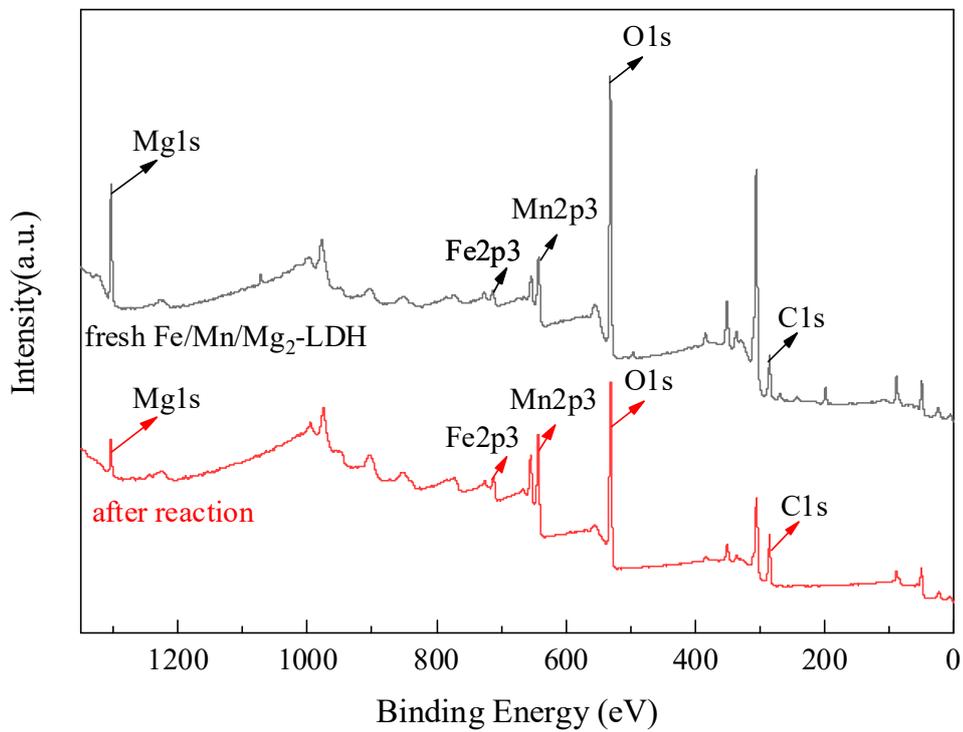


Figure S6. Full XPS spectrum of Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction

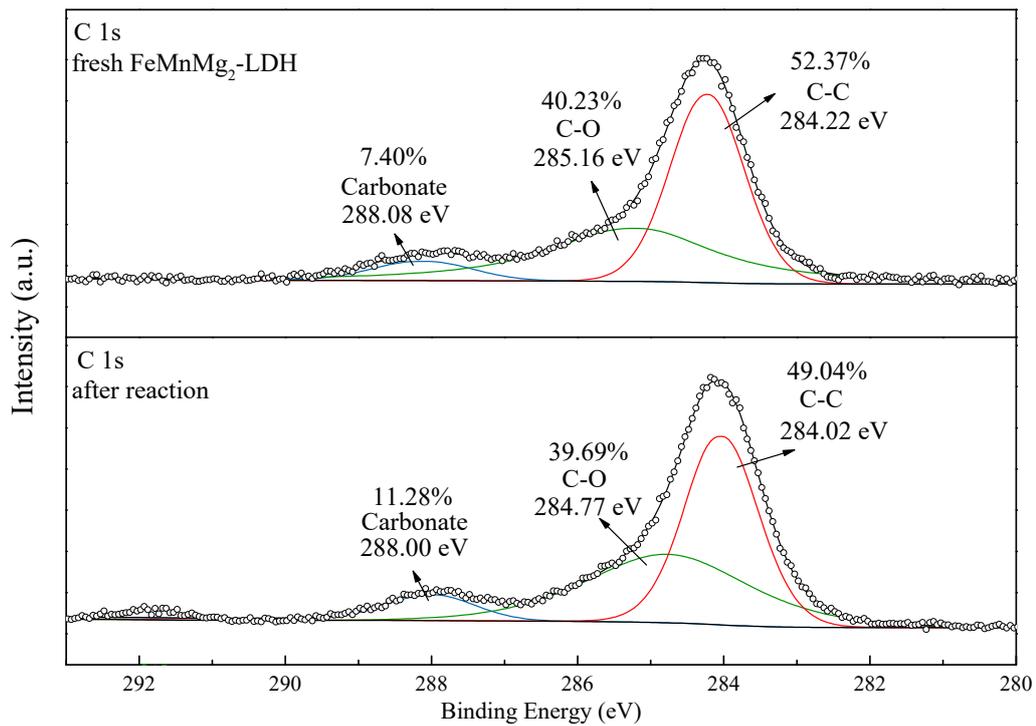


Figure S7. XPS spectra of C 1s on the Fe/Mn/Mg<sub>2</sub>-LDH before and after reaction

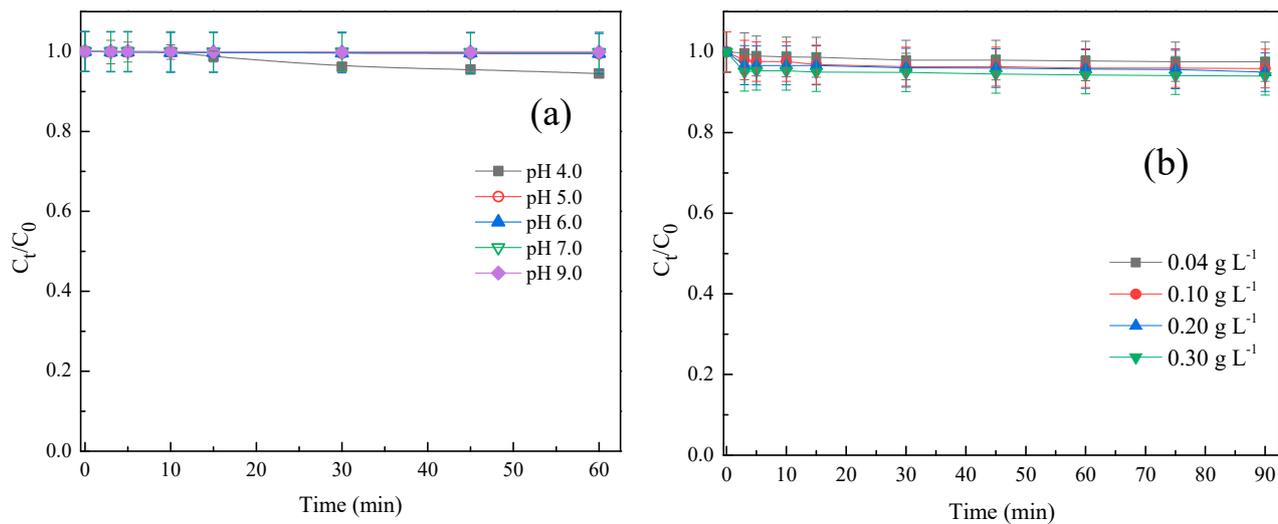


Figure S8. Effect of pH and the dosage of Fe/Mn-LDH on the adsorption of Orange II by Fe/Mn-LDH (Experimental conditions: (a)  $[\text{Fe/Mn-LDH}] = 0.16 \text{ g L}^{-1}$ ,  $[\text{Orange II}]_0 = 50 \text{ } \mu\text{mol L}^{-1}$ , pH 6.0; (b)  $[\text{Orange II}]_0 = 50 \text{ } \mu\text{mol L}^{-1}$ , pH 6.0)

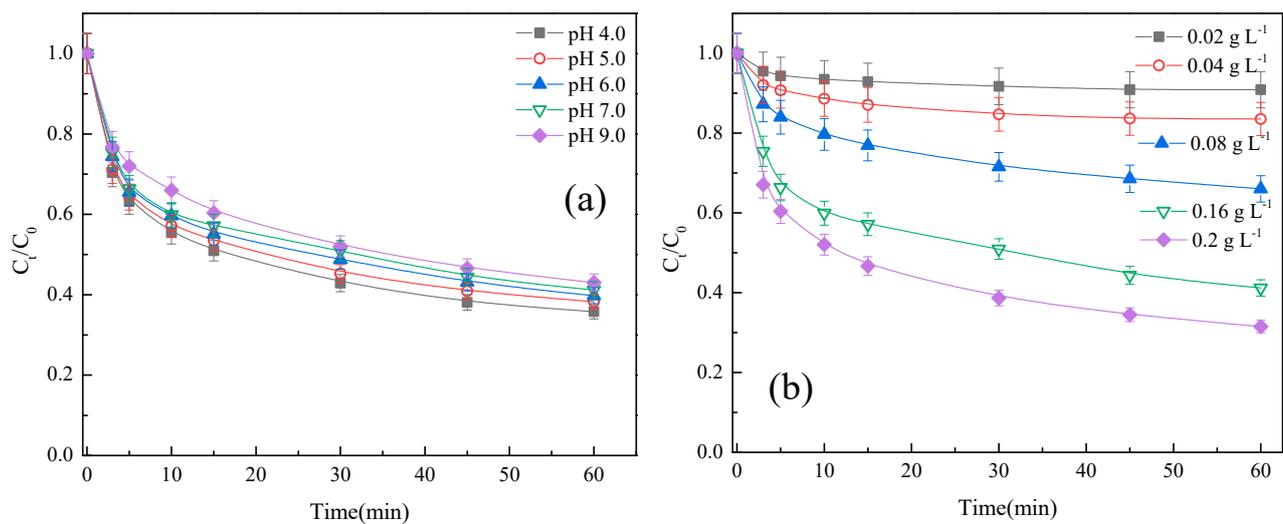


Figure S9. Effect of pH and the dosage of Fe/Mn/Mg<sub>2</sub>-LDH on the adsorption of Orange II by Fe/Mn/Mg<sub>2</sub>-LDH (Experimental conditions: (a) [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>; (b) [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, pH 7.0)

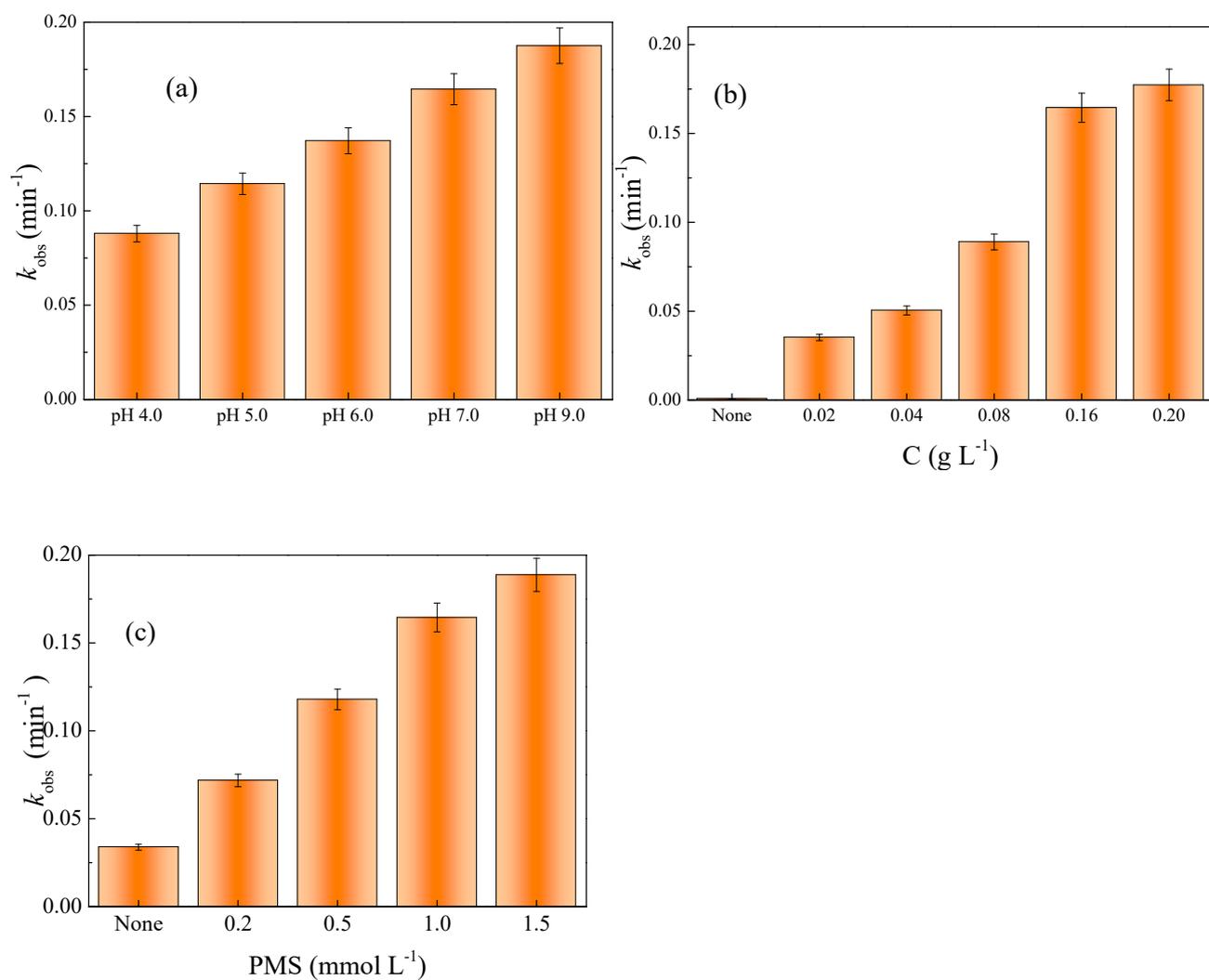


Figure S10. Effect of pH, Fe/Mn/Mg<sub>2</sub>-LDH, and PMS concentration on the  $k_{\text{obs}}$  in the Fe/Mn/Mg<sub>2</sub>-LDH/PMS system (a) pH (b) Fe/Mn/Mg<sub>2</sub>-LDH dosage (c) PMS concentration (Experimental conditions: (a) [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, [PMS] = 1.0 mmol L<sup>-1</sup>; (b) [PMS] = 1.0 mmol L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, pH 7.0; (c) [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, pH 7.0)

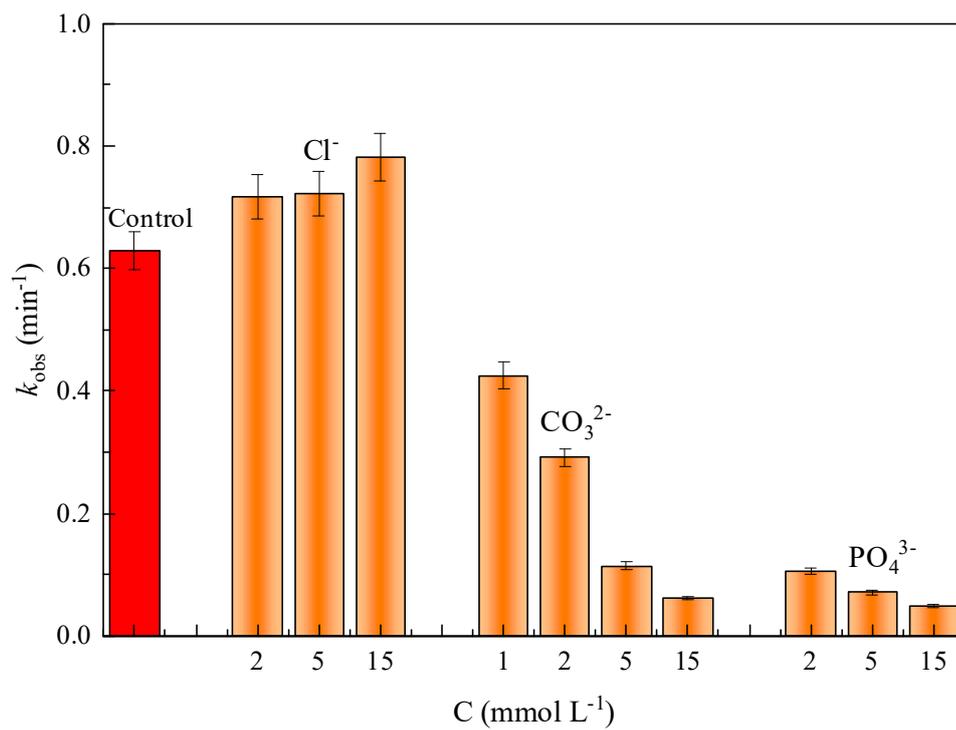


Figure S11. Effect of co-existing anions on the  $k_{\text{obs}}$  in Fe/Mn/Mg<sub>2</sub>-LDH/PMS system (Experimental conditions: [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, [PMS] = 1.0 mmol L<sup>-1</sup>, pH 7.0)

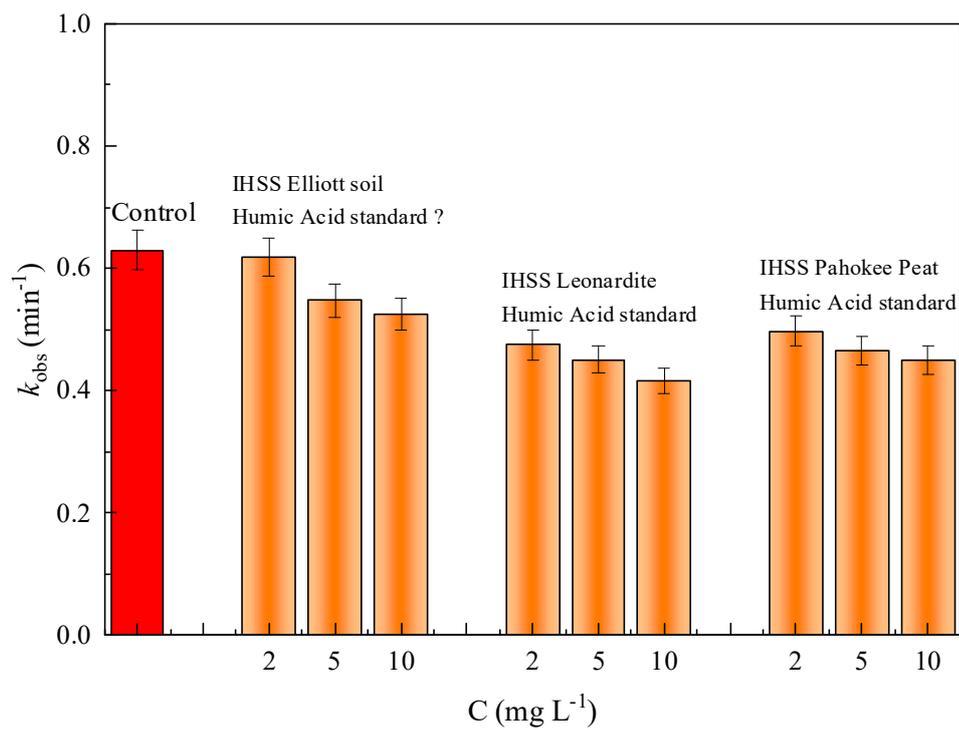


Fig S12. Effect of different humic acids on the  $k_{\text{obs}}$  in Fe/Mn/Mg<sub>2</sub>-LDH/PMS system (Experimental conditions: [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, [PMS] = 1.0 mmol L<sup>-1</sup>, pH 7.0)

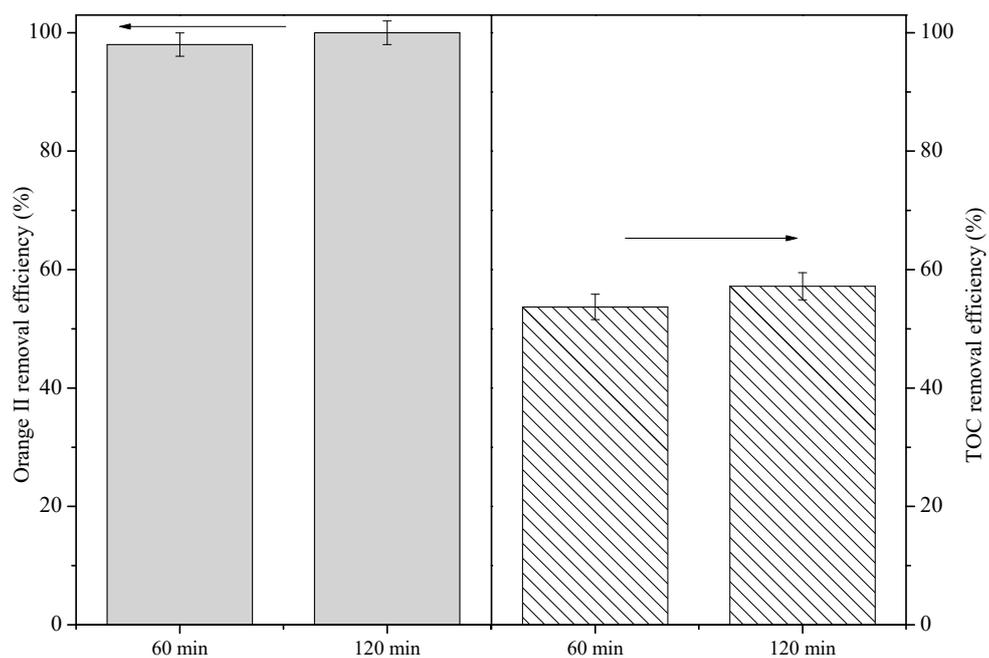


Figure S13. Catalytic performance of Fe/Mn/Mg<sub>2</sub>-LDH in PMS activation for Orange II and TOC removal (Experimental conditions: [Fe/Mn/Mg<sub>2</sub>-LDH] = 0.16 g L<sup>-1</sup>, [Orange II]<sub>0</sub> = 50 μmol L<sup>-1</sup>, [PMS] = 1.0 mmol L<sup>-1</sup>)

## References

1. Lu, H.; Zhu, Z.; Zhang, H.; Zhu, J.; Qiu, Y. Simultaneous removal of arsenate and antimonate in simulated and practical water samples by adsorption onto Zn/Fe layered double hydroxide. *Chem. Eng. J.* 2015, 276, 365–375.
2. Xie, L.; Zhong, Y.; Xiang, R.; Fu, G.; Xu, Y.; Cheng, Y. Sono-assisted preparation of Fe(II)-Al(III) layered double hydroxides and their application for removing uranium (VI). *Chem. Eng. J.* 2017, 328, 574–584.
3. Zhou, Y.; Jiang, J.; Gao, Y.; Ma, J.; Pang, S.; Li, J.; Lu X.; Yuan, L. Activation of Peroxymonosulfate by Benzoquinone: A Novel Nonradical Oxidation Process. *Environ. Sci. Technol.* 2015, 49; 12491-12950.
4. Huang, G.; Wang, C.; Yang, C.; Guo P.; Yu, H. Degradation of bisphenol A by peroxymonosulfate catalytically activated with  $Mn_{1.8}Fe_{1.2}O_4$  nanospheres: synergism between Mn and Fe. *Environ. Sci. Technol.* 2017, 51, 12611-12618.
5. Ding, Y.; Xia, X.; Ruan Y.; Tang, H. In situ  $H^+$ -mediated formation of singlet oxygen from  $BaBiO_3$  for oxidative degradation of bisphenol A without light irradiation: Efficiency, kinetics, and mechanism. *Chemosphere*, 2015, 141, 80–86.
6. Fang, G.; Dionysiou, D.D.; Al-Abed, S.R.; Zhou, D. Superoxide radical driving the activation of persulfate by magnetite nanoparticles: Implications for the degradation of PCBs. *Appl. Catal. B.* 2013, 129, 325-332.
7. Zhang, J.; Shao, X.; Shi, C.; Yang, S. Decolorization of Acid Orange 7 with peroxymonosulfate oxidation catalyzed by granular activated carbon. *Chem. Eng. J.* 2013, 232, 259–265.
8. Yang, B.; Liu, H.; Zhang, J. High-valent metals in advanced oxidation processes: A critical review of their identification methods, formation mechanisms, and reactivity performance. *Chem. Eng. J.* 2023, 460, 141796.