J. Phys. Chem. A **2004,** *108,* 2675−2681

Oxidation of Safranine T in Aqueous Solution Using Fenton's Reagent: Involvement of an Fe(III) Chelate in the Catalytic Hydrogen Peroxide Oxidation of Safranine T

P. K. Malik*

Department of Chemical Engineering, Jadavpur University and Centre for Surface Science, Department of Chemistry, Jadavpur University, Kolkata 700032, India

Received: September 22, 2003; In Final Form: December 16, 2003

This study addresses the chemistry and kinetics of oxidation of a basic dye, Safranine T (C. I. Basic Red 2) by the classic Fenton's reagent (Fe^{2+} and H_2O_2). The kinetic study suggests that the chemistry involved in this system differs to some extent from that reported for the classic Fenton's chemistry in aqueous solution. Thus, participation of an Fe(III)−organic complex in the catalytic decomposition of H_2O_2, thereby producing an active oxidant, seems to be a step in the oxidation mechanism. Stoichiometric measurements of the hydrogen peroxide consumption per mole of Fe^{2+} used, poor oxidation of dye by the combination of Fe^{3+} and H_2O_2, and the formation of a shoulder at around 385 nm suggest a possible formation and participation of an Fe(III)−organic complex. The oxidation data indicates that Safranine T can be most effectively oxidized at a pH of around 3. The Fe(III) chelate catalyzed peroxide oxidation of Safranine T follows pseudo-first-order kinetics. The activation energy for the Fe(III) chelate catalyzed peroxide oxidation of the dye was determined to be 75.91 kJ mol^{-1}.

Introduction

Generation of hydroxyl radicals by the Fe^{2+}-catalyzed decomposition of hydrogen peroxide (known as the Fenton reaction) in the dark has been the subject of numerous studies during the past decade.[1−4] The oxidizing species generated in the Fenton reaction have been discussed by many investigators, but are still controversial[5−10] The participation of the hydroxyl radical as the active oxidant is not yet universal, and doubts as to its very existence in the system have been raised.[7,10] In classic Fenton's chemistry, it is generally considered that the reaction between hydrogen peroxide and Fe^{2+} in acidic aqueous medium (pH ≤3) produces hydroxyl radicals [eq 1] and can involve the reactions, which are presented below [eqs 1−6].[5,11−13] The rate constants are reported at 298 K in $M^{-1}\ s^{-1}$ for a second-order reaction rate.[14,15]

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \qquad k_1 = 63 \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + Fe^{2+} \qquad k_2 = 0.002{-}0.01 \qquad (2)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad k_3 = 3 \times 10^8 \qquad (3)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HOO^{\bullet} + H_2O \qquad k_4 = 2.7 \times 10^7 \qquad (4)$$

$$Fe^{2+} + HOO^{\bullet} \rightarrow Fe^{3+} + HOO^- \qquad k_5 = 1.2 \times 10^6 \qquad (5)$$

$$Fe^{3+} + HOO^{\bullet} \rightarrow O_2 + H^+ + Fe^{2+} \qquad k_6 < 2 \times 10^3 \qquad (6)$$

The hypothesis of Haber and Weiss[16] that the Fenton reaction involves the formation of hydroxyl radical as the actual oxidant has been proved by many techniques, including electron paramagnetic resonance (EPR) spin-tapping technique. Although several researchers have offered evidence for the formation of the hydroxyl radical as the principle active oxidant in the Fenton system,[17−19] it has also been reported by others[20] that this species is not only the active oxidant but that some type of high-valent iron-oxo species also exists.[7,10,21−23] Yamazaki and Piette[24] observed three types of oxidizing species (free hydroxyl radical, bound hydroxyl radical, and high-valence iron species, which is probably a ferryl ion, $Fe^{IV} = O$) using EPR spin-trapping. Kremer[25] hypothesized the formation of "FeO^{3+}" in dark Fe(III)/H_2O_2 reactions.

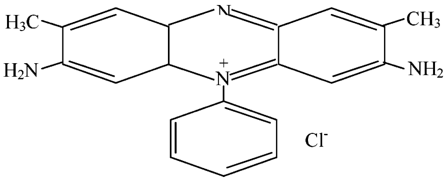

Figure 1. Structure of Safranine T.

This study is aimed at understanding the chemistry and kinetics of oxidation of a basic dye, Safranine T, in aqueous solution by the Fenton's reagent. The role of some conditions such as pH, initial [H_2O_2] and [Fe^{2+}], and temperature were examined in order to provide a full description of this system. Due to the importance as an environmental pollutant, Safranine T was selected for the study.

Materials and Methods

Safranine T was provided by Aldrich (purity, ~95%) and used as received. Figure 1 displays the structure of this dye. Ferrous sulfate and hydrogen peroxide (purity, 30%) were an AR grade product of E. Merck (India). The rest of the used reagents were at least reagent grade and purchased from E. Merck (India). Aqueous solutions used for oxidation reactions were prepared with double distilled water.

---

* To whom correspondence should be addressed. Phone: +91-33-24146411. Fax: +91-33-24146266. E-mail: pkmd14@yahoo.co.in.

10.1021/jp031082r CCC: $27.50

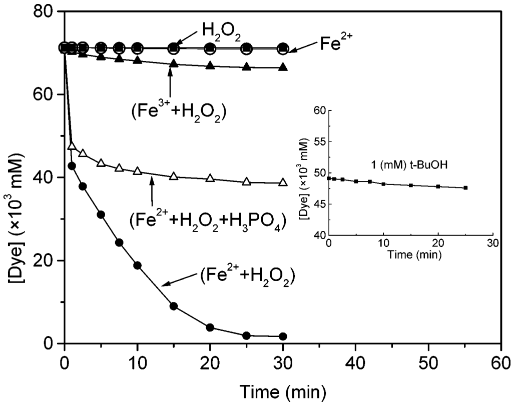

Figure 2. Time-dependent changes in the concentration of Safranine T on treatment with various reagents. Inset, changes in [dye] on addition of t-BuOH after initiation of the second stage oxidation by the Fenton's reagent. Experimental conditions: $[Fe^{2+}]_0$ or $[Fe^{3+}]_0 = 4.46 \times 10^{-2}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; pH = 3; temperature = 30 °C.

Reaction mixtures were prepared in 100 mL beakers by taking an appropriate amount of stock dye solution followed by adding ferrous ion and diluting with double distilled water to 25 mL, and adjusting the pH to 3. After the adjustment of pH, the solution was placed in a thermostated water-bath at 30 °C. Stirring was provided by a magnetic stirrer. The reactions were initiated by adding hydrogen peroxide. After initiating the reaction, the reaction mixture was taken in a spectrometric quartz cell (1 cm path length) and the changes in the absorbance with time were measured. The cell was kept at a temperature of 30 °C maintained by a water-bath throughout the experiment. A Shimadzu (Japan) UV−vis spectrophotometer (model 160A) was used for absorbance measurements. The concentrations of the dye in the reaction mixture at different times were determined by measuring absorbances at maximum wavelength (λ_{max} = 520 nm) and computing concentrations from the calibration curve. The effect of each parameter was studied by fixing the values of other parameters. Dilute H_2SO_4 and NaOH were used for pH adjustment.

Hydrogen peroxide was analyzed by an iodometric titration with $Na_2S_2O_3$ solution.[26] Ferrous ions were tested by the phenanthroline method.[27] Concerning the measurement of ferrous and hydrogen peroxide, separate experiments were conducted in beakers.

Results and Discussion

Change of Concentration of Safranine T with Time. In Figure 2, the results obtained by treating the Safranine T with H_2O_2 alone, Fe^{2+} alone, and Fenton's reagent ($Fe^{2+} + H_2O_2$) are reported. The results indicate that the concentration of Safranine T remained constant after a reaction time of 30 min with Fe^{2+} alone. On the other hand, H_2O_2 utilized alone yielded very poor oxidation of Safranine T, although H_2O_2 has an oxidation potential of 1.77 V. In combination, however, H_2O_2 and Fe^{2+} brought about a drastic reduction in the concentration of Safranine T. Results from the experiment showed that Safranine T was oxidized by the Fenton's reagent rapidly in the first minute and somewhat less rapidly after that time period. The reason for the rapid oxidation in the first minute may be explained by the fact that a large amount of hydroxyl radical, which is a powerful oxidant, is generated quickly by the reaction of H_2O_2 and Fe^{2+} (eq 1), making possible the swift oxidation of Safranine T in the first minute of reaction.

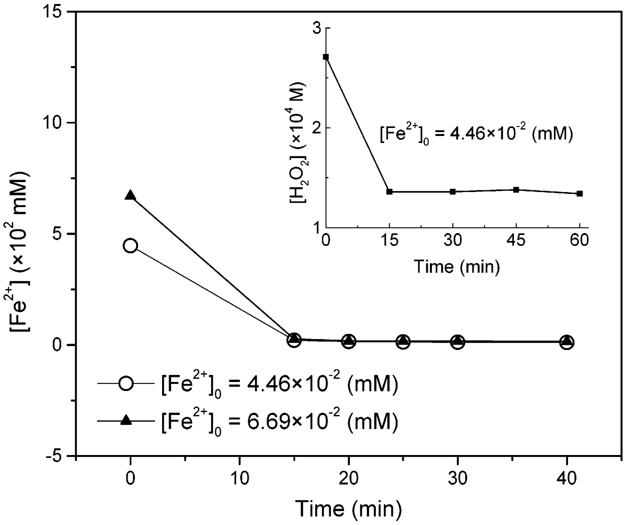

Figure 3. Time-dependent changes in $[Fe^{2+}]$ during the oxidation. Inset, time-dependent changes in $[H_2O_2]$ during the oxidation. Experimental conditions: $[dye]_0 = 71.3 \times 10^{-3}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; pH = 3; temperature = 30 °C.

Fe(III) has lower catalytic activity than Fe(II) and may form a complex with the degradation intermediates.[28−30] The hydroperoxyl radical is largely unreactive toward organic compounds.[31] Also, the Haber−Weiss cycle (eqs 7−9)

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{7}$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+ \qquad k_8 = 3 \times 10^8 \tag{8}$$

$$O_2^{\bullet -} + H^+ + H_2O_2 \rightarrow O_2 + {}^{\bullet}OH + H_2O \tag{9}$$

does not constitute an effective source of $^{\bullet}OH$ radical in aqueous solution containing F(II)/Fe(III) and H_2O_2 under any conditions.[32] Consequently, the oxidation rate after the first minute of reaction should be very slow due to the slow production of Fe(II) from Fe(III). The detection of ferrous ions (Figure 3) supports the lower generation of Fe(II) from Fe(III). Furthermore, the experiment in combination of Fe^{3+} and H_2O_2 under the same conditions shows poor bleaching of the dye (Figure 2). Thus, it may be hypothesized that the oxidation of dye in the first minute produces some intermediate which is capable of forming a complex with Fe(III). This Fe(III)−organic complex is able to produce an active oxidant by catalyzing the hydrogen peroxide decomposition faster than the ferric aquo-complexes do and, thus, continues the oxidation of dye after the first minute reaction.

To confirm the formation of Fe(III)−organic complex, UV−vis spectra of solutions were performed. Figure 4a shows spectra from H_2O_2 only, dye only, a mixture of Fe^{2+} and H_2O_2, a mixture of dye and H_2O_2, and a mixture of Fe^{3+} and dye at pH 3. Figure 4b shows spectra from oxidation of the dye by the Fenton's reagent at different times. It can be clearly seen from these figures that oxidation of the dye results in the formation of a shoulder at around 285 nm. In the absence of dye under otherwise identical conditions, the mixture of Fe^{2+} and H_2O_2 exhibits an absorption maximum at 300 nm (Figure 4a). The shoulder at 285 nm may be ascribed to the formation of Fe(III)−organic complex.

Addition of phosphoric acid to the solution of the Fe(III)−organic complex (pH becomes 2.45) obtained after 30 min oxidation results in the blue shift of the shoulder toward attaining a Fe(III)−phosphate nature (Figure 5). Furthermore, addition of solid ammonium bifluoride to the solution of Fe(III)−organic complex, whence its pH becomes 4.7, suitable for the formation

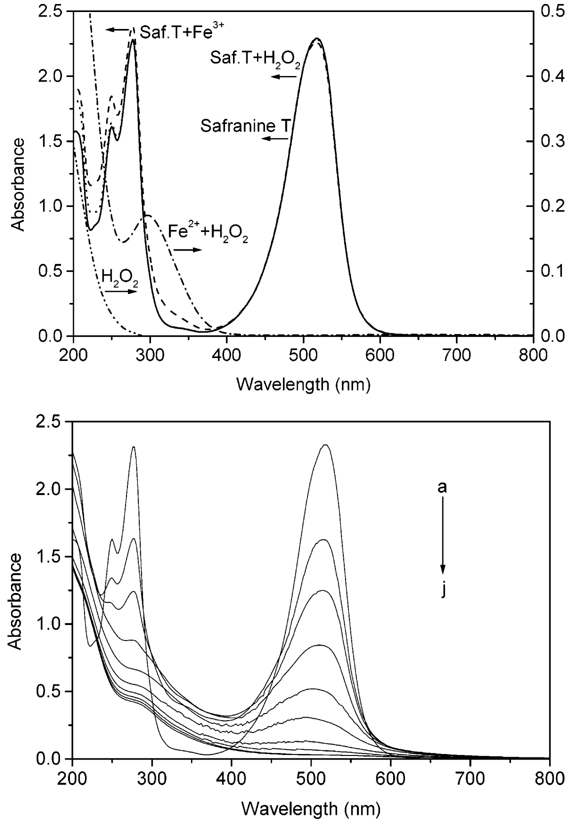

Figure 4. (a) UV−visible spectra of the studied system in aqueous solution. Experimental conditions: $[dye]_0 = 85.5 \times 10^{-3}$ mM; $[Fe^{2+}]_0$ or $[Fe^{3+}]_0 = 4.46 \times 10^{-2}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; pH = 3; temperature = 30 °C. (b) Time-dependent changes in UV−Visible spectra of Safranine T on oxidation by the Fenton's reagent ($a = 0$, $b = 1$, $c = 5$, $d = 10$, $e = 15$, $f = 20$, $g = 25$, $h = 30$, $i = 35$, $j = 60$ min). Experimental conditions: $[dye]_0 = 85.5 \times 10^{-3}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; $[Fe^{2+}]_0 = 4.46 \times 10^{-2}$ mM; pH = 3; temperature = 30 °C.

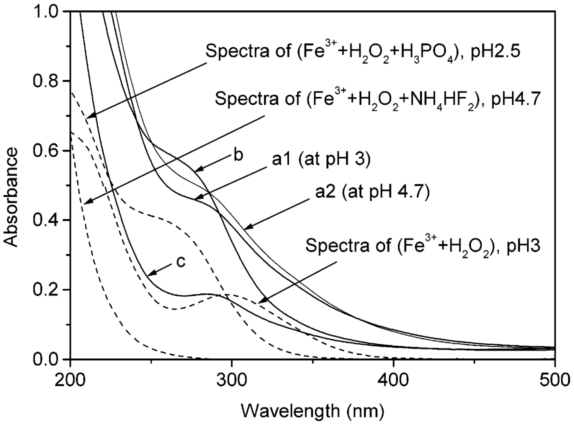

Figure 5. UV−visible spectra of the aqueous solution of Fe(III)−organic complex before (curve a1 and a2) and after addition of H_3PO_4 (curve b) or NH_4HF_2 (curve c). Experimental conditions: $[dye]_0 = 85.5 \times 10^{-3}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; $[Fe^{2+}]_0$ or $[Fe^{3+}]_0 = 4.46 \times 10^{-2}$ mM; pH = 3, otherwise mentioned; temperature = 30 °C.

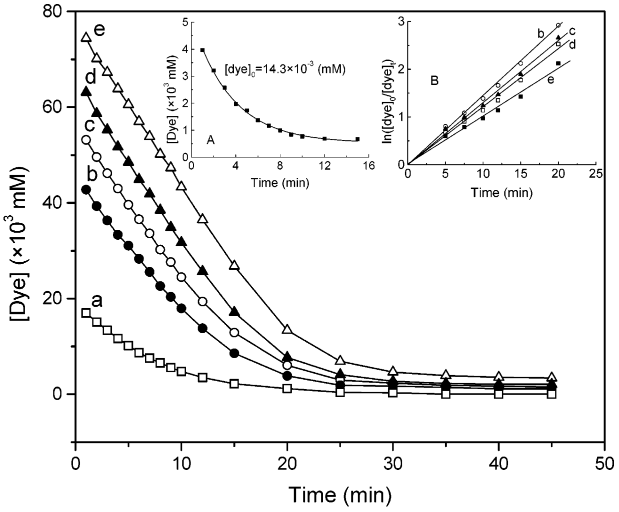

Figure 6. Effect of initial concentration of dye on oxidation ($a = 71.3 \times 10^{-3}$, $b = 85.5 \times 10^{-3}$, $c = 99.8 \times 10^{-3}$, $d = 114 \times 10^{-3}$ mM). Inset (B), kinetics of Fe(III) chelate catalyzed peroxide bleaching of Safranine T monitored at 520 nm. Experimental conditions: $[Fe^{2+}]_0 = 4.46 \times 10^{-2}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; pH = 3; temperature = 30 °C.

of Fe(III)−fluoride complexes,[33] results in a decrease of absorbance of the shoulder for the Fe(III)−organic complex (Figure 5). These results suggest the formation of an Fe(III)−organic complex of stability lower than those of Fe(III)-phosphate or Fe(III)−fluoride complexes. The existence of such Fe(III)−organic complexes having stabilities lower than those of the Fe(III)−phosphate or Fe(III)−fluoride complexes has been reported in the literature.[34] Additionally, the oxidation of the dye by the Fenton's reagent in the presence of phosphoric acid under otherwise identical conditions of reaction exhibits almost cessation of the second stage oxidation. Therefore, the formation of the active Fe(III)−organic complex and its role in the oxidation of Safranine T can be suggested. It has been reported that some Fe(III)−organic chelators can catalyze the hydrogen peroxide decomposition, thereby accelerating the degradation of organic compounds.[31,35−37]

Researchers have firmly established that complexes of Fe(III) with organic ligands (e.g., porphyrin and pyridyl-type) may react with peroxides or other oxidants to form a high-valent oxoiron (ferryl) species, Fe=O, where iron is formally in the +IV or +V oxidation state[20,37,38] and the species is capable of oxidizing organic compounds.[1−3,29,30] To determine the nature of the oxidant, the second stage reaction was repeated with the addition of t-BuOH (1 mM) which is a well-known scavenger for the hydroxyl radical or ferryl species.[40] The results, shown in the inset in Figure 2, bring out the cessation of the second stage reaction. These data confirm that only the hydroxyl radical and/or ferryl species and no other transient oxygen species are involved in the Fe(III) chelate catalyzed peroxide oxidation of the dye.

It can be seen from Figure 3 (inset picture) that 1.36×10^{-4} M hydrogen peroxide is utilized at the end of the process. The consumption ratio of hydrogen peroxide to ferrous ions is higher than the anticipated 1:1. Experimentally, it has been found that Safranine T hardly oxidized at all in the duration of 30 min if only hydrogen peroxide is used. Because reaction 2 is a very slow process, the consumption of hydrogen peroxide by the ferric ions can be neglected. The above result can be ascribed to the catalytic decomposition of hydrogen peroxide by the Fe(III)−organic complex. Cessation of the reaction after the first minute on using the initial almost 1:1 H_2O_2 and Fe^{2+} concentration suggests the above mechanism. Rivas et al.[41,42] reported the consumption of hydrogen peroxide by its catalytic decomposition with the Fe(III)−organic complex during the oxidation of *p*-hydroxy benzoic acid using the Fenton-like system.

Experiments carried out at different initial dye, Fe^{2+} and H_2O_2 concentrations (Figures 6−8) showed that a steady oxidation rate is maintained in the second stage for the initial concentration ratios of $[Fe^{2+}]/[dye] < 1$ and $[H_2O_2]/[Fe^{2+}] > 3$. When the

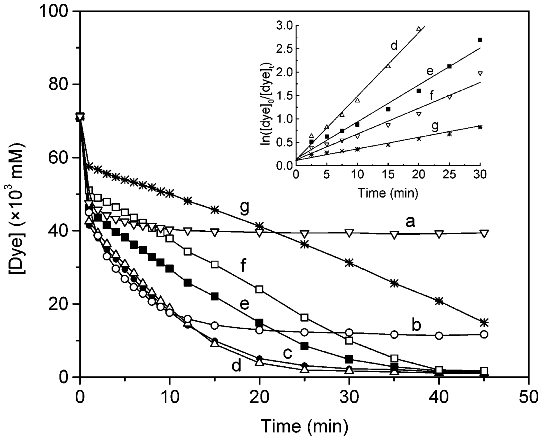

Figure 7. Effect of initial concentration of H_2O_2 on oxidation of Safranine T ($a = 0.39 \times 10^{-4}$, $b = 0.68 \times 10^{-4}$, $c = 1.36 \times 10^{-4}$, d $= 2.71 \times 10^{-4}$, e $= 5.43 \times 10^{-4}$, f $= 10.86 \times 10^{-4}$, g $= 21.72 \times 10^{-4}$ M). Inset, kinetics of Fe(III) chelate catalyzed peroxide bleaching of Safranine T monitored at 520 nm. Experimental conditions: $[Fe^{2+}]_0 = 4.46 \times 10^{-2}$ mM; $[dye]_0 = 71.3 \times 10^{-3}$ mM; pH = 3; temperature = 30 °C.

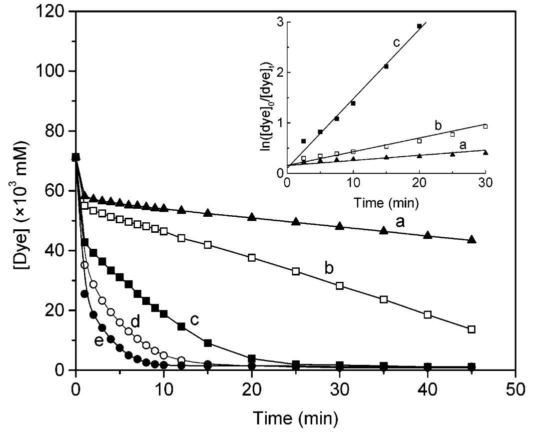

Figure 8. Effect of initial concentration of Fe^{2+} on oxidation of Safranine T ($a = 0.89 \times 10^{-2}$, $b = 2.23 \times 10^{-2}$, $c = 4.46 \times 10^{-2}$, d $= 6.69 \times 10^{-2}$, e $= 8.93 \times 10^{-2}$ mM). Inset, kinetics of Fe(III) chelate catalyzed peroxide bleaching of Safranine T monitored at 520 nm. Experimental conditions: $[dye]_0 = 71.3 \times 10^{-3}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; pH = 3; temperature = 30 °C.

$[Fe^{2+}]_0/[dye]_0$ is >1 at the $[H_2O_2]_0/[Fe^{2+}]_0 > 3$ or when the $[H_2O_2]_0/[Fe^{2+}]_0$ is <3 at the $[Fe^{2+}]_0/[dye]_0 < 1$, the steady rate of oxidation is disturbed. The reason for this result is probably due to the contribution of oxidant produced from a different source along with the oxidant generated by the Fe(III)−organic complex. It may be hypothesized that the former is generated by the reaction of $^{\bullet}OH$ and Fe^{2+} since the rise in Fe^{2+} concentration increases the rate of $^{\bullet}OH + Fe^{2+}$ reaction. It has been reported that Fe^{2+} could yield oxoiron (IV) on reaction with an oxidant like hydrogen peroxide or ozone at pH 3:[43−45]

$$Fe^{2+} + {}^{\bullet}OH \rightarrow FeO^{2+} + H_2O \tag{10}$$

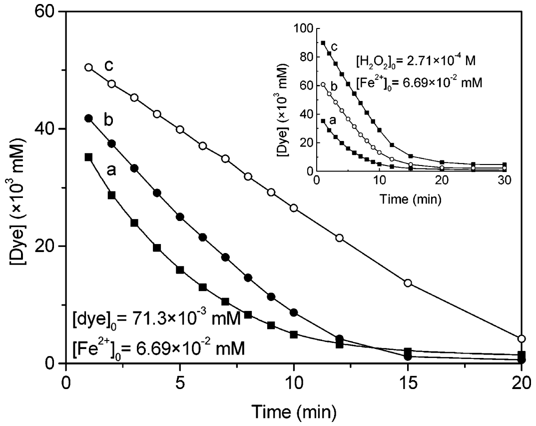

Figure 9. Time-dependent changes in [dye] on increasing the concentration of hydrogen peroxide ($a = 2.71 \times 10^{-4}$, $b = 10.84 \times 10^{-4}$, $c = 16.26 \times 10^{-4}$ M) at fixed $[Fe^{2+}]_0$ and $[dye]_0$. Inset, time-dependent changes in [dye] on increasing the concentration of dye ($a = 71.3 \times 10^{-3}$, $b = 142.5 \times 10^{-3}$, $c = 171 \times 10^{-3}$ mM) at fixed $[Fe^{2+}]_0$ and $[H_2O_2]_0$. Experimental conditions: $[Fe^{2+}]_0 = 6.69 \times 10^{-2}$ mM; pH = 3; temperature = 30 °C.

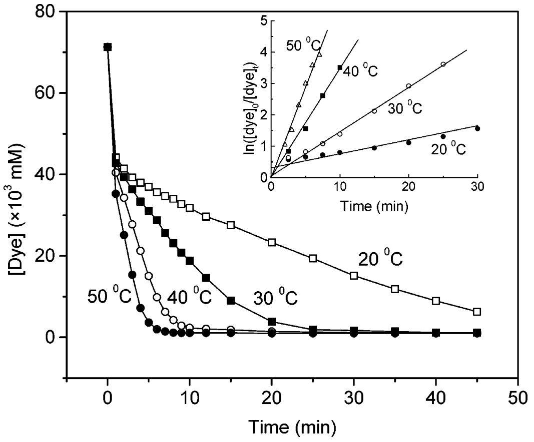

Figure 10. Effect of temperature on oxidation of Safranine T. Inset, kinetics of Fe(III) chelate catalyzed peroxide bleaching of Safranine T monitored at 520 nm. Experimental conditions: $[dye]_0 = 71.3 \times 10^{-3}$ mM; $[Fe^{2+}]_o = 4.46 \times 10^{-2}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; pH = 3.

The assumption of the generation of an oxidant by the reaction $^{\bullet}OH$ and Fe^{2+} is supported by the fact that the scavenging of the hydroxyl radicals by using excess H_2O_2 under otherwise identical conditions of reaction leads to a steady rate of oxidation (Figure 9) Also, under otherwise identical conditions of reaction, the decrease in $[Fe^{2+}]_0/[dye]_0$ to <1 by increasing the initial concentration of Safranine T at fixed $[H_2O_2]_0/[Fe^{2+}]_0$ value of above 3 resulted in a steady rate of oxidation (inset of Figure 9). Therefore, the steady concentration of an Fe(III)−organic complex can be suggested during the second stage reaction at the initial concentration ratios of $[Fe^{2+}]/[dye] < 1$ and $[H_2O_2]/[Fe^{2+}] > 3$. Taking into account the above observations and borrowing some mechanistic ideas from the literature,[40,46,47] the reaction mechanism of Fe(III) chelate catalyzed peroxide oxidation of Safranine T could perhaps be hypothesized as

$$LFe(III) + H_2O_2 \rightarrow LFe(V){=}O \tag{11}$$

$$\leftrightarrow L^{\bullet+}Fe(IV){=}O + H_2O \tag{12}$$

$$L^{\bullet+}Fe(IV){=}O + dye \rightarrow LFe(III) + \text{oxidation products} \tag{13}$$

With the pseudo-steady-state assumption for the Fe(III)−organic complex under the above initial concentration ratios, the second stage oxidation reaction, i.e., the Fe(III) chelate catalyzed peroxide oxidation of the dye, can be described by pseudo-first-order kinetics with respect to the dye concentration (eq 14):

$$\ln([dye]_0/[dye]_t) = k_{obs}t \tag{14}$$

where k_{obs} represents the pseudo-first-order rate constant. In this case, a plot of $\ln([dye]_0/[dye]_t)$ versus time in every experiment

TABLE 1: Pseudo-First-Order Rate Constants for the Fe(III) Chelate Catalyzed Peroxide Oxidation of Safranine T at Different Initial Concentrations of Dye, H_2O_2, and Fe^{2+} and at Different Temperatures

[dye]$_o$ mM	k_{obs} min^{-1}	$[H_2O_2]_0$ M	k_{obs} min^{-1}	$[Fe^{2+}]_0$ mM	k_{obs} min^{-1}	temp. °C	k_{obs} min^{-1}
71.3×10^{-3}	0.137	2.72×10^{-4}	1.37	0.89×10^{-2}	0.006	20	0.035
85.5×10^{-3}	0.128	5.43×10^{-4}	0.078	2.23×10^{-2}	0.022	30	0.137
99.8×10^{-3}	0.123	10.86×10^{-4}	0.055	4.46×10^{-2}	0.137	40	0.362
114×10^{-3}	0.099	21.72×10^{-4}	0.021			50	0.605

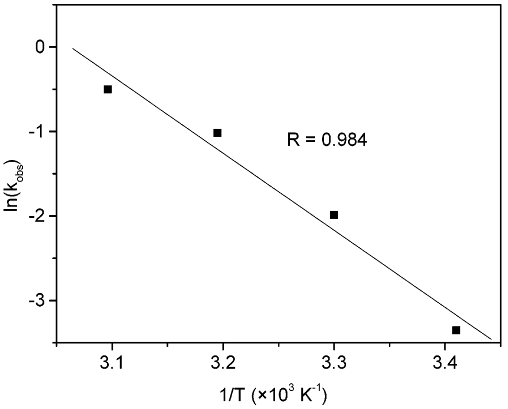

Figure 11. Arrhenius plot for the Fe(III) chelate catalyzed peroxide oxidation of Safranine T.

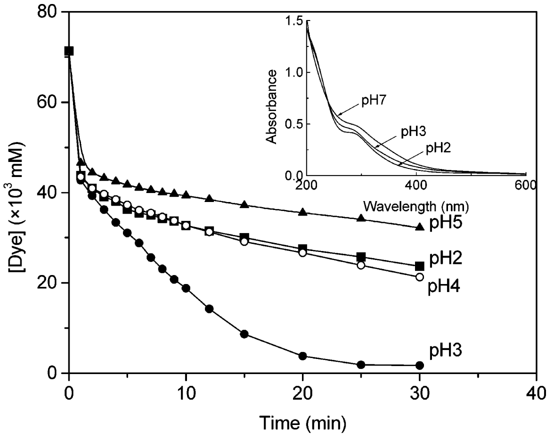

Figure 12. Effect of pH on oxidation of Safranine T. Inset, UV−visible spectra of the aqueous solution of active Fe(III)-organic complex at different pH. Experimental conditions: $[dye]_0 = 71.3 \times 10^{-3}$ mM; $[Fe^{2+}]_0 = 4.46 \times 10^{-2}$ mM; $[H_2O_2]_0 = 2.71 \times 10^{-4}$ M; temperature = 30 °C.

must lead to a straight line with slope of $k_{obs.}$ Insets in Figures 6−8 and 10 show these plots for experiments in which the initial concentration of dye, H_2O_2, Fe(II), and the temperature were varied. As it can be observed, points lie in satisfactory straight lines with correlation coefficients >0.98. All of these results support the pseudo-first-order kinetics assumed. The k_{obs} values were calculated from the experimental data and are shown in Table 1.

Effect of Temperature. Oxidation of Safranine T was carried out with $[Fe^{2+}]_0/[dye]_0 < 1$ and $[H_2O_2]_0/[Fe^{2+}]_0 > 3$ at four different temperatures in the range of 20−50 °C. Results (Figure 10) showed that the temperature exerts a strong effect on the Fe(III) chelate catalyzed peroxide oxidation of the dye. The oxidation rate increases with temperature due to an increment in the pseudo-first-order rate constant. The data exhibit Arrhenius-type behavior with an activation energy of 75.91 kJ mol^{-1}, calculated from the usual $\ln(k_{obs})$ versus $1/T$ plot (Figure 11).

Effect of pH on Degradation of Dye. The oxidation of Safranine T as a function pH is shown in Figure 12. It is evident that a change in the pH of the solution to either side of the value of 3 leads to a decrease in the extent of oxidation in the second stage. This demonstrates that the pH value for the most effective oxidation of Safranine T is almost 3. Lu et al.[48] found that the optimum pH of dichlorvos oxidation using classic Fenton's reagent is between 3 and 4. They also found that the rate of oxidation decreased when the solution pH is 2.5. The decrease in oxidation rate at pH > 3 could be explained based on the formation of $Fe(OH)_3$, which has lower catalytic activity in the decomposition of H_2O_2.[29] It can be calculated that, when the value of pH raises beyond 3, $Fe(OH)_3$ appears,[49] leading to a decrease in Fe^{3+} concentration and, subsequently, the oxidation rate. To confirm the stability of the active Fe(III)−organic complex at different pH, UV−vis spectra of the solution of the complex obtained after 30 min of oxidation were performed after adjusting the pH to different values. It can be clearly seen from the results (inset in Figure 12) that a higher pH value results in red shift and softening of the shoulder for the active Fe(III)−organic complex, suggesting instability of the active Fe(III)-organic complex at higher pH. This may be a reason of decrease in the oxidation rate at pH > 3.

Effect of H_2O_2 Concentration on Dye Degradation. As Figure 7 shows, for the initial $[H_2O_2]/[Fe^{2+}] > 3$ and initial $[Fe^{2+}]/[dye] < 1$ at pH 3 and 30 °C, the rate of oxidation of Safranine T both in the first minute and after that time period decreases with increase in the initial concentration of hydrogen peroxide. Increasing the $[H_2O_2]_0$ value accelerates reaction 4 whose effect is the consumption of the very reactive $^{\bullet}OH$ radicals to give less reactive $HO_2^{\bullet}$ radicals. This reaction (eq 4) reduced the probability of attack of the organic molecule by hydroxyl radicals, and caused the dye oxidation rate to drop[50,51] in the first minute. Thus, H_2O_2 in excess becomes a scavenger of hydroxyl radicals, in accordance with reaction 4. Under the conditions of $[Fe^{2+}]_0/dye]_0 < 1$ and $[H_2O_2]_0/[Fe^{2+}]_0 > 3$, the Fe(III)−organic complex limits the rate of dye oxidation in the second stage. As the efficiency of hydroxyl radicals scavenging by hydrogen peroxide gets increased with the increase in the latter's concentration, the efficiency of dye oxidation and, therefore, the formation of the active Fe(III)−organic complex in the first stage of reaction decreases with the increase in H_2O_2 concentration. Hence, the rate of Fe(III) chelate catalyzed peroxide oxidation of Safranine T decreases with the increase in hydrogen peroxide concentration.

Effect of Fe^{2+} Concentration on Dye Degradation. Figure 8 shows how the concentration of Safranine T changes if initially different amounts of ferrous ions were added. The results indicate that the rate of oxidation is remarkably dependent on the initial concentration of the Fe^{2+} at fixed $[H_2O_2]_0$ and $[dye]_0$. When the initial amount of ferrous ions increased, the oxidation rate of Safranine T increased as well both in the first and second stages of oxidation. The reason is that as the added amount of ferrous ion directly influence the production of hydroxyl radical a lower initial $[Fe^{2+}]$ would cause fewer $^{\bullet}OH$ radicals and, hence, the Fe(III)−organic complex to take part in oxidation. Lou and Lee[52] reported that the oxidation efficiency of BTX linearly increased with increasing Fe^{2+} concentration.

Conclusion

The kinetics and mechanism of oxidation of Safranine T in aqueous solution was studied using classic Fenton's reagent. The oxidation of the dye in this system underwent a two-stage reaction; the first minute of reaction occurs swiftly and then somewhat less rapidly. In the process, the complexation of Fe(III) and the oxidation intermediate of the dye occurred. This Fe(III)−organic complex is highly active in catalytic decomposition of hydrogen peroxide to produce an oxidant capable of oxidizing the Safranine T. Cessation of the Fe(III) chelate catalyzed peroxide oxidation of the dye on using t-BuOH suggests the generation of $^{\bullet}OH$ and/or ferryl species as the oxidant by the Fe(III)−organic complex. The Fe(III) chelate catalyzed peroxide oxidation of Safranine T follows pseudo-first-order rate dependence on dye concentration.

Acknowledgment. The author is thankful to the Centre for Surface Science, Jadavpur University, Kolkata, India, for providing necessary laboratory facilities. Thanks are also due to Prof. S. P. Moulik and Prof. S. K. Sanyal of Jadavpur University for providing valuable guidance.

References and Notes

(1) Arnold, S. M.; Hickey, W. J.; Harris, R. F. Degradation of atrazine by Fenton's reagent: condition optimization and product quantification. *Environ. Sci. Technol.* **1995**, *29*, 2083−2089.

(2) Pignatello, J. J.; Day, M. Mineralization of methyl parathion insecticide in soil by hydrogen peroxide activated with iron (III)-NTA or HEIDA complexes. *Hazard. Waste Hazard. Mater.* **1996**, *13*, 237−244.

(3) Hislop, K. A.; Bolton, J. R. The photochemical generation of hydroxyl radicals in the UV−visyferrioxalateyH O 2 2 system. *Environ. Sci. Technol.* **1999**, *33*, 3119−3126.

(4) Chen, R.; Pignatello, J. J. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environ. Sci. Technol.* **1997**, *31*, 2399−2406.

(5) Walling, C.; Fenton's reagent revised. *Acc. Chem. Res.* **1975**, *8*, 125−131.

(6) Stubbe, J.; Kozarich, J. W. Mechanisms of bleomycininduced DNA degradation. *Chem. Rev.* **1987**, *87*, 1107−1136.

(7) Bossmann, S. H.; Oliveros, E.; Gob, S.; Siegwart, S.; Dahlen, E. P.; Payawan, L., Jr.; Straub, M.; Worner, M.; Braun, A. M. New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. *J. Phys. Chem. A* **1998**, *102*, 5542−5550.

(8) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. A Radical Account of "Oxygenated Fenton Chemistry". *Acc. Chem. Res.* **1998**, *31*, 159−162.

(9) Goldstein, S.; Meyerstein, D. Comments on the Mechanism of the "Fenton-Like" Reaction. *Acc. Chem. Res.* **1999**, *32*, 547−550.

(10) Kremer, M. L. Mechanism of the Fenton reaction. Evidence for a new intermediate. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3595−3607.

(11) Haber, F.; Weiss, J. The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. R. Soc. London A* **1934**, *134*, 332−351.

(12) Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. Reactions of ferrous and ferric ions with hydrogen peroxide. Part I—the ferrous ion reaction. *Trans. Faraday Soc.* **1951**, *47*, 462−500.

(13) Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. Reactions of ferrous and ferric ions with hydrogen peroxide. Part II—the ferric ion reaction. *Trans. Faraday Soc.* **1951**, *47*, 591−616.

(14) De Laat, J.; Gallard, H. Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environ. Sci. Technol.* **1999**, *33*, 2726−2732.

(15) Lin, S.-S.; Gurol, M. D. Catalytic decomposition of hydrogen peroxide on iron oxide: kinetics, mechanisms, and implications. *Environ. Sci. Technol.* **1998**, *32*, 1417−1423.

(16) Haber, F.; Weiss, J. The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. R. Soc. London A* **1934**, *134*, 332−351.

(17) Dixon, W. T.; Norman, R. O. C. Electron spin resonance studies of oxidation. Part III. Some alicyclic compounds. *J. Chem. Soc.* **1964**, 4850−4860.

(18) Buettner, G. R. Free Radical. *Biol. Med.* **1987**, *3*, 259−303.

(19) Rosen, G. M.; Tsai, P.; Barth, E. D.; Dorey, G.; Casara, P.; Spedding, M.; Halpern, H. J. A One-Step Synthesis of 2-(2-Pyridyl)-3*H*-indol-3-one *N*-Oxide: Is It an Efficient Spin Trap for Hydroxyl Radical? *J. Org. Chem.* **2000**, *65*, 4460−4463.

(20) Rahhal, R.; Richter, H. W. Reduction of Hydrogen Peroxide by the Ferrous Iron Chelate of Diethylenetriamine-*N*,*N*,*N*9,*N*0,*N*0-pentaacetate. *J. Am. Chem. Soc.* **1988**, *110*, 3126−3133.

(21) Groves, J. T.; Watanabe, Y. Oxygen Activation by Metalloporphyrins Related to Peroxidase and Cytochrome P-450. Direct Observation of the O−O Bond Cleavage Step. *J. Am. Chem. Soc.* **1986**, *108*, 7834−7836.

(22) Kean, R. T.; Oertling, W. A.; Babcock, G. T. Characterization of Six-Coordinate Ferryl Protoheme by Resonance Raman and Optical Absorption Spectroscopy. *J. Am. Chem. Soc.* **1987**, *109*, 2185−2187.

(23) Sychev, A. Y.; Isak, V. G. Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O and H O and of the oxidation of organic substrates. *Russ. Chem. Rev.* **1995**, *12*, 1105−1129.

(24) Yamazaki, I.; Piette, L. H. EPR spin trapping study on the oxidizing species formed in the reaction of the ferrous ion with hydrogen peroxide. *J. Am. Chem. Soc.* **1991**, *113*, 7588−7593.

(25) Kremer, M. L. *Int. J. Chem. Kinet.* **1985**, *17*, 1299−1314.

(26) Kolthof, I. M.; Sandell, E. B.; Meehan, E. J.; Buckstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: New York, 1969; pp 1862−1867.

(27) Rand, M. C., Greenberg, A. E., Taras, M. J., Eds.; *Standard Methods for the Examination of Water and Wastewater*, 14th ed.; APHA-AWWA-WPCF: Washington, 1975; p 208.

(28) Pignatello, J. J. Dark and photoassisted Fe^{3+}-catalysed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* **1992**, *26*, 944−951.

(29) Sun, Y.; Pignatello, J. J. Photochemical reactions involved in the total mineralization of 2,4-D by Fe^{3+}/H_2O_2/UV. *J. Environ. Qual.* **1993**, *27*, 304−310.

(30) Li, Z. M.; Comfort, S. D.; Shea, P. J. Destruction of 2,4,6-trinitrotoluene by Fenton oxidation. *J. Environ. Qual.* **1997**, *26*, 480−487.

(31) Pignatello, J. J.; Liu, D.; Huston, P. Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environ. Sci. Technol.* **1999**, *33*, 1832−1839.

(32) Rush, J. D.; Bielski, B. H. J. Pulse Radiolytic Studies of the Reaction of $HO_2^{\bullet}/O_2^{\bullet-}$ with Fe(II)/Fe(III) ions. The Reactivity of $HO_2^{\bullet}/O_2^{\bullet-}$ with Ferric Ions and Its Implication on the Occurrence of the Haber-Weiss Reaction. *J. Phys. Chem.* **1985**, *89*, 5062−5066.

(33) Kolthof, I. M.; Sandell, E. B.; Meehan, E. J.; Buckstein, S. *Quantitative Chemical Analysis*, 4th ed.; Macmillan: New York, 1969; pp 855−856.

(34) Furia, T. E. *CRC Handbook of Food Additives*, 2nd ed.; CRC Press: West Palm Beach: FL: 1972; pp 271−294.

(35) Sun, Y.; Pignatello, J. Chemical Treatment of Pesticide Wastes. Evaluation of Iron (III) Chelates for Catalytic Hydrogen Peroxide Oxidation of 2,4-D at Circumneutral pH. *J. Agric. Food Chem.* **1992**, *40*, 322−327

(36) Walling, C.; Goosen, A. Mechanism of the Ferric Ion Catalyzed Decomposition of Hydrogen Peroxide. Effect of Organic Substrates. *J. Am. Chem. Soc.* **1973**, *95*, 2987−2991

(37) Salem, I. A.; El-Maazawi, M.; Zaki, A. Kinetics and mechanism of decomposition of hydrogen peroxide in the presence of metal complex. *Int. J. Chem. Kinet.* **2000**, *32*, 643−666.

(38) Dong, Y.; Fujii, H.; Hendrich, M. P.; Leising, R. A.; Pan, G.; Randall, C. R.; Wilkinson, E. C.; Zang, Y.; Que, L., Jr.; Fox, B. G.; Kauffmann, K.; Munck, E. A High-Valent Nonheme Iron Intermediate. Structure and Properties of $[Fe_2(.mu.\text{-}O)_2(S\text{-}Me\text{-}TPA)_2](ClO_4)_3$. *J. Am. Chem. Soc.* **1995**, *117*, 2778−2792.

(39) Arasasingham, R. A.; Cornman, C. R.; Balch, A. L. Detection of Alkyl Peroxo and Ferryl, (FeIV: O)2+, Intermediates during the Reaction of *tert*-Butyl Hydroperoxide with Iron Porphyrins in Toluene. *J. Am. Chem. Soc.* **1989**, *111*, 7800−7805.

(40) Pierre, J. L.; Fontecave, M. Iron and activated oxygen species in biology: The basic chemistry. *Iometals* **1999**, *12*, 195−199.

(41) Rivas, F. J.; Beltran, F.; Frades, J.; Buxeda, P. Oxidation of *p*-hydroxybenzoic acid by Fenton's reagent. *Water Res.* **2001**, *35*, 387−396.

(42) Rivas, F. J.; Beltran, F. J.; Garcia-araya, J. F.; Navarrete, V.; Gimeno, O. Co-oxidation of *p*-hydroxybenzoic acid and atrazine by the Fenton's such as system $Fe(III)/H_2O_2$. *J. Hazard. Mater.* **2002**, *91*, 143−157.

(43) Bary, W. C.; Gorin, M. H. Ferryl Ion, A Compound of Tetravalent Iron. *J. Am. Chem. Soc.* **1932**, *54*, 2124−2125.

(44) Kremer, M. L. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3595−3605.

(45) Logager, T.; Holcman, J.; Sehested, K.; Pedersen, T. *Inorg. Chem.* **1994**, *33*, 3523−3529.

(46) Meunier, B. Metalloporphyrins as Versatile Catalyst for Oxidation Reactions and Oxidative DNA Cleavage. *Chem. Rev.* **1992**, *92*, 1411−1456.

(47) Freire, R. S.; Pessoa, C. A.; Mello, L. D.; Kubota, L. T. Direct electron transfer: an approach for electrochemical biosensors with higher selectivity and sensitivity. *J. Braz. Chem. Soc.* **2003**, *14* (2), 230−243.

(48) Lu, M.-C.; Chen, J.-N.; Chang, C.-P. Oxidation of dichlorovos with hydrogen peroxide using ferrous ion as catalyst. *J. Hazard. Mater*. **1999**, *69* (3) 277−288.

(49) Snoeyink, V. L.; Jenkins, D. *Water Chemistry*; Wiley: New York, 1982; pp 262−269.

(50) Moon, D. K.; Maruyama, T.; Osakada, K.; Yamamoto, T. Chemical oxidation of polyaniline by radical generating reagent. *Chem. Lett.* **1991**, 1633−1636.

(51) Khan, M. D. A.; Watts, R. J. Mineral-catalyzed peroxidation of tetrachloroethylene. *Water Air Soil Pollut*. **1996**, *88*, 247−260.

(52) Lou, J. C.; Lee, S. S. Chemical oxidation of BTX using Fenton's reagent. *Hazard. Waste Hazard. Mater* **1995**, *12* (2), 185−193.