Substituent effects on azo dye oxidation by the FeIII–EDTA–H2O2 system

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

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Abstract

The effect of substituents on the oxidation of azo dyes in the Fe^{III}–EDTA–H$_2$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 Fe^{III}–EDTA–H$_2$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 ·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 ·OH is proposed. In addition, the optimal levels of H$_2$O$_2$ needed for the process have been examined. It appears that high levels of H$_2$O$_2$ could reduce decolorization by scavenging the ·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 (Paszczynski et al., 1992; Spadaro et al., 1992). However, this organism is not suitable for treating industrial effluents at the present time.
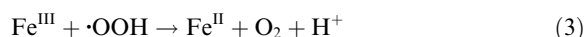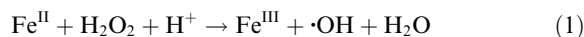
Advanced oxidation processes (AOPs) refer to remediation processes that generate the highly reactive hydroxyl radical (·OH) to degrade organic pollutants (Cha et al., 1996; Hong et al., 1996; Bahorsky, 1997). AOPs have been used for degrading a wide variety of

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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 $\cdot$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 H_2O_2 to produce $\cdot$OH as shown in Eqs. (1)–(3) (Walling, 1975).

$$Fe^{II} + H_2O_2 + H^+ \rightarrow Fe^{III} + \cdot OH + H_2O \qquad (1)$$

$$Fe^{III} + H_2O_2 \rightarrow Fe^{II} + \cdot OOH + H^+ \qquad (2)$$

$$Fe^{III} + \cdot OOH \rightarrow Fe^{II} + O_2 + H^+ \qquad (3)$$

In photochemical AOPs, $\cdot$OH is produced in combinations such as UV–H_2O_2, UV–TiO_2, or UV–O_3 (Ruppert et al., 1994; Vinodgopal and Kamat, 1995; von Gunten and Oliveras, 1997).

Hydroxyl radicals generated using Fe^{III}–H_2O_2, UV–TiO_2, and UV–TiO_2–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 CO_2 by the Fe^{III}–H_2O_2 system (Spadaro et al., 1994). In the study reported here, we examine the effect of ring substituents on azo dye degradation by an Fe^{III}–H_2O_2 system containing EDTA (in part, to simulate some of the co-contaminants found in industrial waste from dying operations). Production of $\cdot$OH and consumption of H_2O_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 [(Fe(NO$_3$)$_3 \cdot$ 9H$_2$O)], hydrogen peroxide (H_2O_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 $\cdot$OH generating system, $Fe^{III}NO_2$–EDTA–H_2O_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 $\cdot$OH generation. The color developed was monitored at 532 nm using a UV-visible spectrophotometer (Model UV-265, Shimadzu, Kyoto, Japan). The concentration of $\cdot$OH was equated with thiobarbituric acid active substances using an extinction coefficient, ϵ, of 153 mM^{-1} cm^{-1}.

2.4. Estimation of H_2O_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 µg) and potassium iodide (10 mM) for 5 min. If the reaction mixture contains H_2O_2, the peroxidase oxidizes iodide to tri-iodide, which has a strong absorbance at 355 nm ($\epsilon = 255$ mM^{-1} cm^{-1}; Cotton and Dunford, 1973). The H_2O_2 concentration was calculated from the tri-iodide absorption at 355 nm.

2.5. Decolorization of azo dyes by Fe^{III}–EDTA–H_2O_2

A Fe^{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 H_2O_2 (10 mM) were added to the Fe^{III}–EDTA mixture. After a 10-min interval, the amount of dye remaining was monitored at the λ_{max} for that dye using a spectrophotometer.

2.6. Products from Orange II oxidation

Dyes were reacted with Fe^{III}–EDTA–H_2O_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 × 25 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
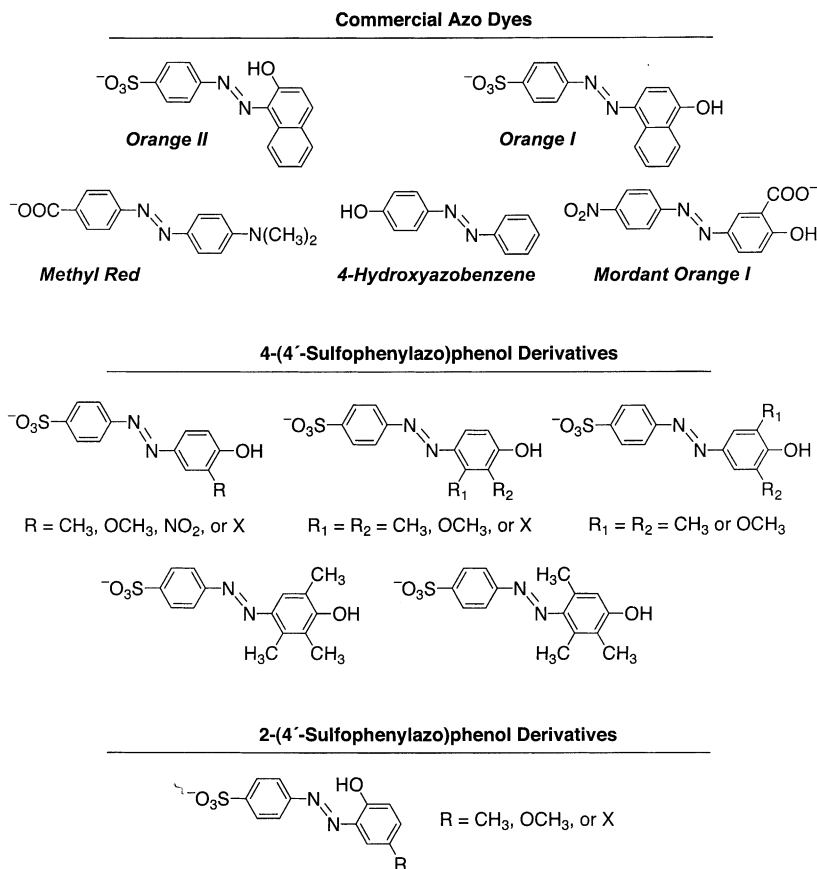
Fig. 1. Structures of the azo dyes and model compounds used in this study.

monitored at 254 nm using a UV detector. The flow rate of eluent was 1 ml min^{-1}. 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^{III}–H_2O_2, UV–TiO_2, and UV–SnO_2–TiO_2, 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′-sulfopheny-lazo)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	λ_{max} (nm)	Reaction time (min)	Absorbance decrease at λ_{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	λ_{max} (nm)	Reaction time (min)	Absorbance decrease at λ_{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	λ_{max} (nm)	Reaction time (min)	Absorbance decrease at λ_{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 ·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
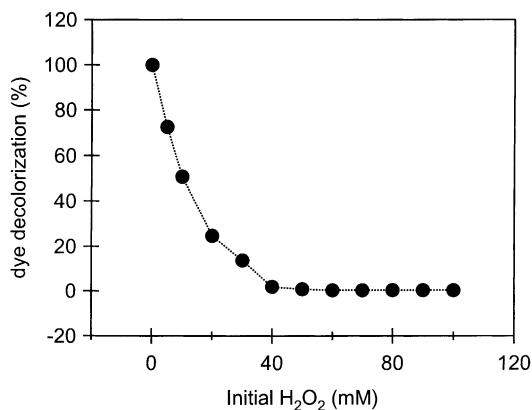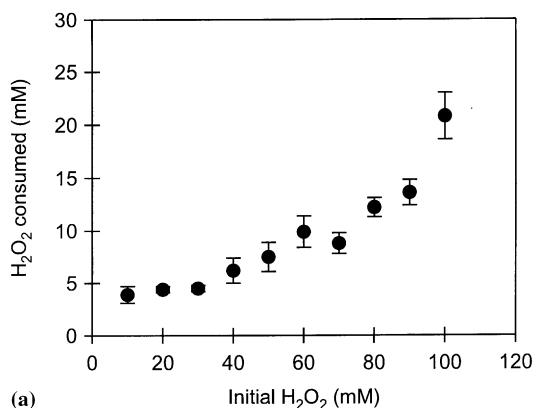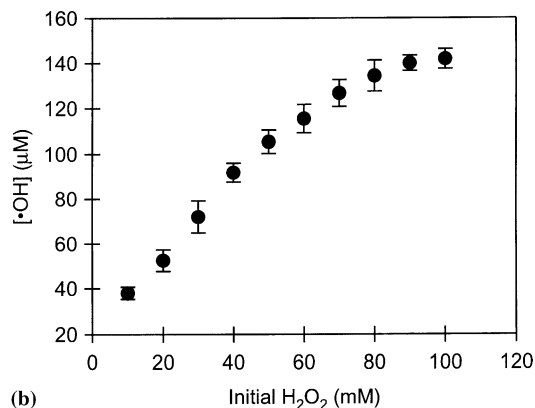
Fig. 2. Correlation of the amount of dye decolorized by the Fe^{III}–EDTA-H_2O_2 system with the calculated charge densities of (a) phenolate and (b) phenol forms of azo dyes.

Fig. 3. A proposed mechanism for the degradation of Orange II by Fe^{III}/H_2O_2.

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 Hoigné, 1994, 1991). The results in Fig. 2 suggest that the oxidation of azo dyes under the conditions of this study are initiated by ·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

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, ·OH removes an electron from the phenolate anion to produce the corresponding resonance-stabilized phenoxy radical. Then another ·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 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 ·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_2O_2 concentration and ·OH production

The degree of azo dye decolorization increases nonlinearly with the initial concentration of added H_2O_2 (Fig. 4). To investigate this further, we determined the

Fig. 4. Degree of oxidation of Orange II at various H_2O_2 concentrations. Reaction conditions: [dye] = 200 μM, [Fe^{III}] = 2 mM, [H_2O_2] = 5–100 mM, EDTA = 2 mM, pH 7.0, and reaction time = 7 min at 25°C.

Fig. 5. Effect of H_2O_2 concentration on (a) H_2O_2 consumption and (b) ·OH production. Reaction conditions: [deoxyribose] = 3 mM, [Fe^{III}] = 2 mM, [H_2O_2] = 10–100 mM, EDTA = 2 mM, pH 7.0, and reaction time = 10 min at 25°C.

amount of H_2O_2 remaining after 10 min and the amount of ·OH generated over 10 min, both as a function of the amount of H_2O_2 added in the Fe^{III}–EDTA–H_2O_2. The amount of residual H_2O_2 increased slowly between 10 and 50 mM but rapidly above 50 mM initial H_2O_2 (Fig. 5(a)). Levels of ·OH, as determined by the deoxyribose method, increased linearly between 10 and 80 mM H_2O_2, but leveled out above 80 mM initial H_2O_2 (Fig. 5(b)). A comparison of the trends in Figs. 5(a) and (b) suggests that this increase in H_2O_2 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_2O_2 levels increase at high H_2O_2 concentrations because Fe^{III} becomes limiting, and that high levels of residual H_2O_2 scavenge ·OH as shown in Eq. (4) (Walling and Kato, 1971).

$$·OH + H_2O_2 \rightarrow H_2O + ·OOH \tag{4}$$

These findings suggest that remediation systems based on the Fenton reaction may become less efficient at elevated H_2O_2 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_2O_2 is needed for generating the ·OH, very high levels H_2O_2 could reduce decolorization by scavenging the ·OH.

References

Bahorsky, M.S., 1997. Textiles. Water Environ. Res. 69, 658–664.

Bandara, J., Mielczarski, J.A., Kiwi, J., 1999. 2. Photosensitized degradation of azo dyes on Fe, Ti, and Al oxides. Mechanism of charge transfer during the degradation. Langmuir 15, 7680.

Barbeni, M., Minero, C., Pelizzetti, E., Borgarello, E., Serpone, N., 1987. Chemical degradation of chlorophenols with Fenton's reagent ($Fe^{2+} + H_2O_2$). Chemosphere 16, 2225–2237.

Brown, M.A., DeVito, S.C., 1993. Predicting azo dye toxicity. Crit. Rev. Environ. Sci. Technol. 23, 249–324.

Brown, D.H., Hitz, H.R., Schafer, L., 1981. The assessment of the possible inhibitory effect of dye-stuffs on aerobic wastewater. Experience with a screening test. Chemosphere 10, 245–261.

Cha, D.K., Song, J.S., Sarr, D., Kim, B.J., 1996. Hazardous waste treatment technologies. Water Environ. Res. 68, 575–586.

Chivukula, M., Spadaro, J.T., Renganathan, V., 1995. Lignin peroxidase-catalyzed oxidation of sulfonated azo dyes generates novel sulfophenyl hydroperoxides. Biochemistry 34, 7765–7772.

Cotton, M.L., Dunford, H.B., 1973. Nature of compounds I and II as determined from the kinetics of the oxidation of ferrocyanide. Can. J. Chem. 51, 582–587.

Dieckmann, M.S., Gray, K.A., Zepp, R.G., 1994. The sensitized photocatalysis of azo dyes in a solid system: a feasibility study. Chemosphere 28, 1021–1034.

Fujita, S., Peisach, J., 1982. The stimulation of microsomal azoreduction by flavins. Biochim. Biophys. Acta 719, 178–189.

Gutteridge, J.M.C., 1981. Thiobarbituric acid-reactivity following iron-dependent free-radical damage to amino acids and carbohydrates. FEBS Lett. 128, 343–346.

Haag, W.R., Mill, T., 1987. Direct and indirect photolysis of water-soluble azodyes: kinetic measurements and structure–activity relationships. Environ. Toxicol. Chem. 6, 359–369.

Halliwell, B., Gutteridge, J.M.C., 1981. Formation of a thiobarbituric-acid-active substance from deoxyribose in the presence of iron salts. The role of superoxide and hydroxyl radicals. FEBS Lett. 128, 347–352.

Halliwell, B., Gutteridge, J.M.C., Aruoma, O.I., 1987. The deoxyribose method: a simple test-tube assay for determination of rate constants for reactions of hydroxyl radicals. Anal. Biochem. 165, 215–219.

Ho, P.C., 1986. Photooxidation of 2,4-dinitrotoluene in aqueous solution in the presence of hydrogen peroxide. Environ. Sci. Technol. 20, 260–267.

Hong, A., Zappi, M.E., Kuo, C.H., Hill, D., 1996. Modeling kinetics of illuminated and dark advanced oxidation processes. J. Environ. Eng. 122, 58–62.

Huang, M.T., Miwa, G.T., Lu, A.Y.H., 1979. Rat liver cytosolic azoreductase. Purification and characterization. J. Biol. Chem. 254, 3930–3935.

Joseph, J.M., Destaillats, H., Hoffmann, M.R., 2000. The sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions. J. Phys. Chem. 104, 301–307.

Kulla, H.G., Klausener, F., Meyer, U., Lüdeke, B., Leisinger, T., 1983. Interference of aromatic sulfo groups in the microbial degradation of the azo dyes Orange I and Orange II. Arch. Microbiol. 135, 1–7.

Lin, S.H., Chen, M.L., 1997. Treatment of textile wastewater by chemical methods for reuse. Water Res. 31, 868–876.

Nam, S., Renganathan, V., 2000. Non-enzymatic reduction of azo dyes by NADH. Chemosphere 40, 351–357.

Nam, S., Tratnyek, P.G., 2000. Reduction of azo dyes with zero-valent iron. Water Res. 34, 1837–1845.

Paszczynski, A., Pastigrigsby, M.B., Goszczynski, S., Crawford, R.L., Crawford, D.L., 1992. Mineralization of sulfonated azo dyes and sulfanilic acid by Phanerochaete chrysosporium and Streptomyces chromofuscus. Appl. Environ. Microbiol. 58, 3598–3604.

Pignatello, J.J., 1992. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environ. Sci. Technol. 26, 944–951.

Rafii, F., Franklin, W., Cerniglia, C.E., 1990. Azoreductase activity of anaerobic bacteria isolated from human intestinal microflora. Appl. Environ. Microbiol. 56, 2146–2151.

Ruppert, G., Bauer, R., Heisler, G., 1994. $UV–O_3$, $UV–H_2O_2$, $UV–TiO_2$ and the photo-Fenton reaction – comparison of advanced oxidation processes for wastewater treatment. Chemosphere 28, 1447–1454.

Russ, R., Rau, J., Stolz, A., 2000. The function of cytoplasmic flavin reductases in the reduction of azo dyes by bacteria. Appl. Environ. Microbiol. 66, 1429–1434.

Sedlak, D.L., Andren, A.W., 1991. Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. Environ. Sci. Technol. 25, 1419–1427.

Spadaro, J.T., Renganathan, V., 1994. Peroxidase-catalyzed oxidation of azo dyes: mechanism of disperse yellow 3 degradation. Arch. Biochem. Biophys. 312, 301–307.

Spadaro, J.T., Gold, M., Renganathan, V., 1992. Degradation of azo dyes by the lignin-degrading fungus Phanerochaete chrysosporium. Appl. Environ. Microbiol. 58, 2397–2401.

Spadaro, J.T., Isabelle, L., Renganathan, V., 1994. Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation. Environ. Sci. Technol. 28, 1389–1393.

Tanaka, K., Padermpole, K., Hisanaga, T., 2000. Photocatalytic degradation of commercial azo dyes. Water Res. 34, 327–333.

Tratnyek, P.G., 1998. Correlation analysis of the environmental reactivity of organic substances. In: Macalady, D.L. (Ed.), Perspectives in Environmental Chemistry. Oxford, New York, pp. 167–194.

Tratnyek, P.G., Hoigné, J., 1991. Oxidation of substituted phenols in the environment: a QSAR analysis of rate constants for reaction with singlet oxygen. Environ. Sci. Technol. 25, 1596–1604.

Tratnyek, P.G., Hoigné, J., 1994. Kinetics of reactions of chlorine dioxide (OClO) in water. II. Quantitative structure–activity relationships for phenolic compounds. Water Res. 28, 57–66.

Vaidya, A.A., Datye, K.V., 1982. Environmental pollution during chemical processing of synthetic fibers. Colourage 14, 3–10.

Vinodgopal, K., Kamat, P.V., 1995. Enhanced rates of photocatalytic degradation of an azo dye using SnO_2/TiO_2 coupled semiconductor thin films. Environ. Sci. Technol. 29, 841–845.

von Gunten, U., Oliveras, Y., 1997. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural systems. Water Res. 31, 900–906.

Walling, C., 1975. Fenton's reagent revisited. Acc. Chem. Res. 8, 125–131.

Walling, C., Kato, S.I., 1971. The oxidation of alcohols by Fenton's reagent. The effect of copper ion. J. Am. Chem. Soc. 93, 4275–4281.

Weber, E.J., 1996. Iron-mediated reductive transformations: investigation of reaction mechanism. Environ. Sci. Technol. 30, 716–719.

Zollinger, H., 1987. Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments. VCH, New York.