Fenton Degradation of Malachite Green Catalyzed by Aromatic Additives

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Fenton degradation of malachite green (MG) catalyzed by various kinds of aromatic additives was examined. It was found that the aromatic additives exhibited catalysis immediately or after an induction period to accelerate the MG degradation in the Fenton reaction. EPR, GC−MS, and redox potential measurements were employed to obtain details of the reaction process. A reaction mechanism is proposed for the interaction between Fenton reagents (Fe^{2+}/Fe^{3+}, H_2O_2) and the aromatic compounds, which involves the generation and redox cycle of hydroquinone-like intermediates in the Fenton reaction. The Fenton reaction rates of MG after addition of various kinds of aromatic additives were in the following order: hydroquinone > salicylic acid > *p*-hydroxylbenzoic acid > *m*-hydroxylbenzoic acid > *p*-benzoquinone > carboxylic aromatics > amido aromatics, which is also quite consistent with their ability to be transformed into hydroquinone-like compounds. Hydroquinone-like compounds can react with ferric ions to regenerate ferrous ions and are regenerated continuously from quinone or semiquinone by reacting with $HO_2^{\bullet}$, which accelerates the Fenton reaction.

Introduction

The Fenton reaction has been proven to be an effective method to treat organic pollutants in wastewater.[1−4] The mechanism and kinetics of the Fenton reaction have been studied by many researchers.[3,5] The brief mechanism in the simple Fenton system involves the formation of hydroxyl and hydroperoxyl radicals as shown below:[6−8]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad k_1 = 58\ M^{-1}\ s^{-1} \tag{1}$$

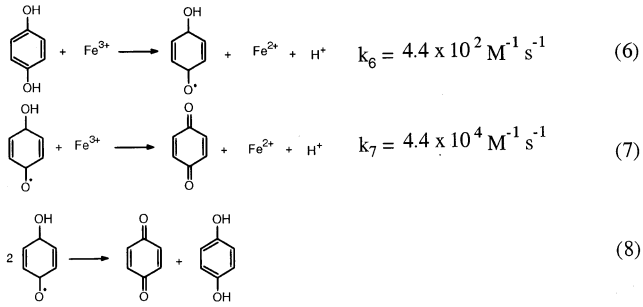
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad k_2 = 0.02\ M^{-1}\ s^{-1} \tag{2}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \tag{3}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \tag{4}$$

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{5}$$

However, organic compounds presented in the Fenton system greatly affect the rates of the reaction propagation.[9] Many kinds of inorganic and organic compounds can interact with the iron ions and hence greatly influence the mechanism and kinetics of the Fenton reaction. A few works had been done to observe the effects of additives such as Cl^-, $H_2PO_4^{3-}$ [10,11] and sodium oxalate[12,13] on the Fenton degradation of organic compounds. Hydroquinone has also been found to greatly catalyze the Fenton degradation of organic compounds,[14−16] which was attributed to the fact that it can quickly reduce ferric ions to ferrous ions, and hence accelerates the slow step of the Fenton reaction (eq 2).



Many aromatic compounds, such as phenol,[16] Orange II,[3] aniline[17] and benzene,[18] generate hydroquinone or hydroquinone-like intermediates by $^{\bullet}OH$ attack in the Fenton reaction. What is more, those aromatic compounds are common and abundant in the organic wastewaters, especially in the dye-contained wastewater. However, little work has been done to study the effect of those aromatic compounds on the Fenton reaction.

The present work studied the interaction between Fe^{2+}/Fe^{3+}, H_2O_2, aromatic additives, and the target pollutant (and its intermediates) and also the redox cycle of hydroquinone/quinone in the reaction. The details of the influence of the aromatic additives on the Fenton reaction were analyzed by observing the changes in the concentrations of MG (as a probe molecule), H_2O_2, and the additives and by measuring the redox potential variation of solution. EPR technique was used to detect the active radicals generated in the reaction solution. The Fenton degradation intermediates of the aromatic additives were analyzed with the GC−MS technique. A reaction mechanism is proposed for the interaction between the Fenton reagents and the aromatic compounds which involves the generation of hydroquinone or hydroquinone-like intermediates and the redox cycle of hydroquinone/quinone in the Fenton reaction. Aromatic derivatives are the main pollutants in wastewater; most dye-contaminated wastewaters contain various kinds of aromatic

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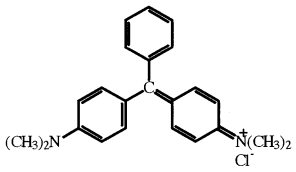
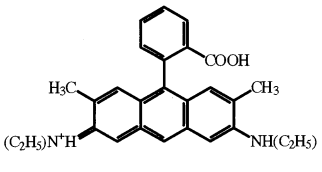
derivatives such as phenol and hydroquinone. A detailed study on their effect on the Fenton reaction would allow better understanding of the Fenton reaction mechanism and be significant and useful to apply the Fenton reaction to treatment of actual wastewater containing complicated components.

Experimental Section

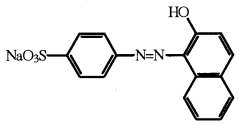
Materials. Malachite green (MG), Orange II, Rhodamine 6G, salicylic acid, *m*-hydroxylbenzoic acid, *p*-hydroxylbenzoic acid, 1,4-hydroquinone, 1,2-hydroquinone, resorcinol, *p*-benzoquinone, aniline, *o*-phthalic acid, sodium oxalate, potassium fluoride, ethylenediaminetetraacetic acid (EDTA), malonic acid, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 7H_2O$, and hydrogen peroxide were of laboratory reagent grade and used without further purification. Deionized and doubly distilled water was used throughout this study.



Malachite green (MG)



Rhodamine 6G (RD6G)



Orange II

Procedures and Analyses. Reaction solutions were freshly prepared from air-saturated stock solution of $FeCl_3$ (5 mM) at pH 1.9 and dye (0.1 mM) at pH 4.8 and adjusted to the desired pH with $HClO_4$ and NaOH solutions. All experiments were carried out under the following conditions: 1×10^{-4} M Fe^{3+}, 2×10^{-3} M H_2O_2, 1×10^{-5} M dye at pH 2.8 except mentioned elsewhere.

At the given reaction time intervals, samples (3.5 mL) were taken out and analyzed by measuring the UV−vis spectra of MG at 617 nm where MG is strongly absorbent (Orange II at 484 nm, RD6G at 525 nm) with a Lambda Bio20 UV−vis spectrophotometer (Perkin-Elmer Co.). The H_2O_2 concentration was determined by a photometric DPD (*N*,*N*-diethyl-*p*-phenylenediamine) method (λ = 551 nm, ϵ = 21 000 M^{-1}), in which the DPD reagent is oxidized by H_2O_2 based on the peroxidase catalyzed reaction in a phosphate buffer (pH = 6.8).[19,20] The fluorescence spectra were recorded with a F-4500 luminescence photometer. The fluorescence quenching of the target by iron ions was prevented by adding a specified amount of EDTA to the detected solution. A Brucker model EPR 300E spectrometer was used to measure the electron paramagnetic resonance (EPR) signals with the following setting: center field = 3486.70 G; sweep width = 100.0 G; microwave frequency = 9.82 GHz, and power = 5.05 mW. To minimize measurement errors, the same quartz capillary tube was used for all of the EPR measurements. All samples were analyzed immediately to avoid further reactions. The redox potential was recorded with a pHs-3C model pH meter with a Pt working electrode and a calomel reference electrode.

Results and Discussion

Fenton Degradation of MG and Orange II in Separate and Mixed Solution. Figure 1 shows the Fenton degradation of MG (1×10^{-5} M) and Orange II (1×10^{-5} M) separately and in mixture. These two dyes were selected because they have different molecular structures with little interference to each other in UV−vis detection. The degradation rates of both MG and Orange II were altered in the mixed Fenton system compared with the separated case: The degradation of MG in the mixed system was accelerated after an induction period, whereas that of Orange II was depressed to some extent. The depression of the degradation of Orange II can be attributed to the competitive trap of hydroxyl radicals by MG; however, the degradation of MG was surprisingly accelerated in the presence of Orange II. The results show that Orange II or some intermediates generated in the degradation of Orange II (an induction period at the beginning of the MG degradation implies that it is mostly some intermediates of Orange II) could accelerate the degradation of MG in the Fenton system. The disappearance of H_2O_2 in the MG or Orange II solution and in the mixed MG/Orange II solution is also shown in Figure 1b. To enlarge the relative change of the H_2O_2 concentration, the initial H_2O_2 concentration was reduced to 4×10^{-4} M in Figure 1b. The H_2O_2 concentration change in the mixed system was much greater than that in the MG system or in the controlled reaction but a little less than that in the Orange II system, which confirms that Orange II or some intermediates generated in the Orange II degradation promoted the disappearance of H_2O_2 and, hence, accelerated the generation of hydroxyl radicals and the degradation of MG in the Fenton system. These results showed that the Fenton degradation rate of the target compound and the H_2O_2 disappearance rate were closely related to the presence of other compounds (or intermediates). Because MG was found to have little influence on the H_2O_2 disappearance rate herein-

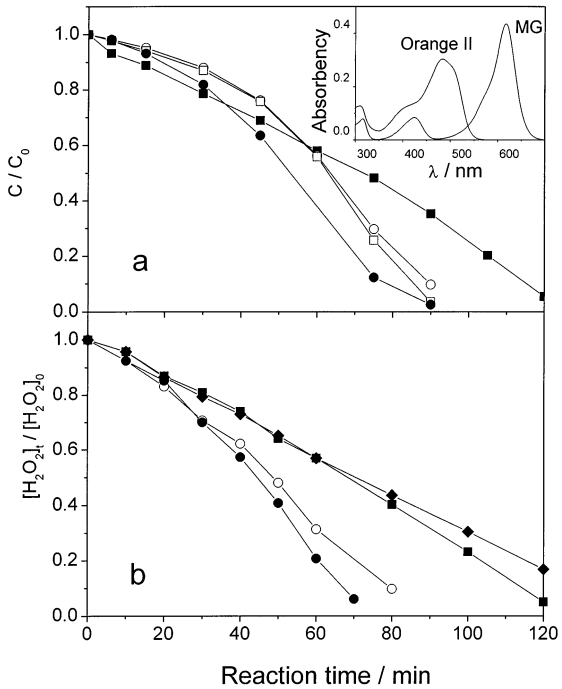


Figure 1. (a) Fenton degradation of MG (1×10^{-5} M) and Orange II (1×10^{-5} M). Fe^{3+}, 1×10^{-4} M; H_2O_2, 2×10^{-3} M. (■) MG degradation in the absence of Orange II; (□) MG degradation in a MG/Orange II mixed solution; (○) Orange II degradation in a MG/Orange II mixed solution; (●) Orange II degradation in the absence of MG. (b) Variations of the H_2O_2 concentration in the Fenton reaction. MG, 1×10^{-5} M; Orange II, 1×10^{-5} M; Fe^{3+}, 1×10^{-4} M; and H_2O_2, 4×10^{-4} M. (◆) in the absence of MG and Orange II; (■) in a MG solution; (●) in an Orange II solution; (○) in a MG/Orange II mixed solution.

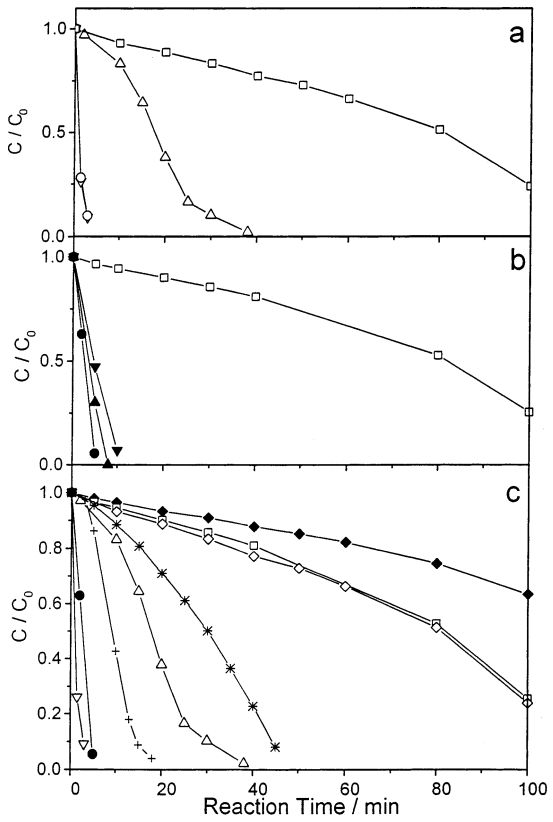
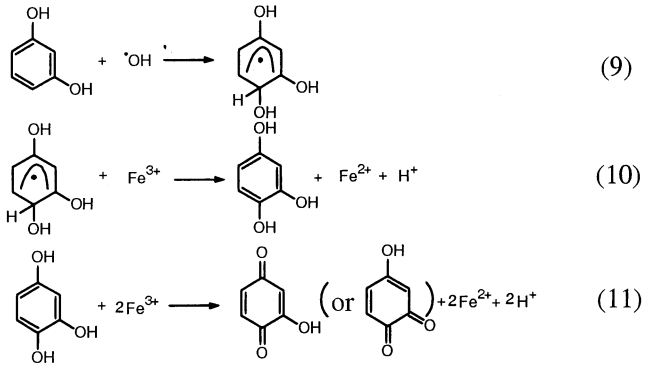


Figure 2. Fenton degradation of MG (1×10^{-5} M) in the presence of (a) hydroquinone (1×10^{-5} M), (b) hydroxybenzoic acids (1×10^{-5} M), (c) aromatic compounds (1×10^{-5} M). (□) Blank reaction; (▽) 1,4-hydroquinone; (○) 1,2-hydroquinone; (△) resorcinol; (▼) *m*-hydroxybenzoic acid; (●) salicylic acid; (▲) *p*-hydroxybenzoic acid; (◆) aniline; (◇) trimethylbenzylammonium chloride; (*) *o*-phthalic acid; (+) *p*-benzoquinone. Fe^{3+}, 1×10^{-4} M; H_2O_2, 2×10^{-3} M.

before, it was chosen as the target compound to examine the apparent Fenton reaction rate below.

The iron ions are the center of the Fenton reactions because the reactive radicals are produced by its redox reactions. The influence of organic compounds or their degradation intermediates on the activity of iron ions may be caused by their (i) complexing the iron ions as ligands or (ii) changing the redox cycle of iron ions as redox agents. In the previous studies, photolysis of Fe^{3+}−L complexes was found to greatly promote the Fenton reaction.[11,12] Photo-Fenton degradation of atrazine in the presence of oxalate was much faster than that in the absence of oxalate. However, the present work was wholly carried out in the dark. Many ligands such as F^-, PO_4^{3-}, EDTA, malonic acid, and oxalate, which do not belong to aromatic derivatives, were added into the Fenton reaction here. All of them showed a negative effect on the Fenton degradation of MG; in particular, those that complex with iron ions more tightly depressed the MG degradation more.

Fenton Degradation of MG in the Presence of Various Kinds of Aromatic Additives. Figure 2a shows the Fenton degradation of MG in the presence of 1,4-hydroquinone, 1,2-hydroquinone, and resorcinol. 1,2-Hydroquinone and 1,4-hydroquinone have been confirmed having an effect of assisted catalysis in the Fenton system for the degradation of organic compounds,[14,15] whereas another di-hydroxyl substituted benzene, resorcinol, was usually ignored in those studies. The study showed the Fenton reaction rate in the presence of resorcinol was much slower than that in the presence of 1,4-hydroquinone or 1,2-hydroquinone, although the addition of these compounds all greatly accelerated the Fenton reaction of MG. It was more interesting that the Fenton reaction of MG exhibited an initial induction period in the presence of resorcinol. The catalysis of 1,4-hydroquinone and 1,2-hydroquinone could be attributed to their reaction with ferric ions (eqs 6−8) in which ferrous ions were concomitantly regenerated and hydroquinones were transformed to quinones. Because of the molecular structure, resorcinol is unable to be directly oxidized by ferric ions into a quinone structure. However, resorcinol tends to be attacked by hydroxyl radicals in the Fenton reaction to generate a hydroxyl-substituted hydroquinone which can promote the Fenton reaction (eqs 9−11). Therefore, resorcinol also showed promotion to the Fenton reaction although it is much weaker than that in the presence of other two di-hydroxyl substituted benzene. The initial induction period in curve c in Figure 2a confirms that the resorcinol did not directly accelerate the reaction but the intermediates generated in the Fenton reaction accelerated the Fenton degradation of MG.



The Fenton degradation of MG in the presence of salicylic acid, *p*-hydroxybenzoic acid, and *m*-hydroxybenzoic acid are displayed in Figure 2b. The carboxyl group is a meta-orientating and inhibitory group to hydroxyl radical electrophilic substitution. A carboxyl group at the meta site of the phenol would be adverse to the attack of hydroxyl radicals on the para and ortho sites of phenol, which generates a hydroquinone intermediate. Because of the effect of the carboxyl group on the phenyl moiety, the abilities of these compounds to be transformed to hydroquinone-like compounds by the hydroxyl radicals were in the following order: salicylic acid > *p*-hydroxybenzoic acid > *m*-hydroxybenzoic acid. Their tendencies to accelerate the Fenton reaction of MG also entirely fit the same order.

Aniline and aniline-like compounds exist in the form of ammonium in the acidic media (the Fenton system). Ammonium on the phenyl ring is a strong inhibitory group for hydroxyl radical electrophilic substitution to the phenyl ring, and the positive charge on the molecule also reduces its interaction with the ferric ions. The process of aniline-like compounds being transformed into hydroquinone by hydroxyl radicals would be slower than the other kinds of aromatic compounds. Moreover, aniline added to the Fenton system would trap •OH radicals competitively with MG. The Fenton degradation of MG was depressed to some extent in the presence of the aniline in the initial induction period of MG degradation (about 100 minutes). The addition of aniline-like compounds is unfavorable to the Fenton reaction (Figure 2c) because they need a long induction period and are not easily transformed into hydroquinone-like intermediates. The Fenton degradation of MG in the presence of another ammonium compound, *N*,*N*,*N*-trimethylbenzylammonium chloride, was also carried out. Although the MG degradation in the presence of *N*,*N*,*N*-trimethylbenzylammonium

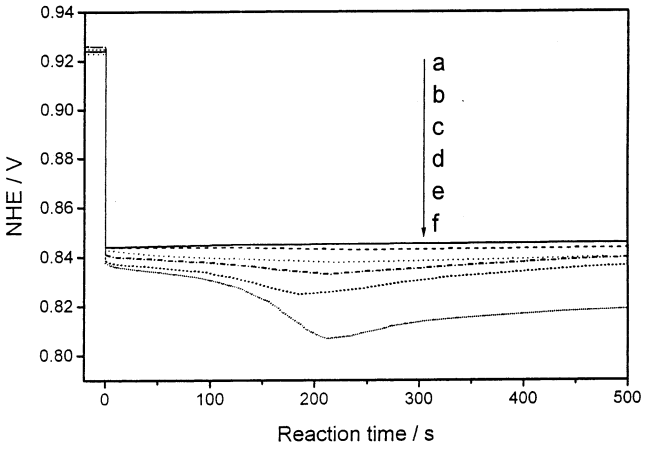


Figure 3. Variation of the Pt electrode potential in the presence of salicylic acid at different concentrations in the Fenton reaction. Fe^{3+}, 1×10^{-4} M; H_2O_2, 2×10^{-3} M. The concentration of salicylic acid: (a) 0; (b) 0.25×10^{-5} M; (c) 0.5×10^{-5} M; (d) 1×10^{-5} M; (e) 2×10^{-5} M; (f) 5×10^{-5} M. H_2O_2 was added into each reaction solution at the zero time.

chloride was slower than those in the presence of most other aromatic additives, it showed a quicker degradation rate than that in the presence of aniline. The adverse influence from the ammonium group was depressed by the methylene moiety between the phenyl and ammonium groups here.

It is more interesting that a great number of other aromatic compounds besides hydroquinone were also found to promote the Fenton reaction. Most of the aromatic additives, which were shown in Figure 2, accelerated the Fenton degradation of MG to some extent. It should also be noted that the degradation of MG in the presence of these aromatic compounds exhibited an induction period at the beginning of the reaction, which suggests some degradation intermediates of these aromatic compounds play a role to promote the Fenton reaction. The Fenton reaction rates of MG with various kinds of additives were in the following order: 1,4-hydroquinone ~ 1,2-hydroquinone > salicylic acid > *p*-hydroxylbenzoic acid > *m*-hydroxylbenzoic acid > *p*-benzoquinone > 1,3-hydroquinone > carboxylic aromatics > amido aromatics (in the form of ammonium in the acidic medium), which is surprisingly consistent with the order of their ability to be transformed into hydroquinone-like compounds.

Fenton Degradation of Dyes in the Presence of Salicylic Acid at Different Concentrations. To understand the details of the effect of these aromatic compounds, the changes of various factors in the Fenton reaction were studied in the presence of salicylic acid, which had been found to greatly promote the Fenton degradation of MG. The changes in the Pt electrode potential in the Fenton reaction are displayed in Figure 3. The Pt electrode potential continuously decreased with increasing the salicylic acid concentration, which means that a higher concentration of ferrous ions were formed which resulted in a quicker Fenton reaction rate. The initial decrease of the Pt electrode potential implies that at least one kind of intermediate of salicylic acid played an important role in the regeneration of ferrous ions in the Fenton reaction. The minimum and subsequent increase of the curve can be attributed to the destruction of the intermediates.

The Fenton degradation rates of MG (1×10^{-5} M) in the presence of salicylic acid at the different concentrations are shown in Figure 4a. The MG degradation rate greatly increased upon addition of salicylic acid with a maximum rate at about 2.5×10^{-5} M of salicylic acid and then decreased with further

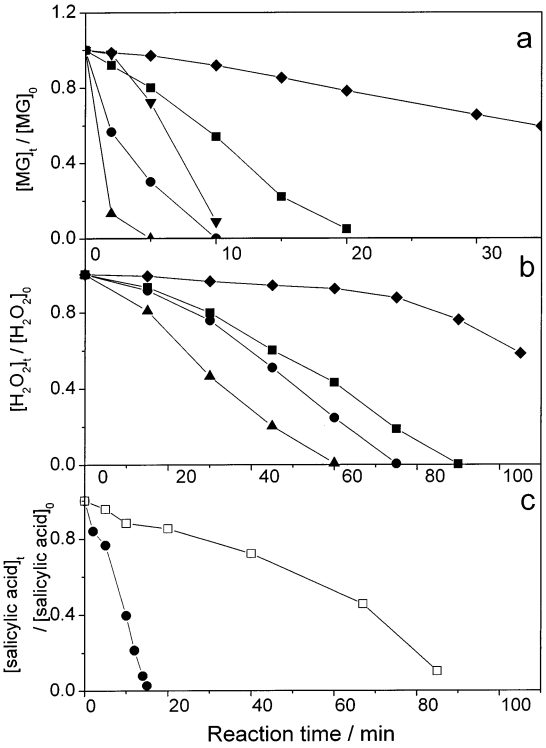


Figure 4. Concentration variations of (a) MG, (b) H_2O_2, and (c) salicylic acid in the Fenton degradation of MG (1×10^{-5} M) in the presence of salicylic acid at different concentrations. Fe^{3+}, 1×10^{-4} M; H_2O_2, 2×10^{-3} M (4×10^{-4} M for b). The concentration of salicylic acid: (◆) blank reaction; (□) 0.2×10^{-5} M; (■) 0.5×10^{-5} M; (●) 1×10^{-5} M; (▲) 2.5×10^{-5} M; (▼) 5×10^{-5} M.

increases of the salicylic acid concentration. The effect of salicylic acid is so great that it can significantly accelerate the Fenton reaction of MG at a very low concentration.

The hydrogen peroxide disappearance rate is an important index to indicate the Fenton reaction rate and can be used to confirm the conclusions obtained from the Fenton degradation of the dye. Figure 4b shows the variation of the H_2O_2 concentration in the Fenton degradation of MG in the presence of salicylic acid at various concentrations. The changes of the hydrogen peroxide disappearance rate had similar tendencies to that of the dye degradation rate in the Fenton reaction.

The variation of the salicylic acid concentration recorded with the fluorescence spectra in the Fenton reaction of MG is shown in Figure 4c. The *y* axis of Figure 4c was given as $[\text{salicylic acid}]_t/[\text{salicylic acid}]_0$ for readily comparing of the relative degradation rate of salicylic acid under various conditions. The salicylic acid decomposition was accelerated concomitantly with the degradation of the dye. The data show that salicylic acid in the Fenton reaction is not only a catalyst but also a reactant which was attacked by the hydroxyl radicals formed in the reaction process.

The Fenton degradation of Rhodamine 6G was also examined in the presence of different concentrations of salicylic acid. The results were similar to those of MG, indicating that the influence of salicylic acid on the Fenton reaction should be general for different target pollutants.

The results for the decomposition of dyes and salicylic acid, the disappearance of H_2O_2, and the changes in the Pt electrode potential show that the Fenton reaction rate of the target pollutant can be greatly influenced by additives owing to the interaction of the additives (or their degraded intermediates) with the iron ions, leading to significant changes in the generation of $^{\bullet}OH$ radicals (also see EPR results).

TABLE 1: GC−MS Data and Identified Molecular Structures of Intermediates Formed in the Fenton Degradation of Salicylic Acid

GC Peak	intermediates	relative time (min)	relative intensities of GC peak	MS data[a]						
A		5.17	1.1%	98 (5%)	54 (58%)	53 (11%)	28 (11%)	26 (100%)		
B		5.67	0.8%	106 (34%)	105 (15%)	91 (100%)	79 (18%)	77 (19%)	65 (16%)	51 (25%)
C	phenol	7.75	18.7%	94 (100%)	74 (4%)	66 (75%)	65 (40%)	55 (20%)	50 (17%)	39 (90%)
D	1,2-hydroquinone	11.78	17.4%	110 (80%)	92 (10%)	82 (17%)	81 (43%)	64 (100%)	63 (53%)	
E	2,5-dihydroxyl benzoic acid	13.14	1.9%	168 (13%)	154 (4%)	137 (9%)	136 (49%)	108 (29%)	80 (49%)	79 (24%)
F	salicylic acid	13.53	56.8%	138 (20%)	121 (7%)	120 (77%)	93 (8%)	92 (100%)	65 (22%)	64 (60%)
G	2,3-dihydroxyl benzoic acid	13.97	2.9%	168 (15%)	154 (6%)	137 (7%)	136 (51%)	108 (32%)	80 (57%)	79 (18%)

[a] The data in parentheses represent relative intensities.

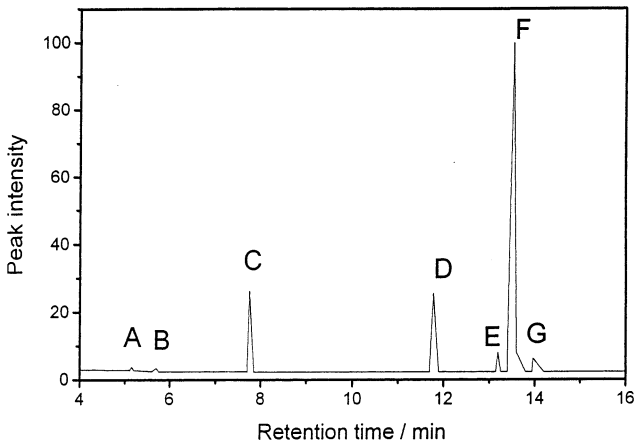


Figure 5. GC chromatogram of the GC−MS determination of the degraded intermediates in the Fenton oxidation of salicylic acid. Fe^{3+}, 1×10^{-4} M; H_2O_2, 2×10^{-3} M; and salicylic acid, 1×10^{-3} M. The peak intensity reflects MS detector response in single ion mode. Peaks A−G denote the intermediates produced in the degradation process. These peaks are defined in detail in Table 1.

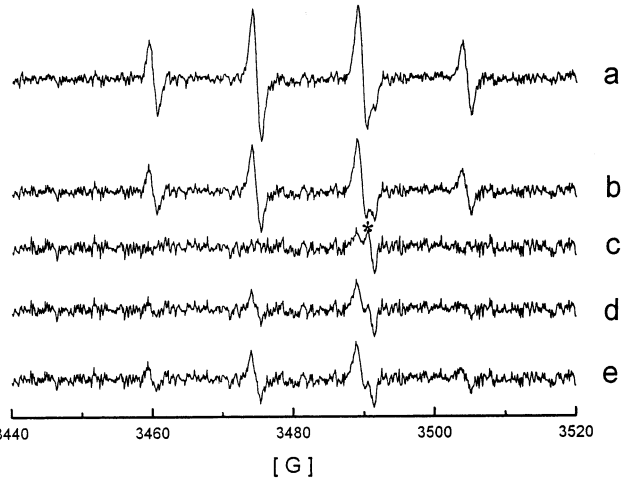


Figure 6. DMPO spin-trapping EPR spectra of hydroxyl radicals in the presence of additives (1×10^{-4} M). Fe^{3+}, 1×10^{-4} M; H_2O_2, 0.01 M; MG, 1×10^{-5} M; and DMPO, 0.1 M. (a) salicylic acid; (b) *o*-phthalic acid; (c) propane diacid; (d) $H_2PO_4^-$ ions; (e) blank reaction. *EPR signal of quartz capillary tube.

GC−MS Spectra. The GC−MS technique was used to analyze the intermediates of these additives in the Fenton reaction. The GC chromatogram of the GC−MS determination of the Fenton degradation of salicylic acid is shown in Figure 5. Besides the reactant (salicylic acid), six obvious peaks appeared in the GC chromatogram. Their structures identified from the MS data and contents are listed in Table 1. Some kinds of hydroquinone-like intermediate compounds, such as 1,2-hydroquinone, 2,5-dihydroxyl benzoic acid, and 2,3-dihydroxyl benzoic acid, were found in the reaction process; what is more, the amounts of these intermediates were relatively great in the Fenton reaction. Most of them should have catalysis in the Fenton reaction. GC−MS measurements for the Fenton degradation intermediates of other aromatic compounds also found the generation of hydroquinone-like compounds.

EPR Measurement. EPR is a convenient and effective technique to detect the formation of radicals or radical intermediates related to the Fenton reaction rate.[9,21] The DMPO spin-trapping EPR technique has confirmed that hydroxyl radicals are generated in the Fenton reaction. The amount of $^{\bullet}OH$ radicals formed is closely relative to the Fenton reaction rate. Figure 6 shows the DMPO spin-trapping EPR spectra in the presence of various kinds of additives. Comparing with the blank reaction, the intensity of the DMPO−$^{\bullet}OH$ signals changed greatly in the presence of various kinds of additives. Malonic acid and $H_2PO_4^{3-}$ ions depressed greatly the Fenton reaction by complexing with the iron ions, so that the DMPO−$^{\bullet}OH$ signal intensities were much lower. Salicylic acid and *o*-phthalic acid promoted the Fenton reaction as they were transformed into hydroquinone-like intermediates, which greatly increased the EPR signal intensities in the Fenton system. These tendencies agree well with those of the MG degradation rates above.

Catalytic Mechanism of the Aromatic Additives. It is surprising that so small of an amount of additives can continuously and significantly accelerate the Fenton reaction (for example, 5×10^{-6} M salicylic acid for 1×10^{-5} M MG, see Figure 4). Some other interesting phenomena were also found: (i) the promotion effect of the hydroquinone on the Fenton reaction is continuous in the whole reaction process although the hydroquinone would be quickly exhausted by the ferric ions at the beginning of the reaction; (ii) *p*-benzoquinone also showed good catalysis in the Fenton degradation of MG even though it does not react with the ferric ions. These two phenomena could be explained by the potential data for the reactions[22,23]

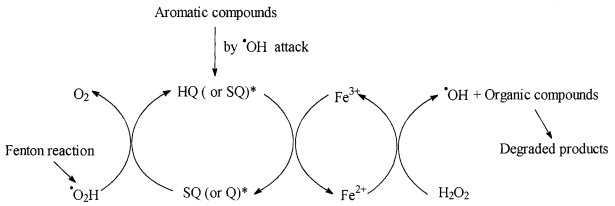
$$HO_2^{\bullet}(aq) + H^+ + e \rightarrow H_2O_2(aq) \qquad 1.44\ V \qquad (12)$$

$$O_2 + H^+ + e \rightarrow HO_2^{\bullet}(aq) \qquad -0.046\ V \qquad (13)$$

$$p\text{-benzoquinone} + 2e + 2H^+ \rightarrow p\text{-hydroquinone} \quad 0.6992\ V \qquad (14)$$

Although H_2O_2 does not directly react with *p*-benzoquinone to produce semiquinone or hydroquinone, $HO_2^{\bullet}$ radicals are generated through the Fenton reaction (eqs 2 and 5) and abundant in the Fenton system. Semiquinone or hydroquinone

SCHEME 1: Catalytic Mechanism of Aromatic Compounds in the Fenton Degradation of Organic Compounds



are regenerated by the reaction between quinone and the $HO_2^\bullet$ radicals:[23,24]

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \quad (2)$$

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \quad (5)$$

$$HO_2^\bullet + \text{quinone} \rightarrow \text{semiquinone} + O_2 \qquad k_{15} = 1 \times 10^9\ M^{-1}\ s^{-1} \quad (15)$$

$$HO_2^\bullet + \text{semiquinone} \rightarrow \text{hydroquinone} + O_2 \qquad k_{16} = 1 \times 10^9\ M^{-1}\ s^{-1} \quad (16)$$

$$2\ \text{semiquinone} \rightarrow \text{hydroquinone} + \text{quinone} \quad (17)$$

Therefore, the hydroquinone added or generated in the Fenton reaction was not one-off in the Fenton reaction but continuously regenerated through the reactions between quinone (or semiquinone) and $HO_2^\bullet$. As a result, quinone can also promote the Fenton reaction and hydroquinone can continuously and greatly catalyze the Fenton reaction. A brief mechanism is showed in Scheme 1. The proposed mechanism explains well the significant catalysis of these aromatic organic additives in the Fenton reaction.

MG is also an aniline-like compound, which needs a long induction period to generate hydroquinone-like intermediates. Orange II can be regarded as a phenol-like compound. Compared to MG, Orange II is more quickly transformed into hydroquinone-like compounds with a much shorter induction period. When Orange II and MG coexist in the Fenton system, the Orange II degradation rate would be depressed and the MG degradation rate would be accelerated after a shorter induction period in which some hydroquinone-like intermediates were generated from the Fenton degradation of Orange II, which explains well the results in Figure 1.

Conclusions

Aromatic compounds can catalyze the Fenton reaction when they are transformed into hydroquinone-like intermediates by hydroxyl radicals. Their capability to promote the Fenton reaction is closely related to their easiness to be transformed into hydroquinone-like intermediates. Hydroquinone-like compounds significantly promote the Fenton reaction by accelerating the regeneration of ferrous ions which is the slow step (eq 2) in the mechanism of the simple Fenton reaction. On the other hand, the hydroquinone-like compounds are continuously regenerated from quinone or semiquinone by reacting with $HO_2^\bullet$ to continuously promote the Fenton reaction.

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