Application of *Fenton*-Based Reactions for Treating Dye Wastewaters: Stability of Sulfonated Azo Dyes in the Presence of Iron(III)

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

Fenton- and photo-assisted *Fenton* advanced oxidation processes generate reactive oxygen species from hydrogen peroxide and are candidates for the remediation of dye wastewaters. The purpose of this study was to investigate interactions of iron (III) with hydroxyazo dyes. The *o*-hydroxyazo dyes *Acid Orange 7* (AO7; 4-[(2-hydroxynaphthalen-1-yl)azo]benzenesulfonic acid sodium salt) and *Acid Orange 10* (AO10; 7-hydroxy-8-(phenylazo)naphthalene-1,3-disulfonic acid disodium salt) represent dyes allegedly able to chelate Fe^{III} through the chromophore. The *p*-hydroxyazo dye *Acid Orange 20* (AO20; 4-[(4-hydroxynaphthalen-1-yl)azo]benzenesulfonic acid sodium salt) represents an analogous structure that is unable to chelate Fe^{III} due to the position of the OH group. Reactions were carried out at pH 2–3 in perchlorate or chloride media in the absence of peroxide. No evidence was found by UV/VIS spectroscopy for complexation of Fe^{III} by the *o*-hydroxyazo chromophore. Instead, Fe^{III} apparently coordinated or formed an ion pair with the sulfonate group, and, when only one sulfonate group was present (*i.e.*, AO7), the dye formed a co-precipitate with iron(III) hydrous oxides and perchlorate ion. Dye precipitation was seeded by colloidal iron hydrolysis product nuclei. By contrast, the *p*-hydroxyazo dye (AO20) was rapidly oxidized by iron(III). The net Fe^{2+}/oxidized AO20 ratio was 2:1, and a minor yield of 1,4-naphthoquinone was obtained. The major initial oxidation product, which was not identified, formed a reversible complex with Fe^{2+}. Results of this study indicate that the effectiveness of *Fenton*-based methods for treating certain azo dyes that form insoluble ferric salts may be compromised by removal of the catalyst from solution. However, the degradation of certain other azo dyes might be assisted by direct thermal oxidation by iron(III).

Introduction. – *Fenton*-based advanced oxidation processes (AOPs) seem to be well-suited for treating wastes from dye manufacture and textile- and paper-dyeing operations. An important class of dyes for these applications are acid dyes [1]. Acid dyes comprise a large group of relatively low molecular mass, mainly monoazo compounds that bear up to three sulfonic acid groups [2]. Wastewater is produced from dying operations at a rate of 100 to 130 liters per kilogram of dyestuff applied [3]. Conventional wastewater treatment methods are ineffective for removing color from these wastestreams. For example, highly soluble acid dyes cannot be destabilized by coagulation, and are not efficiently removed by carbon adsorption [4]. And, since dyestuffs are chosen in part for their resistance to microbial attack, biological treatment processes are often ineffective, unless wastewaters are pre-treated with strong oxidants or reductants [5][6]. *Fenton* and photo-assisted AOPs involving iron and hydrogen

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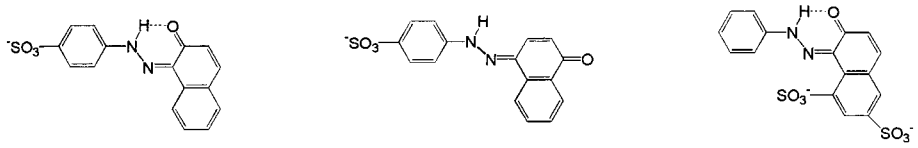
peroxide enable dye degradation by OH· radicals in homogeneous solution and have the potential to achieve deep oxidation of the dye to carbon dioxide and other nontoxic by-products.

The efficacy of various *Fenton*-based AOPs has been demonstrated with simulated and actual acid dye wastewaters. *Kuo* [7] first demonstrated that acid dye solutions were decolorized by 99% with up to 83% removal of chemical oxidation demand by reaction with 3.3 mM ferrous sulfate ($FeSO_4$) and 26 mM hydrogen peroxide (H_2O_2) at pH 3.5 for 5 h at 50°. *Tang* and *Chen*[8] compared dye removal using *Fenton*'s reagent (Fe^{2+}/H_2O_2) with H_2O_2/Fe powder. Greater dye-removal efficiencies were obtained with the Fe-powder system, but the increased removal was attributed to dye adsorption on the Fe powder, not faster transformation reactions. Decolorization of acid dye solutions by *Fenton*'s reagent was increased with the addition of UV light [9]. Complete decolorization of *Acid Orange 7* (AO7; *Fig. 1*) was observed within 2 h, and up to 95% mineralization occurred in less than 8 h [9]. Comparable dye transformation rates were achieved when iron was immobilized in *Nafion* membranes or alginate beads in the presence of H_2O_2 and light [11][12]. In general, mineralization of acid dyes by *Fenton*-based AOPs is significantly slower than transformation of the primary dye chromophore; however, integration of *Fenton*-based AOPs with other wastewater-treatment methods improves the overall removal of chemical and biological oxidation demand [13][14].



Acid Orange 7 (AO7) *Acid Orange 20* (AO20) *Acid Orange 10* (AO10)

Fig. 1. *Structures of the sulfonated azo dyes shown in the hydrazone form, the dominant tautomer in polar solvents* [10]

Few studies have investigated the mechanisms of dye degradation by *Fenton*-based AOPs. *Spadaro et al.* [15] followed the appearance of degradation products from the oxidation of substituted (phenylazo)benzene and (phenylazo)naphthalene dyes by Fe^{3+} and H_2O_2 at pH 2.8. They suggested that degradation of such monoazo dyes is initiated by hydroxyl-radical attack on the azo group and results in cleavage of the azo bond from one of the aromatic moieties and formation of an unstable aryldiazene intermediate. The products depend upon the structure of the dye and upon which side of the azo group the OH· radical attacks. Similar mechanisms have been proposed for the oxidation of monoazo dyes by non-*Fenton*-based AOPs [16][17]. Naphthoquinone, arene sulfonic acid and carboxylic acid products have been identified from the oxidation of azo dyes having naphthalenyl and benzyl moieties [15][16][17].

The mechanisms by which hydroxyazo dyes (*e.g.*, *Fig. 1*) are degraded with *Fenton*-based AOPs are not well characterized. Hydroxy groups are common substituents of acid dyes [18]. It is conceivable that a dye compound with the OH group located *ortho* to the azo group could chelate the metal ion at the chromophoric site, as in **A** or **B**. *Nadtochenko* and *Kiwi* [19] attributed decreases in AO7 absorbance in solutions

containing only the dyestuff and iron(III) to the formation of a 1:1 dye/Fe^{3+} complex through the chromophoric group as in **B**. They proposed that the initiating degradation step under photo-*Fenton* reaction conditions (UV light, Fe^{3+}, H_2O_2) is ligand-to-metal electron transfer within the excited state.

A **B**

Other evidence suggests that iron complexation of the chromophore may not be important for *o*-hydroxyazo dyes. Metal-ion complexes of monohydroxyazo dyes are known to have low stabilities in acidic dye applications [20]. *Drew* and *Fairbairn* [21] found that when sulfonate groups are present in monohydroxyazo dyes, coordination or ion pairing with the sulfonate group takes place in preference to complexation with the chromophore. Stable iron(III) complexes have been reported only for *o,o′*-dihydroxyazo dyes [22]. For these compounds, distinct hypsochromic shifts and peak broadening in the dye absorbance spectra were observed on addition of Fe^{3+}. Thus it appears that iron salts may be formed when *Fenton*-based AOPs are applied to acid dye wastewaters. Under certain conditions, dye oxidation proceeds [9]; however, if the solubility of the dye salts is low, the iron catalyst may be removed from solution and oxidation slowed or halted.

The purpose of this study was to determine the stability of hydroxyazo acid dyes in the presence of ferric ions (Fe^{3+}). To test whether dyes from this class formed soluble iron(III) complexes or insoluble iron(III) salts, we chose three monoazo dyes with related structures. Their structures are given in *Fig. 1* in the dominant hydrazone tautomeric form.

Experimental. – *Chemicals.* The sulfonated azo dyes used in this study were *Acid Orange 7* (AO7; 4-[(2-hydroxynaphthalen-1-)azo]benzenesulfonic acid sodium salt; >85% pure; *Aldrich*, Milwaukee, WI), *Acid Orange 20* (AO20; 4-[(4-hydroxynaphthalen-1-yl)azo]benzenesulfonic acid sodium salt; >85% pure; *Fluka*, Switzerland), and *Acid Orange 10* (AO10; 7-hydroxy-8-(phenylazo)naphthalene-1,3-disulfonic acid disodium salt; >85% pure; *National Aniline and Chemical Co.*). Iron(III) perchlorate, sodium perchlorate, benzenesulfonic acid sodium salt, 4-hydroxybenzenesulfonic acid sodium salt dihydrate, and *FerroZine*® iron reagent (4,4′-[3-(pyridin-2-yl)-1,2,4-triazine-5,6-diyl]bis[benzenesulfonic acid]monosodium salt hydrate) were obtained from *Aldrich* (Milwaukee, WI). Iron(III) chloride hexahydrate, NaCl, NaOH, EtOH, AcOEt, MeCN, and alumina (80–200 mesh) were from *Fisher Scientific* (Fairlawn, NJ), phosphoric, hydrochloric, and perchloric acids from *J. T. Baker* (Phillipsburg, NJ), and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) and potassium dihydrogen phosphate from *Mallinckrodt* (Paris, KY). All compounds were used as received, except AO7 and AO20 which were purified as described below. All solns. were prepared with high-purity (18 MΩ·cm) distilled, deionized H_2O (*Barnstead NANOpure* system). Glassware was soap-and-water washed followed by rinsing with high-purity water.

Dye Purification. AO7 was purified by recrystallization from a minimal amount of H_2O. The hot soln. was filtered through #41 ashless filter paper (*Whatman*) in a heated glass funnel. The filtrate was cooled slightly and extracted with AcOEt to remove a hydrophobic impurity. The aq. phase was cooled overnight at 4°. The crystals were collected on #41 filter paper, rinsed with H_2O, and vacuum dried. HPLC: only 1 peak on detection at 254 nm (general arom. compounds) and 478 nm (AO7 maxima). Anal. (*Galbraith Laboratories*, Knoxville, TN) calc. for $C_{16}H_{12}N_2NaO_4S \cdot 0.5\,H_2O$: C 53.5, H 3.2, N 7.8; found: C 53.5, H 3.35, N 7.76.

AO20 was purified by column chromatography (alumina). The dye was dissolved in MeOH and coated on alumina by slow evaporation of the solvent. The dye-coated alumina was seated on a column (49 cm × 3 cm i.d.) of fully-activated alumina. Elution at 1.5 ml/min with EtOH (200 ml), EtOH/H_2O 8:2 (*v*/*v*; 500 ml), EtOH/H_2O 6:4 (250 ml), and EtOH/H_2O 1:1 (250 ml) gave AO20 fractions which were identified by HPLC, evaporated and freeze-dried. Anal. (*Perkin-Elmer 2400* CHN elemental analyzer) calc. for $C_{16}H_{12}N_2NaO_4S \cdot 4\,H_2O$: C 45.4, H 2.83, N 6.62; found: C 45.5, H 3.21, N 6.15.

Dye Stability. Stock solns. containing ferric perchlorate (or chloride) and perchloric (or hydrochloric) acid were diluted to the target iron concentration and pH. Sodium perchlorate (or chloride) was added to adjust the ionic strength. At time zero, a small aliquot of concentrated dye soln. was added to the iron soln. At each sampling time, the soln. was centrifuged for 20 min at 340 *g*, and several milliliters were removed from the top. Absorbance measurements (*Hewlett-Packard 8452A* diode-array spectrophotometer) were made in 1-cm quartz cuvettes at the absorbance maximum for the dye (486 nm for AO7, 476 nm for AO20, and 478 nm for AO10). Replicate measurements were made on identically prepared solutions, *1*) containing dye only with no iron, and *2*) containing iron only with no dye. The effect of colloidal polynuclear iron hydrolysis species on AO7 stability was investigated by adjusting the soln. pH to 2.7 with NaOH instead of by dilution [23]. At the end of the experiment, Na_2EDTA was added to solns. to enable mass-balance determination of the dye compound. All sample manipulations for these and following experiments were undertaken in a darkened room, and all sample vessels were foil-covered to minimize possible photochemical reactions.

Acid Orange 20 *Oxidation.* In the dark, an aliquot of a concentrated AO20 soln. was added to a large-volume iron(III) perchlorate soln. to achieve nominal concentrations of 0.071 mM AO20, 0.125 mM Fe^{III}, and 23 mM $NaClO_4$ at pH 2 (to prevent formation of polynuclear Fe species). Over time, aliquots were removed to monitor dye and product concentrations. AO20 and ionic org. products were quantified by ion-pair chromatography. Separations were achieved on a C_{18} column (*ODS-5*, 250 mm, 4.6 mm i.d., 5 μm packing; *Alltech*) in an *Agilent-1100* instrument equipped with a diode-array detector gradient elution (modified from that of *Alonso* [24]): 100% of *B* for 5 min → *B*/*A* 4:6 within 13 min; *B* = 10 mM phosphate and 5 mM $(Bu_4N)OH$ in MeOH/H_2O 36:63 (*v*/*v*) at pH 6.5, *A* = MeOH. Compounds were detected by monitoring at 254 nm (general arom. compounds), 272 nm (substituted benzene sulfonates), and 476 nm (AO20) with bandwidths of 2 nm. A reference wavelength of 700 nm (10-nm bandwidth) was used. To prevent column contamination and chromatographic interference, dissolved iron was removed by addition of NaOH, filtration through 0.2-μm *Teflon* filters (*Gelman Acrodisk*) and re-acidification to pH 2 with perchloric acid. The limit of detection for AO20 was 0.001 mM by this method.

Non-ionic products were determined by CH_2Cl_2 extraction of aliquots of the reaction mixture. Extracts were dried (Na_2SO_4) and analyzed by GLC/MS (*Hewlett Packard 5890GC/5970MSD*). Upon product identification, subsequent quantifications were performed with flame-ionization detection. Both methods utilized a *PTE-5* capillary column (30 m, 0.25-mm i.d., 0.25 μm film thickness; *Supelco*, Bellefont, PA), and a temp. program beginning at 60° and ramping at 5° per min to 250°, with a final isotherm at 250° for 10 min. Injector and detector temp. were held at 250°.

Fe^{2+} Concentrations were quantified by complexation with *FerroZine*® reagent [25] at pH 2. Absorbance measurements were made at 562 nm to minimize interference from unreacted dye; however, background corrections were still applied by subtracting the absorbance (562 nm) of a duplicate sample volume to which an equivalent volume of pH 2 perchloric acid had been added in place of the *FerroZine*® reagent. The detection limit was 0.002 mM Fe^{2+}.

Results and Discussion. – *Reaction of Fe^{III} Ion with* o*-Hydroxyazo Dyes AO7 and AO10.* Chelation of Fe^{3+} by the *o*-hydroxyazo moiety is expected to affect the VIS absorption band of the dye. Consistent with a recent report [19], the VIS absorbance at 486 nm of AO7 solutions decreased in the presence of excess Fe^{III} (*Fig. 2*). However, the changes were atypical for a chelation reaction in homogeneous solution; they often occurred over long time periods (hours), and application of the *Benessi-Hildebrand* method [26] or the method of variations [27] to the absorbance data to obtain a stability constant gave nonlinear and/or non-reproducible correlations, and so failed to provide a reliable value. Instead, we believe the spectral changes are due to formation of an insoluble iron salt of the dye, although the appearance of a precipitate was not always

evident to the eye. Presumably the iron is outer- or inner-sphere associated with the sulfonate group (*Eqn. 1*).

$$\text{dye}-SO_3^- + Fe^{III} \rightarrow Fe^{III} \cdot \text{dye}-SO_3^-{}_{(\downarrow)} \quad (1)$$

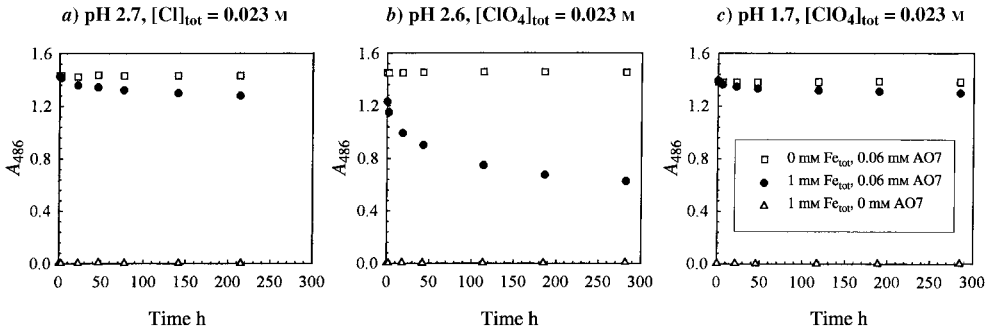


Fig. 2. *Stability of* Acid Orange 7 *absorbance at 486 nm in the presence of iron(III) with varying counter ion and pH*. The absorbances of iron-only controls (△) were less than 0.008 and indicated minimal polynuclear iron hydrolysis species in solution.

Several experiments confirmed precipitation rather than chelation by the chromophoric group. First, the spectral changes depended markedly on the anion of the background electrolyte. The decrease in dye absorbance at 486 nm was faster and more extensive in $NaClO_4$ than in NaCl media (*Fig. 2,a vs. b*). Since ClO_4^- and Cl^- have little tendency to coordinate Fe^{3+} – complexation of Fe^{3+} by ClO_4^- is negligible, while that by Cl^- is less than 10% of total iron at these concentrations (MINEQL+; Environmental Research Software) – they are expected to have little effect on the spectrum of the putative $Fe^{III} \cdot$ AO7 complex or on the position of equilibrium at identical pH and ionic strength. We interpret the dependence of spectral changes on the anion to mean that $Fe^{III} \cdot$ AO7 salt is less soluble in ClO_4^- solutions. Interestingly, the solubility of AO7 monosodium salt is lower in 0.1M $NaClO_4$ than in 0.1M NaCl.

Secondly, the spectral changes depended on pH and on the way the pH was adjusted, again supporting precipitation over chelation. In the most likely chelate structure (**A**), acid-base equilibria of the dye itself are not involved in chelation. Therefore, formation of the $Fe^{III} \cdot$ dye complex should be favored as the pH declines due to increasing abundance of the hexaaquo species ($Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$; $pK_a = 2.45$ at ionic strength of 30 mM [28]), which should more readily coordinate the dye than the monohydroxy or higher hydrolysis species. However, the opposite was observed (*Fig. 2,b vs. c*); the AO7 absorbance at 486 nm decreased much more at pH 2.6 ($[Fe^{3+}]/[Fe(OH)^{2+}] = 0.7$) than at pH 1.7 ($[Fe^{3+}]/[Fe(OH)^{2+}] = 5.7$). Further experimentation with 0.06 mM AO7 and 1 mM Fe^{3+} revealed that the decrease in AO7 absorbance was sensitive to the presence of colloidal polynuclear iron hydrolysis species, suggesting that the solutions were oversaturated with respect to $Fe^{III} \cdot$ dye$-SO_3^-$ salt and that precipitation was nucleated by the colloids.

To test whether this was true, we compared Fe^{III} solutions at the same pH (2.7–2.8) adjusted by two different methods: *a*) diluting acidified concentrated stock solutions (10 mM Fe^{III}, pH 1.7) to the target pH with purified H_2O, and *b*) neutralizing solutions (1 mM Fe^{III}, pH 1.7) to the target pH dropwise with NaOH. Addition of strong base causes locally high pH at the interface between the drop and the bulk solution, forming iron hydrous oxide colloids that do not redissolve readily [23]. The spectra of dye-free, NaOH-adjusted Fe^{III} solutions tailed off much further into the VIS region due to scattering by colloids than did spectra of the same that were pH-adjusted by dilution (*Fig. 3*), confirming that some iron hydrolysis species were formed by base neutralization. When a small volume of concentrated AO7 stock solution was added to the NaOH-adjusted Fe^{III} solution, an immediate decrease in dye absorbance occurred; whereas dye added to Fe^{3+} solutions prepared by dilution exhibited no initial decrease in dye absorbance relative to an Fe-free control (*Fig. 3*). Elemental analysis of the orange-colored precipitate formed in a preparative-scale reaction (1 mM Fe^{III}, 1 mM AO7, pH 2.8, 23 mM total perchlorate) gave, after rinsing with electrolyte and vacuum drying, a compound of composition $C_{16}H_{20}Cl_{0.8}Fe_{1.4}N_2$ when normalized to the N

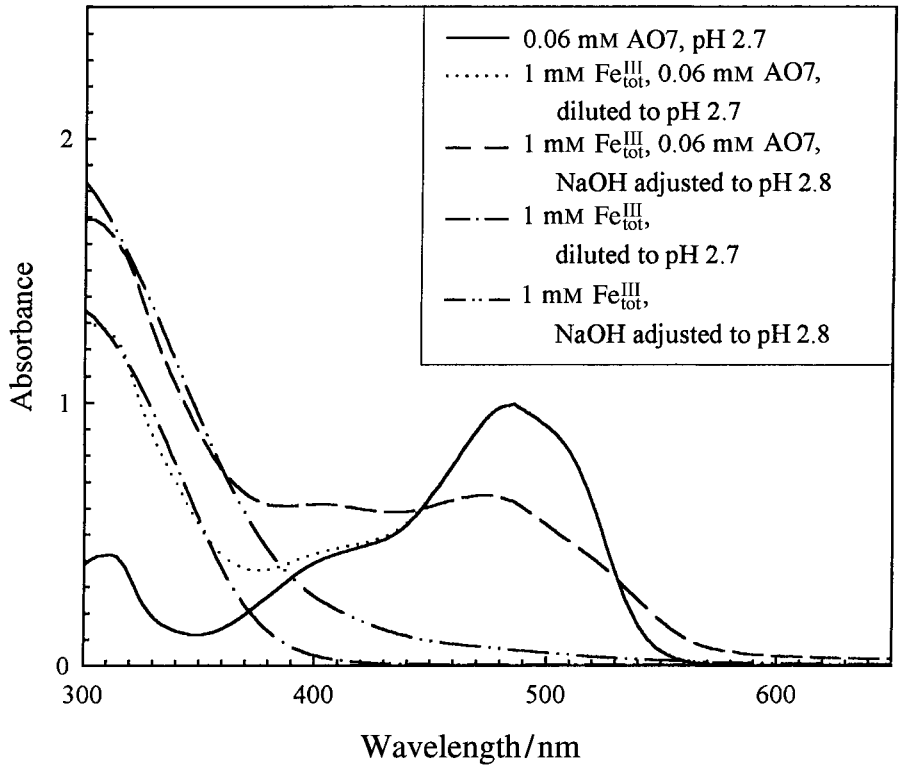


Fig. 3. *Effect of iron colloids on the absorbance of* Acid Orange 7. Iron was added as $FeCl_3$ and the background electrolyte was NaCl ($[Cl]_{tot} = 24$ mM). Fe^{III} solutions without dye and pH-adjusted by NaOH addition (– · · –); Fe^{III} solutions without dye and pH-adjusted by dilution (– · –); AO7 added to Fe^{III} solutions pH-adjusted by NaOH (– –); AO7 added to Fe^{III} solutions pH-adjusted by dilution (···); dye only (—).

content (38.4% C, 3.96% H, 5.44% N, 14.9% Fe, and 2.5% Cl). The Fe/dye ratio of 1.4 obviously indicates a co-precipitation of iron hydrous oxides with iron dye species as opposed to adsorption of dye molecules on an iron oxide surface. H-Content in excess of the stoichiometric amount expected for AO7 likely reflects the incorporation of waters of hydration and hydroxide ions for charge balance.

Experiments conducted on precipitated reaction mixtures verified that AO7 had not been transformed. The concentration of dissolved Fe^{2+} was less than the detection limit of 0.002 mM (< 0.2% yield). Addition of EDTA with mixing for one to several days resulted in re-solubilization of the precipitate and regeneration of more than 98% of the initial AO7, as determined by HPLC.

Lastly, evidence against Fe^{III} complexation of the *o*-hydroxyazo chromophore was obtained in experiments with AO10, which is identical to AO7, except that it has two sulfonate groups. The VIS spectrum at wavelengths above 425 nm of 0.06 mM AO10 in a perchlorate solution at pH 2.8 was unchanged in the presence of 1 mM Fe^{III} (*Fig. 4*). This indicates no complexation of iron with the chromophore. The enhanced solubility of the $Fe^{III} \cdot$ AO10 sulfonate salt over the $Fe^{III} \cdot$ AO7 salt is due possibly to the extra sulfonate group in the AO10 molecule.

Nadtochenko and *Kiwi* [19] postulated that AO7 forms a 1:1 complex with Fe^{III} ions in solution. We prepared solutions to replicate the experimental conditions of these authors' study. An aliquot of concentrated AO7 solution was added to a pH 2.8

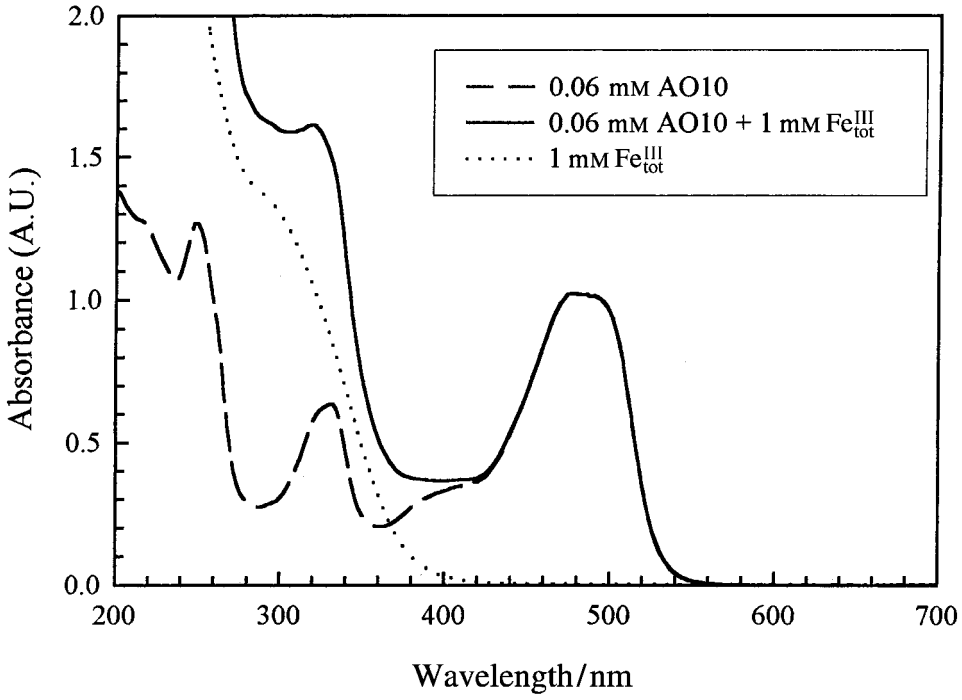


Fig. 4. *Absorbance spectrum of* Acid Orange 10 *in the absence of presence of iron(III) ions.* Solutions were prepared at pH 2.8 with a background electrolyte of $NaClO_4$ (23 mM). Iron was added as the iron(III) perchlorate salt.

$FeCl_3$ solution to give nominal solution concentrations of 2.9 mM AO7 and 0.9 mM Fe^{III}. A flocculent precipitate formed immediately upon mixing. *Nadtochenko* and *Kiwi* did observe precipitate formation in their solutions, but only after increasing the $FeCl_3$ concentration to 4 mM.

Reaction of Fe^{III} Ion with p-*Hydroxyazo Dye AO20*. Chelation of Fe^{III} by the chromophore of AO20 is not possible since the OH group is located in the *para* position; hence, no change in the VIS spectrum of AO20 was expected in the presence of Fe^{III} ions. However, when AO20 was added to solutions containing an excess of Fe^{III} at pH 2 or 3, a rapid color change from orange to pink occurred, the intensity of the dye band in the VIS region decreased, and the λ_{max} shifted from 476 to 486 nm (*Fig. 5*). The decrease in AO20 concentration was accompanied by the appearance of reduced iron in solution (*Fig. 6*). EDTA failed to restore the spectrum corresponding to the lost AO20, confirming that the dyestuff was degraded and not complexed. Furthermore, AO20 degradation was inhibited by prior complexation of Fe^{III} with EDTA. Together, these results indicate that AO20 is easily oxidized by Fe^{III}. Interestingly, *p*-hydroxyazo dyes are more readily oxidized by oxo(porphyrinato)iron [29] and horseradish peroxidase [30] than are *o*-hydroxyazo dyes, possibly due to intramolecular H-bonding in the latter that may inhibit removal of an electron. The only by-product identified in our experiments by liquid chromatography or by gas chromatography and MS or FID detection was 1,4-naphthoquinone, produced in only 4% yield based on initial AO20.

The reaction stoichiometry was determined by following Fe^{2+} spectrophotometrically in aliquots of the reaction mixture after complexation with ferrozine. The typical

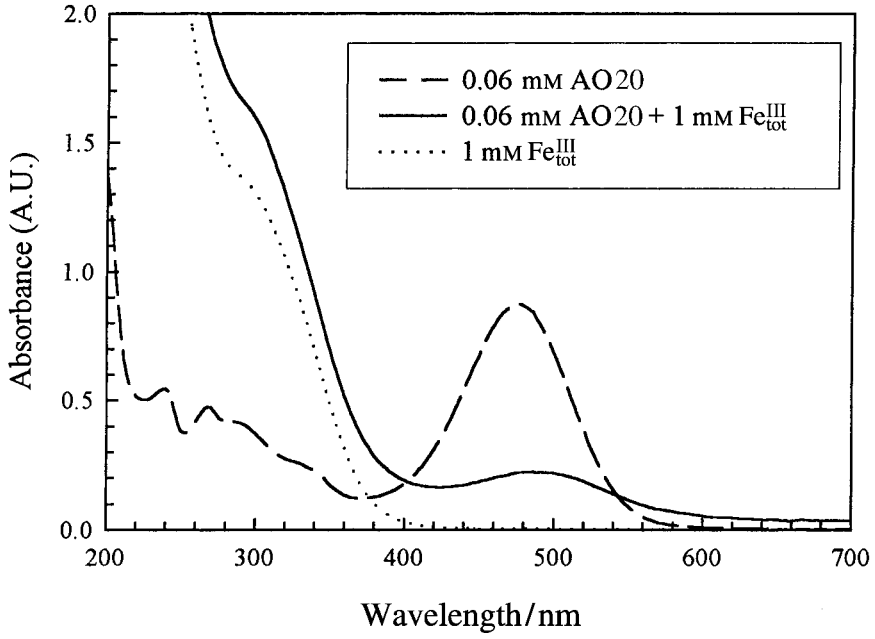


Fig. 5. *Absorbance spectrum of* Acid Orange 20 *in the absence and presence of iron(III) ions.* Solutions were prepared at pH 2.8 with a background electrolyte of $NaClO_4$ (23 mM). Iron was added as the iron(III) perchlorate salt.

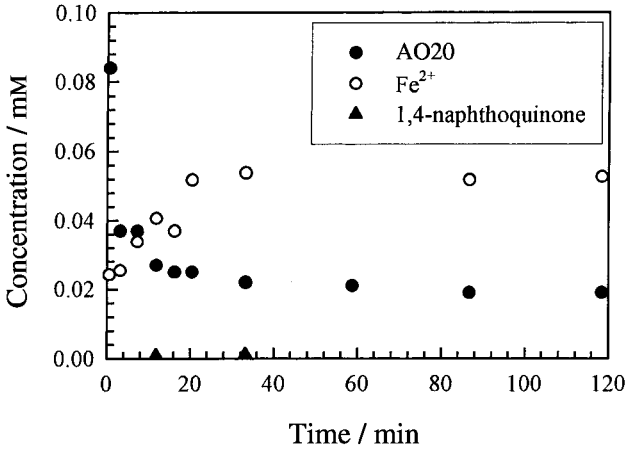


Fig. 6. *Oxidation of* Acid Orange 20 *with iron(III) perchlorate.* Initial concentrations were 0.071 mM dye and 0.125 mM Fe^{III}, at pH 2 and $[ClO_4]_{tot} = 23$ mM. Fe^{2+} Measurements were made 60 s after ferrozine addition to sample aliquots and reflect an apparent 1:1 reaction stoichiometry (see text for discussion of reaction stoichiometry).

development time for the ferrozine complex is 1 min, which also proved adequate for control samples of Fe^{2+} in the same solution matrix. However, in the samples, but not in the controls, we found that after an immediate color change within 1 min, the color of the Fe^{2+} · ferrozine complex continued to develop slowly for an additional 30 min (*Fig. 7*). A 1 min development time gave an apparent Fe^{2+}/oxidized dye ratio of 1.0 (*e.g.*, *Fig. 6*); however, extending the development time to 30 min gave an Fe^{2+}/oxidized dye ratio of 2.3. In several experiments similar to that in *Fig. 6*, the 30 min development

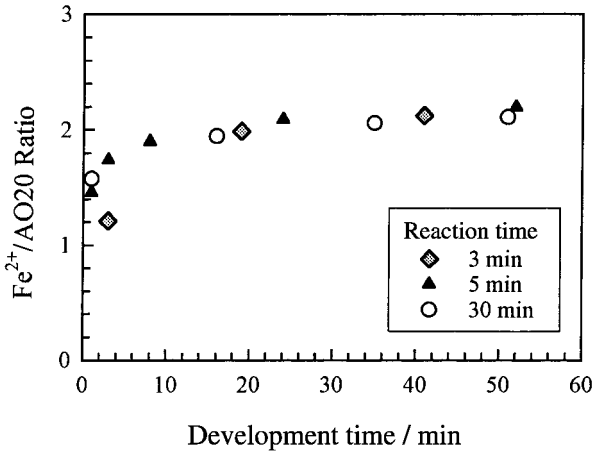


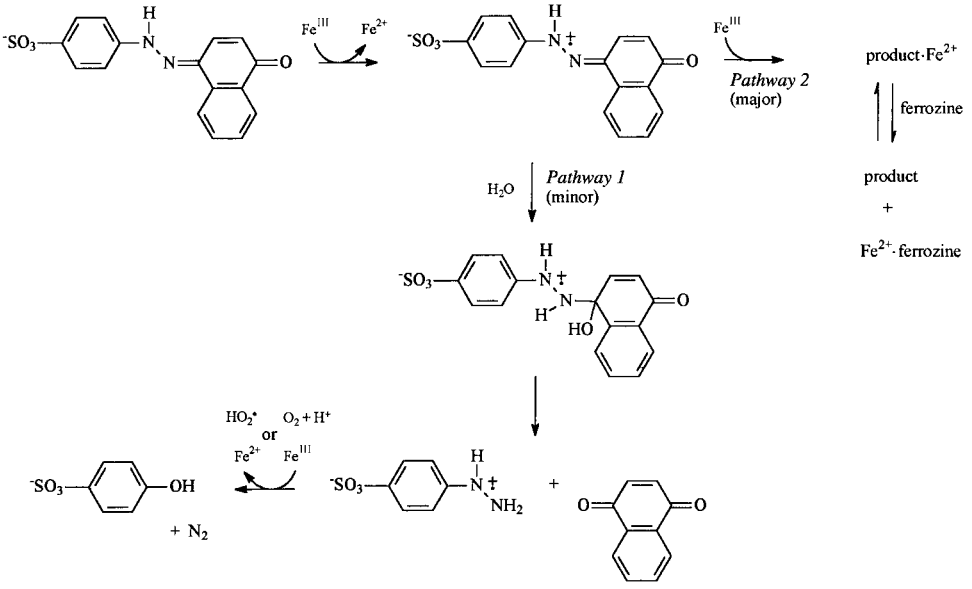
Fig. 7. *Formation of* Fe^{2+} · *ferrozine complex in* N_2*-purged solutions.* The reaction was initiated with 0.095 mM iron(III) perchlorate and 0.0122 mM AO20 at pH 2. Solution aliquots were removed after reaction times of 3, 5, and 30 min and mixed with ferrozine reagent. Complex formation is reported as reacted Fe^{2+}/dye stoichiometry calculated for 100% dye oxidation.

time gave an average 2:1 stoichiometry for all dye-plus-Fe^{III} reaction times of 1 min or longer.

Complete disappearance of AO20 was observed only when Fe^{III} was present initially in at least two-fold molar excess over the dye. A dye oxidation experiment with initial concentrations of 0.125 mM Fe^{III} and 0.043 mM AO20 gave 0.085 mM Fe^{2+} (30 min development time), and no dye compound was detectable by HPLC. Whereas, experiments with a stoichiometric deficiency of Fe^{III} had unreacted dye remaining in solution. For example, in the experiment of *Fig. 6*, in which 1.48 mol of Fe^{III} were added per mol of dye, 97–98% of Fe^{III} was ultimately reduced, and 27% of the initial AO20 remained (expected: 14% based on 2:1 stoichiometry). The unreacted AO20 in aliquots treated with ferrozine reagent did not further react during the extended color development; thus, the second equiv. of Fe^{2+} produced is not coupled to further AO20 oxidation.

The proposed mechanism for AO20 oxidation by Fe^{III} is shown in the *Scheme*. The reaction is initiated by one-electron removal from the azo group yielding a dye radical cation and the first equivalent of Fe^{2+}. A plausible minor pathway (*Pathway 1*) is hydrolysis of the dye radical cation to give 1,4-naphthoquinone (4%) and an unstable (sulfophenyl)hydraziniumyl radical. The hydraziniumyl radical is oxidized rapidly by O_2 or Fe^{III} to give 4-hydroxybenzenesulfonic acid [31][32]. Due to chromatographic interference, 4-hydroxybenzenesulfonic acid in yields comparable to 1,4-naphthoquinone could not be resolved by HPLC. If Fe^{III} and not O_2 is the oxidant in this step, the Fe^{2+} so generated would be very small relative to the total Fe^{2+} produced in the reaction.

Scheme. *Postulated Mechanism for Oxidation of* Acid Orange 20. *FerroZine®* was added to solutions as a colorimetric reagent for the Fe^{2+} assay.



The major route (*Pathway 2*) involves a second one-electron oxidation by Fe^{III} to produce a species that strongly complexes the reduced Fe^{2+}. This complex is formed reversibly and exchanges slowly with ferrozine when exposed to excess ferrozine in the assay. The exchange gives rise to the prolonged color development and accounts for the observed second equivalent of Fe^{2+}. If an oxidation by-product were binding a portion of Fe^{2+}, only the unbound species would be quantified in the 1 min ferrozine assay. We have not identified the species responsible for complexation of Fe^{2+} in *Pathway 2*.

An alternative explanation for the 2nd equiv. of Fe^{2+} is reaction of the AO20 radical cation in step 1 with O_2 to produce H_2O_2, which then slowly reduces Fe^{III} to Fe^{2+} in the presence of the ferrozine ligand (*Eqn. 2*). Reduction of Fe^{III} by H_2O_2 in the presence of the ferrozine reagent can be observed in control solutions. However, the pathway in *Eqn. 2* can be ruled out because Fe^{III} reaction with AO20 in N_2-purged compared to O_2-saturated solutions gave the same Fe^{2+}/oxidized dye stoichiometry and the same rate of slow color development in the ferrozine assay.

$$AO20^{+\bullet} + O_2 + H^+ \rightarrow AO20^{2+} + HO_2^{\bullet} \quad (2a)$$

$$HO_2^{\bullet} \rightarrow 1/2\ H_2O_2 + 1/2\ O_2 \quad (2b)$$

$$\text{ferrozine} + Fe^{III} + 1/2\ H_2O_2 \rightarrow Fe^{2+} \cdot \text{ferrozine} + 1/2\ O_2 + H^+ \quad (2c)$$

Relevance to Dye Waste Treatment Technology. The results of this research point out possible limitations or possible benefits of *Fenton*-based AOPs for treating acid dye wastewaters depending on the dye. Typical wastestreams contain *ca.* 1 gram dyestuff per liter of solution [3]. Such concentrations correspond to *ca.* 3 mM for the acid dyes considered in our study. *Fenton* treatment would be initiated by adding H_2O_2 and catalytic amounts (typically, 0.1 – 1 mM) of iron. At a dye/Fe^{III} ratio of 3 : 1, we observed immediate precipitation of AO7. Acid dyes that form poorly soluble Fe^{III} salts could remove the iron catalyst from solution and slow down or stop the oxidation process. Furthermore, light scattering by particles could reduce the efficiency of photo-*Fenton* treatments. Certainly, dye removal by *Fenton*-based AOPs has been achieved for a few acid dyes tested [7][9]; however, no comprehensive study has been conducted to assess whether azo-dye stability toward precipitation in the presence of Fe^{III} affects reaction rates. On the other hand, certain acid dyes may accelerate *Fenton*-degradation rates. The key step in hydroxyl-radical generation is the reduction of H_2O_2 by Fe^{2+} [33]. Azo dyes such as AO20 are partially oxidized by Fe^{III} and also provide reducing equivalents for the *Fenton* reaction.

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