

Photochemical Degradation of Dimethyl Phthalate by Fe(III)/tartrate/H₂O₂ System

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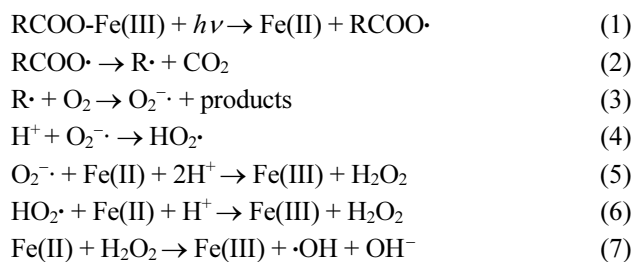
Photochemical degradation of dimethyl phthalate (DMP) in Fe(III)/tartrate/H₂O₂ system was investigated utilizing fluorescent lamps as the primary light source. Effects of initial pH, light source, and initial concentration of each reactant on DMP photodegradation was examined. The results show that the system was able to effectively photodegrade DMP utilizing visible light. Fluorescent lamp, halide lamp, UV lamp and sunlight could all be used as the light sources. The optimal pH ranged among 3.0–4.0 for the system. Increases of the initial concentrations of Fe(III) and H₂O₂ accelerated the photodegradation of DMP, whereas excessively high initial tartrate concentration resulted in the decrease of photodegradation efficiency and rate of DMP.

Key Words : Photochemical degradation, Ferric, Tartrate, H₂O₂, Dimethyl phthalate

Introduction

In recent years, various iron systems has been attracting extensive attention due to generating ·OH in photochemical process. Photo-Fenton system based on the mixed solution of Fe(III) and H₂O₂ is the most attractive one, which has been successfully applied in the processing of a variety of organic pollutants such as pesticides, dyes, textile wastewater, endocrine disrupting compounds, explosives owing to strong oxidative ability, high mineralization degree for medium-low concentrations of organic wastewater.^{1–6} However, photo-Fenton system commonly employs UV lamp as the light source, which will bring about extra energy consumption cost.

It has been reported recently that Fe(III) coordinated with some carboxylates and formed various complexes such as Fe(III)-citrate and Fe(III)-oxalate that decomposed by intensively absorbing visible lights at relatively higher wavelengths even up to 450 nm.^{7,8} The generated Fe(II) and carboxyl radicals underwent a secondary photochemical process and yielded ·OH, which eventually degraded the target organic matter.^{9–12} Main photochemical reactions of the Fe(III)-carboxylate complex are listed as follows:^{13,14}



Although Fe(III)-carboxylate is highly active in the photolysis under visible light, the complex cannot effectively degrade organic pollutants owing to the insufficient ·OH derived from the low concentration of H₂O₂ that is produced in the secondary photochemical process.

Fe(III) and tartrate are extensively distributed in natural aqueous phase, which can forms a 1:1 complex with the stability constant (logK) of 7.49 (25 °C).¹⁵ It is previously reported that photoproduction and determination of hydroxyl radicals in aqueous solutions of Fe(III)-tartrate complex.¹⁶ However, the application of photolysis characteristics of the complex has little been reported. This research investigated and determined the absorption of visible light by the Fe(III)-tartrate complex, to which was then added H₂O₂ to elevate its concentration in the system, establishing a novel Fe(III)/tartrate/H₂O₂ system. Then the feasibility and basic principles of the system in processing organic pollutants were studied utilizing an endocrine disruptor dimethyl phthalate (DMP) and fluorescent lamp as the model pollutant and primary light source (simulating the sunlight), respectively. The study deepened and enriched photochemical theory of Fe(III)-carboxylate complex and photo-Fenton reaction, clarified the migration and transformation of organic pollutants in the natural environment, and provided the theoretical and practical basis for application of iron system on the treatment of pollutants.

Experimental

Reagents. FeCl₃·6H₂O was utilized as the Fe(III) source. Sodium tartrate was used as the source of tartrate ligand. 30 wt % H₂O₂ aqueous solution was used. Solution pH values were adjusted by NaOH and HCl. Methanol used as the HPLC mobile phase was of chromatography grade, and all the other reagents were of analytical grade. Double distilled water was utilized throughout the experiment.

DMP was used as the pollution processing target. It is reported that the aqueous solubility of DMP is about 21–26 mmol·L⁻¹ (about 4000–5000 µg·mL⁻¹). However, levels DMP in environmental samples typically found in concentrations of ranged from µg·L⁻¹ to lower mg·L⁻¹. So, DMP concentration of 20.0 µmol·L⁻¹ (3.9 mg·L⁻¹) was mainly employed

in this study.

Apparatus. UV-3010 UV-vis spectrophotometer (Hitachi) was used to measure UV-vis spectra of solutions. LC-2010 high performance liquid chromatograph (Shimadzu) was used to determine the concentrations of DMP and $\cdot\text{OH}$ generated. Two 30 W fluorescent lamps ($\lambda_{\text{max}} = 410 \text{ nm}$) was used as the main light source for photochemical reactions unless specifically identified. Besides, a 250 W metal halide lamp ($\lambda_{\text{max}} \geq 365 \text{ nm}$, China), two 30 W UV lamps ($\lambda_{\text{max}} = 254 \text{ nm}$) and sunlight were also used instead of the fluorescent lamps to test the effects of light sources.

Experimental Procedure. Reaction solutions with desired concentrations were prepared in a dark room using Fe(III), tartrate, H₂O₂ and DMP stock solutions, and pH value of the solution was adjusted. The resulting solutions were then transferred into six 10 mL stoppered quartz cuvettes (cuvette capacity had been corrected), which were then irradiated. The solutions were sampled at different time intervals to determine DMP concentrations.

Analysis Methods. DMP concentrations were determined by HPLC. The conditions were listed as follows: SHIMADZU VP-ODS-C18 column (15 cm \times 4.6 mm, 5 μm), 50% (volume fraction) methanol solution was used as mobile phase, flow rate was set at 1.0 mL $\cdot\text{min}^{-1}$, column temperature was set at 25 $^{\circ}\text{C}$, UV detector wavelength was set at 228 nm, injection volume was 20 μL , retention time was 6.7 min. Concentrations of $\cdot\text{OH}$ generated during irradiation were determined utilizing 5.6 mmol $\cdot\text{L}^{-1}$ benzene as the scavenger that yielded phenol.¹⁷ The measured concentration of phenol was equivalent to the accumulated concentration of $\cdot\text{OH}$ within a selected time. The concentration of phenol was determined by HPLC fitted with a VP-ODS-C18 column in conjunction with a UV detector selected at 270 nm. Temperature of the column was set at 25 $^{\circ}\text{C}$. Mobile phase was methanol-water mixture (60/40, v/v) at a flow rate of 1.0 mL $\cdot\text{min}^{-1}$. Injection volume was 20 μL and retention time was 3.01 min.

Degradation efficiency of DMP (E) was calculated by following formula: $E (\%) = (1 - c/c_0) \times 100\%$, where c_0 is the initial concentrations of DMP, c is the residual concentration of DMP in the solution after t time of irradiation.

Results and Discussion

UV-Vis Spectra of Different Solutions. Fe(III) mainly exists as Fe-OH complexes primarily in the form of $\text{Fe}(\text{OH})^{2+}$ at pH 3.0. As shown in Figure 1, Fe(III) solution exhibited an absorption at 295 nm at pH 3.0. Upon the addition of sodium tartrate, the absorption apparently bathochromically shifted to 345 nm (Curve 4) due to the formation of Fe(III)-tartrate complex. Meanwhile, the absorbances of the Fe(III)-tartrate complex were all higher than those of the Fe(III)-OH complexes in the Fe(III) solution at the wavelengths ranging from 320-500 nm. Therefore, the photochemical activity of Fe(III)-tartrate complex outweighed that of Fe(III)-OH complexes in the range of 320-500 nm visible lights.

In addition, UV-vis spectra of the three mixed solutions of Fe(III)/tartrate (Curve 4), Fe(III)/tartrate/H₂O₂ (Curve 5) and

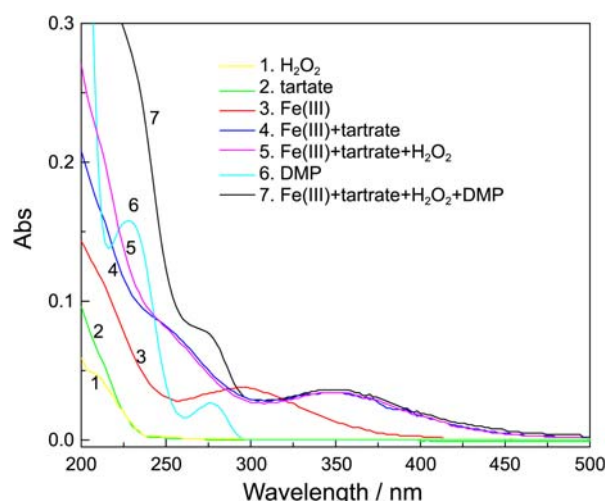


Figure 1. UV-vis spectra of different solutions. $c_0(\text{Fe(III)}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{tartrate}) = 100.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{H}_2\text{O}_2) = 400.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{DMP}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, pH = 3.0

Fe(III)/tartrate/H₂O₂/DMP (Curve 7) almost overlapped in the range of 300-500 nm. Thus, it was reasonable to conclude that light-absorbing substances in the above three solutions ranging from 300-500 nm all corresponded to the Fe(III)-tartrate complex.

Photodegradation of DMP by the Fe(III)/tartrate/H₂O₂ Complex System (Comparison Experiment). The comparison study of photolysis efficiencies of various Fe(III)/carboxylate complexes including Fe(III)/oxalate, Fe(III)/citrate and Fe(III)/tartrate was carried out, and the result showed that the concentrations of Fe(II) and $\cdot\text{OH}$ generated from photolysis of Fe(III)/tartrate system were higher than that of Fe(III)/oxalate and Fe(III)/citrate, which implied Fe(III)/tartrate system was superior to other systems (data is available in supplementary material).

Photodegradation efficiencies of DMP in different systems were investigated for comparison. DMP concentration was hardly affected after being directly irradiated for 100 min, even if tartrate was added, its concentration only slightly decreased. As shown in Figure 2(a), under irradiation for 100 min, the additions of H₂O₂, Fe(III), Fe(III) and tartrate, and Fe(III) and H₂O₂ degraded 7.8%, 11.2%, 47.4% and 64.2% of DMP, respectively. After Fe(III), H₂O₂, tartrate and DMP were mixed and left still in the dark room for 100 min, no concentration variations of DMP were detected (not shown in figures). However, 97.6% of DMP was degraded by being irradiated for 100 min.

In order to explain the different photodegradation ability of five systems including H₂O₂, Fe(III), Fe(III)/H₂O₂, Fe(III)/tartrate and Fe(III)/tartrate/H₂O₂, concentrations of $\cdot\text{OH}$ generated from the five systems were determined. Figure 2(b) shows that the concentrations of $\cdot\text{OH}$ generated by the five systems follow the ascending order: $\text{H}_2\text{O}_2 < \text{Fe(III)} < \text{Fe(III)/tartrate} < \text{Fe(III)/H}_2\text{O}_2 < \text{Fe(III)/tartrate/H}_2\text{O}_2$, which is consistent with the ascending order of the photodegradation of DMP. The concentration of $\cdot\text{OH}$ generated by the Fe(III)/tartrate/H₂O₂ system was 7.3 and 2.9 times larger than

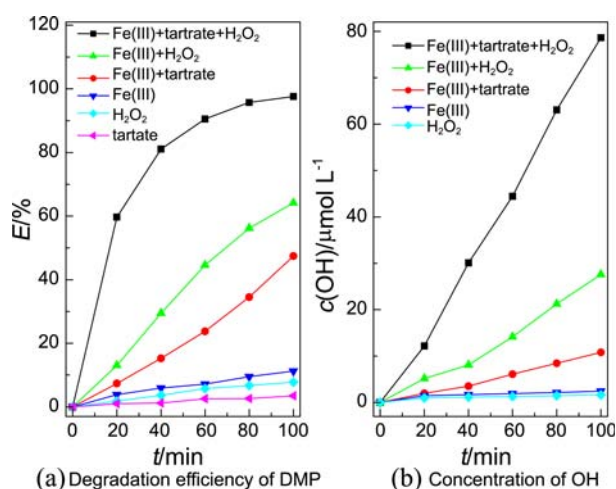


Figure 2. Degradation efficiency of DMP and concentrations of ·OH generated by various systems (comparison experiments). $c_0(\text{Fe(III)}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{tartrate}) = 100.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{H}_2\text{O}_2) = 400.0 \mu\text{mol}\cdot\text{L}^{-1}$, pH = 3.0, 3.8×10^4 Lux, (a) $c_0(\text{DMP}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, (b) $c_0(\text{C}_6\text{H}_6) = 5.6 \mu\text{mol}\cdot\text{L}^{-1}$

those generated by the Fe(III)/tartrate system and Fe(III)/H₂O₂ system at pH 3.0 after 100 min of irradiation, respectively. Therefore, the Fe(III)/tartrate/H₂O₂ system is more potent in the degradation of organic matter than the other systems.

The systems discussed above could degrade DMP owing to the generation of ·OH under irradiation. However, ·OH radicals were produced in different pathways, which led to different concentrations of ·OH that degraded DMP to various extents.

The concentrations of ·OH generated by the H₂O₂ solution were minimal, which could be attributed to ·OH derived from the photolysis of H₂O₂ ($\text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot\text{OH}$) by being irradiated with the light wavelength below 380 nm (some lights of fluorescent lamps were shorter than 380 nm).¹⁸ The concentrations of ·OH generated by the Fe(III) solution were also low, which could be attributed to weak photolysis of Fe(III)-OH complexes in Fe(III) solution under the irradiation of visible light following the equation $\text{Fe}(\text{OH})^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH}$.¹⁹

Photochemical reaction in Fe(III)/H₂O₂ system mainly included the photolysis of $\text{Fe}(\text{OH})^{2+}$ and the Fenton reaction that took place between Fe(II) and H₂O₂ (Eq. (7)) produced ·OH. The generation of ·OH was further accelerated by cycling of Fe(III)/Fe(II) in the system, whereas it was contrarily inhibited by the weak absorption of visible light by $\text{Fe}(\text{OH})^{2+}$.

Fe(III)-tartrate complex formed in the Fe(III)/tartrate system could absorb visible light and rapidly photolyze, generated ·OH following Eqs. (2)–(7), and then formed Fe(III)/Fe(II) cycling in the system. However, insufficient ·OH was produced owing to the limited generation of H₂O₂ in this system.

Although an extra addition of H₂O₂ in the Fe(III)/tartrate system did not change the generation pathway of ·OH, insufficient H₂O₂ was supplemented. As a result, the increase of H₂O₂ concentration in the system accelerated the reaction

in Eq. (7) as well as the cycling of Fe(III)/Fe(II), leading to the generation of more ·OH. Compared to the Fe(III)/H₂O₂ system, this system increased the concentration of Fe(II) by means of the rapid photolysis of the Fe(III)-tartrate complex under visible light, which resulted in the larger concentration of ·OH.

Effects of Initial pH on the Photodegradation of DMP.

Effects of initial pH on the photodegradation of DMP were investigated in range of pH 2.0–6.0. As shown in Figure 3, up to 97.6% and 91.9% of DMP could be degraded at pH 3.0 and 4.0 under the irradiation of 100 min. Excessively high or low pH values all inhibited the degradation of DMP in this system.

The concentrations of ·OH generated from Fe(III)/tartrate/H₂O₂ system with different initial pH value were measured after 100 min of irradiation. The results shown in Figure 3 indicated that the effects of initial pH on the concentration of ·OH generated was in accordance to that on the degradation of DMP.

The effects of initial pH on the photodegradation efficiencies of DMP can be explained by the following three reasons. First, Fe(III) in the solution was hydrolyzed more significantly at higher pH ($20.0 \mu\text{mol}\cdot\text{L}^{-1}$ Fe(III) may be hydrolyzed into $\text{Fe}(\text{OH})_3$ in the aqueous solution at pH ≥ 2.89 theoretically), which decreased the concentration of the Fe(III)-tartrate complex, resulting in the decreases of ·OH concentration and DMP degradation efficiency. Secondly, increased pH changed dissociation equilibrium of tartaric acid (25 °C: $K_{a1} = 9.20 \times 10^{-4}$, $K_{a2} = 4.31 \times 10^{-5}$), leading to increase of tartrate concentration in the solution (at 25 °C, distribution fraction of tartrate in the sodium tartrate solution is calculated as 9.49×10^{-4} at pH 3.00, whereas the value at pH 2.00 is calculated as 1/56 of the former one at 1.69×10^{-5}). The coordination between Fe(III) and tartrate was facilitated, which thus increased the concentration of Fe(III)-tartrate complex and further promoted the degradation of DMP. Thirdly, higher pH was conducive to the secondary photochemical process of the Fe(III)-tartrate complex that also promoted the degradation of DMP. In short, multiple

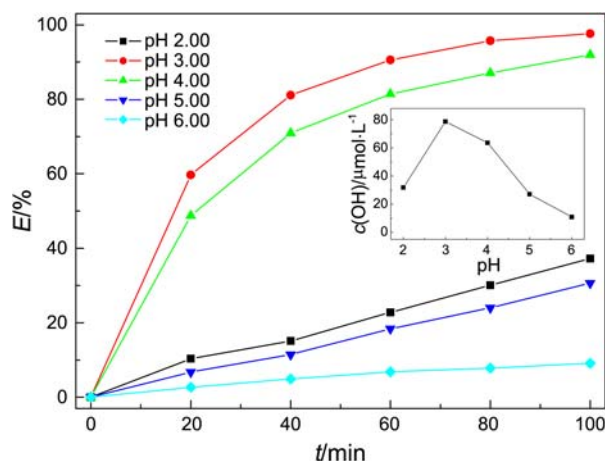


Figure 3. Effects of initial pH on the photodegradation of DMP. $c_0(\text{Fe(III)}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{tartrate}) = 100.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{H}_2\text{O}_2) = 400.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{DMP}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$

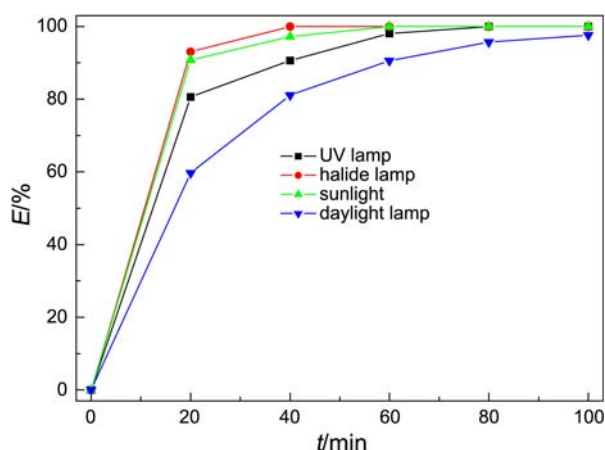


Figure 4. Effects of light sources on the photodegradation of DMP. $c_0(\text{Fe(III)}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{tartrate}) = 100.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{H}_2\text{O}_2) = 400.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{DMP}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, pH = 3.00

factors including the hydrolysis equilibrium of Fe(III), dissociation equilibrium of tartaric acid and secondary photochemical reaction of the Fe(III)-tartrate complex synergetically contributed to the influence of initial pH on DMP photodegradation.

Degradation of DMP Under Different Light Sources.

As shown in Figure 4, DMP concentration decreased by 97.6% when the mixed solution of Fe(III), H₂O₂, tartrate and DMP was irradiated under two 30 W fluorescent lamps (irradiation intensity was about 3.8×10^3 Lux) for 100 min. 100% of DMP was degraded under the irradiation of two 30 W UV lamps (irradiation intensity was $2.1 \times 10^3 \mu\text{W}\cdot\text{cm}^{-2}$) for 80 min. The reaction was significantly facilitated by being irradiated with the 250 W metal halide lamp (irradiation intensity was 5.4×10^4 Lux), the degradation efficiencies of DMP reached 93.0% and 100.0% after 20 min and 40 min, respectively. When the mixture was irradiated by the sunlight (cuvette was placed at an approximately 45° angle with the incident light of sunlight, irradiation intensity ranged among $5.2\text{--}5.4 \times 10^4$ Lux), the degradation efficiencies of DMP were 97.2% and 100.0% after 40 min and 60 min, respectively.

Although the light sources differ in irradiation intensities, wavelengths and irradiation ways that cannot be compared, they can all be used for the Fe(III)/tartrate/H₂O₂ system. Meanwhile, the system has also been verified to be able to utilize sunlight as the light source to save energy in the practical application. In this paper, fluorescent lamp was used instead to acquire a stable light source.

Effects of the Initial Concentrations of Each Reactant on the Photodegradation of DMP. Photodegradation efficiencies of DMP under different initial concentrations of reactants were detected at pH 3.0, and the experimental data was fitted with pseudo-first order kinetics equation $\ln C/C_0 = -kt$, pseudo-first rate constant k (min^{-1}) was obtained.

As shown in Figure 5(a) and (b), the degradation efficiencies and rate constants of DMP increased with increasing initial concentrations of Fe(III) and H₂O₂. In the presence of excessive tartrate, the increase of Fe(III) concentration actually

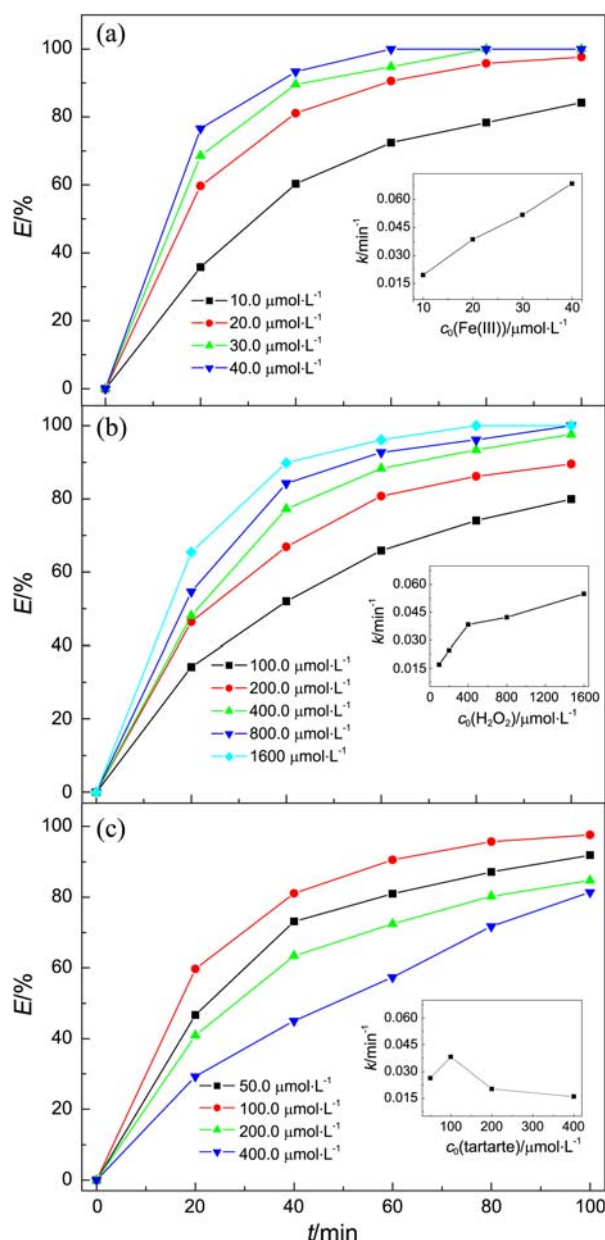


Figure 5. Effects of initial concentrations of each reactant on the photodegradation of DMP. $c_0(\text{Fe(III)}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{tartrate}) = 100 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{H}_2\text{O}_2) = 400.0 \mu\text{mol}\cdot\text{L}^{-1}$, $c_0(\text{DMP}) = 20.0 \mu\text{mol}\cdot\text{L}^{-1}$, pH = 3.00. (a) Effects of initial Fe(III) concentrations; (b) Effects of initial H₂O₂ concentrations; (c) Effects of initial tartrate concentrations.

increased the concentration of the Fe(III)-tartrate complex in the system, which inevitably increased the concentration of $\cdot\text{OH}$, leading to the increases of both degradation efficiency and degradation rate of DMP.

Figure 5(c) shows that when the initial tartrate concentration increased from $50.0 \mu\text{mol}\cdot\text{L}^{-1}$ to $100.0 \mu\text{mol}\cdot\text{L}^{-1}$, the degradation efficiency of DMP increased from 91.9% to 97.6% and the rate constant increased from 0.026 min^{-1} to 0.038 min^{-1} . Considering that Fe(III) and tartrate formed a 1:1 complex, excessive tartrate could re-coordinate with Fe(III) generated in the system, which thus facilitated the

cycling of Fe(III)/Fe(II) in the photoreaction. As a result, in the initial tartrate concentration range among 50.0-100.0 $\mu\text{mol}\cdot\text{L}^{-1}$, the degradation efficiency and rate of DMP increased with increasing initial tartrate concentration. However, when the initial tartrate concentration continuously increased to 400.0 $\mu\text{mol}\cdot\text{L}^{-1}$, the degradation efficiency and rate constant of DMP reversely reduced to 81.4% and 0.016 min^{-1} . The results may be ascribed to the increased $\cdot\text{OH}$ scavenging effect owing to the increase of tartrate concentration, which reduced the utilization of $\cdot\text{OH}$ and accordingly decreased the degradation efficiency and rate of DMP.

Conclusions

(1) Fe(III)-tartrate primarily absorbed light in the Fe(III)/tartrate/ H_2O_2 system, and the Fe(III)-tartrate complex outweighed Fe(III)-OH complexes in the utilization of visible light; (2) Degradation efficiency of DMP employing the Fe(III)/tartrate/ H_2O_2 system was higher than the Fe(III)/tartrate, Fe(III)/ H_2O_2 and Fe(III)-OH complex system. At the initial pH of 3.0, up to 97.6% of 20.0 $\mu\text{mol}\cdot\text{L}^{-1}$ DMP could be degraded by being irradiated with two fluorescent lamps for 100 min in the presence of the initial concentrations of Fe(III), tartrate and H_2O_2 at 20.0 $\mu\text{mol}\cdot\text{L}^{-1}$, 100.0 $\mu\text{mol}\cdot\text{L}^{-1}$ and 400.0 $\mu\text{mol}\cdot\text{L}^{-1}$, respectively; (3) At pH 3.00, the concentration of $\cdot\text{OH}$ generated by the Fe(III)/tartrate/ H_2O_2 system was 7.3 and 2.9 times larger than that generated by the Fe(III)/ H_2O_2 and Fe(III)/tartrate system, indicating that the former could oxidize organic matter more potently; (4) Fluorescent lamp, UV lamp, halide lamp and sunlight could all be used as the light sources for the Fe(III)/tartrate/ H_2O_2 system to effectively photodegrade DMP; (5) Optimal pH for the degradation of DMP utilizing the Fe(III)/tartrate/ H_2O_2 system ranged among 3.0-4.0; (6) Increases of the initial concentrations of Fe(III) and H_2O_2 could elevate the photodegradation efficiency and rate of DMP. Although the increase of initial tartrate concentration could increase the

degradation efficiency and rate of DMP to a certain extent, excessive tartrate would conversely decrease them.

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