



Strategies comparison of eliminating the passivation of non-aromatic intermediates in degradation of Orange II by Fe³⁺/H₂O₂

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ABSTRACT

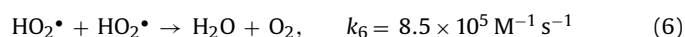
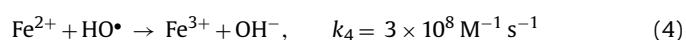
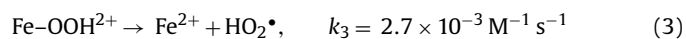
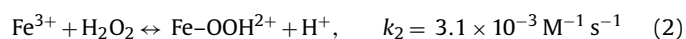
The degradation kinetics of Orange II by Fe³⁺/H₂O₂ was examined under various conditions in the presence of the non-aromatic organic intermediates such as malonic acid (MA), oxalic acid (OX) and EDTA. Various strategies were adopted to eliminate the passivation of the non-aromatic organic intermediates in the Fenton-like degradation of Orange II. UV irradiation, visible irradiation, hydroquinone (HQ) additive and their hybrid were used to accelerate the decoloration of Orange II; however, some of them were failed to show a good performance in the presence of non-aromatic organics, especially for the mineralization of Orange II. Aluminum ions additive released the ferric ions via a competitive chelation process, and accelerated the reaction obviously. From the decoloration and the mineralization data of Orange II, UV irradiation combined with Al³⁺ ion additive was regarded as the most favorable strategy for deep mineralization of Orange II by Fe³⁺/H₂O₂ in the presence of non-aromatic intermediates. However, by considering the decoloration of Orange II with moderate mineralization, the combination of visible irradiation and Al³⁺ ion additive might present the best performance.

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1. Introduction

Synthetic dyes have been extensively used in textile, paper and printing industries and significant losses were discharged in the effluent during the manufacture and dyeing processes. Many of them are very toxic and carcinogenic [1], resistant to biological degradation, and their color removal by bioprocess is difficult and always not complete [2,3]. Therefore, decoloration and decomposition of azo-dye using the Fenton reagent has been actively discussed [4,5].

Fenton and photo-Fenton reactions have been proven to be effective methods to treat organic pollutants in wastewater, and their mechanisms and kinetics have been widely studied [6–15]. The generally accepted free radical chain mechanism for the Fenton reaction is shown below [10,16–18], of which Eq. (3) acts as the rate-determining step.



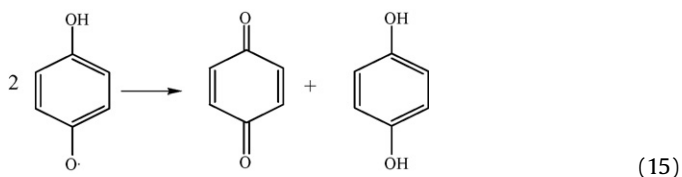
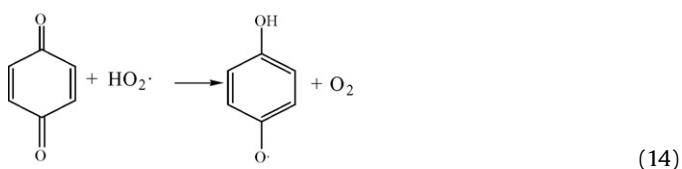
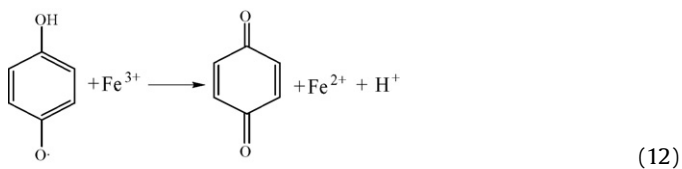
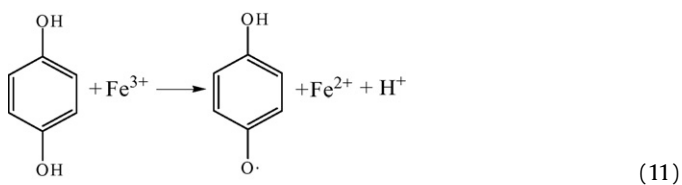
Although Fenton reagent is regarded as a powerful oxidant, deeply mineralization of organic pollutants is always difficult in Fenton reaction treatment of wastewater [19]. Great amounts of non-aromatic intermediates such as malonic acid, propanoic acid, acetic acid, oxalic acid are generated during the Fenton-like degradation of organics [7,18,20]. These non-aromatic intermediates can interact strongly with the ferric ions (e.g. $\log \beta[\text{Fe}(\text{ox})_3^{3-}] = 20.3$, ox = oxalate ion) to form complex. It is commonly accepted that the interactions between ferric ions and organic ligands restrain the reaction rate in Fe³⁺/H₂O₂ system [10,20–23], and result in an incomplete mineralization [24].

Passivation of organic ligands in Fe³⁺/H₂O₂ system is very harmful to the practical applications in dealing with the organic pollutants in the wastewater [24,25]. However, the non-aromatic intermediates are unavoidable generated during the treatment of high TOC of wastewater with Fe³⁺/H₂O₂ system; hence, seeking effective strategies to eliminate or weaken the passivation effect of the non-aromatic intermediates is of importance.

Many efforts have been carried out to improve the Fenton reaction [8,26–30]. UV irradiation which was introduced into the Fenton or Fenton-like processes constantly reduced Fe³⁺ to Fe²⁺ (Eqs. (7) and (8)), and resulted in a reaction rate improvement by the participation of additional photogenerated Fe²⁺ [26]. In the presence of colored substances such as dye, visible light irradiation can also

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promote the Fenton process through an electro-transfer from the excited dye into Fe^{3+} ions (Eqs. (9) and (10)), which enhances the catalytic cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ [31]. Hydroquinone and hydroquinone-like substances can quickly reduce Fe^{3+} to Fe^{2+} (Eqs. (11) and (12)); meanwhile, the resulting quinone rapidly react with $\text{HO}_2\cdot$ generating in the Fenton reaction (Eq. (13)) and regenerate hydroquinone (Eqs. (14) and (15)), which build up a hydroquinone cycle to accelerate the key $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle of Fenton reaction [25,27,32,33]. These favorable results were also observed in our previous works [27].



Most of the above experiments were carried out comparing with the neat reaction system (neat substance with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$), in which increase in kinetics was observed. However, the practical wastewater is much complex than the above mimic neat systems. Further investigations on the performances of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system in the presence of organic ligands (either original or reaction-generated) are needed for its practical application in wastewater treatment. In this work, UV irradiation, visible irradiation, HQ additive, inert metal ions (Al^{3+}) additive and their combined uses were introduced to observe their effects on the degradation kinetics of Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of non-aromatic intermediates or not, which are common and unavoidable in the degradation of organic pollutants with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. New strategies to eliminate the passivation effect of non-aromatic intermediates in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system were suggested, which were different with the previous strategies.

2. Materials and methods

2.1. Chemicals

Orange II (sodium *p*-(2-hydroxy-1-naphthylazo) benzene sulphonate, GR) was supplied by Acros Organics. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, H_2O_2

30 wt.%, HCl, 1,4-hydroquinone, malonic acid (MA), EDTA, oxalic acid (OX) were all AR grade. All chemicals were used without further purification double distilled water was used throughout the work.

2.2. Reaction procedures and analytical methods

All experiments were conducted in a cylindrical quartz (100 ml) tube under magnetic stirring at an initial pH 2.8 (adjusted with 0.1 M HCl). UV irradiation was carried out using a 300 W high-pressure mercury lamp, while visible light source was a 1000 W halogen lamp. Both light sources (either UV or visible light) were surrounded by a quartz jacket to allow for water cooling. The short wavelength components ($\lambda < 420 \text{ nm}$) of the visible light were cut off using a glass optical filter (JB420). In a typical procedure, desired concentrations of Orange II, ferric ion and the possible additive were firstly mixed under stirring for 20 min. Then H_2O_2 was added into the solution. The reaction was timed as soon as the H_2O_2 was added. At given reaction time intervals, 2.0 ml samples were taken out and immediately immited into a 1.0 ml phosphate buffer solution to avoid further reaction (total phosphate concentration of 0.05 M, pH 8.0). The residual concentration of Orange II was then determined by measuring its absorbance at 484 nm on a UV-vis spectrophotometer (Unico, 4802). The TOC was measured on a TOC analyzer (LiquiTOC Elementar). All the solutions were passivated with phosphate buffer and measured immediately to avoid further reaction. Without special indication, the concentrations of ferric ion, hydrogen peroxide and HQ used throughout this work were 1.0×10^{-4} , 4.0×10^{-3} and 4.0×10^{-5} M, respectively.

3. Results and discussion

3.1. Degradation of various concentrations of Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$

Fig. 1 shows the effect of $[\text{Orange II}]_0$ on its degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. It can be seen that the oxidation of Orange II includes three different kinetic stages: An initial stage (or inductive stage), a self-catalytic stage (during which the oxidation of Orange II is self-accelerated) and a passivation stage [27,34]. The first 5, 5–30 and >30 min in Fig. 1 can approximately correspond with the three stages, respectively.

In the initial stage, the degradation of Orange II should be described as a pseudo-first-order reaction kinetics with regard to dye [34]. As shown in Fig. 1, the rate constants k were 0.010, 0.013, 0.010 and 0.011 min^{-1} for different $[\text{Orange II}]_0$ of 1.0×10^{-4} , 2.0×10^{-4} , 3.0×10^{-4} and 4.0×10^{-4} M in the first 5 min, respec-

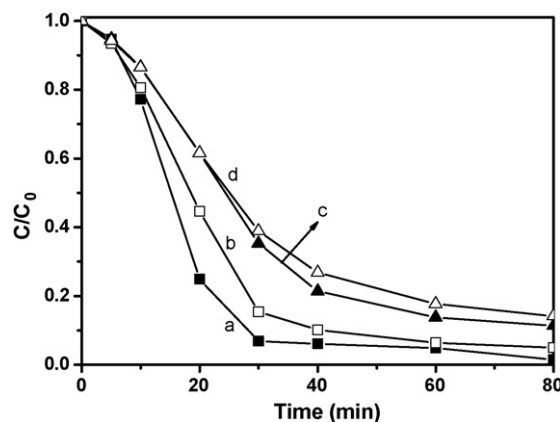


Fig. 1. Degradation of (a) 1.0×10^{-4} M, (b) 2.0×10^{-4} M, (c) 3.0×10^{-4} M, (d) 4.0×10^{-4} M Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the dark.

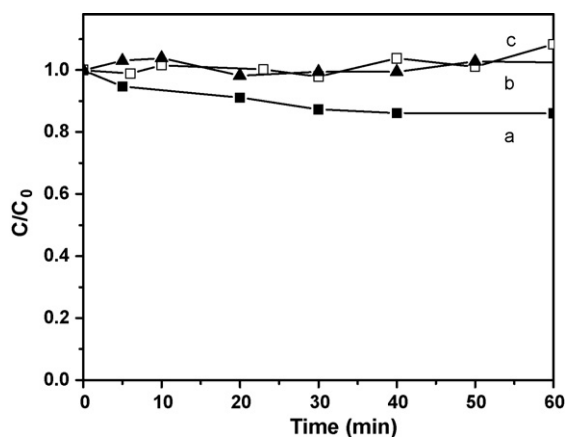


Fig. 2. Degradation of 2.0×10^{-4} M Orange II in the presence of 5.0×10^{-4} M (a) malonic acid, (b) oxalic acid, (c) EDTA by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the dark.

tively (It is supposed that the reaction rate was calculated as $r = kC$, in which C was $[\text{Orange II}]_t$). Although it had been suggested that Orange II was coordinated with the ferric ion [35], which affected the reaction rate, the rate constants k for different $[\text{Orange II}]_0$ were almost similar and presented in the region $k = 0.012 \pm 0.002 \text{ min}^{-1}$. Thus, the rate-determining factors in the initial stage are independent of the $[\text{Orange II}]_0$. The reactions between $\text{Fe}^{3+}/\text{Fe}^{2+}$ and H_2O_2 (Eqs. (1)–(6)) induce the oxidation reaction, and $[\text{Fe}^{3+}]_0$ and $[\text{H}_2\text{O}_2]_0$ determine the reaction rate in the initial stage.

The degradation rate in the self-catalytic stage can be illuminated by $k_{1/2}$, which is the temporal rate constant at $C/C_0 = 1/2$ and was calculated as follow:

$$k_{1/2} = \frac{\Delta(C/C_0)}{t} \quad (16)$$

t is 10 min, the time interval for sample measuring, while $\Delta(C/C_0)$ is the relative concentration change of Orange II in the time interval that contains the point of $C/C_0 = 1/2$. The rate constants $k_{1/2}$ for various $[\text{Orange II}]_0$ of 1.0×10^{-4} , 2.0×10^{-4} , 3.0×10^{-4} and 4.0×10^{-4} M was 0.046, 0.037, 0.028 and 0.027 min^{-1} , respectively, several times higher than that in the initial stage. It has reported that hydroquinone-like intermediates were identified in degradation of Orange II and were found accelerated the Fenton-like reaction by promoting the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle [25,27].

In the passivation stage, the degradation rate decreased obviously. Further degradation of Orange II and its hydroquinone-like intermediates leads to the generation of non-aromatic intermediates, such as oxalate, propanoic acid, malonic acid and acetic acid [4,7,20]. Non-aromatic intermediates do not promote the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle different from the hydroquinone-like intermediates. On the contrary, they chelate well with ferric ions, and depress the reaction between ferric ions and H_2O_2 (Eq. (2)), and so decrease the degradation rate.

3.2. Effects of the non-aromatic organics on the degradation of Orange II

Malonic acid and oxalic acid are the most common non-aromatic intermediates generated in the Fenton-like degradation of organics [7,20], and complex well with Fe^{3+} ($\log \beta[\text{Fe}(\text{ox})_3^{3-}] = 20.3$, $\log \beta[\text{Fe}(\text{MA})_3^{3-}] = 15.4$) so they were selected as additives to observe their effects on the degradation of Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. EDTA, another organic ligand, was also used as an additive, since it chelates strongly with ferric ions ($\log \beta[\text{Fe}(\text{EDTA})] = 25.1$). All the three additives greatly depressed the reaction, especially when oxalic acid (Fig. 2, curve b) and EDTA (Fig. 2, curve c) were introduced into the solution. The chelation between these additives and

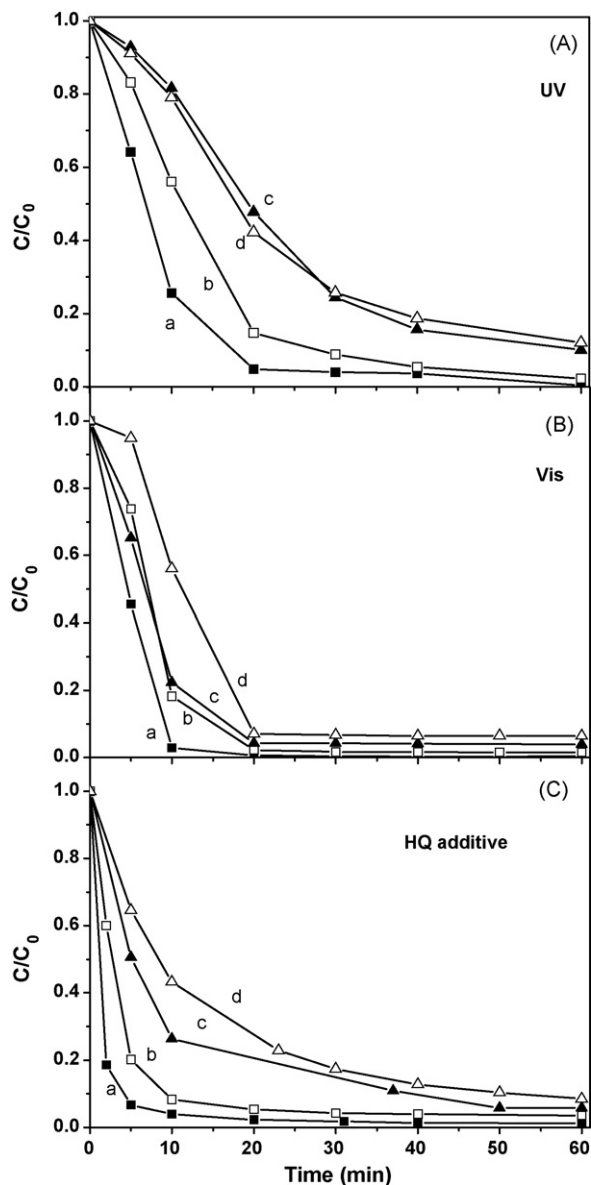


Fig. 3. Degradation of (a) 1.0×10^{-4} M, (b) 2.0×10^{-4} M, (c) 3.0×10^{-4} M, (d) 4.0×10^{-4} M Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (A) under UV irradiation, (B) under visible irradiation, and (C) in the presence of HQ.

ferric ions should be the main reason for such results, similar as that had happened in the passivation stage of Fig. 1. It was reported that EDTA could retard the Fe-catalyzed oxidation of benzoylformic acid by H_2O_2 [21]. Walling [10] also observed that the Fenton oxidation of organic substrates (including bound and free EDTA) was retarded by excess EDTA.

3.3. Effects of UV irradiation, visible irradiation and HQ additive on the degradation of Orange II

Fenton reaction can be accelerated by both UV irradiation [8,26] and HQ additive [27–29]. Furthermore, when there are dyes, visible irradiation can also promote the reaction via an electron transfer between dye* molecule and ferric ion [30]. Fig. 3 presents the effects of UV, visible irradiation and HQ additive on the degradation of Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. It was clearly observed that UV irradiation accelerated the processes of all the three stages; visible irradiation mainly accelerated the processes of the inductive stage and the self-

catalytic stage; while HQ additive only accelerated the process of the inductive stage.

UV irradiation was effective for accelerating all the three stages, but its effect was weakened for higher $[\text{Orange II}]_0$ (Fig. 3A). The half-life $t_{1/2}$ of Orange II under UV irradiation for $[\text{Orange II}]_0 = 1.0 \times 10^{-4} \text{ M}$ was ca. 6.89 min, 2.18 times shorter than that in the dark (15.04 min); However, $t_{1/2}$ of Orange II under UV irradiation for $[\text{Orange II}]_0 = 4.0 \times 10^{-4} \text{ M}$ was 17.81 min, only 1.41 times shorter than that in the dark (25.20 min). UV irradiation accelerates the reduction of Fe^{3+} to generate Fe^{2+} , in other words, it accelerates the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle by Eqs. (7) and (8), thus it speeds up the reaction.

Differ with UV irradiation, the visible irradiation was effective for all concentrations of $[\text{Orange II}]_0$. The half-life $t_{1/2}$ of Orange II under visible irradiation for $[\text{Orange II}]_0 = 1.0 \times 10^{-4} \text{ M}$ was 4.53 min, 3.32 times shorter than that in the dark. As well as that for $[\text{Orange II}]_0 = 4.0 \times 10^{-4} \text{ M}$ under visible irradiation was 11.14 min, 2.26 times shorter than that in the dark. Although Orange II is the target substance in this reaction, higher concentration of Orange II also favors the visible absorption, and then favors reaction by accelerating the generation of Fe^{2+} via an electron transfer process from excited dye. On the other hand, since the promotion effect of visible irradiation is based on the photon absorption of Orange II, its efficiency is inescapably weakened with the degradation of Orange II. As shown in Fig. 3B, curve d ($[\text{Orange II}]_0 = 4.0 \times 10^{-4} \text{ M}$), there was more rapid degradation than others in 10–20 min region, which was obviously different from that in Fig. 3A and C and was attributed to the higher absorption of higher concentration of dye.

It demonstrates from Fig. 3C that HQ additive showed an excellent exhibition in the inductive stage, and 81.4% of Orange II was degraded in 2 min in the case of $[\text{Orange II}]_0 = 1.0 \times 10^{-4} \text{ M}$, as well as 80.8% in 5 min in the case of $[\text{Orange II}]_0 = 2.0 \times 10^{-4} \text{ M}$. In other words, the inductive stage of the reaction was eliminated, and the degradation of Orange II was directly advanced to the second stage by the addition of HQ. HQ can quickly reduce Fe^{3+} to Fe^{2+} , meanwhile, the resulting quinone rapidly reacts with HO_2^{\bullet} to regenerate hydroquinone, which builds up a hydroquinone/semiquinone cycle to accelerate the key $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle of the Fenton reaction [25,27,32,33]. Comparing with UV irradiation and visible irradiation strategies, HQ additive has the highest priority if we only focus on the forefront of the reaction. However, with the increase of the reaction time, also with the increase of the concentration of dye, the validity was depressed quickly. As mentioned before, HQ is a consumable, which means its efficiency would be weakened accompanying with the reaction time: the degradation of Orange II was obviously slackened after 10 min of reaction. In the case of $[\text{Orange II}]_0 = 4.0 \times 10^{-4} \text{ M}$, the $\Delta C/C_0$ in the second 20 min was only 14.7% with the HQ additive while that under UV was 23.6%.

3.4. Effects of UV irradiation, visible irradiation and HQ additive on the degradation of Orange II in the presence of non-aromatic organics

One of the key problems that hinder $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system from the practical application is that its reaction rate is readily depressed by the intermediates generated during the reaction [25], as shown in Fig. 1. The non-aromatic intermediates generated during the reaction can complex with the ferric ions, which depresses of the reaction between ferric ions and H_2O_2 . Some previous literatures [19] suggested that ferric ions react with H_2O_2 via a transitional intermediate $[\text{Fe}(\text{H}_2\text{O}_2)]^{3+}$. The passivation effect of the non-aromatic intermediates would become serious if the TOC value of the wastewater is high. So, if we appeal to an entirely mineralization of the organic pollutants in the wastewater, a relative readily method which can eliminate the passivation effect of the non-aromatic intermediates would be desired. Hereinafter, the degradations of Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of non-

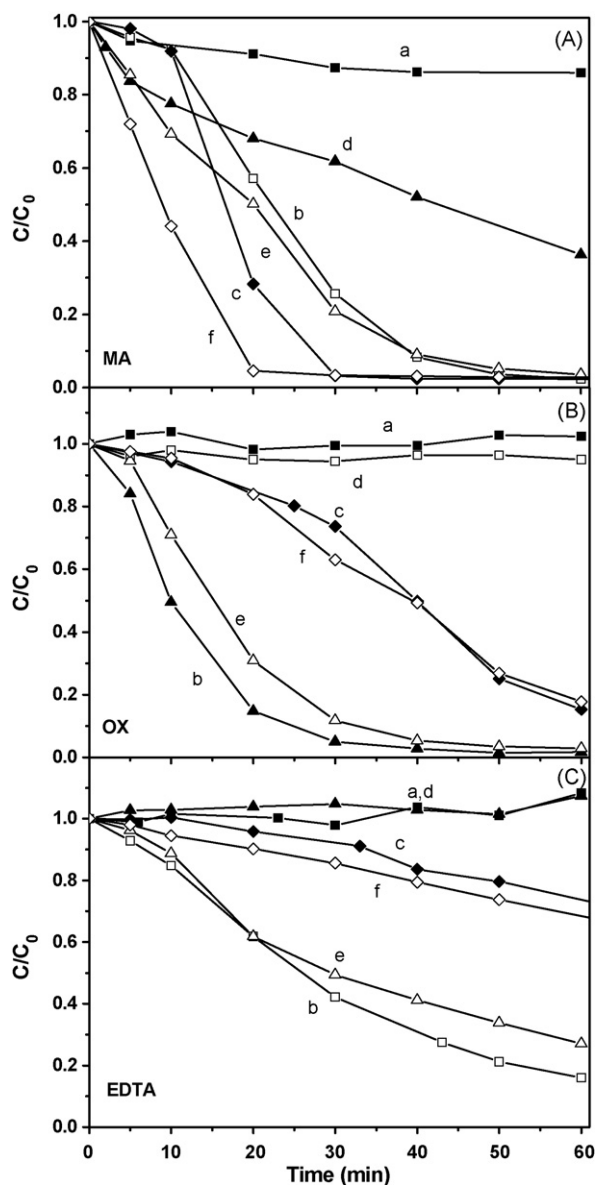


Fig. 4. Degradation of $2.0 \times 10^{-4} \text{ M}$ Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (a) in the dark, (b) under UV irradiation, (c) under visible irradiation, (d) with HQ additive, (e) under UV irradiation combined with HQ additive, (f) under visible irradiation combined with HQ additive in the presence of $5.0 \times 10^{-4} \text{ M}$ (A) malonic acid, (B) oxalic acid, and (C) EDTA.

aromatic intermediates such as malonic acid, oxalic acid and EDTA were observed under the UV irradiation, visible irradiation with or HQ additive (Fig. 4).

UV irradiation is an effective method in improving the degradation of Orange II (see Fig. 3A), even in the presence of non-aromatic organics. The degradation rate of Orange II in the presence of malonic acid increased from 13.8% to 91.8% in the first 40 min, twice than that in the presence of HQ. Even in the presence of other two strong ligands, oxalic acid and EDTA, the degradation rates also reached 97.3% and 69.2% in the first 40 min, respectively. Consequently, UV irradiation had an extremely excellent performance in eliminating the passivation of non-aromatic intermediates, which was coincident with other researches [25].

Visible irradiation exhibited an extremely excellent performance in accelerating the degradation of Orange II (see Fig. 3B) in the absence and the presence of non-aromatic organics. Although the degradation rates of Orange II in the first 40 min only reached

50.1% and 16.4% in the presence of oxalic acid and EDTA, respectively, as shown in Fig. 4. But comparing with the entirely blocked status in the dark, the degradation rates were greatly enhanced. Furthermore, visible irradiation showed the best performance in promoting the degradation of Orange II in the presence of malonic acid, and the degradation rate increased from 13.8% (in the dark) to 97.6% in the first 40 min. This promotion is attributed to the electron transfer from the excited dye to Fe^{3+} as shown in Eqs. (9) and (10) [5]. It can be concluded that chelation between ligands and Fe^{3+} ions does not greatly block the electron transfer between the excited dye and Fe^{3+} . Therefore, visible irradiation acts as a desire method to accelerate the reaction here.

Although HQ additive had an extremely excellent performance in accelerating the degradation of Orange II (see Fig. 3C), its performance in presence of non-aromatic organics was not good. The degradation rate in the presence of malonic acid was only increased from 13.8% to 47.9% in the first 40 min (note that 80.8% Orange II was degraded in just 5 min without any ligand as shown in Fig. 3C). For the other two ligands which have strong complex abilities with Fe^{3+} ions, the promotion effects of HQ additive were almost negligible.

Combination of UV and HQ additive accelerated a little the degradation of Orange II in the presence of non-aromatic organics. However, its effect was less than a simple sum of that of UV irradiation and HQ additive (Fig. 4A); furthermore, in the presence of oxalic acid and EDTA (Figs. 4B and C), the degradation of Orange II under UV irradiation was even weakened by the HQ additive. In the presence of powerful ligands, HQ additive is incapable of reducing Fe^{3+} to Fe^{2+} ; on the contrary, it consumes the active oxygen species existing in the solution, which results in a decrease of the reaction rate.

Under visible irradiation, the situations of HQ additive in the presence of non-aromatic organics were somewhat different with that under UV irradiation. In the case of malonic acid, the degradation rate of Orange II increased from 71.7% to 95.4% in the first 20 min with the addition of HQ. Even for the other two powerful ligands, the promotion effects also existed. Although HQ additive in the dark was proved to be ineffective in the presence of EDTA, it promoted the degradation of Orange II a little comparing with that just under visible irradiation. Similar result had been observed in the previous works [25], and it was explained in their work that the hydroquinone/quinone transformation pathway was much more facile under visible irradiation. HQ, under visible irradiation, gives another reaction pathway for the quinone cycle besides the $\text{HO}_2\cdot$ pathway, and exerts the hydroquinone driving force and, ultimately, the iron recycle is improved.

As results, UV irradiation is usually the most favorable strategy for the degradation of Orange II if high concentrations of ligands are presented in the wastewater. However, if the ligands combine weakly with Fe^{3+} , visible irradiation combined with HQ additive is also preferred.

3.5. Effect of inert Al^{3+} ions on the degradation of Orange II

It was suggested that the chelation between non-aromatic intermediates and ferric ions passivate the reaction in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system; thereby, any method which can liberate the ferric ions would possibly benefit the degradation of organic pollutants in the wastewater by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. Al^{3+} ions chelated well with the non-aromatic organics such as malonic acid and oxalic acid ($\log \beta[\text{Al}(\text{ox})_3] = 19.8$, $\log \beta[\text{Al}(\text{MA})_3] = 14.1$). Fig. 5 shows the degradation of Orange II in the presence of 2.0×10^{-3} M Al^{3+} by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. There was no degradation in the absence of Fe^{3+} ions. Al^{3+} ions are quite stable, and cannot react with H_2O_2 to produce active oxygen species. When Al^{3+} and Fe^{3+} coexisted, Orange II was degraded, which should be due to the reaction of iron ions with H_2O_2 . Al^{3+} ions here could not promote the degradation rate of Orange II; on the contrary, they

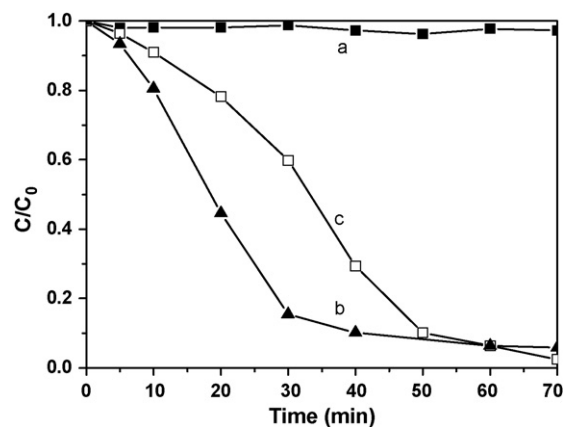


Fig. 5. Degradation of 2.0×10^{-4} M Orange II by H_2O_2 (a) in the presence of Al^{3+} alone, (b) in the presence of Fe^{3+} alone, and (c) in the presence of Al^{3+} and Fe^{3+} . $[\text{Al}^{3+}] = 2.0 \times 10^{-3}$ M.

depressed the reaction. It seems that the interactions of Al^{3+} ions with Orange II stable the dye. The $k_{1/2}$ for $[\text{Orange II}]_0 = 2.0 \times 10^{-4}$ M was 0.021 min^{-1} , lower than that without Al^{3+} ions. But if we sought to the entirely process of the degradation of Orange II, Al^{3+} ions exhibited a fascinating performance: Al^{3+} ions also weakened the passivation of the non-aromatic organics, which made the degradation rate outstrip that with Fe^{3+} alone after 70 min.

Al^{3+} ions greatly accelerated the degradation of Orange II in the presence of malonic acid: the degradation rate increased from 14.0% (Fig. 4A) to 79.9% (Fig. 6A) in the first 60 min in the dark. Surely, Al^{3+} ions chelated well with malonic acid, which released many Fe^{3+} ions. The Fe^{3+} ions released promoted not only the interac-

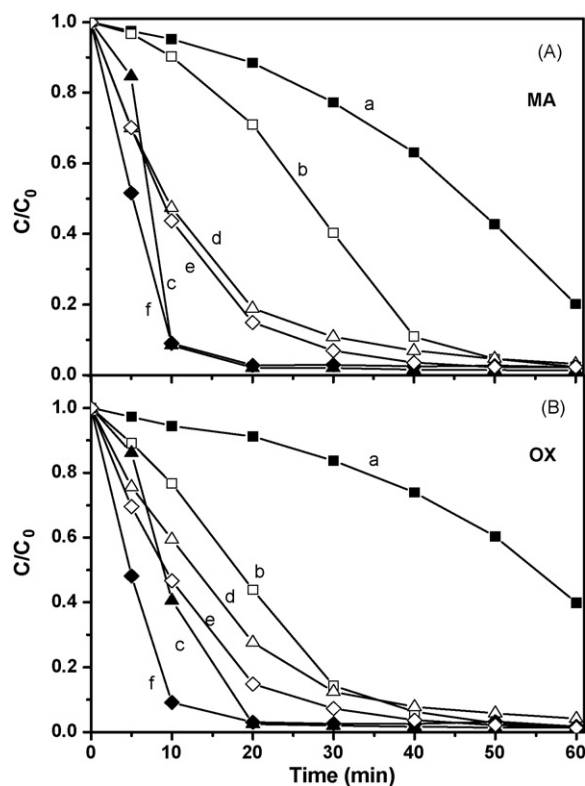


Fig. 6. Degradation of 2.0×10^{-4} M Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (a) in the dark, (b) under UV irradiation, (c) under visible irradiation, (d) with HQ additive, (e) under UV irradiation combined with HQ additive and (f) under visible irradiation combined with HQ additive in the presence of Al^{3+} with 5.0×10^{-4} M (A) malonic acid, (B) oxalic acid. $[\text{Al}^{3+}] = 2.0 \times 10^{-3}$ M.

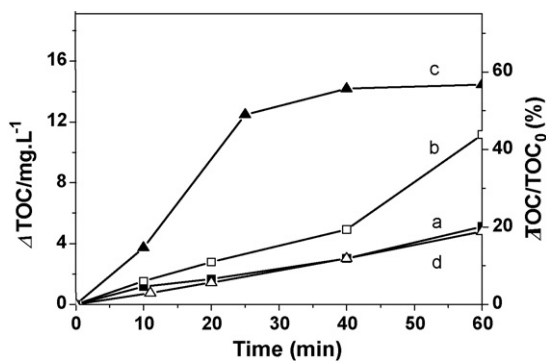


Fig. 7. TOC value decreased in the degradation of 2.0×10^{-4} M Orange II solution by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (a) in the dark, (b) under UV irradiation, (c) under visible irradiation, and (d) in the presence of HQ. Note: The original TOC value of the Orange II solution (25.49 mg/L) was regarded as 100% on the percentage axis.

tion between Fe^{3+} ions and H_2O_2 , but also the interaction between Fe^{3+} ions and HQ additive; the reaction in the presence of HQ additive and Al^{3+} ions (Fig. 6A, Curve d) gave a $t_{1/2}$ of 9.6 min, while that without Al^{3+} was 42.4 min. Similar results were also obtained under visible irradiation and UV irradiation in the absence and the presence of HQ additive. In a word, Al^{3+} ions promoted the degradation of Orange II under all conditions in the presence of malonic acid.

More effective results were also observed when Al^{3+} ions acted as the additive in the presence of oxalic acid (Fig. 6B). Because of the powerful chelation between oxalic acid and Fe^{3+} , the reaction almost stopped in the dark both in the absence and the presence of hydroquinone. While Al^{3+} ions acted as the additive, 40.2% and 95.9% of Orange II were degraded in 60 min in the dark in the absence and the presence of hydroquinone, respectively. Interestingly, Al^{3+} ions promoted the degradation rate more under visible irradiation; therefore, with the Al^{3+} ion additive, visible irradiation (in absence and presence of HQ) gave the best performance, while UV irradiation accelerated most the degradation of Orange II (Fig. 4B) without the Al^{3+} additive.

So the combination of visible irradiation and Al^{3+} ions in the presence of HQ additive exhibits the best performance for organics decoloration, hence, it is the most favorable strategy for the decoloration of organic pollutants in wastewater by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$.

3.6. Mineralization of Orange II in the absence of non-aromatic organics

HQ additive presented an extremely excellent performance in promoting the decoloration of Orange II (Fig. 3C); however, it had no contribution to the mineralization of Orange II (Fig. 7), and the ΔTOC was the same as that just in the dark. UV irradiation promoted the mineralization of Orange II and the ΔTOC was doubled than that in the dark in 60 min. Inspiringly, ΔTOC increased rapidly with the reaction proceeding. The mineralization rate under visible irradiation was the highest: 48.61% in the first 25 min. However, the promotion effect of visible light irradiation is photo-absorbance-dependent; therefore, the mineralization was quickly abated after 25 min of reaction.

3.7. Mineralization of Orange II in the presence of non-aromatic organics

Fig. 8 presents the effects of non-aromatic organics on the mineralization of Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. These organics depressed the mineralization of Orange II. ΔTOCs in the presence of EDTA and oxalic acid were higher under UV irradiation than those under other conditions. e.g. In the presence of oxalic acid, ΔTOCs in 60 min were only 3.80, 2.88, 3.80 mg/L in the dark, under visible irradiation, and

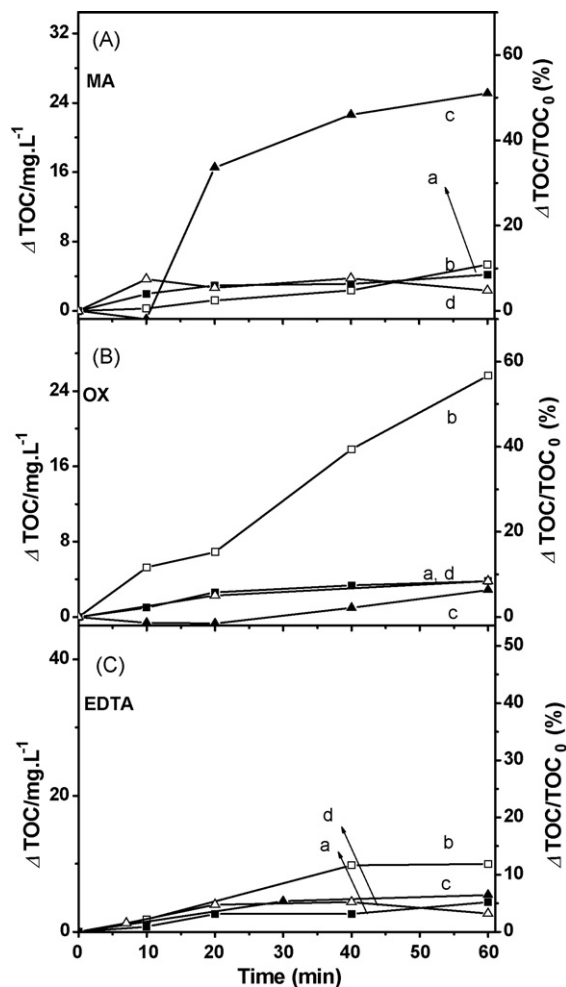


Fig. 8. Mineralization of 2.0×10^{-4} M Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (a) in the dark, (b) under UV irradiation, (c) under visible irradiation, (d) in the presence of HQ with 5.0×10^{-4} M (A) malonic acid, (B) oxalic acid, (C) EDTA. Note: The original TOC value of the Orange II solution combined with organic ligand was regarded as 100% on the percentage axis.

in the presence of HQ additive, respectively. However, the condition under UV irradiation was an exception, the ΔTOC in this case reached 29.58 mg/L. Unfortunately, it was not only attributed to the Fenton-like reaction, but also partly attributed to the UV photolysis of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, in which the photolytic production, $\text{C}_2\text{O}_4^{\bullet-}$, will further dissociate to its entirely mineralized products CO_2 and $\text{CO}_2^{\bullet-}$ [36–38]. The ΔTOC of UV photolysis of sole $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ was 8.56 mg/L (mineralization rate of 71.3%) in 60 min in our experiment. Certainly, reaction would also be promoted to a certain extent by another UV photolytic product, Fe^{2+} , which can react with H_2O_2 to generate to HO^{\bullet} .

ΔTOC of Orange II in the presence of malonic acid was maximum (25.08 mg/L) under visible irradiation, which was consistent with the decoloration results shown in Fig. 4. ΔTOCs in the dark or with HQ additive were much smaller; and that under UV irradiation also increased slightly. Different mineralization result under visible irradiation was mainly due to the weak chelation between malonic acid and Fe^{3+} ions, which did not largely block the photo-induced electron transfer from excited dye to Fe^{3+} ions. HQ additive partly eliminated the passivation of malonic acid in the decoloration of Orange II (Fig. 4A), but it showed no effect on the mineralization of Orange II (ΔTOC was only 2.37 mg/L in 60 min). The promotion effects of HQ additive in the presence of oxalic acid and EDTA were also negligible.

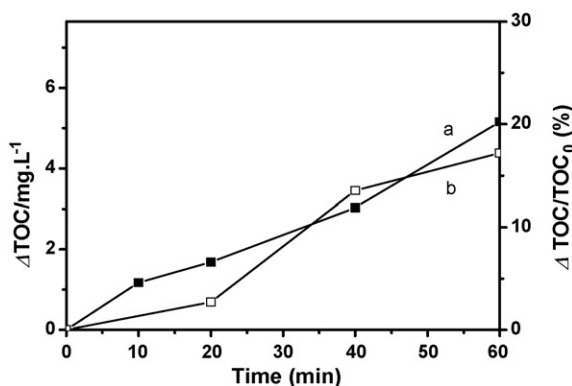


Fig. 9. Mineralization of 2.0×10^{-4} M Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (a) in the presence of Fe^{3+} alone, (b) in the presence of Al^{3+} and Fe^{3+} . Note: The original TOC value of the Orange II solution (25.49 mg/L) was regarded as 100% on the percentage axis.

Thereby, the non-aromatic intermediates are harmful for the mineralization of organic pollutants existed in wastewater. In the presence of weak ligand such as malonic acid, visible irradiation would be desirable for improving the mineralization of Orange II. HQ additive benefits the decoloration of Orange II; however, it does not obviously affect the mineralization of Orange II.

3.8. Effect of Al^{3+} ions on the mineralization of Orange II

Fig. 9 presents the ΔTOCs in the presence of Al^{3+} ions or not. Comparing with that in the presence of Fe^{3+} ions alone, when Al^{3+} ions and Fe^{3+} ions coexisted in the solution, the mineralization rate was lower in the first 20 min, but it increased subsequently and had an ascendant after 40 min, which was consistent with the decoloration of Orange II as shown in Fig. 5.

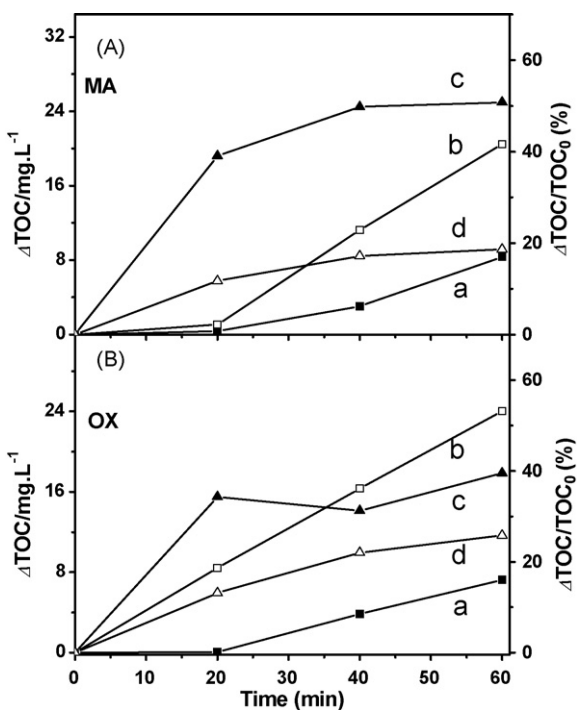


Fig. 10. Mineralization of 2.0×10^{-4} M Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ (a) in the dark, (b) under UV irradiation, (c) under visible irradiation, (d) in the presence of HQ in the presence of Al^{3+} with 5.0×10^{-4} M (A) malonic acid, (B) oxalic acid. $[\text{Al}^{3+}] = 2.0 \times 10^{-3}$ M. Note: The original TOC value of the Orange II solution combined with organic ligand was regarded as 100% on the percentage axis.

Fig. 10 presents the effects of Al^{3+} ions on the mineralization of Orange II in the presence of malonic acid and oxalic acid. Although the mineralization of Orange II was greatly depressed by non-aromatic organics (Fig. 8), there also had an excellent result in the presence of Al^{3+} ions; in other words, Al^{3+} ions eliminated the passivation of non-aromatic organics effectively.

3.8.1. In the presence of malonic acid

Al^{3+} ions greatly accelerated both the decoloration (Fig. 6A) and the mineralization of Orange II (Fig. 10A) in the presence of malonic acid, and the ΔTOC of the mineralization of Orange II in the dark was 8.37 mg/L in 60 min, twice than that without Al^{3+} ions. When HQ acted as the additive, the mineralization rate of Orange II was also doubled after adding the Al^{3+} ions into the reaction solution. Although HQ additive showed an excellent performance in the decoloration of Orange II in the presence of Al^{3+} ions, the mineralization rate of Orange II in the presence of Al^{3+} ions still maintained a similar level as that without HQ additive.

It is worth noting that Al^{3+} ions presents a quite good performance in mineralizing of Orange II under UV irradiation in the presence of malonic acid and the ΔTOC in 60 min reached 20.46 mg/L, almost four times than that without Al^{3+} ions. Although Al^{3+} ions did not greatly accelerate the UV photo-Fenton decoloration of Orange II, it did improve the mineralization rate of Orange II. Combination of Al^{3+} ions and UV irradiation eliminates the passivation of malonic acid available.

Under visible irradiation, Al^{3+} ions also improved the mineralization rate of Orange II in the presence of malonic acid. Although the chelation between Fe^{3+} ions and malonic acid did not block much the photo-induced electron transfer from excited dye to Fe^{3+} ions, it still affected the decoloration and the mineralization of Orange II. When Al^{3+} ions were introduced, the release of Fe^{3+} ions promoted the photo-induced electro-transfer from the excited dye to Fe^{3+} ions, which hastened the mineralization of the dye solution.

3.8.2. In the presence of oxalic acid

Similar results were also obtained in the presence of oxalic acid (Fig. 10B). With the introduction of Al^{3+} ion, ΔTOC of the dye solution increased from 3.80 and 3.61 mg/L to 7.26 and 11.67 mg/L in 60 min in the dark and in presence of hydroquinone, respectively. UV irradiation gave the best performance in mineralizing of Orange II in the presence of Al^{3+} ion, and had a ΔTOC of 24.03 mg/L in 60 min, which was almost similar with that absence Al^{3+} . But if we get rid of the photolysis of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, which also gave an apparent TOC removal, Al^{3+} ions improved the mineralization rate of Orange II obviously.

Al^{3+} additive induced a prominent enhancement about ΔTOC when visible irradiation was introduced: increased from 2.88 to 17.85 mg/L, 4.61 times than that in absence of Al^{3+} . Surely, Al^{3+} additive released Fe^{3+} , which benefited the electron transfer from excited dye to Fe^{3+} . The mineralization process significantly slower after 20 min, that was due to the entirely decoloration of dye.

4. Conclusions

Al^{3+} additive benefits much the Orange II degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in presence of the non-aromatic intermediates. The competitive complex of Al^{3+} with Fe^{3+} for the non-aromatic intermediates releases the free Fe^{3+} ion, which effectively eliminates the passivation of the non-aromatic intermediates. UV irradiation combined with Al^{3+} additive was found as the most favorable strategy for the mineralization of orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of the non-aromatic intermediates. However, if we just seek for the decoloration of wastewater, visible irradiation combined with Al^{3+} might have the best performance. Although hydroquinone-

like intermediate is regarded as the main reason of inducing the appearance of self-catalytic stage in degradation of neat Orange II by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, and hydroquinone accelerates much the decoloration of Orange II, it may be a gamble to introduce hydroquinone into the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system, as no obvious improvement was observed in mineralization of Orange II with hydroquinone additive under various conditions in this work.

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