

Supporting Information

Drastic enhancement on Fenton oxidation of organic contaminants by accelerating Fe(III)/Fe(II) cycle with L-cysteine

Lianshun Luo,^a Yuyuan Yao,^{*a} Fei Gong,^a Zhenfu Huang,^a Wangyang Lu,^a
Wenxing Chen,^a and Li Zhang^{*ab}

^a Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, PR China. E-mail: yyy0571@126.com; Fax: +86 571 86843255; Tel.: +86 571 86843810

^b The School of Material Science and Chemical Engineering, Ningbo University, Ningbo 325211, China. E-mail: zhangli2@nbu.edu.cn; Fax: +86 15869369738; Tel.: +86 574 87609986

Table S1. The changes of the pH value of MB dye solution under different concentrations of Cys. Conditions: [MB] = 10 μ M, T = 20°C.

Cys concentration (μ M)	The changes of the pH value of MB solution								
	2.01	3.00	4.04	5.03	5.47	6.05	6.49	6.96	
0	2.01	3.00	4.04	5.03	5.47	6.05	6.49	6.96	
20	2.01	3.00	4.04	5.03	5.47	6.05	6.49	6.95	
100	2.01	3.00	4.03	5.03	5.48	6.05	6.47	6.92	
200	2.01	3.00	4.03	5.02	5.48	6.04	6.46	6.88	

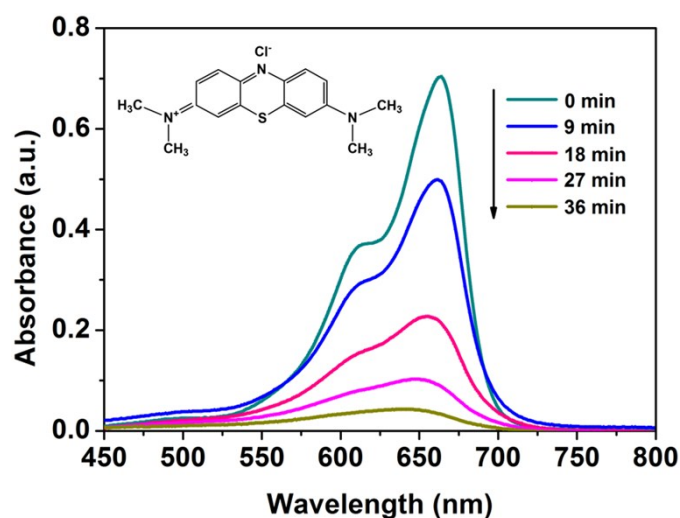


Fig. S1 UV-vis spectra of MB removal in the Fenton-Cys system, and the inset shows the chemical structure of MB.

Conditions: [H₂O₂] = 0.4 mM; [Fe(III)] = 7.5 μ M; [Cys] = 20 μ M; [MB] = 10 μ M; initial pH 3.0; T = 20°C.

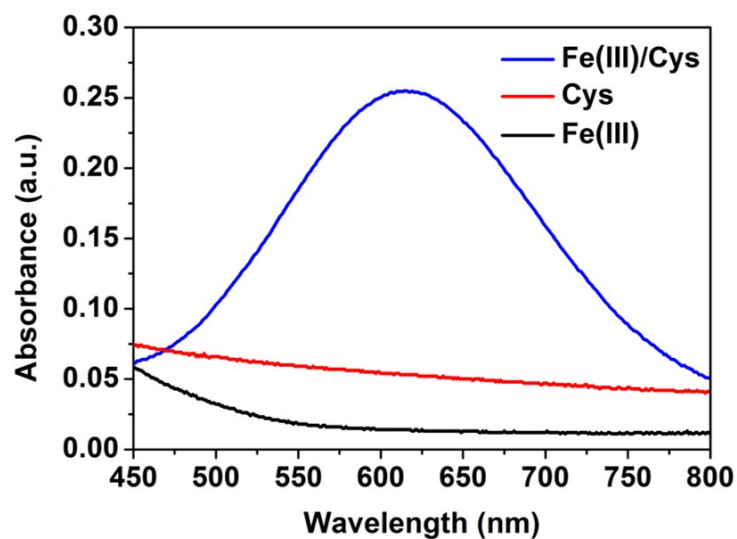


Fig. S2 The UV-vis spectra of Fe(III) solution, Cys solution and Fe(III)/Cys solution. Condition: $[\text{Fe(III)}] = 7.5 \mu\text{M}$, $[\text{Cys}] = 20 \mu\text{M}$, initial pH 3.0, $T = 20^\circ\text{C}$.

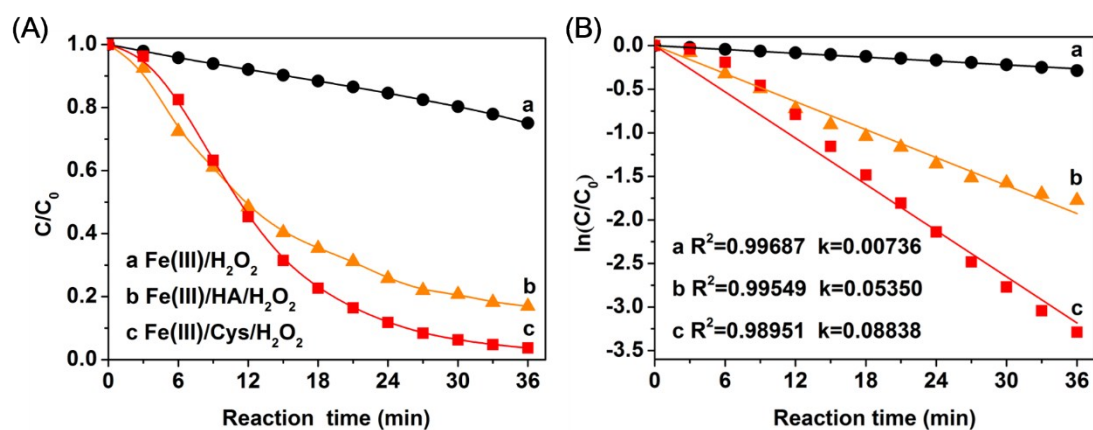


Fig. S3 (A) Concentration changes of MB in different systems; (B) The apparent rate constants (k_{obs}) in different systems. (a) Fenton system; (b) Fenton-HA system; (c) Fenton-Cys system. Conditions: $[\text{H}_2\text{O}_2] = 0.4 \text{ mM}$; $[\text{Fe(III)}] = 7.5 \mu\text{M}$; $[\text{Cys}] = [\text{HA}] = 20 \mu\text{M}$; $[\text{MB}] = 10 \mu\text{M}$; initial pH 3.0; $T = 20^\circ\text{C}$.

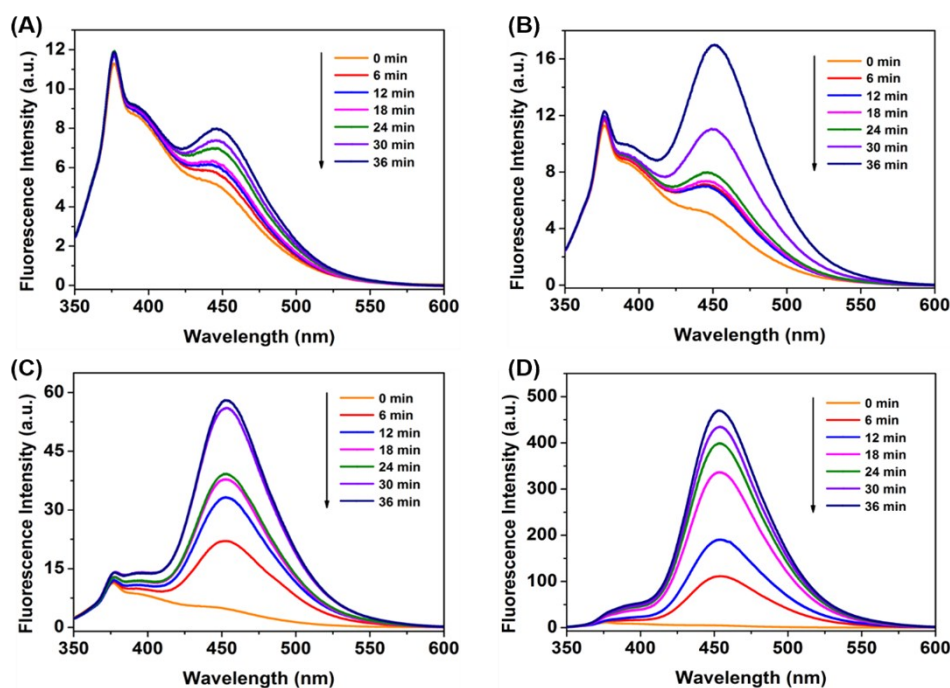


Fig. S4 Spectral changes in the emission spectra of coumarin ($[\text{coumarin}] = 0.05 \text{ mM}$) with reaction time in different systems. (A) H_2O_2 system; (B) Cys/ H_2O_2 system; (C) Fenton system; (D) Fenton-Cys system. Conditions: $[\text{H}_2\text{O}_2] = 0.4 \text{ mM}$; $[\text{Fe(III)}] = 7.5 \text{ }\mu\text{M}$; $[\text{Cys}] = 20 \text{ }\mu\text{M}$; initial pH 3.0; $T = 20^\circ\text{C}$.

Test S1. Effect of several common anions on MB removal

Industrial dyes wastewater contains a large amount of common anions which are widely used in the textile dyeing industry. For example, Cl^- is used widely in the textile dyeing industry to accelerate dye transfer from the aqueous to the fiber phase. Therefore, it is essential to investigate the effect of common anions on the removal of MB. In this study, several common anions (Cl^- , SO_4^{2-} and NO_3^-) were selected to investigate their influence on MB removal. As shown in Table S2, the addition of different concentration of anions inhibited the removal of MB in different degrees in the two systems. In order to further assess the inhibitory effect of anions on the MB removal, we employed inhibitory rate, which was defined as $[(R_0 - R_n)/R_0] \times 100\%$ (R_0 represent the MB removal rate without the addition of anions, and R_n represent the MB removal rate with the addition of different concentrations of anions). As can be shown in Table S2, the inhibitory rate of the Fenton-Cys system was much lower compared with the Fenton system at the same concentration of anions, which indicated that the addition of Cys to the Fenton system remarkably weakened the inhibitory effect of anions on MB removal.

Furthermore, the COD removal rate was also measured to evaluate the mineralization degree of dye in the two systems. It was found that the COD declined by 27.7% (from 49.4 to 35.7 mg/L) and 38.7%

(from 54.4 to 33.3 mg/L) for the Fenton system and the Fenton-Cys system, respectively. The result suggested that the addition of Cys to Fenton system improved the COD removal, moreover, its addition did not increase the COD value. Based on the above results, the addition of Cys to Fenton system might be a promising way to degrade organic contaminants rapidly in wastewater treatment.

Table S2. Effect of several common anions (Cl^- , SO_4^{2-} and NO_3^-) on MB removal. Conditions: $[\text{Fe(III)}] = 7.5 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 0.4 \text{ mM}$, $[\text{Cys}] = 20 \mu\text{M}$, $[\text{MB}] = 10 \mu\text{M}$, initial pH 3.0, $T = 20^\circ\text{C}$, reaction time = 36 min.

Cl ⁻ concentration (μM)	Fenton system		Fenton-Cys system	
	Removal rate (%)	Inhibitory rate (%)	Removal rate (%)	Inhibitory rate (%)
0.0	24.9	0	96.3	0
0.5	16.1	35.3	87.2	9.4
1.0	10.6	57.4	85.7	11.0
2.0	8.3	66.7	71.5	25.8
5.0	5.9	76.3	54.5	43.4
SO ₄ ²⁻ concentration (μM)	Removal rate (%)	Inhibitory rate (%)	Removal rate (%)	Inhibitory rate (%)
0.0	24.9	0	96.3	0
0.5	17.4	30.1	85.5	11.2
1.0	15.3	38.6	86.4	10.3
2.0	14.5	41.8	78.7	18.3
5.0	14.3	42.6	80.4	16.5
NO ₃ ⁻ concentration (μM)	Removal rate (%)	Inhibitory rate (%)	Removal rate (%)	Inhibitory rate (%)
0.0	24.9	0	96.3	0
0.5	23.5	5.6	91.3	5.2
1.0	20.2	18.9	88.6	8.0
2.0	20.8	16.5	88.6	8.0
5.0	16.1	35.3	84.2	12.6