Promoted discoloration of methyl orange in H₂O₂/Fe(III) Fenton system: Effects of gallic acid on iron cycling

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ABSTRACT

The promoting effect of gallic acid (GA) on the discoloration of methyl orange (MO) in H₂O₂/Fe(III) Fenton process was investigated in this study. The MO discoloration rate in H₂O₂/Fe(III) system with GA was significantly higher than that with sulfuric acid. Central composite design based on the response surface methodology (RSM) was adopted to evaluate the effects of initial Fe(III) concentration, initial pH and molar ratios of H₂O₂/Fe(III) and GA/Fe(III) on the discoloration rate constant k_{app} . The RSM model was derived and optimal molar ratios of H₂O₂/Fe(III) = 100:1 and GA/Fe(III) = 2:1 were obtained. The H₂O₂/Fe(III)/GA system also showed good adaptability with minor decreasing trend in alkaline circumstance. Reaction mechanisms for the promoted formation of hydroxyl radical (HO·) by GA were proposed. GA could not only form complexes with Fe(III) to Fe(II) and prevent the precipitation of Fe(III) subsequently, but also accelerate the reduction of Fe(III) to enhance the formation of HO·. Moreover, the readily oxidizable characteristic of GA makes it a good option with environmental benignity in Fenton system.

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1. Introduction

With global production amounts up to 8×10^5 ton per year, synthetic organic dyes are widely used in textile industry and food industry [1]. However, most of synthetic dyes and their derivatives are harmful to aquatic environment inducing changes in color, odor, eutrophication and bioaccumulation [2]. As conventional biological treatment processes are less effective in degrading most of the dye pollutants, continued efforts including adsorption [3], coagulation [4], membrane [5] and advanced oxidation processes (AOPs) [6] have been conducted in the last decades. Secondary contamination usually becomes another concern for some physico-chemical processes after the transferring of dye pollutants from the aqueous phase.

Fenton process is one of the most effective AOPs, which is based on the catalytic reaction of H₂O₂ with iron ions with following production of hydroxyl radical (HO·) ($E^0 = 1.9\text{--}2.7$ V) [6]. Homogeneous Fenton process has been studied for decades which can degrade various compounds and improve the biodegradability of aqueous effluents. However, the intrinsic drawbacks of homogeneous Fenton process have limited its application. First, Fe(II) is readily oxidized to Fe(III) while the slow reduction of Fe(III) to Fe

(II) after it is formed is always the rate-limiting step in Fenton reaction [7]. As shown in Eqs. (1)–(3), the reaction rate of Fe(III) and H₂O₂ ($k = 0.001\text{--}0.01$ M^{−1} s^{−1}) is much slower than that of Fe(II) and H₂O₂ ($k = 63\text{--}76$ M^{−1} s^{−1}). Second, the Fe(III) precipitates as an iron oxide and/or hydroxide at pH > 4 (Eqs. (4)–(6)) [8]. And the last, the recovering and treatment the large amounts of precipitated iron sludge after treatment increase the cost of Fenton process.

To overcome these limitations, modified Fenton processes with heterogeneous catalysts or complexing agents instead of soluble Fe(II) have received increasing attention recently [9]. Compared with the soluble Fe(II) species, the heterogeneous reaction rate was generally lower than that of homogeneous reaction because of

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either the gradual provision of limited surface reaction sites or slow release of aqueous Fe(II) [10]. Complexing agents are also being considered useful options to perform Fenton process at neutral pH in order to form soluble iron species in a wider range of pH. Many organic complexing agents (e.g. ethylenediaminetetraacetic acid (EDTA) [11], ethylenediamine disuccinate (EDDS) [12] and citric acid [13]) were employed in iron catalyzed of Fenton system. However, the addition of complexing agent may cause some adverse environmental consequences because of their poor degradability and strong heavy metal complexing ability. Based on these considerations, if a complexing agent with environmental benignity (i.e. readily degradable in Fenton system), could accelerate the rate-limiting reduction of Fe(III) in Fenton system simultaneously, it could promote the discoloration of dye pollutants in Fenton system.

Gallic acid (GA), known as 3, 4, 5-trihydroxybenzoic acid is an organic acid, which can be found in gallnuts, grapes, sumac, tea leaves, and oak bark (Fig. 1) [14]. GA has been widely applied in chemical and pharmaceutical industry, which exhibits cytotoxicity against cancer cells, without harming healthy cells and can be used to treat albuminuria and diabetes. Qin et al. observed the promotedalachlor degradation in $\text{H}_2\text{O}_2/\text{Fe(III)}$ system with the addition of protocatechuic acid (PA) [15]. Both PA and GA belong to phenolic acids. It should be noted that not all phenolic acids can form complex with iron, but only those containing the catechol or galloyl moiety can [16]. On the other hand, the binding constant of GA with iron is 4.78 M^{-1} , which is more than 3-fold of that of PA [16]. Moreover, GA is known to be readily oxidized, chemically or electrolytically, in acidic and alkaline solutions [17]. The rate con-

stant for the reaction of GA with $\text{HO}^\cdot$ was determined to be $11.0 \pm 0.1 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ via competition kinetics analysis [18]. Considering the stronger complexing ability of GA, it is necessary to clarify its role in the $\text{H}_2\text{O}_2/\text{Fe(III)}$ system.

This study investigated the effects of GA on the MO discoloration performance and iron cycling in $\text{H}_2\text{O}_2/\text{Fe(III)}$ system. The kinetics of MO discoloration in the $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{GA}$ system was evaluated with response surface approach and the optimal reaction conditions were obtained. The mechanisms for the promoted formation of $\text{HO}^\cdot$ by GA including both complexing and reduction abilities were also tentatively proposed. It is expected to develop a highly efficient Fenton system with environmental benignity for the treatment of recalcitrant dye wastewater.

2. Materials and methods

2.1. Materials

Chemicals used as catalysts (anhydrous iron(III) chloride (FeCl_3)), oxidant (hydrogen peroxide (H_2O_2), 30% w/v), sulfuric acid (H_2SO_4), auxiliary chemicals for initial pH value adjustment (sodium hydroxide (NaOH)), target pollutant (methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$)) and quenching agent (sodium sulfite (Na_2SO_3)) were purchased from Panreac Quimica (Spain). Complexing agent (gallic acid ($\text{C}_6\text{H}_2(\text{OH})_3\text{COOH}$)) was obtained from Sigma-Aldrich (Spain). Hydroxylamine hydrochloride and sodium acetate were purchased from Sinopharm Chemical Reagent (China). All solutions were prepared in deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) produced by a Milli-Q system.

2.2. Fenton reaction experiment and analysis

All experiments were conducted in a 250 mL conical flask in batch mode at ambient temperature. 50 mL of MO solution was first added into the reaction flask followed by the addition of accurately prepared iron complexing solution with FeCl_3 and GA at pre-determined dosage and mixed more than 30 min. The initial pH was adjusted with NaOH (0.1 M) and H_2SO_4 (0.1 M) solution. Thereafter, the reaction was initiated with the addition of H_2O_2 stock solution and run for 60 min. Before analysis was done, all samples were withdrawn from the reactor and immediately treated with excess Na_2SO_3 solution to prevent further oxidation.

Total organic carbon determination was carried out in a TOC-VCSN TOC analyzer. The absorbance of the samples was analyzed with a HACH visible spectrophotometer (DR 3900) at a wavelength of 466 nm, which is the maximum absorption wavelength of MO. The solution pH was measured by a Crison pH meter (GLP 22). Ferrous ions were analyzed based on 1,10-phenanthroline method and total iron ions were analyzed using hydroxylamine hydrochloride as the reducing agent [18]. Spectrum scanning was conducted with a HACH UV-vis spectrophotometer (DR 6000).

2.3. Kinetics and central composite design (CCD)

During the reaction, the discoloration of MO concentration vs. time was exponential in all cases indicating that MO discoloration follows a *pseudo*-first-order kinetics. Indeed, the discoloration of MO by $\text{HO}^\cdot$ can be described by second order kinetics:

$$-\frac{d[\text{MO}]}{dt} = k_{\text{abs}}[\text{MO}][\text{HO}^\cdot] \quad (7)$$

Assuming a quasi steady-state value for $\text{HO}^\cdot$ concentration during treatment (because of its very high reactivity and non accumulation in the medium), Eq. (7) becomes:

$$-\frac{d[\text{MO}]}{dt} = k_{\text{app}}[\text{MO}] \quad (8)$$

Fig. 1. (a) Comparison of MO discoloration rate in the presence and absence of GA at same initial pH; (b) time course of UV-vis spectra of MO in $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{GA}$ system. Conditions: $[\text{MO}]_0 = 50 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe(III)}]_0 = 0.5 \text{ mM}$, $[\text{GA}]_0 = 0.5 \text{ mM}$, $[\text{pH}]_0 = 4.0$.

where $k_{app} = k_{abs}[\text{HO}^\bullet]$, k_{app} (in unit of min^{-1}) and k_{abs} (in unit of $\text{M}^{-1} \text{min}^{-1}$) being the apparent and absolute rate constants respectively.

Central composite design (CCD) is an excellent tool to establish response surface methodology (RSM) models, especially in the case of five level factorial designs. A central composite design (CCD) based on the response surface methodology (RSM) [18], consisting of 30 runs, was composed to evaluate the relative impacts of four variables with five levels on the response k_{app} (Table 1). The independent input variables included the concentration of Fe(III) (X_1), the initial pH (X_2), and the molar ratios of $\text{H}_2\text{O}_2/\text{Fe(III)}$ (X_3) and GA/Fe(III) (X_4). The data were analyzed with the software Design Expert 8.0.

The values of the independent variables were coded as X_i according to Eq. (9):

$$X_i = \frac{x_i - x_0}{\Delta x_i} \quad (9)$$

where X_i is the dimensionless value of an independent variable; x_i represents the real value of the independent variable; x_0 is the real value of the independent variable at the center point and Δx_i is the step change.

The response variable was fitted by a quadratic polynomial Eq. (10):

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=0}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (10)$$

where Y is the predicted response; b_0 is the offset term (constant); b_i , b_{ii} and b_{ij} are the first-order linear, squared coefficient for the factor i and the linear model coefficient for the interaction between factors i and j , respectively; X_i and X_j are the coded values of the independent input variables.

3. Results and discussion

3.1. Promoted discoloration of MO with GA in $\text{H}_2\text{O}_2/\text{Fe(III)}$ system

The effect of GA on the discoloration rate of MO was firstly investigated. As shown in Fig. 1a, the discoloration of MO in the $\text{H}_2\text{O}_2/\text{Fe(III)}$ system in the presence and absence of GA were compared. The initial pH value of the $\text{H}_2\text{O}_2/\text{Fe(III)}$ system without the addition of GA was adjusted to 4.0 with H_2SO_4 . It was found that although under the same pH circumstance, the addition of GA improved the k_{app} of MO significantly compared with the addition of inorganic acid. More than 95% of MO was decomposed with the addition of GA after two minutes while only 25% discoloration efficiency was achieved with the addition of sulfuric acid. Apart from the acidic circumstance induced after the addition of GA, the acceleration of iron cycling may play a more important role for the promoted discoloration process in $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{GA}$ system.

The temporal evolution of UV-vis spectra taking place during the discoloration of MO by $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{GA}$ system is displayed in Fig. 1b. The MO spectrum is characterized by one peak in the ultra-violet region located at 270 nm and by one peak in the visible region located at 466 nm. The peak at 466 nm originates from a conjugated structure formed by the azo bond under the strong influence of the electron-donating dimethylamino group ($-\text{N}=\text{N}-$ chromophore), whereas the other peak at 270 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic rings in the MO molecule. While the absorption spectrum of GA exhibits the characteristic of aromatic ring, i.e. peak dominating around 270 nm. After the startup of the reaction, the peak located at 466 nm of MO disappears immediately. Generally, the azo bond will be firstly attacked by $\text{HO}^\bullet$ and the chromophoric characteristic of the MO will be lost by producing other intermediates which do not absorb in the visible region. $\text{HO}^\bullet$ attack to the azo double bond is reported to be the main process (60%) in AOPs, while the attack to aromatic

Table 1
Experimental design matrix and results of the degradation kinetics of MO in $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{GA}$ system.

Run	Initial actual values				Coded values				Y (min^{-1})	R^2
	X_1 Fe (mM)	X_2 pH	X_3 $\text{H}_2\text{O}_2/\text{Fe}$	X_4 GA/Fe	x_1	x_2	x_3	x_4		
1	0.05	6.0	50	1	−1	−1	−1	−1	0.049	0.997
2	0.05	8.0	50	3	−1	1	−1	1	0.027	0.992
3	0.05	8.0	150	1	−1	1	1	−1	0.023	0.994
4	0.1	7.0	100	2	0	0	0	0	0.14	0.999
5	0.1	7.0	100	0	0	0	0	−2	0.0014	0.988
6	0.15	6.0	150	1	1	−1	1	−1	0.13	0.993
7	0.15	8.0	50	3	1	1	−1	1	0.10	0.994
8	0.15	6.0	50	3	1	−1	−1	1	0.14	0.9904
9	0.05	8.0	50	1	−1	1	−1	−1	0.037	0.991
10	0.05	6.0	150	1	−1	−1	1	−1	0.043	0.997
11	0.1	7.0	200	2	0	0	2	0	0.065	0.991
12	0.1	7.0	100	2	0	0	0	0	0.13	0.992
13	0.1	9.0	100	2	0	2	0	0	0.11	0.977
14	0.1	7.0	100	4	0	0	0	2	0.083	0.992
15	0.15	7.0	10	2	0	0	−2	0	0.051	0.985
16	0.05	8.0	150	3	−1	1	1	1	0.027	0.9911
17	0.15	6.0	150	3	1	−1	1	1	0.13	0.99
18	0.15	8.0	50	1	1	1	−1	−1	0.16	0.99
19	0.1	7.0	100	2	0	0	0	0	0.14	0.99
20	0.1	7.0	100	2	0	0	0	0	0.14	0.991
21	0.01	7.0	100	2	−2	0	0	0	0.011	0.983
22	0.15	8.0	150	1	1	1	1	−1	0.11	0.992
23	0.1	7.0	100	2	0	0	0	0	0.14	0.991
24	0.2	7.0	100	2	2	0	0	0	0.15	0.992
25	0.15	8.0	150	3	1	1	1	1	0.087	0.974
26	0.15	6.0	50	1	1	−1	−1	−1	0.16	0.997
27	0.1	5.0	100	2	0	−2	0	0	0.11	0.976
28	0.05	6.0	150	3	−1	−1	1	1	0.031	0.992
29	0.05	6.0	50	3	−1	−1	−1	1	0.028	0.989
30	0.1	7.0	100	2	0	0	0	0	0.14	0.993

rings accounts for the rest of the observed products [19]. On the contrary to the rapid disappearance in visible region, the decays of the absorbance from 200 nm to 310 nm associated with naphthalene and benzene structures in the molecule were slowly, indicating the slow progresses of aromatic fragmentation and mineralization of their intermediates. 2-propanol, known as an effective scavenging agent for $\text{HO}\cdot$ ($k_{2\text{-propanol}, \text{HO}\cdot} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [20] was used as a scavenger of $\text{HO}\cdot$ and the effect on MO discoloration was evaluated. The addition of 2-propanol obviously inhibited the discoloration of MO (Fig. S1). At 2000 mM of 2-propanol, the degradation of MO was inhibited significantly, indicating that the degradation of MO was mainly due to the reactivity with $\text{HO}\cdot$.

3.2. Regression equation and analysis of variance (ANOVA)

Batch runs 30 (in total) were then conducted to analyze the combined effects of initial pH, initial Fe(III) concentration, and molar ratios of $\text{H}_2\text{O}_2/\text{Fe(III)}$ and $\text{GA}/\text{Fe(III)}$ on the k_{app} of MO, as presented in Table 1 [20,21].

A second-order polynomial regression equation for calculation of the k_{app} value could then be derived as follows:

$$Y(\text{min}^{-1}) = 0.139 + 0.0435X_1 - 0.00573X_2 - 0.00375X_3 + 0.000617X_4 - 0.00391X_1X_2 - 0.00549X_1X_3 - 0.00419X_1X_4 - 0.00238X_2X_3 - 0.0026X_2X_4 + 0.005X_3X_4 - 0.0129X_1^2 - 0.006X_2^2 - 0.0188X_3^2 - 0.0228X_4^2 \quad (11)$$

The predicted and measured k_{app} values are compared in Fig. S2. All the points are quite uniformly distributed on both sides of the regression line, which confirms that the predicted values agreed fairly well with the measured ones [22–25].

3.3. Response surface analysis and optimization conditions

The interactive effect of the initial Fe(III) concentration and pH on the degradation kinetics of MO was obtained after ANOVA

Fig. 2. Response surface plots showing k_{app} value as a function of two variables: (a) initial concentration of Fe(III) (X_1) and pH (X_2); (b) initial concentration of Fe(III) (X_1) and molar ratio of $\text{H}_2\text{O}_2/\text{Fe(III)}$ (X_3); (c) initial concentration of Fe(III) (X_1) and molar ratio of $\text{GA}/\text{Fe(III)}$ (X_4); (d) initial pH (X_2) and molar ratio of $\text{H}_2\text{O}_2/\text{Fe(III)}$ (X_3); (e) initial pH (X_2) and molar ratio of $\text{GA}/\text{Fe(III)}$ (X_4); (f) initial molar ratio of $\text{H}_2\text{O}_2/\text{Fe(III)}$ (X_3) and molar ratio of $\text{GA}/\text{Fe(III)}$ (X_4).

analysis ($F = 9.00$, $p < 0.05$). Fig. 2a showed the k_{app} as a function of the initial concentration of Fe(III) and pH at a fixed H_2O_2 /Fe(III) molar ratio of 100:1 and GA/Fe(III) molar ratio of 2:1. At a low level of Fe(III) (0.05–0.1 mM), there was no obvious change in the k_{app} value with the initial pH from 5.0 to 9.0, while the k_{app} increased gradually when the initial pH decreased from 9.0 to 5.0 at a high level of Fe(III) (>0.1 mM). In addition, elevating the Fe(III) concentration from 0.05 to 0.2 mM could significantly increase the k_{app} over the entire pH range investigated, especially at a lower pH.

Fig. 2b showed the interactive effect of initial concentration of Fe(III) the molar ratio of H_2O_2 /Fe(III) on k_{app} at a fixed GA/Fe(III) molar ratio of 2:1 and initial pH 7.0. ($F = 13.22$, $p < 0.01$). With the increase of molar ratio of H_2O_2 /Fe(III) from 10:1 to 100:1, improvement of the k_{app} was observed. While, the further increase in molar ratio of H_2O_2 /Fe(III) resulted in a decrease of k_{app} , probably due to the fact that the overdosed H_2O_2 would scavenge $HO^\bullet$ at molar ratio of H_2O_2 /Fe(III) higher than 100:1 (Eqs. (3) and (12)) [10,26].

The correlation between the initial concentration of Fe(III) and the molar ratio of GA/Fe(III) on k_{app} (Fig. 2c) exhibited similar trend with Fig. 2b. With the elevated molar ratio of GA/Fe(III) from 0 to 2:1, the k_{app} increased obviously. However, when the molar ratio of GA/Fe(III) exceeded 2:1, a decreasing trend was observed probably due to the competitive effect of GA for $HO^\bullet$, which will be further discussed in Section 3.5. There were no obvious interactive effects between pH and molar ratio of H_2O_2 /Fe(III) ($F = 2.13$, $p = 0.2796$), between pH and molar ratio of GA/Fe(III) ($F = 2.02$, $p = 0.2514$) and between the molar ratio of GA/Fe(III) and the molar ratio of H_2O_2 /Fe(III) ($F = 3.67$, $p = 0.1892$) after ANOVA analysis. As shown in Fig. 2d and e, at given Fe(III) concentration, GA/Fe(III) and H_2O_2 /Fe(III) molar ratios, slight increase of k_{app} value of MO discoloration could be observed with the decrease of pH, which is different from the previous complexing results using EDTA [27] and NTA [18], probably due to the higher stabilities of Fe-EDTA and Fe-NTA than Fe-GA complexes. However, with the increase of initial pH from 5.0 to 9.0, the decrease trend of k_{app} of MO discoloration was rather limited, indicating the less pH-dependent characteristic of H_2O_2 /Fe(III)/GA system. The k_{app} of MO discoloration as a function of the molar ratio of GA/Fe(III) and the molar ratio of H_2O_2 /Fe(III) at a fixed Fe(III) concentration of 0.1 mM and initial pH 7.0 was shown in Fig. 2f. Consistent with Fig. 2b and c, the impact of GA/Fe(III) and H_2O_2 /Fe(III) on the k_{app} of MO discoloration exhibited similar trends. The optimal molar ratios of

H_2O_2 /Fe(III) = 100:1 and GA/Fe(III) = 2:1 were obtained, respectively. It is well known that an iron complexing agent may either promote or inhibit the production of $HO^\bullet$, depending on its stability constants with Fe(III), and depending on the possibility of smaller ligands (e.g. H_2O_2), to approach iron and occupy a free orbital [28]. GA is also a potent scavenger for $HO^\bullet$, which would compete with target pollutant if the concentration of GA exceeds the maximum complexing ability of Fe(III).

3.4. Mineralization by H_2O_2 /Fe(III)/GA system

TOC evolution was monitored to evaluate the mineralization of MO and GA in the H_2O_2 /Fe(III)/GA system. As both MO and GA contributed to the TOC values of the H_2O_2 /Fe(III)/GA system, the TOC variations in the H_2O_2 /Fe(III)/GA system in the presence and absence of MO were compared (Fig. 3). The optimal initial molar ratio of GA/Fe(III) was adopted with 2:1 after CCD optimization. Thus, 0.25 mM of Fe(III) and 0.5 mM of GA were used in Figs. 3 and 5. The initial TOC value of MO in H_2O_2 /Fe(III)/GA system could be obtained via subtracting the TOC values of the system without MO from those with MO. As shown in Fig. 3, the mineralization rate of MO is much slower than its k_{app} . After 5 min the MO degradation reached 100%, while the TOC mineralization efficiencies of MO and GA only reached around 8.3% and 15.9%, respectively. 17.2% of MO and 27.5% of GA were mineralized in the first 60 min, and the TOC values continued to decline. However the decreasing trend is limited, with 27.3% of MO and 35.2% mineralized after 360 min.

As shown in Fig. 1b, the spectrum absorption intensity in the range of 200–300 nm increased after the start-up of the reaction, indicating the formation of intermediates. Even though the absorption intensity was then gradually reduced within the range, the intermediates were not completely mineralized. Oxidative cleavage of the $-N=N-$ group is likely to be the main reaction pathway, as confirmed by the detection of many compounds originating from such a cleavage. As the degradation pathway of MO in Fenton has been extensively investigated in previous studies, the degradation products were not qualitatively analyzed in this study. Amines, benzene sulfonic acid, aniline, benzene and phenol are the main degradation intermediates of MO in this system [29].

3.5. Proposed reaction mechanism

To probe the promoted mechanism of GA in the H_2O_2 /Fe(III)/GA system, the absorption spectra of solution with different GA/Fe(III) molar ratios were investigated (Fig. 4) and a stepwise reaction mechanism for Fe(III) and GA is proposed in Scheme 1. Without

Fig. 3. Evolutions of TOC in H_2O_2 /Fe(III)/GA system. Conditions: $[MO]_0 = 50 \text{ mg L}^{-1}$, $[H_2O_2]_0 = 25 \text{ mM}$, $[Fe(III)]_0 = 0.25 \text{ mM}$, $[GA]_0 = 0.5 \text{ mM}$.

Fig. 4. UV-vis spectra of Fe(III) with different initial molar ratios of GA/Fe(III). Conditions: $[Fe(III)]_0 = 5 \text{ mM}$.

Scheme 1. Possible stepwise reaction mechanism for Fe(III) and GA.

the addition of GA, the Fe(III) solution displayed an absorption in the range of 330–500 nm that can be attributed to the formation of Fe(III)–hydroxy complexes such as $\text{Fe}(\text{OH})^{2+}$ and mainly $\text{Fe}(\text{OH})_2^+$ [14]. Immediately after the mixing of acidic solutions of Fe(III) and GA, a dark blue color developed and the color faded within minutes to give a pale yellow-green solution. The appearance of the blue color can be ascribed to the formation of a 1:1 complex B (Eq. (13)) in which the metal ion is coordinated to two adjacent hydroxy groups of the GA (the third hydroxyl group remains protonated due to its high pK_a) [15].

The $\text{Fe}(\text{GA})^+$ complex B could subsequently decompose to form Fe(II) and the corresponding semiquinone intermediate C. Intermediate C then reacted rapidly with another Fe(III) species to form the quinone D, which was susceptible to secondary reactions (Eq. (15)). According to previous study, the quinone products adsorb at 380 nm with a shoulder at 445 nm ($\epsilon_{380} = 1675 \text{ M}^{-1} \text{ cm}^{-1}$) [14]. A broad peak and a shoulder developed at 380 nm and 445 nm in the visible spectrum respectively, indicating the formation of quinone. In this study, the maximum intensities of 380 and 445 nm were reached with the addition of 2 moles of Fe(III) per mole of GA (Fig. 4). With the increase of GA/Fe molar ratio from 0.5:1 to 4:1, the excess GA would compete with semiquinone for Fe(III) resulting in the decreasing formation of quinone, whereas promoted the formation of $\text{Fe}(\text{GA})_2^-$ complex (E). It is reported that the maximum spectra adsorption of Fe–GA complexes is at 690 nm ($\epsilon_{690} = 1425 \text{ M}^{-1} \text{ cm}^{-1}$) [15]. With the elevated molar ratio of GA/Fe(III) from 0.5:1 to 4:1, the increase of adsorption intensity at 690 nm in Fig. 4 confirmed the increasing formation of Fe–GA complexes. However, when the molar ratio of GA/Fe(III) exceeded 2:1, the

increase of adsorption value at 690 nm become smooth. This is reasonable as the maximum complexing capacity for one molar Fe(III) is two molar GA (Eq. (14)), which is consistent with the most optimum molar ratio result (i.e. 2:1) in response surface analysis (Fig. 2f).

The promoting effect of GA on the iron cycling was also verified by the evolution of ferrous and total iron ions during the reaction. As shown in Fig. 5, the concentration of total iron ions in Fe(III)/ H_2O_2 system decreased dramatically with the startup of the reaction. The ferrous ion in Fe(III)/ H_2O_2 system is also limited ($<0.012 \text{ mM}$), which is in consistent with the slow discoloration of MO in Fig. 1. After the addition of GA, the concentration of total iron ions kept steadily around 0.21 mM. Immediately after the addition of GA, 0.04 mM ferrous ion was formed and a constant concentration around 0.08 mM could be maintained during the reaction, which played an important role in the enhanced discoloration of MO. Qin et al. also found similar effects of protocatechuric acid to promote alachlor degradation in Fe(III)/ H_2O_2 system [18]. The evolution of ferrous and total iron ions during the reaction clearly confirmed the cheating and reducing abilities of GA in Fenton system, which are especially crucial for the maintenance of iron reactivity.

This study showed that the addition of GA to $\text{H}_2\text{O}_2/\text{Fe(III)}$ system not only prevented the Fe(III) from precipitation via complexing, but also enhanced the k_{app} of MO via promoting iron cycling, which offers new insight for the reuse of phenolic acid wastewater as effective complexing and reducing agents simultaneously in Fenton reaction. In addition, phenolic acid and natural organic matter containing phenolic functional group widely exist in soil, plant and water. The promoting effect of GA on iron cycling in this study may play similar role to promote the degradation of pollutants in natural aquatic environment subsequently, which needs further research.

4. Conclusions

This study investigated the promoting effect of GA on the discoloration of MO in $\text{H}_2\text{O}_2/\text{Fe(III)}$ system. Based on the experimental results, the following conclusions can be drawn:

- The k_{app} of MO in $\text{H}_2\text{O}_2/\text{Fe(III)}/\text{GA}$ system was increased significantly compared with those with inorganic acid.
- The RSM model was derived and optimal molar ratios of $\text{H}_2\text{O}_2/\text{Fe(III)} = 100:1$ and $\text{GA}/\text{Fe(III)} = 2:1$ were obtained.

Fig. 5. Evolutions of ferrous and total iron ions in Fe(III)/GA/ H_2O_2 and Fe(III)/ H_2O_2 systems. Conditions: $[\text{MO}]_0 = 50 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2]_0 = 25 \text{ mM}$, $[\text{Fe(III)}]_0 = 0.25 \text{ mM}$, $[\text{GA}]_0 = 0.5 \text{ mM}$.

- GA could not only form complexes with Fe(III) to prevent the precipitation of Fe(III), but also accelerate the reduction of Fe(III) to enhance the formation of HO[•].
- The promoting effect of GA on iron cycling indicates phenolic acid and natural organic matter containing phenolic functional group widely exist in soil, plant and water may play similar role to promote the degradation of pollutants in natural aquatic environment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2016.07.033>.

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