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

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The development of a highly efficient and pH-tolerant Fenton system has been one of the most important and challenging goals in water remediation. Herein, a green natural organic ligand, L-cysteine (Cys), was innovatively introduced into Fenton's reagent to construct an excellent catalytic oxidation system. The introduction of Cys into the Fenton system expanded the effective pH range up to 6.5 and achieved a superior oxidation efficiency, representing about 70% higher removal ratio and 12 times higher reaction rate constant with methylene blue dye as the probe compound. The Cys-driven Fenton reaction presented an outstanding pH adaptability and oxidative activity compared with other common organic ligands or reducing agent-modified Fenton reactions. An investigation of the reaction mechanism indicated that the addition of Cys into the system accelerated the Fe(m)/Fe(m) cycle, and led to a relatively steady Fe(m) recovery, which enhances the generation of hydroxyl radicals ("OH). The presence of Cys in the Fenton system remarkably reduced the apparent activation energy from 95.90 to 47.93 kJ mol⁻¹. The findings from this study provide a feasible approach for a highly efficient and pH-tolerant wastewater treatment process with environmentally benign characteristics, and initiates an inspiring research domain of amino acids in the environmental catalysis field.

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1. Introduction

In recent decades, environmental deterioration issues such as sandy desertification, soil erosion, and water contamination have become increasingly severe, which have resulted in notably widespread changes in natural ecosystems and climatic disturbances. Excessive hazardous pollutants in industrial wastewater have exceeded the natural ecosystem biodegradability. To remedy biodegradation weaknesses, two alternative strategies were formulated and investigated. These are the physical adsorption and chemical catalytic oxidation of contaminants.¹⁻⁴ Although physical adsorption methods present remarkable performance for phase disengagement, adsorbed pollutants cannot be destroyed completely, and the subsequent disposal may bear the risk of secondary pollution.⁵ Advanced oxidation processes (AOPs) have received increasing attention as promising and attractive technologies for the treatment of wastewater because of the generation of highly reactive radicals which can decompose organic pollutants into non-toxic small molecule substances.⁶⁻⁹

Among the AOPs, the Fenton system has been studied extensively because of its fast reaction rate, simple operation and environmental friendliness.^{10,11} In the Fenton system, ferrous ions serve as a catalyst to activate H₂O₂ to generate highly active 'OH and trigger free radical chain reactions, which can oxidize most organic contaminants rapidly and non-selectively.12,13 However, the Fenton system has some limitations during the reaction: (i) the reaction rate of Fe(m) and H_2O_2 (eqn (2)) is much lower than that of $Fe(\pi)$ and H_2O_2 (eqn (1)), which may hinder the Fe(m)/Fe(n) cycle and result in a decline in reaction rates and (ii) Fe(III) will precipitate as iron hydroxides in insoluble form, which slows down or blocks the 'OH generation rate, and thus acidic conditions (pH \leq 3.0) are required to maintain Fe(III) in soluble form.^{14,15} Obviously, Fe(III) precipitation must be reduced and a more effective transformation from Fe(m) to Fe(m) is required to improve the oxidation efficiency of the Fenton reaction.

 $Fe(II) + H_2O_2 \rightarrow OH + OH^- + Fe(III), k = 63 M^{-1} s^{-1}$ (1)

Fe(III) + H₂O₂ \rightarrow Fe(II) + H⁺ + HOO⁺, $k = 0.01-0.02 \text{ M}^{-1} \text{ s}^{-1}$ (2)

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To overcome these problems, polycarboxylates (e.g., citrate, malonate, and oxalate) and aminopolycarboxylic acids (e.g., ethylenediaminetetraacetic acid (EDTA) and ethylenediamine-N,N'-disuccinic acid (EDDS)) were used as organic ligands to solubilize Fe(III) by complexation.16-18 These ligands could form stable complexes with Fe(III) in solution and reduce or eliminate Fe(m) precipitation, which could expand the effective pH and increase the reaction rates. However, they could not enhance the reduction of Fe(III) to Fe(III) because of the lack of reducing capacity, which limited further improvements in oxidation efficiency. In addition, aminopolycarboxylic acids may also suffer from high environmental risks for practical application in view of its poor biodegradability.19-22 Consequently, researchers have developed some feasible measures such as adding additional reductants to remedy limitations of these organic ligands. For example, Wan et al. demonstrated that a significant improvement is achieved in the oxidative decolorization of orange G in the Fe(II)/EDDS/persulfate process with hydroxylamine introduction. In the Fe(II)/EDDS/persulfate/ hydroxylamine system, EDDS could alleviate the formation of iron sludge by complexing, and hydroxylamine was combined to accelerate Fe(II) recovery to improve persulfate activation.²³ Nevertheless, these extra reductants may burden the ecological environment because of their potential toxicity.24 Therefore, an eco-friendly alternative strategy should be developed that could reduce Fe(III) accumulation and accelerate the transformation from Fe(III) to Fe(III) simultaneously.

Compared with the organic ligands mentioned above, Cys possesses more remarkable properties. It has a unique structure with a reducing sulfhydryl group (-SH), which is capable of reducing Fe(III) to Fe(II) directly.^{25,26} Cys can form complexes with Fe(m), which reduces the precipitation of Fe(m). On the other hand, Fe(III)-Cys complexes may present convenient channels for the transformation from Fe(III) to Fe(II) by an internal redox triggered by protonation.²⁷ In addition, Cys is a type of green natural amino acid that exists in organisms, and will not exert a negative impact on the environment. Based on these considerations, Cys may be an ideal candidate that can act as a complexing and reducing agent simultaneously to maintain iron in soluble form and enhance the Fe(III) to Fe(III) transformation for more efficient Fenton oxidation. To the best of our knowledge, researches on the ability of Cys to promote Fenton reactions are almost blank. In this work, we introduced Cys into the Fenton system and investigated the effect of Cys on the oxidation efficiency of the Fenton system with methylene blue (MB) as probe compound. The role of Cys during the reaction process was revealed and electron paramagnetic resonance (EPR) technology combined with radical scavengers was employed to investigate the mechanism of the Cys-driven Fenton reaction. The main influencing factors, such as Cys dosage, catalyst and oxidant concentration, initial pH, reaction temperature were examined. This research not only provides new insight into the development of a highly efficient and pHtolerant Fenton oxidation process for wastewater treatment with environmentally benign characteristics, but also initiates an up-to-date research domain of the application of amino acids in environmental catalysis.

2. Experimental

2.1. Materials and chemicals

Ferric chloride hexahydrate (FeCl₃· $6H_2O$), hydrogen peroxide (H₂O₂) and Cys were analytical grade reagents (Mike Chemical Instrument Co., Ltd., Hangzhou, China). The spin trapping agent 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) was supplied by Tokyo Chemical Industry Co. Ltd., Tokyo, Japan. MB dye was obtained commercially and was used without further purification. All other chemical reagents used were also provided by Hangzhou Mike Chemical Instrument Co., Ltd., China. Doubly distilled water was used throughout this study.

2.2. Experimental procedures

Batch experiments on the catalytic oxidation of the dyes were carried out in 100 mL glass beakers by shaking in a constant temperature shaker water bath (DSHZ-300A, Taicang, Jiangsu) that was adjusted to the required temperature. A reaction volume of 50 mL was used in all experiments. Desired concentrations of MB, Fe(m), H₂O₂ and Cys were added simultaneously at the beginning of each experiment. At predetermined intervals (3 min), samples were withdrawn from the flask for analysis using an ultraviolet/visible (UV/Vis) spectrophotometer (Hitachi U-3010). The initial solution pH was adjusted with NaOH or HClO₄ prior to Fe(m) and H₂O₂ addition. Alcohol quenching experiments with *tert*-butyl alcohol (TBA) were performed by adding desired alcohols into the reaction solution before the addition of H₂O₂.

2.3. Analytical methods

The decoloration efficiency of the dyes was determined using the UV/Vis spectrophotometer. The kinetics of decoloration of the dyes can be described by a pseudo-first-order equation (eqn (3) and (4)):

$$\mathrm{d}C/\mathrm{d}t = -k_{\mathrm{obs}}C\tag{3}$$

$$C_t = C_0 \exp(-k_{\rm obs}t) \tag{4}$$

where C_t is the concentration of the dye solution at time t, C_0 is the initial concentration of the dyes and k_{obs} is the pseudo-first-order rate constant (min⁻¹). k_{obs} values were obtained from the slopes of the regression lines for plots of $-\ln(C_t/C_0)$ versus time (t).

EPR spectra of radicals trapped by DMPO were examined using a Bruker A300 spectrometer at ambient temperature. Settings for the EPR spectrometer were: center field, 3520 G; sweep width, 100 G; microwave frequency, 9.77 GHz; modulation frequency, 100 kHz and power, 12.72 mW. To quantify 'OH, coumarin was used as a chemical probe. 7-Hydroxycoumarin, a product of reaction between coumarin and 'OH, was measured by monitoring its fluorescence emission at 445 nm using a spectrofluorometer (F-7000).²⁸ The excitation wavelength was 332 nm. The Fe(π) concentration was obtained from the difference between the total Fe and the measured Fe(π) concentration, and the concentration of Fe(π) was monitored by spectrophotometric detection of phenanthroline.²⁹ The concentration of H_2O_2 was measured by titanium potassium oxalate colorimetry.³⁰ For more accurate measurement, the concentration of H_2O_2 , Fe^{3+} and Cys increased by 25 times simultaneously. Chemical oxygen demand (COD) was determined by a COD instrument (HACH DR1010, Shanghai), and the concentrations of MB, H_2O_2 , Fe(III) and Cys increased by 5 times simultaneously.

3. Results and discussion

3.1. Oxidative removal of MB

MB, a representative cationic dye, is used widely as a stain in many industries. In this study, MB was selected as the probe compound to compare the oxidation efficiency of different systems. As shown in Fig. 1, with H_2O_2 alone, the removal of MB could be neglected. In the Fenton system, less than 25% of MB was removed in 36 min. Surprisingly, more than 96% of MB was removed in 36 min in the Cys modified Fenton system. UV/Vis spectral changes of MB in the Fenton–Cys system are also shown in Fig. S1.† The experimental results suggested that the introduction of Cys into the Fenton system enhanced the removal of MB significantly.

In order to further investigate the influence of Cys, a general pseudo-first-order kinetic approach $(\ln(C_t/C_0) = -k_{obs}t)$ was employed. As shown in Fig. 2, the Fenton–Cys system gave an almost twelve-fold higher reaction rate constant (0.08838 min⁻¹) than the Fenton system (0.00736 min⁻¹). Furthermore, the utilization efficiency of H₂O₂ was also compared for the Fenton and Fenton–Cys system, which was quantified by the oxidant consumption index (*X*), defined as the number of moles of oxidant consumed per mole of MB removed. Hence, a lower value of *X* indicates a higher utilization efficiency of H₂O₂ to the Fenton system (31.2). Together, these experimental results above demonstrated that the introduction of Cys into the Fenton system



Fig. 1 The concentration changes of MB in different systems. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(III)] = 7.5 \mu M$, $[Cys] = 20 \mu M$, $[MB] = 10 \mu M$, initial pH 3.0, T = 20 °C.



Fig. 2 Comparison of apparent pseudo-first-order rate constants (conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(\text{III})] = 7.5 \text{ }\mu\text{M}$, $[Cys] = 20 \text{ }\mu\text{M}$, $[MB] = 10 \text{ }\mu\text{M}$, initial pH 3.0, $T = 20 \text{ }^\circ\text{C}$) and oxidant consumption indices (conditions: $[H_2O_2] = 10 \text{ }\text{mM}$, $[Fe(\text{III})] = 187.5 \text{ }\mu\text{M}$, $[Cys] = 500 \text{ }\mu\text{M}$, initial pH 3.0, $T = 20 \text{ }^\circ\text{C}$) for the Fenton and Fenton–Cys systems.

increased the utilization efficiency of H_2O_2 and enhanced the oxidation efficiency remarkably.

3.2. Effect of initial pH

The Fenton system is strongly pH dependent and the pH influences the Fenton oxidation reaction significantly.^{31,32} A series of experiments were carried out in which the MB solution pH was adjusted to 2.0, 3.0, 4.0, 5.0, 5.5, 6.0, 6.5 and 7.0 to investigate the effect of pH on MB removal in the Fenton and Fenton–Cys systems. As shown in Table 1, the Fenton–Cys system was superior to the traditional Fenton system in decolorizing MB at the same pH value. The removal of MB in the Fenton–Cys system at pH 6.5 was higher than that achieved in the Fenton–Cys system was consistently higher than that of the Fenton–Cys system at the optimal pH 3.0. Meanwhile, k_{obs} of the Fenton–Cys system at the same initial pH. Hence, the Fenton–Cys system showed a more satisfactory pH adaptability compared with the Fenton system.

MB removal in the Fenton system decreased sharply with increasing pH from 3.0 to 7.0, which occurs primarily because of Fe(m) precipitation as ferric oxyhydroxides,^{33,34} However, MB removal in the Fenton–Cys system was affected slightly by an increase in initial pH from 3.0 to 5.0, which could be interpreted by the complexation between Cys with Fe(m).²⁷ As shown in Fig. S2,† Cys could form colored complex with Fe(m) to maintain Fe(m) in solution, which alleviated Fe(m) precipitation and expended the effective pH range to a certain degree.

The experimental results presented above indicate that the introduction of Cys into a Fenton system broadened the effective pH range up to 6.5 but also enhanced the oxidation efficiency. It has been reported that the addition of other common and intensively investigated organic ligands, such as EDTA, citrate and oxalate to the Fenton system could also extend the pH range.³⁵⁻³⁷ Therefore, we compare Cys with other organic ligands in the performance of expanding pH. As shown in Fig. 3, the addition of these complexants into the Fenton system

Table 1 Effect of initial pH on MB removal rate and k_{obs} in Fenton and Fenton–Cys systems. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(III)] = 7.5 \mu$ M, $[Cys] = 20 \mu$ M, $[MB] = 10 \mu$ M, T = 20 °C, reaction time = 36 min

Initial pH	Fenton system			Fenton-Cys system			
	Removal rate (%)	$k_{ m obs}({ m min}^{-1})$	R^2	Removal rate (%)	$k_{ m obs} ({ m min}^{-1})$	R^2	
2.0	4.5	0.00119	0.993	31.6	0.01023	0.998	
3.0	24.9	0.00736	0.997	96.3	0.08838	0.990	
4.0	22.4	0.00663	0.994	96.6	0.10158	0.996	
5.0	7.4	0.00237	0.985	91.8	0.07681	0.993	
5.5	4.7	0.00084	0.982	76.5	0.04239	0.994	
6.0	2.8	0.00028	0.970	46.6	0.01999	0.978	
6.5	2.7	0.00051	0.970	31.6	0.00614	0.956	
7.0	2.0	0.00043	0.967	8.3	0.00072	0.959	

improves the removal of MB to some extent. However, MB removal in EDTA, citrate and oxalate-modified Fenton reactions was inferior to that achieved in the Cys-driven Fenton reaction, which indicates that the oxidation efficiency of the Cys-driven Fenton reaction was superior to the ligand-driven Fenton reactions.

Some researchers have reported that the introduction of reducing agents into the Fenton system could improve the organic contaminant removal. Among these reducing agents, hydroxylamine (HA) is commonly considered to be one of the most promising reductive chemicals because of its strong reducing property,38 and HA has been introduced into the Fenton process to enhance benzoic acid degradation.³⁹ We compared the removal of MB in the Fenton-HA and Fenton-Cys systems, as shown in Fig. S3,† the addition of HA to the Fenton system enhanced the oxidative removal of MB. However, the removal rate (83%) of MB and k_{obs} in the Fenton-HA system were lower than that in the Fenton-Cys system (96.3%). The experimental results indicated that the introduction of Cys into the Fenton system achieved a more superior oxidation efficiency compared with HA. Therefore, it is necessary to reveal the role of Cys in the Fenton-Cys system and investigate the mechanism of the Cys-driven Fenton reaction.

3.3. Analysis of catalytic oxidation mechanism

In the traditional Fenton reaction, the generation of 'OH is a predominant catalytic oxidation mechanism.⁴⁰⁻⁴² Based on the results presented above, we speculated that the introduction of Cys into the Fenton system promoted the generation of 'OH, and thus improved the oxidation efficiency. To verify our hypotheses, a series of radical scavenging experiments was carried out. TBA was used as a probe compound for the total flux of 'OH because of its high-rate constant reaction with 'OH $(k'_{\text{OH/TBA}} = (3.8-7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}).^{43,44}$ As shown in Fig. 4, the MB removal reaction slowed down and the k_{obs} decreased significantly with increasing concentration of TBA in the Fenton and Fenton-Cys systems, which indicated that 'OH plays an important role in MB removal in the Fenton-Cys system. When same concentration of TBA was added to the two systems, the inhibitory effect on MB removal in the Fenton system was much more obvious than that in the Fenton-Cys system, which could be ascribed to the more generation of 'OH in the Fenton-Cys system.

An EPR experiment was carried out to confirm the role of 'OH by measuring the intensity of the DMPO-'OH adduct signal (Fig. 5(A)).⁴⁵ A typical four-peak spectrum of DMPO-'OH



Fig. 3 Removal rate of MB in different systems at different pH. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(m)] = 7.5 \mu$ M, $[Cys] = [EDTA] = [citrate] = [oxalate] = 20 \mu$ M, $[MB] = 10 \mu$ M, $T = 20 ^{\circ}$ C.



Fig. 4 Effect of TBA on MB removal in the Fenton and Fenton–Cys system. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(m)] = 7.5 \mu M$, $[Cys] = 20 \mu M$, $[MB] = 10 \mu M$, initial pH 3.0, $T = 20 \degree$ C, reaction time = 36 min.

adducts with an intensity ratio of 1:2:2:1 was detected in the Fenton and Fenton-Cys system, which suggests that 'OH was also formed in the Cys-driven Fenton reaction. The intensity of the DMPO-'OH signal of the Fenton-Cys system was at least three times stronger than that in the Fenton system, which indicates that the Fenton-Cys system could generate a higher concentration of 'OH compared with the conventional Fenton system. Furthermore, coumarin was added as a probe molecule to quantify 'OH. The reaction between 'OH and coumarin could generate the 7-hydroxycoumarin with fluorescence, which could be monitored at 445 nm using a spectrofluorometer to achieve the quantification of 'OH. As shown in Fig. 5(B), a markedly enhanced production of 7-hydroxycoumarin was observed in the Fenton system with the addition of Cys whereas the Fenton system, Cys/H₂O₂ system and H₂O₂ alone did not generate a significant level of the hydroxylated product (spectral change shown in ESI Fig. S4[†]). These experimental results demonstrated that the introduction of Cys into the Fenton system promoted the generation of 'OH drastically throughout the reaction and thus showed a much higher oxidation activity.

Based on the aforementioned data and analysis, we assumed that the introduction of Cys into the Fenton system significantly



Fig. 5 (A) EPR spectra of DMPO-'OH adducts in aqueous solution in Fenton and Fenton-Cys system, (B) variations of fluorescence emission intensity of the solution with 0.05 mM coumarin during the reaction for different systems. Conditions: $[H_2O_2] = 0.4$ mM, $[Fe(m)] = 7.5 \mu$ M, $[Cys] = 20 \mu$ M, initial pH 3.0, T = 20 °C.

accelerated the transformation from Fe(III) to Fe(II) and thus generated more 'OH and improved the Fenton oxidation efficiency. To verify our hypothesis, the variation of $Fe(\pi)$ concentration with time in the $Fe(\pi)/H_2O_2$, $Fe(\pi)/H_2O_2$ and $Fe(\pi)/Cys/$ H_2O_2 systems was detected. As can be seen in Fig. 6, in Fe(II)/ H_2O_2 system, the concentration of Fe(II) sharply declined with reaction time, and the Fe(π) concentration was less than 0.1 μ M after 12 min. In $Fe(III)/H_2O_2$ system, the Fe(II) concentration was less than 0.1 µM throughout the reaction. This phenomenon could be interpreted by the rapid reaction between $Fe(\pi)$ and H_2O_2 and the slow recovery of Fe(II) from Fe(III). Conversely, in the Fenton-Cys system, the $Fe(\pi)$ concentration was more than four times higher than that in the Fenton system, and the Fe(II) concentration was relatively steady during the reaction process (the inset of Fig. 4). These results indicated that the introduction of Cys into the Fenton system accelerated the Fe(III)/Fe(II) cycle, lead to a relatively steady Fe(II) recovery and generated more 'OH.

As discussed above, Cys played a major role as complexing agent and reducing agent simultaneously during the reaction process. In addition, it has been demonstrated that 'OH was the primary reactive oxidant in the Cys-driven Fenton reaction. By combining the above experimental results with relevant literature, we propose a mechanism for the more efficient removal of MB in the Fenton–Cys system. First, Cys formed complex with Fe(m) to maintain iron in soluble form, which relieved the Fe(m) precipitation and expanded the effective pH range. Then, the presence of Cys in the Fenton system accelerated the Fe(m)/Fe(n) cycle through the redox reaction, and the redox process between Cys and Fe(m) resulted in the more rapid transformation from Fe(m) to Fe(n), accompanying with the oxidation of Cys to cysteine (eqn (5)).²⁶ This process promoted the generation of 'OH and improved the oxidation efficiency.

$$2Fe(III) + 2HS-CH_{2}-CH-NH_{3}^{+} \longrightarrow COO^{-}$$

$$NH_{3}^{+}-CH_{2}-CH-S-S-CH_{2}-CH-NH_{3}^{+}+ 2Fe(II) + 2H^{+}$$

$$COO^{-} COO^{-}$$
(5)



Fig. 6 Concentration changes of Fe(II) in different systems. And the inset shows more clearly the variation of Fe(II) concentration in the Fenton and Fenton–Cys systems. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(III)] = 7.5 \mu$ M, $[Fe(III)] = 7.5 \mu$ M, $[Cys] = 20 \mu$ M, initial pH 3.0, $T = 20 \degree$ C.



Fig. 7 (A) Effect of Cys concentration on MB removal in Fenton–Cys system, (B) effect of Cys concentration on k_{obs} of MB removal in Fenton–Cys system. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Fe(\text{III})] = 7.5 \mu\text{M}$, $[MB] = 10 \mu\text{M}$, initial pH 3.0, T = 20 °C.

3.4. Effect of other factors on MB removal

3.4.1. Effect of Cys concentration on MB removal. The experimental results and analysis reveal the role of Cys in the Fenton–Cys system for the oxidative removal of MB. The effect of Cys concentration on MB removal should be investigated in the Fenton–Cys system. As shown in Fig. 7(A), the MB removal increased with increase in Cys concentration from 0 to 50 μ M. However, when the Cys concentration exceeded 50 μ M, the MB removal decreased with further increase in Cys concentration, which may be ascribed to the consumption of 'OH by reaction with excess Cys. k_{obs} presented in Fig. 7(B) exhibited a similar variation trend with removal rate. The k_{obs} of MB removal increased from 0.00736 to 0.08863 min⁻¹ when the Cys

concentration increased from 0 to 50 μ M, and then the increase in Cys concentration resulted in a decrease in k_{obs} . A Cys concentration of 20 μ M was selected to obtain the highest decolorization efficiency and economic benefits.

3.4.2. Effect of oxidation and catalyst concentration on MB removal. The oxidative removal of dyes is regulated directly by oxidant and catalyst dosage, therefore, it is essential to investigate the effect of H_2O_2 and Fe(m) concentration on MB removal. As shown in Table 2, the removal rate of MB in the Fenton system improved with increase in H_2O_2 concentration from 0.1 to 2.0 mM. In contrast, in the Fenton–Cys system, the MB removal rate increased rapidly from 60.2% to 98.7% when the H_2O_2 concentration increased from 0.1 to 2.0 mM. Meanwhile, an obvious and continual increase in k_{obs} was observed with increase in H_2O_2 concentration in the Fenton–Cys system, and the k_{obs} of the Fenton–Cys system was consistently higher than that of the Fenton system. This indicated that the introduction of Cys promoted the oxidative removal of MB in the Fenton system significantly at different H_2O_2 concentrations.

The influence of Fe(m) concentration on MB removal in the Fenton and Fenton–Cys system was also investigated. As shown in Table 3, MB removal in the Fenton system increased slowly from 10.5% to 33.7% with increase in Fe(m) concentration from 2.5 to 15 μ M. However, in the Fenton–Cys system, MB removal increased from 69.0% to 97.8% with increasing Fe(m) concentration from 2.5 to 15 μ M. In particular, MB removal in the Fenton–Cys system was much higher than that achieved in the Fenton–Cys system at the same Fe(m) concentration. Furthermore, the variation trend of k_{obs} with Fe(m) concentration presented in Table 3 was similar to that for the MB removal rate with Fe(m) concentration. The experimental results above suggested that the introduction of Cys impelled the Fenton system to achieve a higher oxidation efficiency at the tested H₂O₂ and Fe(m) concentrations.

3.4.3. Effect of temperature on MB removal. Reaction temperature is a critical operating parameter for the Fenton reaction. Therefore, the influence of reaction temperature on MB removal was studied. As shown in Fig. 8(A) and (B), an increase in temperature favors MB removal in the Fenton and Fenton–Cys systems. To further investigate the relationship, kinetic rate constants are presented in Fig. 8(C). k_{obs} in the two systems obviously increased with increasing reaction temperature. Moreover, the k_{obs} for the Fenton–Cys system were much higher than those for the Fenton system at same temperature,

Table 2 Effect of H₂O₂ concentration on MB removal rate and k_{obs} in Fenton and Fenton–Cys systems. Conditions: [Fe(III)] = 7.5 μ M, [Cys] = 20 μ M, [MB] = 10 μ M, initial pH 3.0, T = 20 °C, reaction time = 36 min

H ₂ O ₂ concentration (mM)	Fenton system			Fenton–Cys system		
	Removal rate (%)	$k_{ m obs} \ ({ m min}^{-1})$	R^2	Removal rate (%)	$k_{ m obs} \ ({ m min}^{-1})$	R^2
0.1	17.5	0.00496	0.993	60.2	0.02213	0.965
0.2	19.2	0.00581	0.999	94.0	0.07449	0.986
0.4	24.9	0.00736	0.997	96.3	0.08838	0.990
0.8	20.1	0.00635	0.997	96.0	0.09296	0.998
2.0	25.0	0.00790	0.999	98.7	0.12584	0.999

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Table 3 Effect of Fe(III) concentration on MB removal rate and k_{obs} in Fenton and Fenton–Cys systems. Conditions: $[H_2O_2] = 0.4 \text{ mM}$, $[Cys] = 20 \mu M$, $[MB] = 10 \mu M$, initial pH 3.0, $T = 20 \circ C$, reaction time = 36 min

	Fenton system			Fenton–Cys system		
Fe(III) concentration (μM)	Removal rate (%)	$k_{ m obs} \ ({ m min}^{-1})$	R^2	Removal rate (%)	$k_{ m obs} \ ({ m min}^{-1})$	R^2
2.5	10.5	0.00314	0.999	69.0	0.02985	0.985
5.0	16.8	0.00529	0.997	87.2	0.05367	0.987
7.5	24.9	0.00736	0.997	96.3	0.08838	0.990
10	26.0	0.00802	0.998	97.8	0.09553	0.990
15	33.7	0.01037	0.991	97.8	0.13210	0.975



Fig. 8 (A) Effect of temperatures on MB removal in Fenton system, (B) effect of temperatures on MB removal in Fenton–Cys system, (C) effect of temperature on k_{obs} of MB removal in Fenton and Fenton–Cys systems, (D) Arrhenius plots for MB removal at different temperatures in Fenton and Fenton–Cys systems. Conditions: [H₂O₂] = 0.4 mM, [Fe(III)] = 7.5 μ M, [Cys] = 20 μ M, [MB] = 10 μ M, initial pH 3.0.

which indicated that the Fenton oxidation process for dye removal was more rapid with introduction of Cys at the tested temperature. It can be inferred that Cys play a beneficial role in enhancing Fenton oxidative activity. Further discuss described by an Arrhenius plot (ln *K vs.* 1/*T*), as shown in Fig. 8(D), from which the values of apparent activation energy (E_a) for MB removal were determined as 95.90 and 47.93 kJ mol⁻¹ for the Fenton and Fenton–Cys systems, respectively. This implies that the removal of MB in the Fenton–Cys system could proceed easily at a relatively low energy. Indeed, even under mild

conditions without special temperature and pressure requirements, MB can be removed to a significant extent by the Fenton-Cys system.

4. Conclusions

In this study, the highly efficient and pH-tolerant Cys-driven Fenton oxidation reaction was offered as a promising water remediation method. Compared with the traditional Fenton system, the Fenton–Cys system displayed a superior pH-tolerant

performance (2.0-6.5) and oxidative activity, representing about 12 times higher reaction rate for MB removal. Furthermore, the Cys-driven Fenton reaction presented an outstanding pH adaptability and oxidative activity compared with other common organic ligands or reducing agent-modified Fenton reactions. The introduction of Cys into the Fenton system accelerated the transformation from Fe(m) to Fe(m), and resulted in a more than four times concentration of Fe(II) than that of the Fenton system, which obviously improved the H2O2 utilization efficiency and drastically enhanced the generation of 'OH. In addition, the apparent activation energy of the Fenton system decreased from 95.90 to 47.93 kJ mol⁻¹ with Cys addition. This study provides a viable strategy for constructing a highly efficient and pHtolerant wastewater treatment process with environmentally benign characteristic, and opens up an inspiring research domain of amino acids in the environmental catalysis field.

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