



## Substituent effects on azo dye oxidation by the $\text{Fe}^{\text{III}}$ –EDTA– $\text{H}_2\text{O}_2$ system

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### Abstract

The effect of substituents on the oxidation of azo dyes in the  $\text{Fe}^{\text{III}}$ –EDTA– $\text{H}_2\text{O}_2$  system was examined at pH 7. 4-(4'-sulfophenylazo)phenol and 2-(4'-sulfophenylazo)phenol, with methyl, methoxy, and halo substituents on the phenolic ring, were used as model systems. Oxidation of the naphthol dyes Orange I and Orange II were also examined. All of the dyes tested were decolorized in the  $\text{Fe}^{\text{III}}$ –EDTA– $\text{H}_2\text{O}_2$  system, but the degree of decolorization varied over a factor of 10. Dyes substituted with one or two halogens were oxidized to a greater extent than the corresponding methyl- or methoxy-substituted dyes. One explanation for the effect of halogen substituents is that they make the phenolic moieties more acidic, which favors the phenolate anion, which is more readily attacked by  $\cdot\text{OH}$ . This explanation is supported by the observed correlation between charge density of the phenolate anion and the degree of decolorization. Based on an analysis of products formed from Orange II, a probable mechanism for decolorization of phenolic azo dyes by  $\cdot\text{OH}$  is proposed. In addition, the optimal levels of  $\text{H}_2\text{O}_2$  needed for the process have been examined. It appears that high levels of  $\text{H}_2\text{O}_2$  could reduce decolorization by scavenging the  $\cdot\text{OH}$ . © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Orange I; Orange II; Fenton reagent; Decolorization; Hydroxyl radical

### 1. Introduction

Azo dyes constitute the largest class of dyes used in industry (Zollinger, 1987). Their release into the environment via industrial effluent is a cause for concern because reduction of azo linkages may generate potentially carcinogenic aromatic amines (Brown et al., 1981; Vaidya and Datye, 1982; Brown and DeVito, 1993). Azo dyes are resistant to aerobic biodegradation, but they are easily reduced by enzymes such as reductases and cytochrome P-450 (Huang et al., 1979; Kulla et al., 1983;

Rafii et al., 1990; Brown and DeVito, 1993; Russ et al., 2000). They can also be reduced by chemical systems, such as zero-valent iron, reduced flavin adenine nucleotide, and nicotinamide adenine dinucleotide, under anaerobic or aerobic conditions (Fujita and Peisach, 1982; Weber, 1996; Nam and Tratnyek, 2000). The white-rot fungus *Phanerochaete chrysosporium* is the only organism that is known to completely degrade azo dyes in a nonspecific manner (Paszczyński et al., 1992; Spadaro et al., 1992). However, this organism is not suitable for treating industrial effluents at the present time.

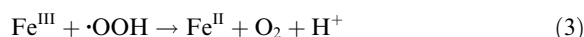
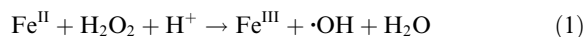
Advanced oxidation processes (AOPs) refer to remediation processes that generate the highly reactive hydroxyl radical ( $\cdot\text{OH}$ ) to degrade organic pollutants (Cha et al., 1996; Hong et al., 1996; Bahorsky, 1997). AOPs have been used for degrading a wide variety of

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environmental pollutants, including chlorophenols, dichlorophenoxyacetic acids, nitroaromatics, and polychlorobiphenyls (e.g., Ho, 1986; Barbeni et al., 1987; Sedlak and Andren, 1991; Pignatello, 1992). The  $\cdot\text{OH}$  can be generated by chemical and photochemical reactions (Walling, 1975; Cha et al., 1996; Bahorsky, 1997; von Gunten and Oliveras, 1997). The most commonly used chemical process, known as the Fenton reaction, involves reaction of ferrous or ferric salts with  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$  as shown in Eqs. (1)–(3) (Walling, 1975).



In photochemical AOPs,  $\cdot\text{OH}$  is produced in combinations such as UV– $\text{H}_2\text{O}_2$ , UV– $\text{TiO}_2$ , or UV– $\text{O}_3$  (Ruppert et al., 1994; Vinodgopal and Kamat, 1995; von Gunten and Oliveras, 1997).

Hydroxyl radicals generated using  $\text{Fe}^{\text{III}}$ – $\text{H}_2\text{O}_2$ , UV– $\text{TiO}_2$ , and UV– $\text{TiO}_2$ – $\text{SnO}_2$  have been shown to decolorize azo dyes (Dieckmann et al., 1994; Vinodgopal and Kamat, 1995; Lin and Chen, 1997; Bandara et al., 1999; Joseph et al., 2000; Tanaka et al., 2000). In a previous report, we established that azo dyes are completely degraded to  $\text{CO}_2$  by the  $\text{Fe}^{\text{III}}$ – $\text{H}_2\text{O}_2$  system (Spadaro et al., 1994). In the study reported here, we examine the effect of ring substituents on azo dye degradation by an  $\text{Fe}^{\text{III}}$ – $\text{H}_2\text{O}_2$  system containing EDTA (in part, to simulate some of the co-contaminants found in industrial waste from dyeing operations). Production of  $\cdot\text{OH}$  and consumption of  $\text{H}_2\text{O}_2$  during this reaction was also investigated.

## 2. Materials and methods

### 2.1. Chemicals

Mordant Orange I, Methyl Red, Orange II, and all substituted phenols were purchased from Aldrich (Milwaukee, WI). Orange I was obtained from TCI America (Portland, OR). All azo dyes were purchased in the highest purity available and used without any further purification. Ferric nitrate [ $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ ], hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and deoxyribose were obtained from Sigma (St. Louis, MO).

### 2.2. Syntheses of azo dyes

The structures of all azo dyes used in this study are shown in Fig. 1. The derivatives of 4-(4'-sulfophenylazo)phenol and 2-(4'-sulfophenylazo)phenol were syn-

thesized and purified as described previously (Nam and Renganathan, 2000). Dye structures were confirmed by fast atom bombardment-mass spectrometry (Chivukula et al., 1995).

### 2.3. Estimation of the hydroxyl radical concentrations

The hydroxyl radical concentration was estimated using the deoxyribose method (Gutteridge, 1981; Halliwell and Gutteridge, 1981; Halliwell et al., 1987). Deoxyribose (3 mM) was reacted with the  $\cdot\text{OH}$  generating system,  $\text{Fe}^{\text{III}}\text{NO}_2$ –EDTA– $\text{H}_2\text{O}_2$ , for 10 min. Total reaction volume was 1 ml. At the end of the reaction, 1 ml of 1% thiobarbituric acid in 50 mM NaOH and 1 ml of 2.8% aqueous trichloroacetic acid (w/v) were added. The mixture was heated over a boiling-water bath for 10 min. Development of blue color indicated  $\cdot\text{OH}$  generation. The color developed was monitored at 532 nm using a UV-visible spectrophotometer (Model UV-265, Shimadzu, Kyoto, Japan). The concentration of  $\cdot\text{OH}$  was equated with thiobarbituric acid active substances using an extinction coefficient,  $\epsilon$ , of  $153 \text{ mM}^{-1} \text{ cm}^{-1}$ .

### 2.4. Estimation of $\text{H}_2\text{O}_2$ concentrations

A portion of the reaction mixture was diluted 100-fold with pH 6, 10-mM phosphate. Then an aliquot (0.1 ml) of the diluted mixture was reacted with 0.9 ml of a solution containing horseradish peroxidase (10  $\mu\text{g}$ ) and potassium iodide (10 mM) for 5 min. If the reaction mixture contains  $\text{H}_2\text{O}_2$ , the peroxidase oxidizes iodide to tri-iodide, which has a strong absorbance at 355 nm ( $\epsilon = 255 \text{ mM}^{-1} \text{ cm}^{-1}$ ; Cotton and Dunford, 1973). The  $\text{H}_2\text{O}_2$  concentration was calculated from the tri-iodide absorption at 355 nm.

### 2.5. Decolorization of azo dyes by $\text{Fe}^{\text{III}}$ –EDTA– $\text{H}_2\text{O}_2$

A  $\text{Fe}^{\text{III}}$ –EDTA complex at pH 7 was formed by mixing ferric nitrate (2 mM) with EDTA (2 mM) and by adjusting the pH to 7. An azo dye (final concentration 0.2 mM) and  $\text{H}_2\text{O}_2$  (10 mM) were added to the  $\text{Fe}^{\text{III}}$ –EDTA mixture. After a 10-min interval, the amount of dye remaining was monitored at the  $\lambda_{\text{max}}$  for that dye using a spectrophotometer.

### 2.6. Products from Orange II oxidation

Dyes were reacted with  $\text{Fe}^{\text{III}}$ –EDTA– $\text{H}_2\text{O}_2$  as described in the preceding section. The oxidation products were analyzed by high-performance liquid chromatography (HPLC) using a C-18 reverse phase column ( $0.46 \times 25 \text{ cm}$ ; Separation Group, Hesperia, CA). Products were eluted with a gradient containing 100-mM phosphate buffer, pH 7.0, and a mixture of deionized water and methanol (1:1). Product elution was

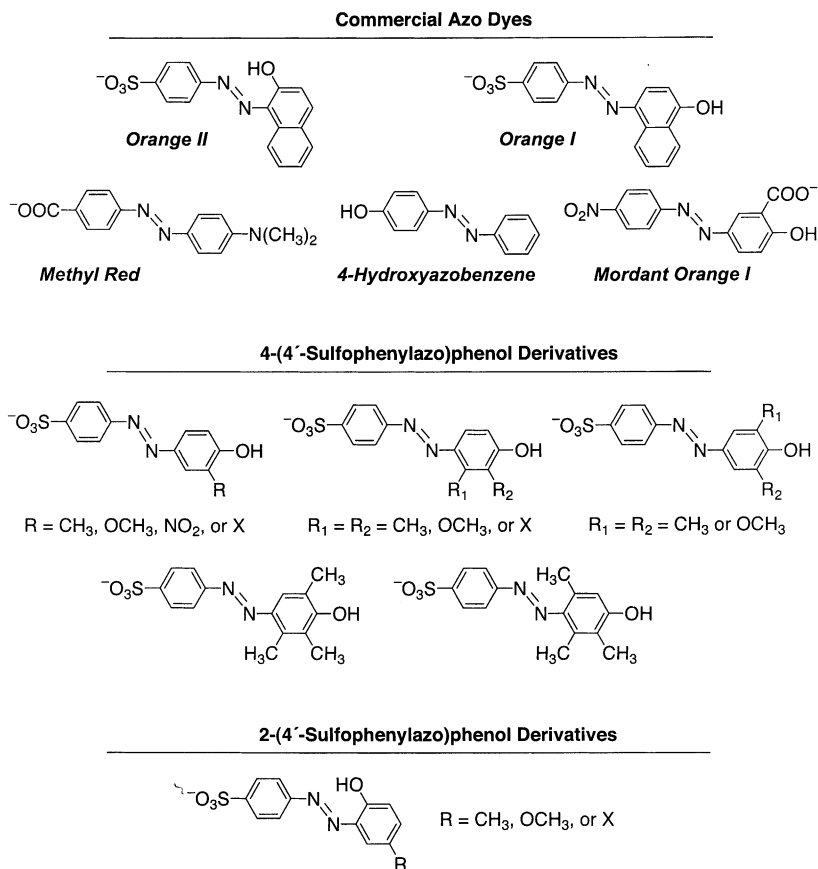


Fig. 1. Structures of the azo dyes and model compounds used in this study.

monitored at 254 nm using a UV detector. The flow rate of eluent was 1 ml min<sup>-1</sup>. Initially, the phosphate buffer concentration was maintained at 100% for 5 min. Then the water-methanol to phosphate buffer ratio was increased from 0 to 100% over 10 min and maintained at 100% concentration for an additional 10 min.

### 2.7. Correlation analysis

The charge densities of phenol and the phenolate ions for all dyes were calculated on the AM1 optimized geometry using the CAChe computer program from Oxford Molecular (Beaverton, OR). Atomic charges on all atoms except hydrogen atoms were also determined.

## 3. Results and discussion

### 3.1. Substituent effects

Advanced oxidation processes, such as Fe<sup>III</sup>-H<sub>2</sub>O<sub>2</sub>, UV-TiO<sub>2</sub>, and UV-SnO<sub>2</sub>-TiO<sub>2</sub>, have been demonstrated to efficiently degrade a variety of azo dyes

(Dieckmann et al., 1994; Spadaro et al., 1994; Vinodgopal and Kamat, 1995; Lin and Chen, 1997; Bandara et al., 1999; Joseph et al., 2000; Tanaka et al., 2000). All of these processes generate ·OH, which is a powerful oxidant (Cha et al., 1996; Bahorsky, 1997). In this study, specificity of ·OH for azo dye oxidation was examined by comparing the degree of decolorization in a fixed time interval for derivatives of 4-(4'-sulfophenylazo)phenol and 2-(4'-sulfophenylazo)phenol. Tables 1 and 2 show the data for methyl, methoxy, and halogen substituted derivatives of these two azo dyes. In addition, oxidation of two other naphthol-based dyes (Orange I and Orange II) were examined, and the results are given in Table 3.

These results suggest that the rate of azo dye oxidation is dependent on dye structure and the nature of substituents. Orange I, a naphthol dye, was decolorized to the greatest extent in the time period used for this study (10 min). The 2-(4'-sulfophenylazo)phenol dyes were decolorized more slowly and its 4-methoxy-substituted derivative was oxidized at the slowest rate. Among the 4-(4'-sulfophenylazo)phenol derivatives, dyes with 2-chloro, 2,5-difluoro, 2,6-difluoro, 2,3-dichloro,

Table 1  
Oxidation of 4-(4'-sulfophenylazo)phenol dyes

	Substituents	$\lambda_{\max}$ (nm)	Reaction time (min)	Absorbance decrease at $\lambda_{\max}$ (%)
1	2-Methyl	358	10	30
2	3-Methyl	362	10	25
3	2-Methoxy	369	10	66
4	3-Methoxy	382	10	30
5	3-Fluoro	352	10	53
6	2-Chloro	354	10	95
7	3-Chloro	359	10	63
8	2-Bromo	362	10	49
9	2-Iodo	368	10	30
10	2,3-Dimethyl	362	10	42
11	2,5-Dimethyl	366	10	37
12	2,6-Dimethyl	359	10	51
13	3,5-Dimethyl	359	10	28
14	2,3-Dimethoxy	362	10	60
15	2,6-Dimethoxy	377	10	46
16	3,5-Dimethoxy	421	10	74
17	2,3-Difluoro	374	10	69
18	2,5-Difluoro	419	10	94
19	2,6-Difluoro	416	10	93
20	2,5-Difluoro	350	10	48
21	2,3-Dichloro	420	10	91
22	2,5-Dichloro	420	10	94
23	2,3,5-Trimethyl	351	10	23
24	2,3,6-Trimethyl	366	10	48

Table 2  
Oxidation of 2-(4'-sulfophenylazo)phenol dyes

No.	Substituents	$\lambda_{\max}$ (nm)	Reaction time (min)	Absorbance decrease at $\lambda_{\max}$ (%)
1	4-Methoxy	324	10	5
2	4-Chloro	318	10	24
3	4-Fluoro	318	10	21

Table 3  
Oxidation of commercial azo dyes

No.	Substituents	$\lambda_{\max}$ (nm)	Reaction time (min)	Absorbance decrease at $\lambda_{\max}$ (%)
1	Orange II	484	10	90
2	Orange I	476	2	98
3	Methyl Red	524	10	71
4	Mordant-Orange I	385	10	67

and 2,5-dichloro substituents were decolorized rapidly and over 90% decolorization was observed (Table 1). Differences in decolorization rates were found among mono-, di-, and tri-methyl derivatives of 4-(4'-sulfophenylazo)phenol. The observed variations in decolorization rates suggest that the susceptibility of azo dyes to

degradation by  $\cdot\text{OH}$  is at least partly determined by their structure.

Further evidence for structural effects on the degree of decolorization was found by correlation analysis (Tratnyek, 1998). A strong correlation was found between the charge density of phenolate anion species of

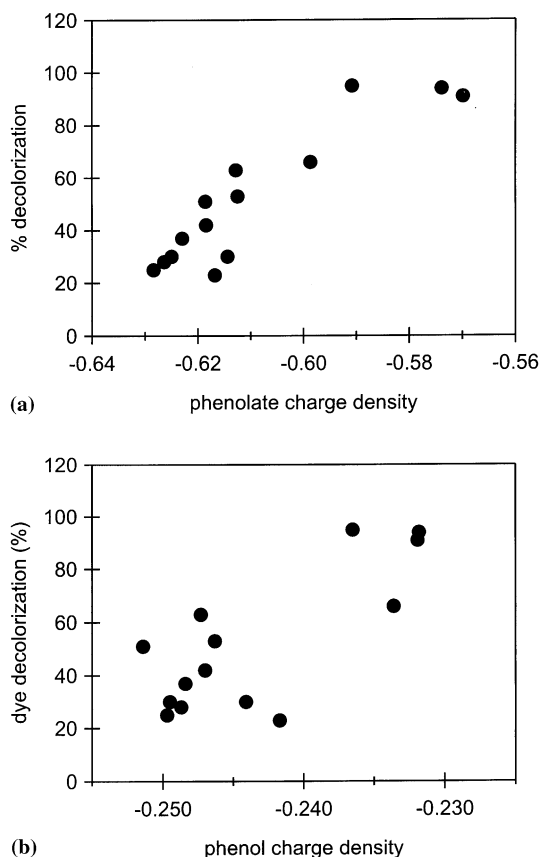


Fig. 2. Correlation of the amount of dye decolorized by the  $\text{Fe}^{\text{III}}$ –EDTA– $\text{H}_2\text{O}_2$  system with the calculated charge densities of (a) phenolate and (b) phenol forms of azo dyes.

the dye and the amount of decolorization (Fig. 2(a)). Dye oxidation did not correlate well with the charge density of the protonated form (Fig. 2(b)) or Hammett constants (data not shown). Because the phenolate is generally more rapidly oxidized, it is fairly common for the kinetics of oxidation to correlate better for substituted phenolates than the phenols (Tratnyek and Hogné, 1994, 1991). The results in Fig. 2 suggest that the oxidation of azo dyes under the conditions of this study are initiated by  $\cdot\text{OH}$  attack on the phenolate anion. The apparent plateau in Fig. 2(a) near 100% decolorization arises because these reactions are too fast to be resolved with the experimental protocol used in this study.

### 3.2. Product analysis and probable mechanism

HPLC analysis of Orange II oxidation products indicated the presence of 4-hydroxybenzenesulfonic acid ( $t_R = 4.4$  min) and 1,2-naphthoquinone ( $t_R = 22.3$  min). A mechanism is suggested in Fig. 3, which is consistent

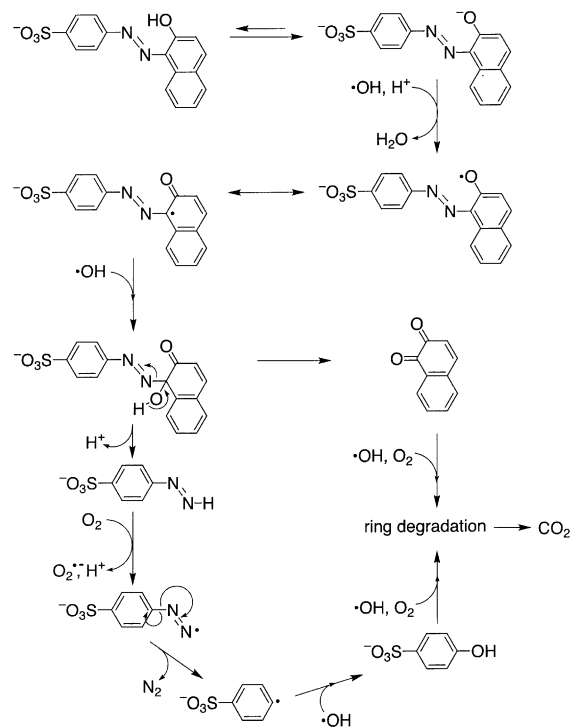


Fig. 3. A proposed mechanism for the degradation of Orange II by  $\text{Fe}^{\text{III}}$ /H<sub>2</sub>O<sub>2</sub>.

with the products observed, the correlation analysis described above, and several previously published studies for related systems (Spadaro and Renganathan, 1994; Spadaro et al., 1994). In the putative rate-limiting step,  $\cdot\text{OH}$  removes an electron from the phenolate anion to produce the corresponding resonance-stabilized phenoxyl radical. Then another  $\cdot\text{OH}$  adds to the C-1 carbon of the naphthol ring, generating an unstable tetrahedral intermediate, which breaks down to produce 1,2-naphthoquinone and 4-sulfophenyldiazene. One-electron oxidation of 4-sulfophenyldiazene, an unstable intermediate, by  $\text{O}_2$  yields a 4-sulfophenyldiazene radical. Since the latter radical is also unstable, it cleaves homolytically to produce a 4-sulfophenyl radical and nitrogen. Addition of  $\cdot\text{OH}$  to the 4-sulfophenyl radical generates 4-hydroxybenzenesulfonic acid. A somewhat different mechanism has been proposed for reaction of singlet oxygen with azo dyes that are subject to formation of the keto-hydrazone tautomer (Haag and Mill, 1987), but this could not apply to the whole range of dyes included in this study.

### 3.3. H<sub>2</sub>O<sub>2</sub> concentration and $\cdot\text{OH}$ production

The degree of azo dye decolorization increases nonlinearly with the initial concentration of added H<sub>2</sub>O<sub>2</sub> (Fig. 4). To investigate this further, we determined the

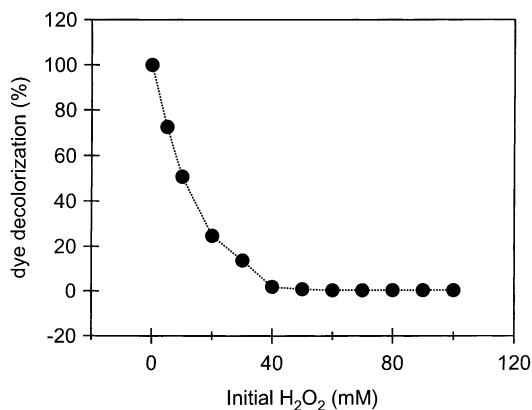
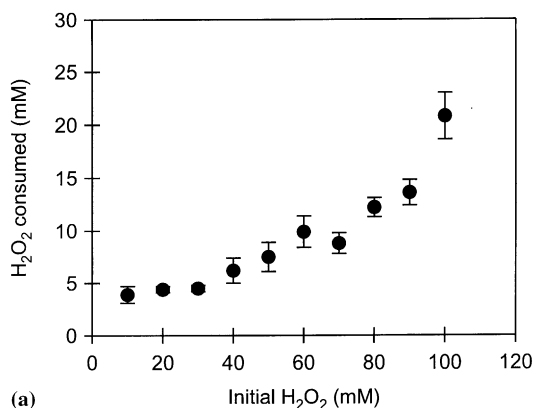
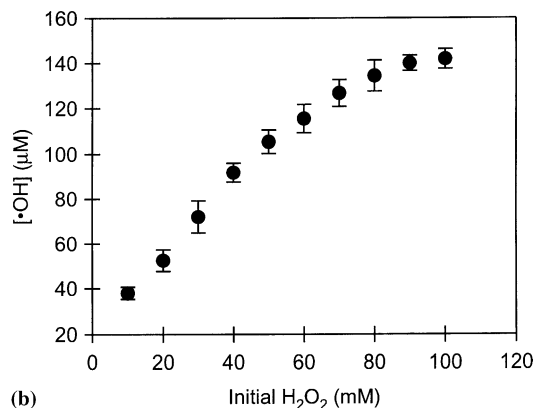


Fig. 4. Degree of oxidation of Orange II at various H<sub>2</sub>O<sub>2</sub> concentrations. Reaction conditions: [dye]=200 μM, [Fe<sup>III</sup>]=2 mM, [H<sub>2</sub>O<sub>2</sub>]=5–100 mM, EDTA=2 mM, pH 7.0, and reaction time=7 min at 25°C.



(a)



(b)

Fig. 5. Effect of H<sub>2</sub>O<sub>2</sub> concentration on (a) H<sub>2</sub>O<sub>2</sub> consumption and (b) ·OH production. Reaction conditions: [deoxyribose]=3 mM, [Fe<sup>III</sup>]=2 mM, [H<sub>2</sub>O<sub>2</sub>]=10–100 mM, EDTA=2 mM, pH 7.0, and reaction time=10 min at 25°C.

amount of H<sub>2</sub>O<sub>2</sub> remaining after 10 min and the amount of ·OH generated over 10 min, both as a function of the amount of H<sub>2</sub>O<sub>2</sub> added in the Fe<sup>III</sup>–EDTA–H<sub>2</sub>O<sub>2</sub>. The amount of residual H<sub>2</sub>O<sub>2</sub> increased slowly between 10 and 50 mM but rapidly above 50 mM initial H<sub>2</sub>O<sub>2</sub> (Fig. 5(a)). Levels of ·OH, as determined by the deoxyribose method, increased linearly between 10 and 80 mM H<sub>2</sub>O<sub>2</sub>, but leveled out above 80 mM initial H<sub>2</sub>O<sub>2</sub> (Fig. 5(b)). A comparison of the trends in Figs. 5(a) and (b) suggests that this increase in H<sub>2</sub>O<sub>2</sub> consumption did not lead directly to ·OH production (as suggested by Eqs. (1)–(3)). A likely explanation for the observed results is that residual H<sub>2</sub>O<sub>2</sub> levels increase at high H<sub>2</sub>O<sub>2</sub> concentrations because Fe<sup>III</sup> becomes limiting, and that high levels of residual H<sub>2</sub>O<sub>2</sub> scavenge ·OH as shown in Eq. (4) (Walling and Kato, 1971).



These findings suggest that remediation systems based on the Fenton reaction may become less efficient at elevated H<sub>2</sub>O<sub>2</sub> levels due to competition for the ·OH.

In conclusion, susceptibility of an azo dye to decolorization by ·OH is affected by substituents on the phenolic ring. Electron-withdrawing substituents, such as chloro and fluoro groups increase the susceptibility of dye to ·OH-dependent oxidation. Whereas H<sub>2</sub>O<sub>2</sub> is needed for generating the ·OH, very high levels H<sub>2</sub>O<sub>2</sub> could reduce decolorization by scavenging the ·OH.

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