Degradation of Orange G Induced by Fe(III)-Oxalate Complex in Irradiated Solution

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The photolysis of orange G in a Fe(III)-oxalate system was investigated under simulated sunlight. Orange G could be effectively photodegraded by the Fe(III)-oxalate system as a result of the formation of the highly oxidizing hydroxyl radical, $^{\bullet}OH$. Orange G degradation followed the first-order kinetics and depended significantly on the initial concentration of Fe (III), oxalic acid and orange G, showing that the photolysis rate increased with increasing iron and oxalic acid concentration and decreased with increasing orange G concentration. The degradation rate constant of orange G changed from 0.0018 min^{-1} to 0.0183 min^{-1} corresponding to the dosage of oxalic acid ranged from 0 to 150 μM under conditions of pH = 4.0, Fe(III) = 20 μM. The interaction of Fe(III) with oxalic acid was characterized using UV-Vis and Fourier transform infrared (FTIR) spectroscopy, indicating that the hydrogen ions on the carboxyl groups were exchanged for Fe(III) ions.

Key Words: Fe(III)-oxalate complex, Photodegradation, Orange G.

INTRODUCTION

Iron is one of the most abundant metals in soils, sediments and surface waters where it may occur in a wide range of chemical forms (species) dependent on the environmental conditions[1]. When the conditions include inorganic or organic ligands, both ferrous iron and ferric iron can easily form stable coordination compounds with them. Simultaneously, these complexes could participate in a series of geochemical cycles in natural waters. The process is often associated with sunlight since the iron complexes have the strong ability of absorbing light energy.

Photochemical processes are important pathways for the transformation and photodegradation of organic pollutants in natural aquatic systems. By irradiation of the Fe(III)-ligand complex, the ligand-to-metal charge transfer would occur and Fe(II) may be produced and the subsequent photochemical reactions between pollutants and radicals can be initiated. Among ligands, oxalic acid had received considerable attention as one of the most common acid molecules in the form of oxalate. Fe(III)-oxalate complex, one of natural photosensitizers with the concentration in natural water from several micromole to several tens of micromole, can generate strong oxidant species, such as hydroxyl radical, *via* a series of photochemical reactions upon sunlight irradiation[2,3]. Gong *et al.*[4] reported the dye indigo carmine with a concentration of 30 mg/L was decolourized by 98.5% in 0.5 h under the

condition of pH = 3 and H_2O_2 = 100 mg/L and the ferrioxalate complexes/H_2O_2/UV was more effective than UV/H_2O_2 and UV/Fe^{3+}. Liu *et al.*[2] suggests that strong oxidative species, $^{\bullet}OH$ and $O_2^{\bullet-}$, are responsible for the enhanced octylphenol ethoxylates photolysis in the presence of Fe(III)-oxalate complexes according to the EPR analysis with DMPO as the spin-trapping reagent.

Dyes constitute a significant part of the wastewater emanated by textile, leather and printing industries. Due to the poor biodegradation and stability of dyes, the wastewater of these industries has to be treated by effective methods. The main disadvantage of the common water treatment processes such as coagulation, ion exchange and adsorption of activity carbon is that these methods just achieved the phase transference of pollutants, instead of their elimination[5]. Advanced oxidation processes are effective for treatment of dyes solution, but it is of high cost. Therefore, the irradiation of Fe(III)-oxalate complex was used here for the photodegradation of azo dye wastewater, specifically orange G, which is widely used in textile, pulp and paper industries.

The aims of this study were as follows: (1) analyzing the photolysis efficiency of orange G in different systems and discussing the related mechanism; (2) investigating the effects of initial iron, oxalic acid and orange G concentrations on the photodegradation of orange G; (3) characterizing the interaction between oxalic acid and Fe(III) by UV-Vis spectra and FTIR.

EXPERIMENTAL

All chemicals were analytical reagent grade and used without further purification. Orange G was purchased from Hengrun Dyestuff Chemical Co. (Guangzhou, China) and stock solution of orange G was prepared at 200 mg L^{-1} in distilled water. Fe(NO)$_3$·9H$_2$O was purchased from Shanghai Chemical Reagent Co. Ltd. and was dissolved in an aqueous solution of 0.1 M H$_2$SO$_4$ as Fe(III) stock solution. All stock solutions were stored in a refrigerator at 4 ºC in the dark and used within 1 week.

Photochemical experiments and analysis: Irradiation of the aqueous solutions of orange G (200 mL) was carried out in a cylindrical reactor equipped with a Xe lamp (Shanghai Jiguang Lighting Corporation, China) to simulate sunlight, which was surrounded with a quartz jacket and the tap water cooling circuit maintained the solution temperature at 25 ± 1 ºC. The irradiation intensity was measured by a radiometer (model FZ-A, Photoelectric Instrument Factory Beijing Normal University, China) and was maintained at *ca.* 10 mW cm^{-2} at λ = 365 nm throughout the experiments. The Fe(III)-oxalate solutions were magnetically stirred for 0.5 h before adding orange G. All solutions for the photolysis experiments were prepared immediately prior to irradiation and were adjusted to the desired pH at 4.0 by 0.1 M HCl or NaOH.

The concentrations of orange G were analyzed directly by a UV-Vis spectrophotometer (UV-550, Jasco, Japan) with maximum absorption wavelength at 495 nm at reaction time of 0, 30, 60, 90, 120 and 150 min.

Characterization of interaction between iron and oxalic acid: The solutions of Fe(III) and oxalic acid were stirred for 1 h in the dark to reach equilibrium. Their light absorption properties were characterized using UV-Vis spectrophotometer. The sample preparations for FTIR were obtained by mixing oxalic acid and Fe(III) at 1:0.1, 1:0.5, 1:1.5 and 1:2 (mol mol^{-1}), stirring for 1 h in the dark, followed by drying at ambient temperature and grinding to yield powder. All samples were stored in a desiccator until the FTIR analysis and KBr of spectrometry-grade was also heated at 25 ºC to remove the adsorbed water before pressing. Then 1 mg dry powdered sample was mixed with 100 mg KBr, followed by compressing the mixture to pellets of 12 mm diameter and investigating by the FTIR spectrometer (Prestige-21, Shimadzu, Japan). Spectra were recorded for a wavenumber from 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

Photodegradation of orange G by Fe(III) solution catalyzed by oxalic acid: Fig. 1A showed the photodegradation of orange G (20 mg/L) in different solutions at pH 4 under Xe lamp irradiation. No significant change over 150 min was observed in the orange G alone solution in dark control experiment. By addition of 40 μM oxalic acid, the concentration of orange G decreased 12 % and in the control experiment of 20 μM Fe(III), about 20% orange G was degraded. In solution containing both oxalic acid and Fe(III), the obvious photodegradation was observed with 40 % orange G removal at the irradiation time of 2.5 h.

Fig. 1B showed the good linear relationship between ln (C$_0$/C) and time (t) for these orange G photodegradation.
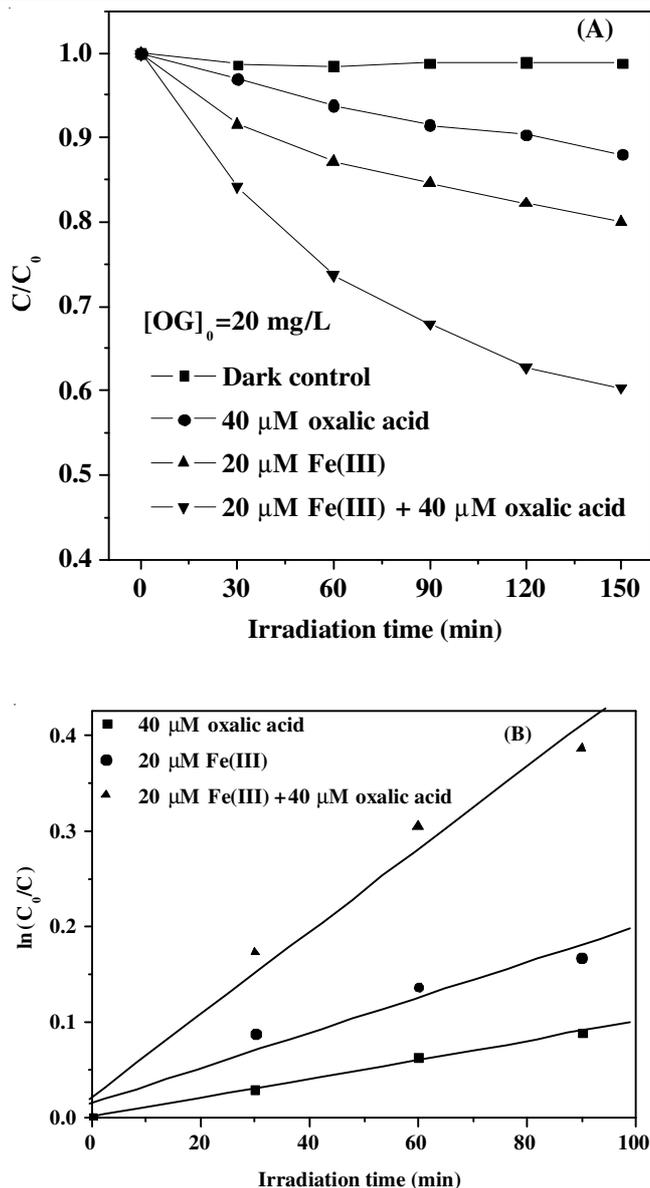
Fig. 1. Photodegradation (A) and kinetics (B) of orange G (OG) (20 mg/L) in the system of Fe(III), oxalic acid and Fe(III)-oxalate complex

The orange G photodecomposition rate constants (k) obtained from the ln (C$_0$/C) = kt plots is 0.001, 0.0018 and 0.0043 min^{-1} corresponding to solutions of oxalic acid, Fe(III) and Fe(III)-oxalate complex, respectively. The degradation of orange G in oxalic acid solution may be due to the possible oxidants (*e.g.* H$_2$O$_2$) that are produced by photolysis of oxalic acid (R1 and R2). On the other hand, the production of •OH from photoreduction of Fe(III) (R3) is responsible for the orange G degradation in the Fe(III) alone solution, where Fe^{III}(OH)$^{2+}$ is an important photoreactive species in acidic solutions. In the presence of oxalic acid at pH 4, Fe(III)-oxalate complexes are the predominant dissolved species[6] such as Fe^{III}(C$_2$O$_4$)$^+$, Fe^{III}(C$_2$O$_4$)$_2^-$ and Fe^{III}(C$_2$O$_4$)$_3^{3-}$. After these complexes absorbed light, a ligand-to-metal charge-transfer (LMCT) from oxalic acid to Fe(III) was initiated, which produces Fe(II) and C$_2$O$_4$•$^-$. Photodegradation of orange G by Fe(III)-oxalate complex can be described by a mechanism involving reactions R1-R7[6,7], then •OH is formed by the Fenton reaction (R8).

$$H_2C_2O_4 + O_2 + h\nu \rightarrow H_2C_2O_4^{\bullet+} + O_2^{\bullet-} \quad (1)$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (2)$$

$$Fe^{III}(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + {}^{\bullet}OH \quad (3)$$

$$Fe^{III}(C_2O_4)_3^{3-} + h\nu \longrightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{\bullet-} \quad (4)$$

$$Fe^{III}(C_2O_4)_3^{3-} + C_2O_4^{\bullet-} \longrightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \quad (5)$$

$$C_2O_4^{\bullet-} \longrightarrow CO_2 + CO_2^{\bullet-} \quad (6)$$

$$C_2O_4^{\bullet-}/CO_2^{\bullet-} + O_2 \longrightarrow 2CO_2/CO_2 + O_2^{\bullet-} \quad (7)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (8)$$
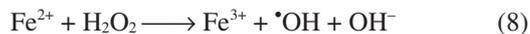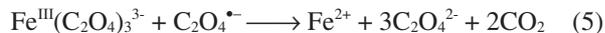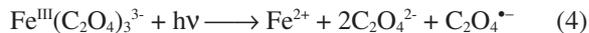
Effect of Fe(III) concentration on orange G photodegradation in Fe(III)-oxalate systems: The dosage of Fe(III) is one of the important factors influencing oxidation reaction of orange G. Under the conditions of 40 μM oxalic acid, 20 mg/L orange G and at pH 4, the effect on orange G degradation of the initial Fe(III) concentration in the range of 0-120 μM with irradiation was analyzed. Fig. 2 showed the concentration profile variation and kinetics curves of orange G at different initial Fe(III) concentration of 0, 10, 20, 40, 80 and 120 μM in 40 μM oxalate solution, corresponding to the k value of 0.001, 0.0038, 0.0043, 0.005, 0.006 and 0.0085 min^{-1}, respectively. As can be seen in Fig. 2, the higher the Fe(III) dosage, the faster the orange G degradation rate, which can be attributed to that an increase of Fe(III) supplement was supposed to accelerate the $^{\bullet}$OH generation rate and should consequently enhance the oxidation rate of orange G. It was also noted that the increase rate of k value was not in accordance with the rate of Fe(III) amount increasing. It was due to higher Fe(III) concentrations favoured the occurrence of the scavenging reaction (R9 and R10) and excess Fe(III) would compete with orange G for the available active radicals such as $^{\bullet}$OH and $O_2^{\bullet-}$.
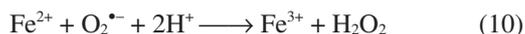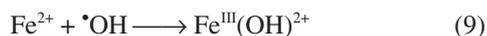
$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{III}(OH)^{2+} \quad (9)$$

$$Fe^{2+} + O_2^{\bullet-} + 2H^+ \longrightarrow Fe^{3+} + H_2O_2 \quad (10)$$

Effect of oxalic acid concentration on orange G photodegradation in Fe(III)-oxalate systems: The oxalic acid concentration as an important parameter for orange G degradation was studied in the solutions containing 20 μM Fe(III) and 20 mg/L orange G under irradiation. Fig. 2 showed orange G photodegradation curves and kinetics curves for oxalic acid concentration of 0, 20, 60, 80, 120 and 150 μM in 20 μM Fe(III) solutions, corresponding to the k value of 0.0018, 0.004, 0.006, 0.0092, 0.0132 and 0.0183 min^{-1}, respectively. This result clearly shows the enhancement of orange G photodecomposition with increasing oxalate concentration. At a given pH value, the oxalic acid with different concentration could complex Fe(III) with different structures corresponding to different photoactivities[8]. As inferred from Fig. 3, the Fe(III)-oxalate complex formed at higher oxalic acid concentration were thought to have higher photoactivity and may be much more efficiently photolyzed than other species, greatly enhancing orange G photodegradation in the presence of oxalic acid. These results were consistent with the previous work that in ferrioxalate systems the rates of atrazine transformation and Fe(II) formation were considerably higher at the higher initial oxalate concentration[8].
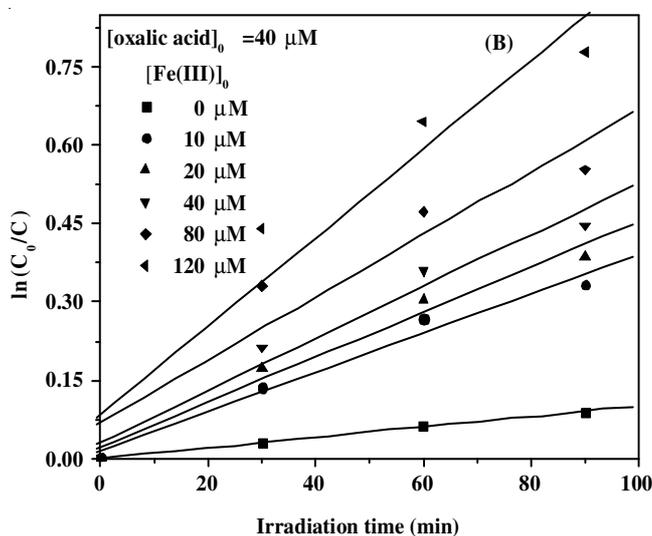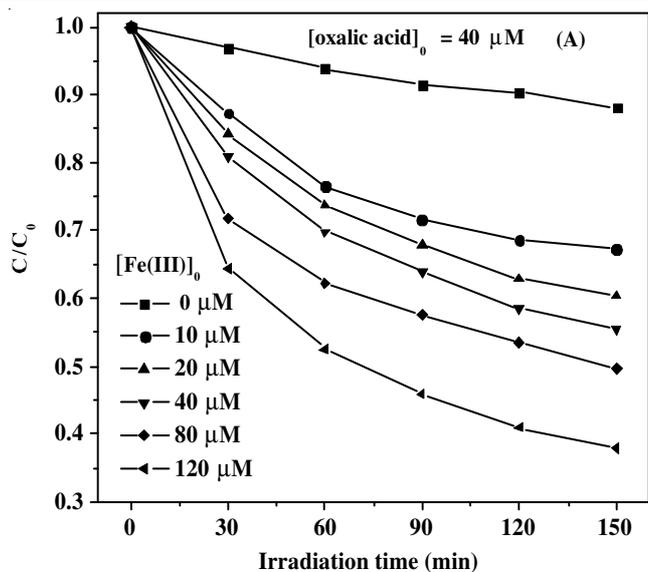
Fig. 2. Effect of Fe(III) concentration on the photodegradation (A) and kinetics (B) of orange G (20 mg/L)
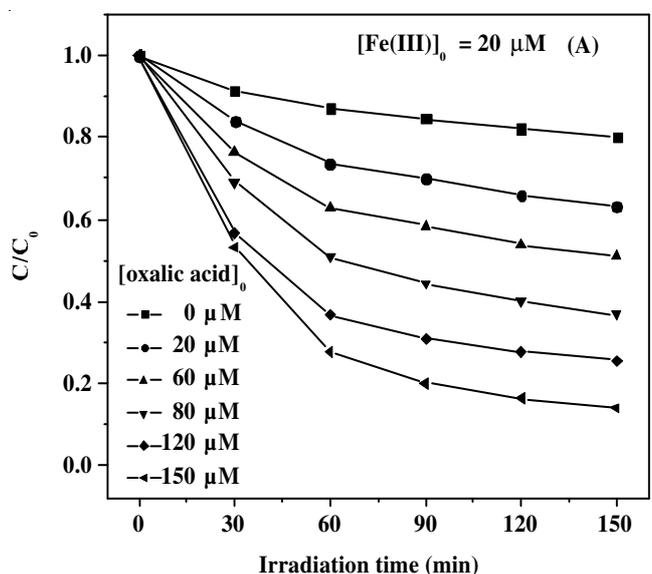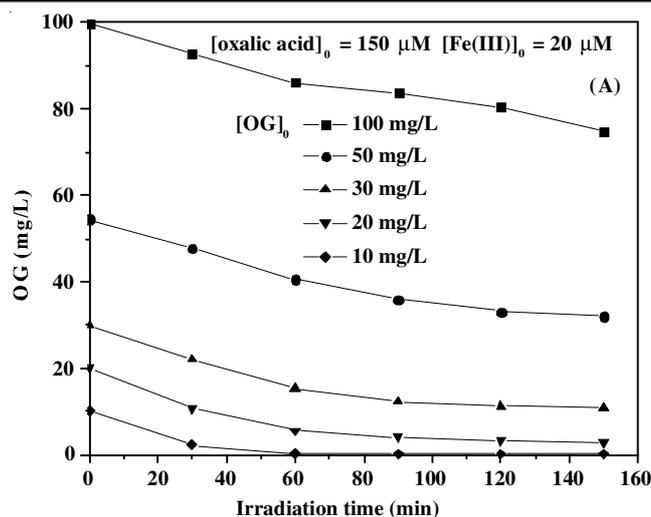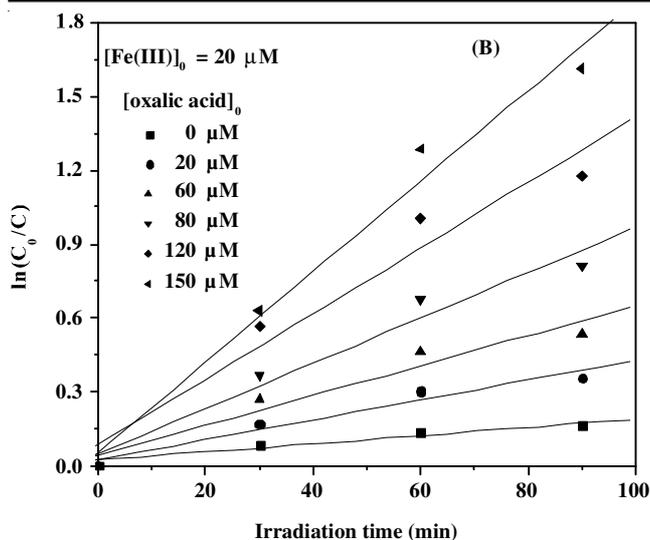
Fig. 3.   Effect of oxalic acid concentration on the photodegradation (A) and kinetics (B) of orange G (20 mg/L)

Comparing the results of Fig. 2 and Fig. 3, it should be noted that the degradation of orange G was more sensitive to the initial concentration of oxalic acid compared to that of Fe(III). After irradiation, the Fe(III)-oxalate complex can undergo ligand to metal charge-transfer in aqueous solutions, which produced Fe(II), $C_2O_4^{\bullet-}$ and CO_2, suggesting the generation of Fe(II) was in parallel to the depletion of oxalic acid. Apparently, more oxalic acid would increase the production of Fe(II) and more $^{\bullet}OH$ followed. It can be inferred oxalic acid in the Fe(III)-oxalate systems simultaneously plays the roles of a carboxylate ligand and a reductant of Fe(III).

Effect of the initial concentrations of orange G: A series of experiments were performed to examine the effect of the initial orange G concentration under the following conditions of 20 µM Fe(III), 150 µM oxalic acid, pH 4 and Xe lamp illumination and the photodegradation curves of orange G were showed in Fig. 4A. The experimental data fitted using the first-order mode were presented in Fig. 4B. The degradation rate of orange G was almost up to 100 % under the following initial concentrations of 20 µM Fe(III), 150 µM oxalic acid and 10 mg/L orange G. The k values for orange G photodegradation in solutions containing 20 µM Fe(III) and 150 µM oxalic acid were 0.0516, 0.0183, 0.0101, 0.0047 and 0.002 min⁻¹ corresponding to initial orange G concentration of 10, 20, 30, 50 and 100 mg/L, respectively. It was seen from Fig. 4 that the degradation rate was accelerated as the initial orange G concentration decreased. Possible explanation for this observation was that a relative lower concentration of $^{\bullet}OH$ resulted from the increasing concentration of orange G but the same dosage of hydrogen peroxide and ferrous ion, which slowed down the oxidation rate of orange G[9].

Characterization of Fe(III)-oxalate complexes by UV-Vis: The UV-Vis spectra of 0.1 mM Fe(III), 0.3 mM oxalic acid and the complex of 0.3 mM oxalic acid and 0.1 mM Fe(III) were shown in Fig. 5(A). It can be seen that oxalic acid solution hardly had absorption from 225 nm to 450 nm and the absorbance of Fe(III) generally decreased with the wavelength (λ) increasing. The absorption of solutions containing both oxalic acid and Fe(III) exhibited a new broad peak around
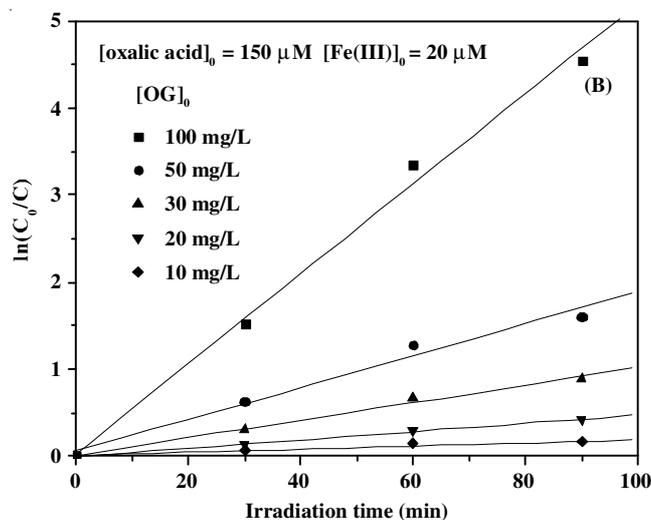
Fig. 4.   Effect of initial orange G concentration on the photodegradation (A) and kinetics (B) of orange G

280 nm, which was stronger than that of alone Fe (III) or alone oxalic acid solution. This new peak can be attributed to the fact that Fe(III) could be complexed by carboxyl groups in oxalic acid according to ligand to metal charge-transfer. Fig. 5(B) illustrated the complex of 0.3 mM Fe(III) and oxalic acid with different concentration ranging from 0 mM to 0.4 mM. As the concentration of oxalic acid added in Fe(III) solution increasing, the absorbance around 280 nm increased due to the binding of Fe(III) with oxalic acid, indicating that the iron species formed at high oxalic acid concentration exhibited generally high photoabsorption. The result provided additional evidence for observations from Fig. 3.

Characterization of Fe(III)-oxalate complexes by FTIR: FTIR spectra is one of the most powerful methods to study the structure and bonding of metal complexes or compounds and it has been used to characterize the interactions between metal and ligands according to variations of peaks. Fig. 6 presented the FTIR spectra of different molar ratios of oxalic acid and Fe (III) at 1:0.1 (a), 1:0.5 (b), 1:1.5 (c) and 1:2 (d). As seen from Fig. 6, there were significant differences. With increasing the Fe (III) concentration, the intensities of C=O (ca. 1614 cm⁻¹) and C-O (ca. 1260 cm⁻¹) stretching vibrations of-COOH were decreasing and disappearing and
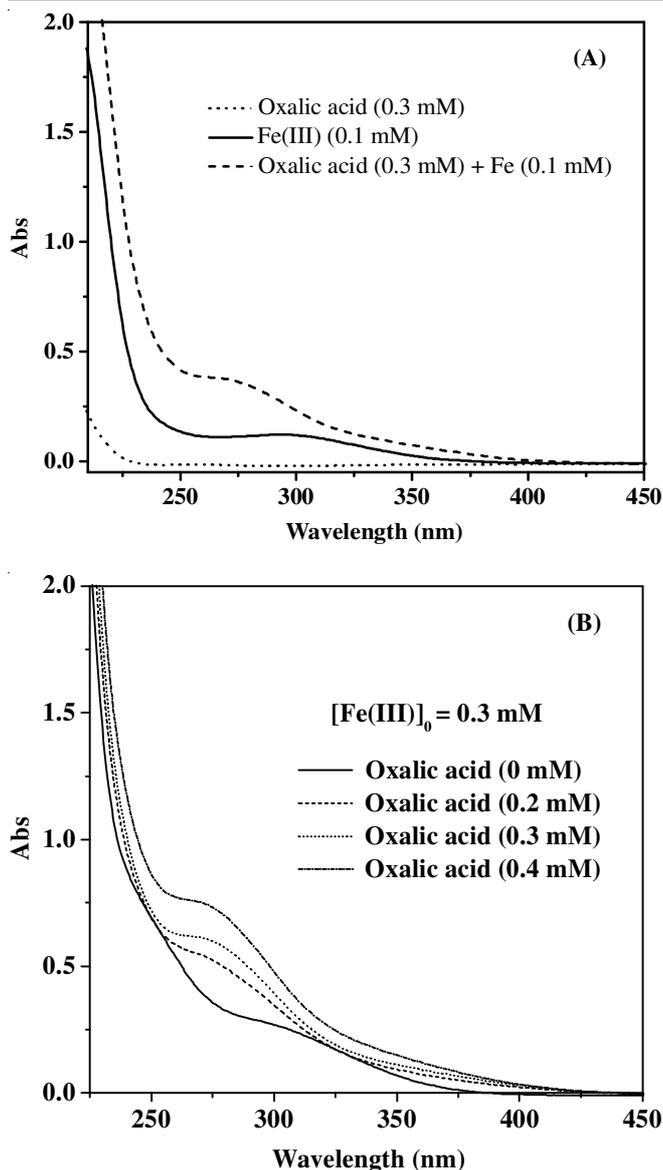
Fig. 5. UV-Vis spectra of Fe(III)-oxalate complexes
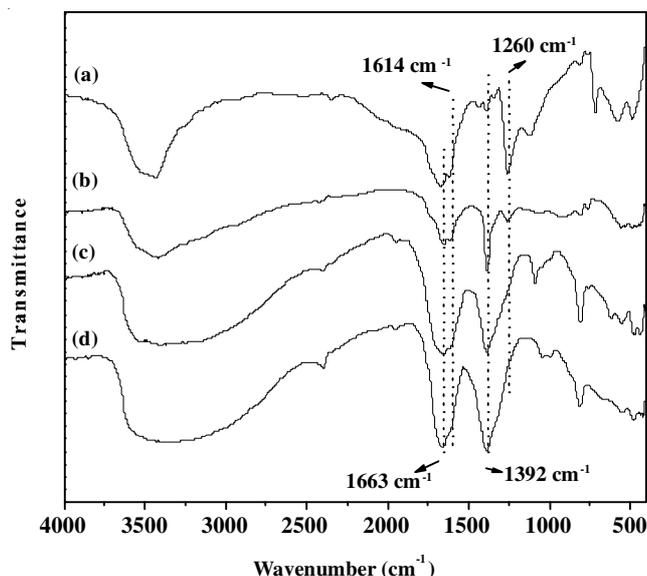
the bands assigned to the asymmetric and symmetric -COO-stretching (*ca.* 1663 and 1392 cm^{-1}) were increasing. The result indicated that a part of carboxylic acid was deprotonated by the ligand exchange with the iron and ultimately was transformed to carboxylate[10] and the band at 1392 cm^{-1} could be assigned to -COO-Fe.

Conclusion

The presence of Fe(III)-oxalate complexes enhanced the photodegradation rate of aqueous orange G under Xe lamp irradiations. The reaction kinetics fitted the first order reaction and the photolysis efficiency was dependent on Fe(III) dosage, oxalate concentration and initial orange G concentration. OH radical is responsible for the increase of orange G photolysis rate in the presence of Fe(III)-oxalate complexes. The degradation of orange G was more sensitive to the initial concentration of oxalic acid compared to that of Fe(III). The results of UV-Vis and FTIR characterization showed that ligand exchange between carboxylic functional groups of oxilic acid and Fe(III) was the dominant interaction mechanism, leading to the formation of iron species that absorb more light energy to degrade organic substances effectively.

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Fig. 6. FTIR spectra of different molar ratios of oxalic acid and Fe(III) (1:0.1 (a), 1:0.5 (b), 1:1.5 (c), 1:2 (d))