

# Photo-Fenton degradation of dye in methanolic solution under both UV and visible irradiation

Feng Chen, Yinde Xie, Jianjun He<sup>1</sup>, Jincai Zhao\*

*The Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*

Received 12 June 2000; received in revised form 21 August 2000; accepted 31 October 2000

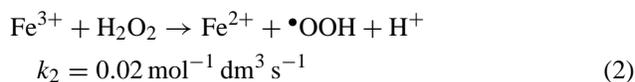
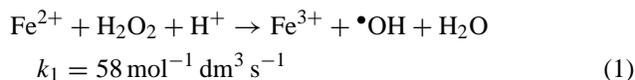
## Abstract

The photodegradation of methyl orange was examined in methanolic solution under both UV and visible irradiations in the presence of ferric ions and H<sub>2</sub>O<sub>2</sub>. The spin-trapping EPR technique was utilized to reveal the photo-Fenton reaction mechanism in the methanolic solution. It was found that different radicals were generated under UV and visible light irradiations. Possible mechanism of the photo-Fenton reaction in methanolic solution under both UV and visible light irradiations was proposed on the basis of experimental results. The intermediates produced during the photo-Fenton reaction were detected by IR and GC–MS spectra. © 2001 Published by Elsevier Science B.V.

*Keywords:* Photo-Fenton reaction; UV–VIS spectra; Spin-trapping EPR technique

## 1. Introduction

Early studies have shown that the Fenton reaction is efficient in the degradation of organic compounds [1–4]. The active species can be generated by the inter-reaction of hydrogen peroxide with ferrous and ferric ions as shown below in [5,6]:

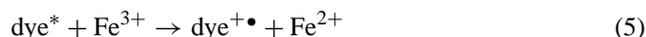


Since the reaction rate constant of reaction (2) is much lower than that of reaction (1), the transformation between the ferric ions and the ferrous ions, and the production of active species (hydroxyl radicals and superoxide radicals) are clogged greatly by the reaction (2). It was found that UV illumination of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> or Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> system increased significantly the Fenton degradation rate of many organic substances such as chlorophenoxy herbicides [7], quinine [8], xylydine [9], phenols [10], and anisole [11]. The effect

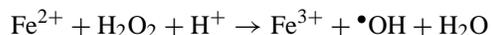
of UV light is attributed to the direct •OH radical formation and regeneration of Fe<sup>2+</sup> from photolysis of the complex [Fe(OH)]<sup>2+</sup> in solution as following mechanism [12–14]:



It is known that only about 3–5% of solar irradiance reaching the surface of the earth is UV light, while artificial UV light sources typically consume large quantities of electrical power, and what is more, they are expensive and often unstable. In the recent years, studies [13,15,16] have been reported on the photo-Fenton degradation of dyes pollutants under visible light irradiation in which visible light was also found accelerate apparently the reaction since it could be absorbed by the dye in solution. The brief mechanism of the photo-Fenton reaction under visible irradiation is shown below:



and reaction (1)

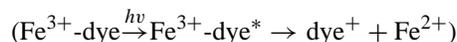


Different from the effect of UV light, that of visible light is attributed to the regenerated of Fe<sup>2+</sup> and the generation of dye<sup>+</sup>•, as it has been found that dye<sup>+</sup>• could hydrolyze or react with some oxidizer such as the dissolved

\* Corresponding author. Fax: +86-10-6487-9375.  
E-mail address: jczhao@ipc.ac.cn (J. Zhao).

<sup>1</sup> Present address: Department of Physical Chemistry, University of Uppsala, Box 532, 5-751 21 Uppsala, Sweden.

oxygen molecules in solution [18,24,25]. In order to explain the interaction among three components of the visible light-assisted photo-Fenton reaction, several models [13,15,16] have been established. Some researchers explained that the intermolecular electron transfer between the excited dye and the ferric ions regenerates the ferrous ions which accelerates the reaction [13,15] as shown in Eq. (5); some researchers explained that the intramolecular electron transfer of the dye complex with the ferric ions contributes a main effect [16], since the electron transfer takes place more efficiently in the inner of the complex



Dye pollutants from the textile and photographic industry are a principal source of environmental contamination. There is above  $16 \times 10^9 \text{ m}^3$  of dye-containing wastewater per year drains into environment water in China, the studies on the visible light-assisted photo-Fenton degradation of dyes are much more significant to us.

Although the Fenton reaction has been known for more than a century, the detailed reaction mechanisms are still intense and controversial discussion. Researchers [5–8,27] had thought that the reaction of  $\text{Fe}^{2+}$  with  $\text{H}_2\text{O}_2$  lead to direct formation of a  $\bullet\text{OH}$  radical. However, this mechanism was questioned from the thermodynamic calculations and it was also found that the intermediates generated during the Fenton reaction were different from those generated during the  $\text{H}_2\text{O}_2$  photolysis reaction with some special organic compounds [19]. An intra-complex two electron-transfer reaction was suggested and a  $\text{Fe}^{(\text{IV})}$  intermediate complex was confirmed during the Fenton reaction in aqueous system.

In this work, methanol was selected as solvent, which is different from water and is proved to be an effective

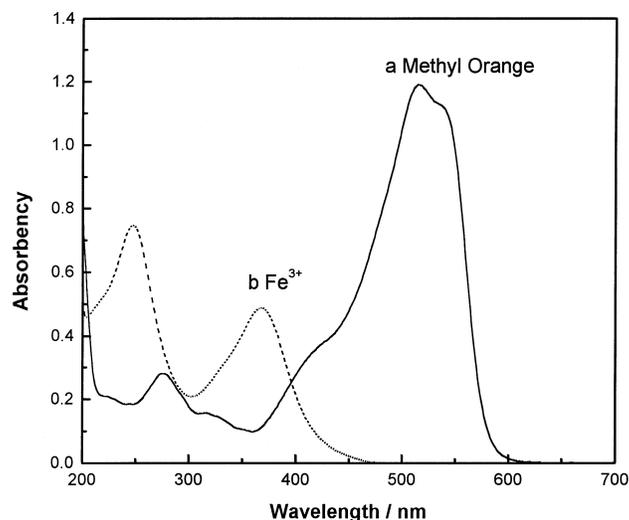


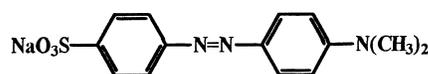
Fig. 1. UV–VIS absorption spectra of (a) methyl orange (—) and (b)  $\text{Fe}^{3+}$  (---) in methanolic solution.

intermediates produced during the photo-Fenton reaction were also detected by IR and GC–MS spectra.

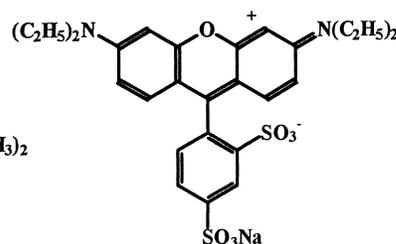
## 2. Experimental section

### 2.1. Materials

Methyl orange, sulforhodamine B (SRB),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , methanol were of laboratory reagent grade and used without further purification. The UV–VIS spectra of methyl orange,  $\text{FeCl}_3$ , in methanolic solution are displayed in Fig. 1. UV–VIS spectra detection showed that  $\text{Fe}^{2+}$  in methanolic solution had no notable absorbency from 200 to 700 nm.



Methyl Orange



Sulforhodamine B

scavenger of the hydroxyl radical [7,17,20,21], to study the reaction process of the photo-Fenton degradation of methyl orange under both UV and visible light. The spin-trapping EPR technique was used to obtain some important information of the interaction among the ferrous (ferric) ions,  $\text{H}_2\text{O}_2$ , and dye in methanolic solution for a better understanding of the mechanism of photo-Fenton reaction. It is also expected to provide an alternative method to remove directly colored organic compounds from organic solvents. Some of the in-

### 2.2. Photoreactor and irradiation devices

A 500 W halogen lamp (Institute of Electric Light Source of Beijing) as a visible light source was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket (Pyrex) to cool the lamp. A round light filter ( $d = 4.5 \text{ cm}$ ) was placed outside the Pyrex jacket to cut off completely light below 450 nm to guarantee irradiation with

visible light. A 100 W Hg lamp (TOSHIBA Lighting and Technology Corporation of Japan) was used as a UV light source. The irradiation of the solutions was carried out in cylindrical Pyrex flasks (volume 60 ml) using 50 ml of solution which was freshly prepared and air-saturated in each case.

### 2.3. Analyses

At given irradiation time intervals, the samples ( $3.5 \text{ cm}^3$ ) were taken out, and immediately analyzed to avoid further reactions by recording variations at the maximum absorption band in UV–VIS spectra of methyl orange using a Lambda Bio 20 spectrophotometer (Perkin-Elmer Co.). Fluorescence spectra were run on a F-4500 fluorescence spectrometer equipped with a computer for data treatment. The Bruker Model EPR 300E spectrometer equipped with an irradiation light source of Quanta-Ray Nd:YAG laser system ( $\lambda = 532$  or  $355 \text{ nm}$ ) was used for measurements of EPR signals. Setting: center field =  $3486.70 \text{ G}$ ; sweep width =  $100.0 \text{ G}$ ; microwave frequency =  $9.82 \text{ GHz}$ ; power =  $5.05 \text{ mW}$ . To minimize measurement errors, the same quartz capillary tube was used throughout the EPR measurements. Samples for infrared spectra (FTS 165) were prepared by removing the solvent from the degraded solution under the reduced pressures and mixing the residue directly with the dried KBr. Samples for gas chromatography–mass spectroscopy (GC–MS; Trio-2000, column BPX70, size  $30 \text{ m} \times 0.25 \text{ mm}$ ) experiments were prepared in a manner except that the residue was dissolved in methanol or ethanol.

## 3. Results and discussion

### 3.1. Photodegradation results

All reactions were carried out in  $1 \times 10^{-3} \text{ mol l}^{-1}$  HCl methanolic solution as we found that the concentration of  $\text{H}^+$  deeply affected the Fenton or photo-Fenton reaction in methanolic solution. The temporal concentration changes taking place during the photo-Fenton degradation of methyl orange under the visible light irradiation in the methanolic solution together with those in the control reactions are displayed in Fig. 2. Methyl orange was scarcely decomposed in a  $\text{H}_2\text{O}_2$  homogeneous solution (curve a) or a  $\text{Fe}^{3+}$  homogeneous solution (curve b) under visible light irradiation within 40 min. Here, 60% methyl orange was disappeared when both  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  were present after 40 min reaction in the dark (curve c), while almost all of the methyl orange was decomposed under the otherwise identical conditions as those of curve c but illuminated by visible light for about 20 min (curve d). An obvious and interesting phenomenon was found here that Fenton reaction could decompose effectively dyes in methanolic solution and visible light accelerated greatly the Fenton degradation of methyl

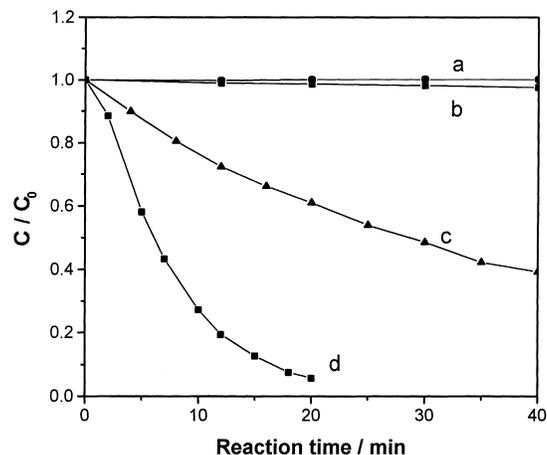


Fig. 2. Degradation of methyl orange ( $2 \times 10^{-5} \text{ mol l}^{-1}$ ) under various conditions; (a) in  $\text{Fe}^{3+}$  ( $2 \times 10^{-5} \text{ mol l}^{-1}$ ) solution under visible light irradiation; (b) in  $\text{H}_2\text{O}_2$  ( $1 \times 10^{-4} \text{ mol l}^{-1}$ ) solution under visible light irradiation; (c) in the presence of  $\text{Fe}^{3+}$  ( $2 \times 10^{-5} \text{ mol l}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $1 \times 10^{-4} \text{ mol l}^{-1}$ ) in the dark; (d) in the presence of  $\text{Fe}^{3+}$  ( $2 \times 10^{-5} \text{ mol l}^{-1}$ ) and  $\text{H}_2\text{O}_2$  ( $1 \times 10^{-4} \text{ mol l}^{-1}$ ) under visible light irradiation.

orange; furthermore, the visible light-assisted photo-Fenton reaction in the methanolic solution fits well with a first-order kinetic reaction after a short induction period at the beginning. Similar experiments were also carried out under UV irradiation, it was found that illumination by UV light could also accelerate greatly the Fenton reaction of methyl orange in methanolic solution. In previous studies [17,20,21], methanol was proved to be an effective scavenger of the hydroxyl radical which mainly causes the decomposition of organic compounds in aqueous solution and hence methanol was often utilized to stop the some reaction by competing with organic compounds for the oxidizer such as  $\bullet\text{OH}$ . It is interesting that the Fenton (photo-Fenton) reaction was not stopped in methanolic solution. The solvent, methanol, seemed to be a transmitter of  $\bullet\text{OH}$  radicals which kept on the Fenton reaction. The active species based on methanol replace the  $\bullet\text{OH}$  radical to work as oxidizer to attack the methyl orange (see EPR results below).

### 3.2. EPR results and photo-Fenton mechanism in methanolic solution

The spin-trapping EPR technique was used to study the reaction mechanism in the methanolic solution. The spin-trapping EPR spectra of UY assisted photo-Fenton reaction in methanolic solution under the various conditions are displayed in Fig. 3. Three groups of characteristic peaks were observed during the reaction process: two groups of sextet peaks and a group of triple peaks (Fig. 3B). The two groups of sextet peaks were confirmed [20,21] as the characteristic peaks of  $\text{DMPO}\cdot\text{OCH}_3$  ( $\alpha_{\text{N}} = 13.6, 21.7$  signed with ( $\Delta$ )) and  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  ( $\alpha_{\text{N}} = 15.2, 21.1$  signed with ( $\circ$ )), respectively. The triple peaks have also been reported in other systems [22] and were left unknown. For

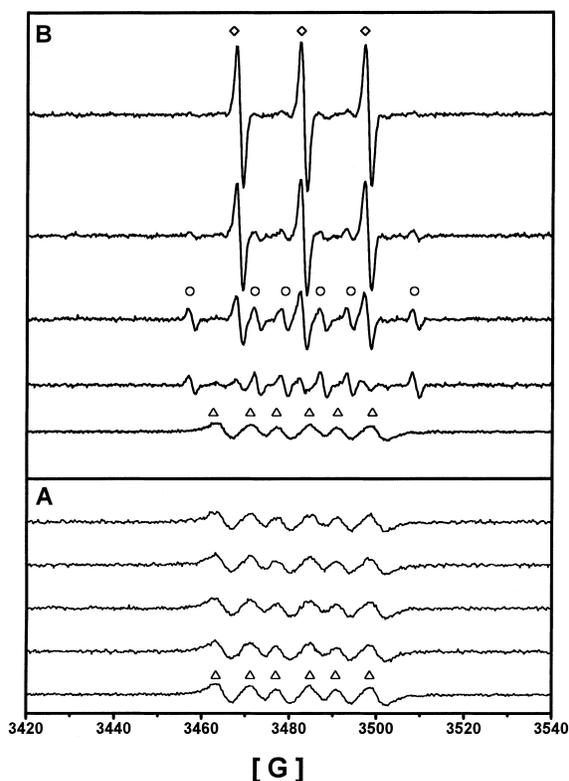
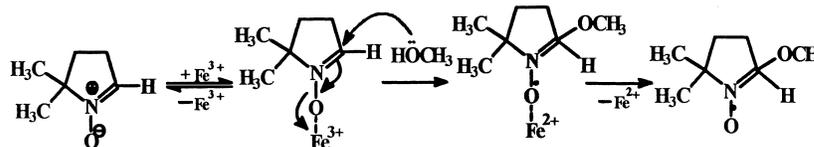


Fig. 3. DMPO spin-trapping EPR spectra under UV irradiation: (A)  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ /methyl orange system in the dark; (B)  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ /methyl orange system under UV irradiation, reaction time of the spectra from under to above: 0, 1, 2, 3, 4 min; the solutions ( $0.3 \text{ cm}^{-3}$ ):  $2 \times 10^{-4} \text{ mol l}^{-1}$  methyl orange,  $2 \times 10^{-4} \text{ mol l}^{-1} \text{ Fe}^{3+}$ ,  $0.1 \text{ mol l}^{-1} \text{ H}_2\text{O}_2$ , and  $0.16 \text{ mol l}^{-1}$  DMPO; irradiation light source: laser  $\lambda = 355 \text{ nm}$ .

the control experiment,  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ /dye system in the dark, the peaks and their intensity had not any change in evidence throughout the whole process (Fig. 3A). It was confirmed [20] that  $\text{Fe}^{3+}$  can complex with DMPO which causes an attack of nucleophilic species, such as methanol. A more detailed mechanism of the interaction between DMPO,  $\text{Fe}^{3+}$  and  $\text{CH}_3\text{OH}$  is shown in Eq. (6). The sextet peaks observed in Fig. 3A were the EPR signals of  $\text{DMPO}\cdot\text{OCH}_3$  (signed with  $\Delta$ ).



(6)

Different from the control experiments, the DMPO-trapping EPR spectra of the  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ /dye system under UV irradiation had an obvious change in a short time (Fig. 3B). A new group of sextet peaks attributed to the signal of  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  (signed with  $\circ$ ) were produced immediately upon UV irradiation which gave an evidence of the production of  $\cdot\text{CH}_2\text{OH}$ . A longer time of irradiation led to the appearance of a new group of triple peaks which had a escalating intensity. The triple peaks (signed with  $\diamond$ ), al-

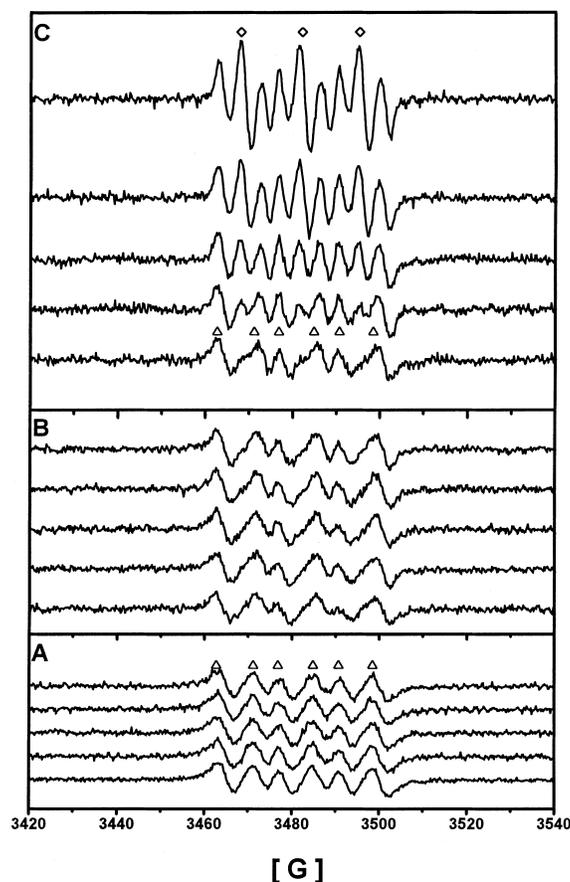


Fig. 4. DMPO spin-trapping EPR spectra under visible irradiation: (A)  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system under visible light irradiation; (B)  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ /methyl orange system in the dark; (C)  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ /methyl orange system under visible light irradiation, reaction time of the spectra from under to above: 0, 1, 2, 3, 4 min; the solutions ( $0.3 \text{ cm}^{-3}$ ):  $2 \times 10^{-4} \text{ mol l}^{-1}$  methyl orange,  $2 \times 10^{-4} \text{ mol l}^{-1} \text{ Fe}^{3+}$ ,  $0.1 \text{ mol l}^{-1} \text{ H}_2\text{O}_2$ , and  $0.16 \text{ mol l}^{-1}$  DMPO; irradiation light source: laser  $\lambda = 532 \text{ nm}$ .

though were left unknown, were contributed to some species after the destruction of DMPO. It was proved that the illumination by UV light increased significantly the generation of active radicals and hence enhanced the Fenton reaction

in methanolic solution which was well fit to the results of dye degradation hereinbefore.

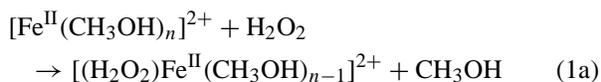
Fig. 4 displayed the spin-trapping EPR spectra of visible light-assisted photo-Fenton reaction of methyl orange in methanolic solution under various conditions. The results observed here had some differences from those under UV irradiation. In the absence of dye, the EPR spectra of the  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system under visible irradiation had no obvious

changes before and after visible light irradiation (Fig. 4A) which means that the generation of radicals in  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system cannot get a perceptible enhancement by visible light irradiation. Similarly, the intensity of the sextet peaks (DMPO- $\bullet\text{OCH}_3$ ) in  $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{dye}$  system also did not change throughout the whole process in the dark reaction (Fig. 4B). Illumination by visible light enhanced greatly the intensity of the sextet peaks in the  $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{dye}$  methanolic system; and a longer time of illumination also resulted in generation of a new group of triple peaks (Fig. 4C) which was caused by the destruction of DMPO. These results supply a proof that the illumination by visible light accelerates effectively the generation of active species and hence accelerates the Fenton reaction in the methanolic solution in and only in the presence of dyes which have the ability to absorb the visible light.

Since azo-dyes such as methyl orange scarcely emit fluorescence, SRB was chosen to reveal the interaction between dye and  $\text{Fe}^{3+}$  ions in methanolic solution. It was found that  $\text{Fe}^{3+}$  ions effectively quenched the fluorescence of SRB which confirmed that dye can transfer electron to  $\text{Fe}^{3+}$  ions in methanolic solution. It has been confirmed [26] that azo-dyes can interact with  $\text{Fe}^{3+}$  in solution and excited azo-dyes can transfer electrons to  $\text{Fe}^{3+}$ . Addition of  $\text{H}_2\text{O}_2$  to this solution strongly enhances the fluorescence quenching of SRB by  $\text{Fe}^{3+}$ . It maybe attribute to the complex of  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{3+}$  ions in methanolic solution which influences the interaction between the dye and  $\text{Fe}^{3+}$  ions.

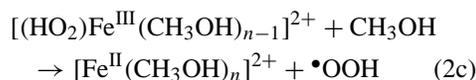
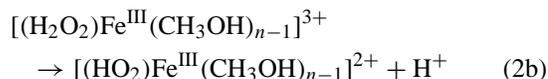
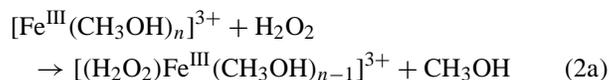
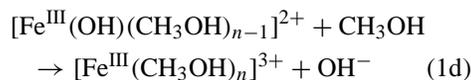
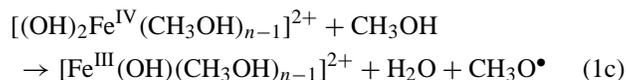
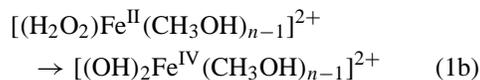
The data above showed that the detailed mechanisms of the photo-Fenton reactions are different not only in the excitation processes at the beginning but also in the active species which promote the photo-Fenton reaction under visible light<sup>2</sup> irradiation and UV irradiation in methanolic solution. On the basis of the above experimental results, a brief mechanism of the photo-Fenton is listed below, in which the generation of  $\text{Fe}^{\text{IV}}$  is involved. The oxoiron(IV), which formed through the complex of the ferrous ions and oxidizer, would react with the targets to generate ferric ions and active radicals as confirmed in some otherwise similar systems [19,23–25]. It is also found that the chelator deeply affect the reaction rate of the Fenton or photo-Fenton reaction [26]<sup>3</sup>.

Fenton reaction (in the dark):

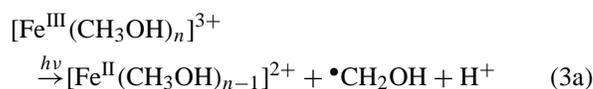


<sup>2</sup> Note that reactions (4a) and (4b) most likely proceed within a  $\text{Fe}^{3+}$ -dye complex.

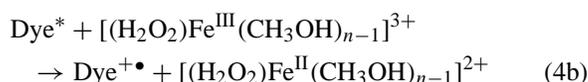
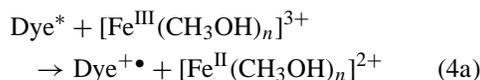
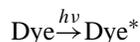
<sup>3</sup> It was found that chelator such as fluoride, oxalate, propandioic acid and salicylate greatly altered the reaction rate of Fenton or photo-Fenton reaction by adding a little amount of them to the reaction system in our current study.



Under UV irradiation



Under visible light irradiation



In fact, under the conditions of Fenton reaction (dark reaction), there are  $\text{CH}_3\text{O}\bullet$  radical and  $\bullet\text{OOH}$  radical generated through the reaction among  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$  and solvent. The reaction between DMPO and  $\text{Fe}^{3+}$  would also take place (Eq. (6)) which produce DMPO- $\bullet\text{OCH}_3$  in the methanolic solution. It can be concluded that there would be DMPO- $\bullet\text{OCH}_3$  and DMPO- $\bullet\text{OOH}$  generated from the above mechanism. But unfortunately, the signals of DMPO- $\bullet\text{OOH}$  ( $\alpha_{\text{N}} = 15.2$ ;  $\alpha_{\text{H}} = 21.1$ ) are just covered by those of DMPO- $\bullet\text{OCH}_3$  in EPR spectra. There are only the signals of DMPO- $\bullet\text{OCH}_3$  could be clearly observed in Fig. 3A. Illumination by UV light led to generation of a large number of  $\bullet\text{CH}_2\text{OH}$  radicals. Considering that DMPO can be destroyed under UV irradiation, the signals of DMPO- $\bullet\text{OCH}_3$  would be lower and the signals of DMPO- $\bullet\text{CH}_2\text{OH}$  and some species from the destruction of DMPO would appear and becomes stronger. All of them fit well to those displayed in Fig. 3B. The signals of DMPO- $\bullet\text{OCH}_3$  could be seen in

Fig. 4A owing to the same reason in Fig. 3A. In the absence of methyl orange, irradiation by the visible light with wavelengths above 450 nm in our experiments of visible light-assisted photo-Fenton reaction or by the laser of wavelength at 532 nm used in EPR measurement, would also not change the EPR signals as shown in Fig. 4B, since no photons could be absorbed by the components in the system throughout the whole process. It is known [26] that azo-dyes can interact with  $\text{Fe}^{3+}$  in solution and excited azo-dyes can transfer electrons to  $\text{Fe}^{3+}$ . In the presence of methyl orange and under the illumination by visible light, the generation of  $\bullet\text{OCH}_3$  radicals would be greatly increased which can be deduced from the above mechanism. On the other hand, the active species generated during the visible light-assisted photo-Fenton reaction appear to attack the DMPO molecule and led to the appearance of a triple peaks.

### 3.3. Formation of intermediates

The visible light assisted photo-Fenton degradation of methyl orange in the methanolic solution was monitored by IR spectroscopic methods (Fig. 5) to investigate the intermediates produced during the dye decomposition process. The sample for IR spectra measurement was prepared from the reaction solution in which about 20% of UV–VIS absorbency of methyl orange remained. Most of the bands of the characteristic IR absorption of the methyl orange (curve a) decreased with increasing the irradiation time. The absorption peaks at wavenumber of 1366 and 1447  $\text{cm}^{-1}$  which are the signals of methyl group almost disappeared; the absorption peak of C–N bond of aromatic tertiary amine ( $\text{Ar-N}(\text{CH}_3)_2$ ) at 1316  $\text{cm}^{-1}$  also almost decreased to zero; what is more, the absorption peaks of C–H bonds of di-substituted benzene at 818 and 845  $\text{cm}^{-1}$  changed their position to 833  $\text{cm}^{-1}$ ; the characteristic absorption peak of phenyl at 1520  $\text{cm}^{-1}$  disappeared. On the other hand, the peaks of sulfonic group at 1200, 1042 and 698  $\text{cm}^{-1}$  decreased slowly comparing to other peaks (curve b) since organic sulfonic group and inorganic sulfate salts have similar absorption in IR spectra; some new IR bands appeared

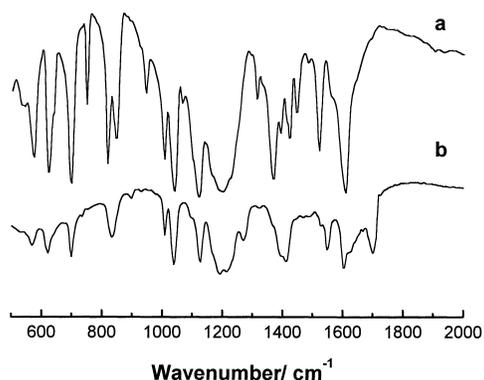


Fig. 5. IR spectra of methyl orange: (a) methyl orange; (b) intermediate of visible light-assisted photo-Fenton degraded methyl orange.

and increased with an increase in the irradiation time: the absorption at 1270  $\text{cm}^{-1}$  is attributed to C–N bonds of aromatic monoamines ( $\text{Ar-NH}_2$ ), the absorption at 1550  $\text{cm}^{-1}$  is attributed to the N=O bonds of nitroso-groups, the absorption at 1700  $\text{cm}^{-1}$  is attributed to the C=O groups. Since the wavenumber of the C=O groups formed is lower than that of normal C=O compounds, a strong absorption at this position means that there are some amido- or conjugated aldo-ketone- or carboxylic intermediates generated during the photo-Fenton reaction (also see the results of GC–MS experiments below). The messages gotten from the IR spectra give an evidence that the degradation of methyl orange was not only a destruction of the azo bond, which has been already known from UV–VIS spectra above, but also a destruction of the aromatic rings of methyl orange. Furthermore, some kinds of the C=O contained and aromatic monoamine intermediates were generated during the reaction.

Formation of intermediates in the degradation process was further confirmed by GC–MS technique. The sample for GC–MS measurement was prepared from the reaction solution in which methyl orange had been entirely decolorized from the UV–VIS spectra measurement. The results of GC–MS measurements are displayed in Fig. 6. The gas chromatogram of the intermediates, formed in the visible light-assisted photo-Fenton degradation of methyl orange in the methanolic solution, gave out five peaks (Fig. 6A), in which three of them have been identified by MS analysis as dimethyl oxalate (Fig. 6B,  $\text{CH}_3\text{OCOCOOCH}_3$ ), dimethyl 2-butenediate (Fig. 6C,  $\text{CH}_3\text{OCOCH}=\text{CHCOOCH}_3$ ), and 4-dimethylamino aniline (Fig. 6D,  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{NH}_2$ ). Some of them, dimethyl oxalate and dimethyl 2-butenediate, contain C=O group and had a strong IR peak around 1700  $\text{cm}^{-1}$ . The intermediates were detected again under the otherwise identical conditions except that ethanol replaced methanol as the solvent to prepare the GC–MS samples. Diethyl oxalate and diethyl 2-butenediate were detected out at this time in which methyl group was substituted with ethyl group when ethanol was used as the solvent instead of methanol. Since methanol (or ethanol) prefers to react with carboxyl group to produce ester at a higher temperature which appears during the gas chromatography measurement, it is deduced that oxalic acid and 2-butenedioic acid formed actually as the intermediates in the visible light assisted photo-Fenton reaction, which meant the entire destruction of the methyl orange.

Combining the analyses of the IR with the GC–MS spectroscopy, it was indicated that the photo-Fenton degradation of methyl orange under visible light irradiation proceeded with the cleavage of the azo-bond, generating 4-dimethylamino aniline, and then underwent a further opening of the phenyl-rings to form small molecular compounds such as oxalic acid and 2-butenedioic acid (see Scheme 1).

In conclusions, Fenton and photo-Fenton degradation of dyes can proceed in methanolic solution. In the pre-

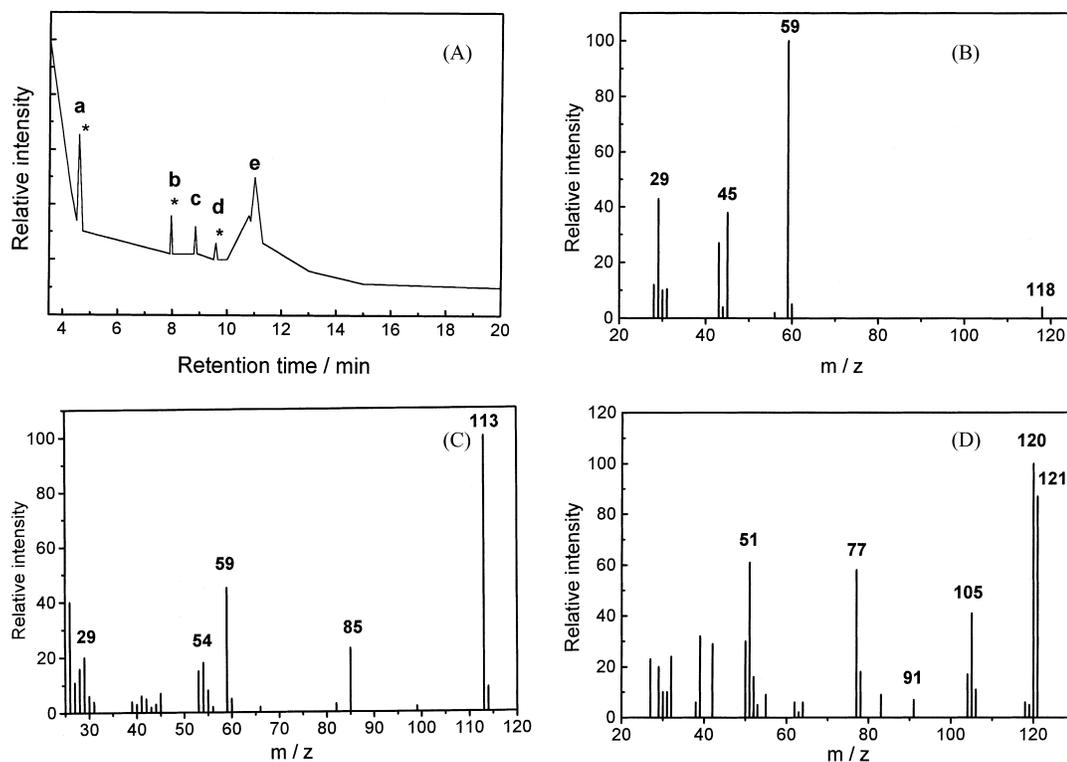


Fig. 6. GC–MS spectra of intermediates of visible light-assisted photo-Fenton degradation of methyl orange: (A) GC spectrum; (B), (C), (D) MS spectra of various components of intermediates.

sence of methyl orange, visible light irradiation strongly accelerates the Fenton reaction.  $\text{CH}_3\text{O}^\bullet$  radical was detected during both the visible light-assisted and UV-assisted photo-Fenton reaction, while  $^\bullet\text{CH}_2\text{OH}$  radical was detected during UV-assisted photo-Fenton reaction. Those two radicals were expected to initiate the photo-Fenton reaction

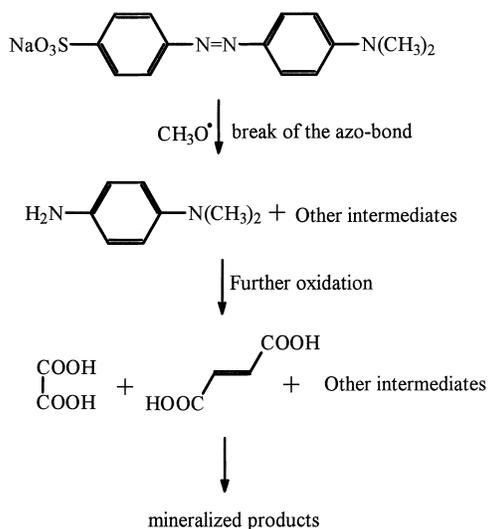
in methanolic solution. The photo-Fenton degradation of methyl orange under visible irradiation led to formation of some fragments of the benzene ring such as oxalic acid and 2-butenedioic acid.

### Acknowledgements

The authors appreciate the financial supports by the National Science Foundation of China (Nos. 29877026, 29725715 and 59772033) and the foundation of Chinese Academy of Sciences; and thank Prof. Jingrong Chen for the assistance in the EPR spectra measurement.

### References

- [1] W.R. Haeg, C.C.D. Yao, *Environ. Sci. Technol.* 26 (1992) 1005.
- [2] J.T. Spadaro, L. Zsabelle, V. Renganathan, *Environ. Sci. Technol.* 28 (1994) 1389.
- [3] W.G. Kuo, *Water Res.* 26 (1992) 881.
- [4] J.H. Carey, E.G. Cosgrove, B.G. Oliver, *Can. J. Chem.* 55 (1977) 2373.
- [5] H.J.H. Fenton, *J. Chem. Soc.* 6 (1894) 899.
- [6] J. Bandeara, C. Marrison, J. Kiwi, C. Pulgarin, P. Pevinger, *J. Photochem. Photobiol. A: Chem.* 99 (1996) 57.
- [7] J.J. Pignatelli, *Environ. Sci. Technol.* 26 (1992) 944.
- [8] A. Nedoloujko, J. Kiwi, *J. Photochem. Photobiol. A: Chem.* 110 (1997) 149.
- [9] V. Nadochenko, *Environ. Sci. Technol.* 32 (1998) 3273.



Scheme 1. Possible mechanism of photo-Fenton degradation of methyl orange in the methanolic solution under visible light irradiation.

- [10] J. Sykora, M. Pado, M. Tatarko, M. Izakovic, J. Photochem. Photobiol. A: Chem. 110 (1997) 167.
- [11] R.G. Zepp, B.C. Faust, J. Holgne, Environ. Sci. Technol. 26 (1992) 313.
- [12] Y. Zuo, J. Holgne, Environ. Sci. Technol. 26 (1992) 1014.
- [13] K. Wu, Y. Xie, J. Zhao, H. Hidaka, J. Mol. Catal. A: Chem. 144 (1999) 77.
- [14] F. David, P.G. David, J. Phys. Chem. 80 (1976) 579.
- [15] K. Wu, T. Zhang, J. Zhao, H. Hidaka, Chem. Lett. 6 (1998) 857.
- [16] F. Herrera, J. Kiwi, A. Lopez, V. Nadtochenko, Environ. Sci. Technol. 33 (1999) 3145.
- [17] T. Wu, T. Lin, J. Zhao, H. Hidaka, N. Serpone, Environ. Sci. Technol. 33 (1999) 1379.
- [18] T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone, J. Phys. Chem. B 103 (1999) 4862.
- [19] S.H. Bossmann, E. Oliveros, S. Gob, S. Siegwant, E.P. Dahlen, L. Payawan, M. Straub, M. Worner, A.M. Braun, J. Phys. Chem. A 102 (1998) 5542.
- [20] K. Makino, T. Hagiwara, A. Hagi, M. Nishi, A. Murakami, Biochem. Biophys. Res. Commun. 172 (1990) 1073.
- [21] M.J. Davies, T.F. Slater, Biochem. J. 240 (1986) 789.
- [22] C.F. Chignall, A.G. Motten, R.H. Sik, C.E. Parker, K. Reszka, Photochem. Photobiol. A 59 (1994) 5.
- [23] C. Walling, K. Amarnath, J. Am. Chem. Soc. 104 (1982) 1185.
- [24] S. Rahhal, H.W. Richter, J. Am. Chem. Soc. 110 (1988) 3126.
- [25] N. Colelough, J.R.L. Smith, J. Chem. Soc., Perkin Trans. 2 (1994) 1139.
- [26] V. Nadtochenko, J. Kiwi, J. Chem. Soc., Faraday Trans. 93 (1997) 2773.
- [27] W.G. Barb, J.H. Baxendale, P. George, K.R. Hargrave, Trans. Faraday Soc. 47 (1951) 462.