

Photo-Fenton degradation of a dye under visible light irradiation

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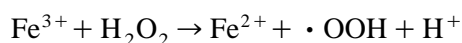
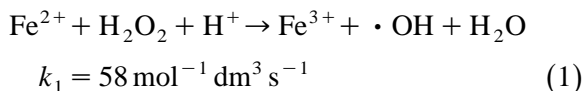
Abstract

The photodegradation of Malachite Green (MG) under visible light irradiation ($\lambda > 470$ nm) in the presence of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was studied in comparison with the dark reaction. It was found that visible light irradiation can accelerate significantly the rate of MG degradation, comparing to that in the dark. This provides possibly another approach to the treatment of dye-polluted waters using visible light or sunlight. Evidence for enhancement of $\cdot\text{OH}$ radical generation by visible light irradiation was obtained using DMPO spin-trapping EPR spectroscopy. A probable degradation mechanism of MG by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ under visible irradiation is discussed, which involves an electron transfer from the excited dye by visible light into Fe^{3+} in the initial photo-Fenton degradation. Conversion of Fe^{3+} to Fe^{2+} was detected in the degradation process of MG. The results of the total organic carbon (TOC) reduction in the photodegradation of MG under visible light irradiation supported the proposed mechanism by comparing to those in the degradation of sodium dodecylbenzenesulfonate (DBS). The photodegradation of MG in a $\text{Fe}^{3+}/\text{C}_2\text{O}_4^{2-}/\text{H}_2\text{O}_2$ system irradiated by UV or visible light and reacted in the dark provided another proof of the proposed mechanism. © 1999 Elsevier Science B.V. All rights reserved.

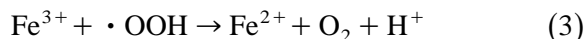
Keywords: Fenton reaction; Photodegradation; Dye

1. Introduction

It has been known that $\cdot\text{OH}$ can be generated by inter-reaction of hydrogen peroxide with Fe^{2+} and Fe^{3+} salts as shown in Eqs. (1)–(3) [1–3]:



$$k_2 = 0.02 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad (2)$$

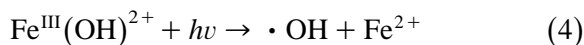


Hydroxyl radicals can oxidize almost all the organic substances and mineralize them to carbon dioxide and water owing to their high oxidation potential ($E^0 = +2.80$ V) [4]. Thus, Fenton treatment has attracted much interest for the destruction of toxic organic compounds in wastewater [5–7]. In recent years, many studies have shown that the oxidizing power of the

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Fenton-type systems can be enhanced greatly under UV light irradiation [3,8–15]. Herbicides 2, 4-dichlorophenoxyacetic acid (2,4-D) [9,10], 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) [9], nitrobenzene [14], anisole [14], phenols [15], substituted phenols [15] and many other aromatic compounds are degraded much more rapidly under the UV illumination of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems than in the dark reactions. Some of them are completely mineralized to CO_2 and HCl [9,10].

The photo-Fenton degradation mechanism under UV irradiation has been studied relatively clear by several researchers [3,9,10,12–14]. In these papers, the effect of UV light is attributed to the direct $\cdot\text{OH}$ radical formation and regeneration of Fe^{2+} from the photolysis of the complex $\text{Fe}(\text{OH})^{2+}$ in solution as follows [12,16]:



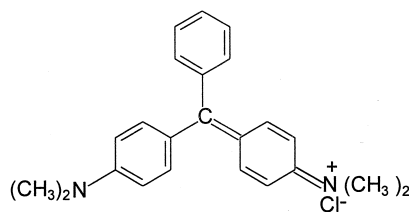
This reaction will occur when no complexing ligands are present and the pH is about 3. The $\cdot\text{OH}$ quantum yield is 0.14 at 313 nm and 0.017 at 360 nm [13]. Visible light irradiation cannot accelerate this reaction. But, to our knowledge, few studies have been reported on the photo-Fenton degradation of organic pollutants under visible light irradiation since most toxic organic pollutants examined cannot absorb visible light. Dye pollutants from the textile and photographic industries are a principal source of environmental contamination [17]. In China, above $1.6 \times 10^9 \text{ m}^3$ of dye-containing wastewater per year drains into environmental water system without treatment. We have reported the photocatalytic degradation of MG in the presence of TiO_2 semiconductor particles under visible light irradiation [18], in which the addition of Fe^{3+} and H_2O_2 increased greatly the photodegradation rate of MG. This work examined the photo-Fenton reactions of MG under irradiation by visible light. It was found that the Fenton degradation of dyes which can absorb strongly visible light could be accelerated greatly by visible irradiation. This provides possibly another good approach to the treatment of dye-

polluted waters using visible light or sunlight because the remaining iron ions can be eliminated easily from the degraded solution by a simple coagulation method. The photo-Fenton degradation mechanism of dyes under visible light irradiation is discussed in comparison with that in the dark. The degradation of MG in a $\text{Fe}^{3+}/\text{C}_2\text{O}_4^{2-}/\text{H}_2\text{O}_2$ system was also examined to reveal some details of interaction of MG with Fe^{3+} . DMPO spin-trapping EPR measurements evidenced an increase in the $\cdot\text{OH}$ radical generation upon visible light irradiation. TOC changes in the degradation process of MG under visible light irradiation and in the dark were also observed compared to those in the degradation of DBS which cannot absorb visible light under otherwise identical conditions.

2. Experimental

2.1. Materials

Malachite Green (MG), sodium dodecylbenzenesulfonate (DBS), hydrogen peroxide, sodium oxalate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$ were of laboratory reagent grade and used without further purification. Deionized and doubly distilled water was used throughout this study.



Malachite green (MG)

2.2. Photoreactor, light source and irradiation procedures

A 500-W halogen lamp (Institute of Electric Light Source of Beijing) as a visible light source

was positioned within a cylindrical Pyrex vessel. A Pyrex jacket with water circulation was used to cool the lamp. A light filter to cut completely light below 470 nm was placed outside the Pyrex jacket to guarantee irradiation with visible light. Solutions for irradiation were freshly prepared from air-saturated stock solutions of FeCl_3 (10 mmol dm^{-3}) at pH 1.9 and MG (1 mmol dm^{-3}) at pH 4.8 and adjusted to the desired pH with HCl and NaOH solutions. A 100-W Hg lamp (Toshiba Lighting and Technology of Japan) was used as an UV light source.

2.3. Analytical methods

At given irradiation time intervals, the samples (3 cm^{-3}) were taken out and then analyzed by observation of variations in UV–VIS spectra of MG at 617 nm where MG has a strong absorbency with Shimadzu-1600A spectrophotometer. The Bruker Model EPR 300E spectrometer equipped with an irradiation light source ($\lambda = 532 \text{ nm}$) of a Quanta-Ray Nd:YAG laser system was used for measurements of EPR signals, setting: center field = 3486.70 G; sweep width = 100.0 G; microwave frequency = 9.82 GHz, power = 5.05 mW. Total organic carbon (TOC) was analyzed in a TOC analyzer (Shimadzu 5000). The Fe^{2+} ions formed in the Fenton and photo-Fenton degradation of dye in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system was determined with 1,10-phenanthroline according to Ref. [19], the Fe(II) -phenanthroline complex was assessed spectrophotometrically at $\lambda_{\text{max}} = 510 \text{ nm}$ ($\epsilon = 1.2 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). The color interference of MG during this determination is negligible because the absorption of both MG and the degraded intermediate products is approximately zero at $\lambda = 510 \text{ nm}$. All samples were immediately analyzed to avoid further reactions.

3. Results and discussion

It was found that the optimal concentrations of ferric chloride and H_2O_2 for the MG degra-

ation were 0.4 mmol dm^{-3} of Fe^{3+} and 0.44 mol dm^{-3} of H_2O_2 when the MG concentration was 0.2 mmol dm^{-3} . These concentrations of Fe^{3+} and H_2O_2 were subsequently used in all the later degradation reactions except mentioned elsewhere.

Fig. 1 shows the degradation of MG in the presence of Fe^{3+} and/or H_2O_2 under visible light irradiation or in the dark detected by the changes in MG concentrations and TOC values. MG was scarcely decomposed over several hours of irradiation (curve a) in the H_2O_2 homogeneous solution and only to a small degree in Fe^{3+} homogeneous solution (curve b) after 180 min of photolysis. About 80% MG was disappeared when both Fe^{3+} and H_2O_2 were present after reaction for 140 min in the dark (curve c). However, MG was degraded completely under the otherwise identical conditions as c but illuminated by visible light for 60 min (curve d). In the dark, ca. 6% TOC removal was observed in the first 90 min and then there was a comparatively rapid decrease in TOC to ca. 50% TOC removal in the subsequent 40 min (curve e). While ca. 68% TOC removal occurred in the first 90 min and 100% TOC was

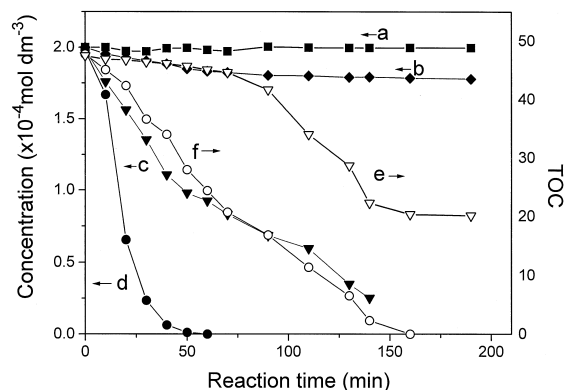
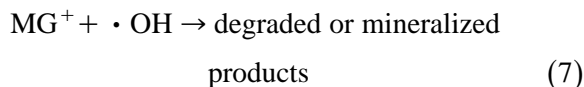
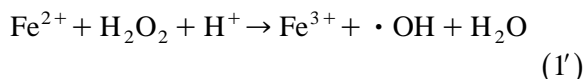
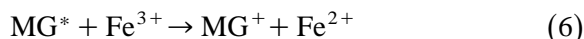


Fig. 1. Degradation of MG (0.2 mmol dm^{-3}) under different conditions and the changes of TOC during the degradation process. (a) in H_2O_2 (0.44 mol dm^{-3}) solution under visible light irradiation, (b) in Fe^{3+} (0.4 mmol dm^{-3}) solution under visible light irradiation, (c) in the presence of Fe^{3+} (0.4 mmol dm^{-3}) and H_2O_2 (0.44 mol dm^{-3}) in the dark, (d) in the presence of Fe^{3+} (0.4 mmol dm^{-3}) and H_2O_2 (0.44 mol dm^{-3}) under visible light irradiation, (e) the same as c and (f) the same as d.

removed after 160 min of visible light irradiation (curve f). We can see directly from these results that visible light irradiation accelerates greatly the degradation of MG. A probable photo-Fenton degradation mechanism under visible light irradiation is suggested as follows:



The degradation of dyes under visible light irradiation involves dye excitation (Eq. (5)) and electron transfer from excited dye molecules into Fe^{3+} ions which are reduced to Fe^{2+} ions (Eq. (6)). Then the generated Fe^{2+} ion reacts with H_2O_2 as Eq. (1) to form $\cdot\text{OH}$ radicals which can mineralize the organic compounds. Here, the first two steps (Eqs. (5) and (6)) are the initial process induced by visible light. There must be a substance that can absorb the visible light then the above overall process can proceed. Thus we selected DBS with little absorbency at wavelengths above 300 nm to carry out its degradation experiment in the presence of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the dark and under visible light irradiation. The degradation of DBS was detected by the changes in TOC and almost the same TOC reduction was observed both in the dark and under visible light irradiation during the same reaction times. This result indicates that visible light irradiation cannot accelerate the Fenton degradation of the substrates that do not absorb the visible light since reactions of Eqs. (5) and (6) cannot occur.

The spin-trapping EPR technique has proven to be useful in detecting radical species and hence to examine the photo-induced electron transfer [20,21] and the photocatalytic reaction pathways [22,23]. Fig. 2 describes the DMPO spin-trapping EPR spectra under various conditions. The four characteristic peaks of DMPO-

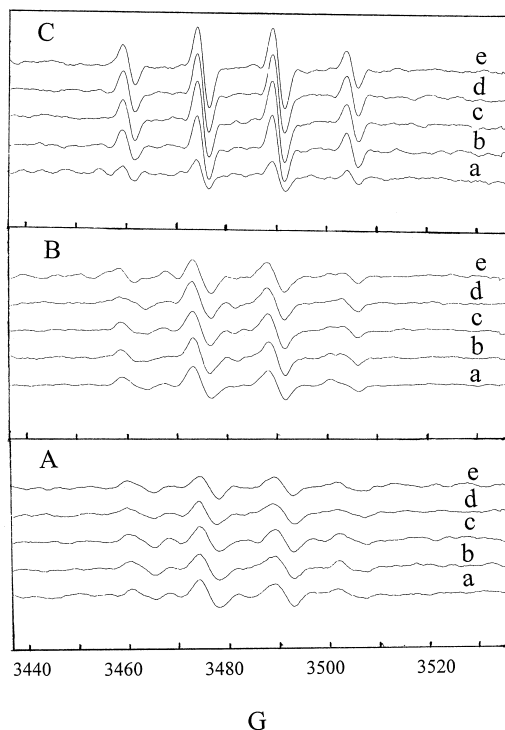


Fig. 2. DMPO spin-trapping EPR spectra under various conditions. (A) $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system under visible irradiation, (B) $\text{MG-Fe}^{3+}/\text{H}_2\text{O}_2$ in the dark, and (C) $\text{MG-Fe}^{3+}/\text{H}_2\text{O}_2$ under visible irradiation, reaction time (a) 0 min, (b) 2 min, (c) 4 min, (d) 6 min and (e) 8 min; the volume of dispersions: 0.3 cm^{-3} , 0.2 mmol dm^{-3} MG, 0.4 mmol dm^{-3} Fe^{3+} , 0.44 mol dm^{-3} H_2O_2 and 0.16 mol dm^{-3} DMPO; irradiation light source: laser $\lambda = 532 \text{ nm}$.

OH adducts with intensity ratio of 1:2:2:1 were observed in all the three cases. For the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system, the intensity of the four characteristic peaks did not change before and after visible irradiation (Fig. 2A), that is, the generation of $\cdot\text{OH}$ radicals in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system cannot be enhanced by visible light irradiation. Similarly, the intensity of the four characteristic peaks in the $\text{MG-Fe}^{3+}/\text{H}_2\text{O}_2$ system also did not change with increasing the reaction time in the dark reaction (Fig. 2B), while the signals of DMPO-OH adducts became stronger apparently upon irradiation by visible light and remained unchanged after visible irradiation for 4 min (Fig. 2C). These results supply a proof for the proposed mechanism that visible light irradiation can enhance the generation of $\cdot\text{OH}$

radicals and hence accelerate the Fenton degradation of MG.

Fig. 3 shows the pH effect on the MG degradation under visible irradiation in the $\text{FeCl}_3/\text{H}_2\text{O}_2$ system. The optimal pH was found to be 2.9 which is similar to that reported in the past papers [6–15]. For example, the most effective pH for the degradation of chlorophenoxy herbicides under UV irradiation was 2.7–2.8 [10] and the optimal value was pH 2.8 in the oxidation of 4-phenylazoaniline or Disperse Yellow 13 in the dark⁴ by Fenton's reagent. So, it seems that the optimal pH value is determined by the nature of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system itself, independent of organic compounds and the light sources used. Faust and Hoigne [12] have reported that the hydrolytic speciation of Fe^{3+} is dependent on the pH value and that $\text{Fe}(\text{OH})^{2+}$ is predominant at somewhat acidic pH values (pH = 2.5–5). Sylva [24] has reported that the precipitation of Fe^{3+} to $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ occurs at pH > 3. In our experimental conditions, the formation of precipitation in the solution was observed at pH > 3.5 which made the photodegradation of MG very slow.

At a constant total concentration of $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$, the initial rate of MG degradation within 20 min of visible irradiation was enhanced drastically with increasing the Fe^{2+} pro-

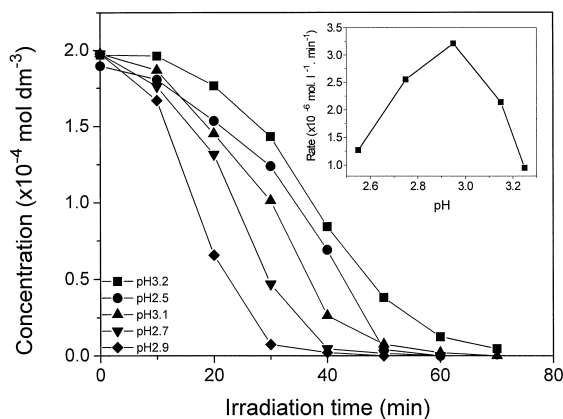


Fig. 3. Effect of pH on the photodegradation of MG (0.2 mmol dm^{-3}) under visible light irradiation by Fe^{3+} (0.4 mmol dm^{-3})/ H_2O_2 (0.44 mol dm^{-3}), inset shows the relationship between the initial rate (20 min) and the pH value.

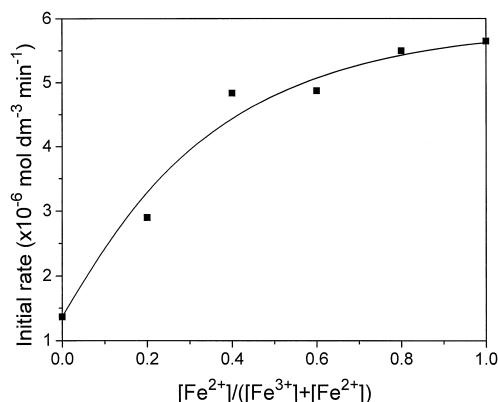


Fig. 4. Degradation rate of MG at various ratios of $[\text{Fe}^{2+}]/([\text{Fe}^{3+}] + [\text{Fe}^{2+}])$ (total concentration: 0.4 mmol dm^{-3}) in addition of H_2O_2 (0.44 mol dm^{-3}) under visible light irradiation.

portion as shown in Fig. 4. That is, substitution of Fe^{3+} with Fe^{2+} promotes the photodegradation of MG. Because there seems to be an induction period in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system as shown in Eqs. (2) and (3), where k_2 is much slower than k_1 [2]. In other words, Fe^{3+} ions must react with H_2O_2 to yield Fe^{2+} first, then the produced Fe^{2+} ions react with H_2O_2 to form $\cdot\text{OH}$ radicals which are the useful oxidant to decompose the organic compounds. The photodegradation of MG in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system was about 4 times faster than that in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system from the results of Fig. 4.

The conversion rate and the amounts of Fe^{2+} ions formed determine the degradation rate of MG. Visible light irradiation enhances greatly the oxidizing power of the Fenton-type systems since light irradiation accelerates the conversion of Fe^{3+} ions to Fe^{2+} ions. In order to elucidate the generation of Fe^{2+} in the degradation process of dye in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system under visible light irradiation and to see whether there is difference in the formation of Fe^{2+} among the dark reaction, UV light irradiation and visible light irradiation, the reaction process of a solutions containing 0.2 mmol dm^{-3} MG, 0.4 mmol dm^{-3} FeCl_3 , 1.2 mmol dm^{-3} 1,10-phenanthroline and 0.44 mol dm^{-3} H_2O_2 at pH 2.9 was detected under the above three conditions. The results are presented in Fig. 5. It do

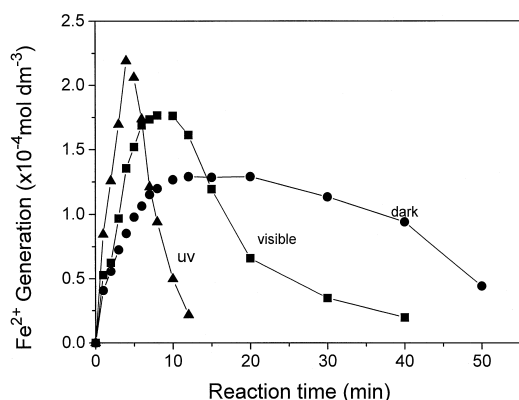


Fig. 5. Conversion of Fe^{3+} to Fe^{2+} during the degradation process of MG (0.2 mmol dm^{-3}) in Fe^{3+} (0.4 mmol dm^{-3})/ H_2O_2 (0.44 mol dm^{-3}) system under different conditions.

prove that the conversion of Fe^{3+} to Fe^{2+} occurs in these process. The maximum concentration of Fe^{2+} formed was 0.22, 0.17 and 0.12 mmol dm^{-3} under UV irradiation, visible light irradiation and in dark reaction, respectively. The time to reach the maximal concentration was 4 min, 8 min and 12 min, respectively. The conversion rate of Fe^{3+} to Fe^{2+} and the maximum concentration of Fe^{2+} formed under UV light irradiation was higher than those in the dark reaction through Eq. (4). Although the reaction of Eq. (4) cannot occur under visible light irradiation, it should be noted that the maximum amount of Fe^{2+} formed and the rate of Fe^{3+} conversion to Fe^{2+} under visible light irradiation were still higher than those in the dark reaction. It must have another path to accelerate the conversion of Fe^{3+} to Fe^{2+} . According to our proposed mechanism, MG has a high absorbency at visible light ranges, so MG can absorb visible light and can be excited to singlet or triplet state. The excited dye injects an electron into Fe^{3+} to yield Fe^{2+} and therefore both the maximum Fe^{2+} concentration and the rate of Fe^{3+} conversion to Fe^{2+} were greater than those in the dark reaction. The electron injection from excited dye into Fe^{3+} is possible from the viewpoint of their oxidation potentials ($\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77 \text{ V}$, $\text{MG}^*/\text{MG}^+ = -1.08 \text{ V}$ [25]). The conversion of Fe^{3+} to Fe^{2+} also

occurred at a relatively slow rate in the dark owing to the slow reactions of Eqs. (2) and (3).

Fig. 6 presents the changes in fluorescence emission spectra of a solution containing 0.5 mmol dm^{-3} MG, 1 mmol dm^{-3} FeCl_3 and 0.44 mol dm^{-3} H_2O_2 at pH 2.9 irradiated by visible light at different times. No fluorescence was observed before irradiation (curve a) since MG is not a fluorescent reagent. A weak fluorescence signal with two peaks at 475 and 520 nm was detected after irradiation for 10 min (curve b) and became stronger with the irradiation time until 30 min (curves c and d). After 30 min, the fluorescence intensity of these two peaks decreased with further irradiation (curve e). While another fluorescence signal with two peaks at 450 and 500 nm was observed after 50 min of photolysis (curve f) and decreased slowly with further irradiation (curves g and h). Finally, it disappeared almost after 200 min of photolysis (curve i). These results indicate that there were at least two intermediates with fluorescence generated during the photodegradation of MG under visible light irradiation although we cannot give their exact molecular structures. Further experiments are needed to supply more detailed information about the intermediates.

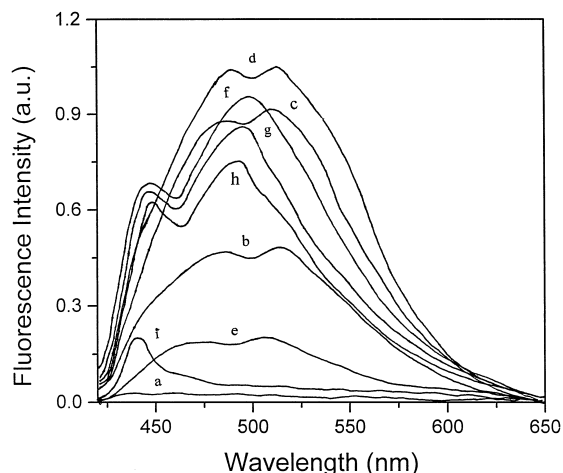
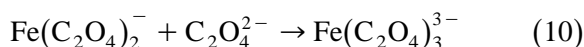
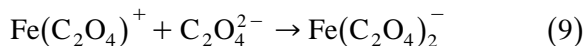
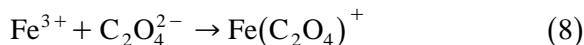
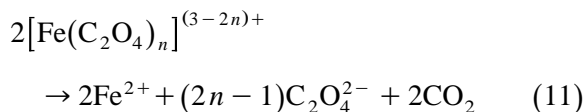


Fig. 6. Changes in fluorescence emission spectra of a solution containing 0.5 mmol dm^{-3} MG, 1 mmol dm^{-3} Fe^{3+} and 0.44 mol dm^{-3} H_2O_2 at pH 2.9 under visible light irradiation and irradiated for (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 60 min, (g) 80 min and (i) 200 min.

In order to testify further the proposed mechanism, we added $C_2O_4^{2-}$ at different concentrations to the reaction system to make the ratio of $C_2O_4^{2-}/Fe^{3+}$ be 1, 2, 3, 5 and 100 and let it react in the dark, under UV irradiation and visible irradiation, respectively. For all the cases, the addition of sodium oxalate inhibited the degradation of MG to some extent in comparison with that in the $C_2O_4^{2-}$ -free system. The degradation rate of MG decreased with an increase in the oxalic ion concentration under visible light irradiation (Fig. 7A), while the degradation of MG was inhibited almost in the dark when the concentration of oxalic ion increased to a certain value (5 $mmol\ dm^{-3}$) (Fig. 7B). Otherwise, the degradation rate of MG was very fast and almost the same even in the presence of $C_2O_4^{2-}$ at higher $C_2O_4^{2-}/Fe^{3+}$ ratios (i.e., 3, 5 and 100) under UV light irradiation (Fig. 7C). As Zuo and Hoigne reported [13], in the presence of oxalate, and pH ranges from 3 to 5, Fe(III)-oxalate complexes are the predominant dissolved species as follows:



and slight Fe^{3+} will exist with increasing the $C_2O_4^{2-}$ concentration. The complexation by oxalate not only increases the quantum yield for the photoreduction of Fe(III) from 0.14 to 1.2 at 313 nm but also extends the absorption band into the visible region to some extent and increases the absorption coefficient. Under UV light irradiation, Fe(III) would be reduced according to the following overall reaction (Eq. (11)) instead of Eq. (4).



the resulting Fe^{2+} would react with H_2O_2 to form $\cdot OH$ radicals. Thus, the degradation of

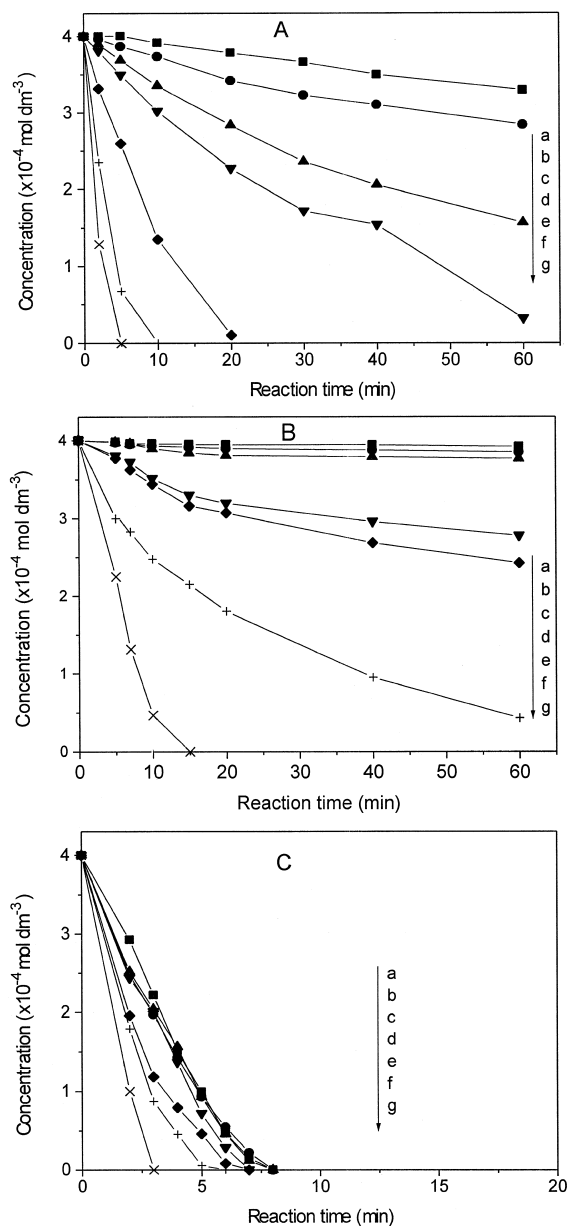


Fig. 7. Degradation of MG ($0.4\ mmol\ dm^{-3}$) at pH 2.9 in (A) Fe^{3+} ($1\ mmol\ dm^{-3}$)/ $C_2O_4^{2-}$ (0–100 $mmol\ dm^{-3}$)/ H_2O_2 ($0.44\ mol\ dm^{-3}$) under visible light irradiation, the $C_2O_4^{2-}$ concentration: (a) 100 $mmol\ dm^{-3}$, (b) 5 $mmol\ dm^{-3}$, (c) 3 $mmol\ dm^{-3}$, (d) 2 $mmol\ dm^{-3}$, (e) 1 $mmol\ dm^{-3}$, (f) 0.5 $mmol\ dm^{-3}$ and (g) 0. (B) Fe^{3+} ($1\ mmol\ dm^{-3}$)/ $C_2O_4^{2-}$ (0–15 $mol\ dm^{-3}$)/ H_2O_2 ($0.44\ mol\ dm^{-3}$) in the dark, $C_2O_4^{2-}$ concentration: (a) 15 $mmol\ dm^{-3}$, (b) 10 $mmol\ dm^{-3}$, (c) 5 $mmol\ dm^{-3}$, (d) 3 $mmol\ dm^{-3}$, (e) 2 $mmol\ dm^{-3}$, (f) 1 $mmol\ dm^{-3}$ and (g) 0. (C) Fe^{3+} ($1\ mmol\ dm^{-3}$)/ $C_2O_4^{2-}$ (0–100 $mmol\ dm^{-3}$)/ H_2O_2 ($0.44\ mol\ dm^{-3}$) under UV light irradiation, the $C_2O_4^{2-}$ concentration: (a) 100 $mmol\ dm^{-3}$, (b) 5 $mmol\ dm^{-3}$, (c) 3 $mmol\ dm^{-3}$, (d) 2 $mmol\ dm^{-3}$, (e) 1 $mmol\ dm^{-3}$, (f) 0.5 $mmol\ dm^{-3}$ and (g) 0.

MG was almost at the same rate when the concentration of $C_2O_4^{2-}$ reached at a certain value, 3 mmol dm^{-3} in our case (Fig. 7C). In the dark, MG cannot absorb light to excited state and free Fe^{3+} ions are also too few to proceed the reactions 2 and 3, therefore, the degradation of MG is retarded with increasing the concentration of oxalic ions (Fig. 7B). According to the proposed degradation mechanism, MG absorbs visible light to the excited state and then injects an electron to Fe^{3+} yielding Fe^{2+} . Since the free Fe^{3+} ions become fewer with an increase in the concentration of $C_2O_4^{2-}$, reaction 6 is inhibited. The total rate of MG degradation is the rate in the dark plus the photo-promoted rate. The dark reaction rate decreases greatly by addition of oxalic ions and only a very small photoreaction of $Fe^{III}(C_2O_4)_n^{3-2n}$ is possible under visible light irradiation ($\lambda > 470 \text{ nm}$) owing to the weak absorption in this region as shown by a absorption threshold of 450 nm in the absorption spectra of the $Fe^{3+}/C_2O_4^{2-}$ solution, therefore, the observed MG degradation rate under visible irradiation decreased obviously with increasing the concentration of $C_2O_4^{2-}$ (Fig. 7A).

4. Conclusion

The degradation of MG in Fe^{3+}/H_2O_2 or Fe^{2+}/H_2O_2 system can be accelerated significantly under visible light irradiation. Dye is excited by visible light, then injects electron to the empty orbit of Fe^{3+} yielding Fe^{2+} which enhances the generation of $\cdot OH$ radicals as demonstrated by DMPO spin-trapping EPR spectra. The degradation behaviors of MG in the dark, under UV irradiation and under visible irradiation in addition of $C_2O_4^{2-}$ at various concentrations to the Fe^{3+}/H_2O_2 system support the proposed mechanism. This provides possibly another approach to the treatment of waste water containing dyes using visible light or sunlight.

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