Pretreatment of Textile Dye Concentrates Using Fenton's Reagent and Ozonation Prior to Biodegradation

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ABSTRACT

The Fenton's reaction and ozonation were tested as means for treating several reactive dye concentrated effluents from jet dyeing and cold pad/batch dyeing of cotton and cotton-polyester blend knits and for treating samples from black and red spent nylon acid dye baths. The concentrated discharges from dyeing operations included 1) a navy azo, disazo jet mixture of predominantly Reactive Black 5, 2) a bright blue containing only the anthraquinone dye, Reactive Blue 19, 3) a dark turquoise mixture primarily containing a copper-phthalocyanine dye, Reactive Blue 21, 4) a purple mixture of predominantly a copper-azo complex, Reactive Violet 5, 5) a nylon acid black mixture of predominantly an azo-chromium complex, 6) a nylon acid red mixture of predominantly the disazo dye, Acid Red 114, and 7) a slack washer concentrate from pad-dyeing the same navy.

Batch laboratory testing using the Fenton's reagent was conducted at pH 3. Weight ratios of typically 10:1 to 20:1 H_2O_2 to ferrous ion were used. Several field tests were also conducted to check the feasibility of in-plant operations. Batch laboratory testing (3 liters) of ozonation was conducted at both pH 3 and 11 with and without the presence of carbonates. Ozone was generated from dry air using Pollution Control Industries laboratory equipment. Testing was generally conducted at room temperature. The concentrated discharges from ozonation and Fenton's reaction were diluted for biodegradation tests. Biodegradation of untreated waters was also evaluated for comparison purposes.

The Fenton's reagent was effective at destroying color from highly colored discharges that contained a minimum of dissolved organics, e.g., those from jet dye machines and Nylon Fast Black BW dyeing operations. It was less effective and more costly if the discharge contained large quantities of sizing, organic dye bath auxiliaries, or natural cotton impurities. Ozonation was able to destroy dye color with minimum influence from other dissolved organics. The treated effluent easily biodegraded to a lower final color, although the final dissolved organic carbon (DOC) was not enhanced by ozonation.

The economics look particularly favorable for batch treating selected discharges with Fenton's reagent. Ozone also looks promising, but the capital commitment, operating costs, and safety considerations could restrict its use.

Copper phthalocyanine dyes are much more difficult to decolorize than the copper azo complexed ones. The copper is freed and does not precipitate at low pH with the Fenton solids even though the solution is decolorized. Increasing the pH with sodium hydroxide and lime of Fenton oxidized solutions to 10 precipitates the copper for both complexes, but increases the color of phthalocyanine oxidized under moderate conditions.

INTRODUCTION

Currently the textile dyeing industry is under considerable pressure to reduce color of process waters directly discharged to a local Publically Owned Treatment Works (POTW). To some extent, the color problem can be remedied in a POTW with proper operation, flocculation in the secondary clarifier, and postchlorination.

However, while the color issue has received considerable attention, more recently, salt (chloride and silicates) content, extensively used in reactive dyeing of cotton, heavy metals (copper in particular) found in selected dyes, and toxicity of organics from the degradation of dyes and dye auxiliaries are being considered within the framework of pretreatment regulations. Furthermore, the Environmental Protection Agency (EPA) is attempting to reduce the hazards associated with landfilling sludges through requirements of the Toxicity Characteristic Leachate Procedure (TCLP). Metals such as chromium and selected organics, including some acknowledged dye breakdown products, e.g., aromatic amines, are the focus of concern.

Additionally, under federal mandate, states are establishing stream water quality standards which will tighten National Pollution Discharge Elimination System (NPDES) permits. Relevant to textile operations is an increased emphasis on color, color reappearance, heavy metals including chromium and copper, and acute and chronic toxicity (often performed with Ceriodaphnia which is known to be sensitive to chlorinated organics and salts). Post-chlorination of a POTW treated effluent (often used as a final oxidation step for disinfection and color removal) can contribute to the formation of chlorinated organics which affect the waters toxicity. New, more stringent regulations are being written and enforcement is tightening.

During the past year, studies at Virginia Tech by Powell et al. (1) and at the University of Delaware by Flaherty and Huang (2) with dye concentrates from reactive dyeing of cotton have shown that a number of non-metallic dye concentrates can be decolorized quite effectively using Fenton's reagent or ozonation. Furthermore, these treated concentrates from reactive dyeing operations were amenable to aerobic biodegradation, but degradation was not enhanced by oxidation pretreatment.

The primary purpose of this effort was to extend the use of Fenton's reagent to a number of non-metallic and metallic dye bath concentrates. The objectives of this effort were to follow:

1. color removal
2. iron and DOC complexed with the resulting sludge
3. the fate of the copper and the chromium in the phthalocyanine and azo-metal complex dyes
4. the effectiveness of Fenton's reagent versus ozonation for pretreatment prior to biodegradation.
5. the cost effectiveness of Fenton's reagent versus chemical reduction with thiourea dioxide of the nylon red and black baths for color removal

BACKGROUND

As reviewed by Powell (3), many different schemes for treating colored waste streams have been investigated. Chemical reduction or anaerobic treatment will decolorize azo dyes by breaking the azo linkage (-N=N-) between the aromatic rings, but these treated discharges are not easily biodegraded (McCurdy et al., 4; Loyd et al., 5). In addition, aromatic amines, reduction products of azo dyes, have been suspected to cause cancer (Eberhard et al., 6). Researchers have identified a particular bacterium which degrades azo dyes. The expected reduction products, aromatic amines, were identified for certain azo dyes (Idaka et al., 7). The biotreatment of a Disperse Blue 79 was found to be unaffected by activated sludge treatment, but degraded in an anaerobic system with 97% removal. The possible degradation products were detected and some removal of these products was noted in subsequent aerobic digestion (Gardner et al., 8). Attempts to measure the biodegradability of the amines has been attempted by other researchers with success. The degradability of the aromatic amines depended heavily on initial biomass concentration (Brown and Laboureur, 9).

Oxidative treatment schemes have been studied for decolorization of dyes by several researchers. Color removal using Fenton's reagent has been known for some time (Yamaguchi et al., 10) and has been shown to decolorize a wide variety of dyes including reactive azo dyes (Gregor, 11). However, the dye solutions studied were formulated in the laboratory and were not actual waste streams. Research has shown that dye solutions can be decolorized with either ozone or chlorine. Dyeings were conducted in the laboratory and the exhausted dyebaths treated for reuse. Actual industrial dye water was not studied in the experiment, however (Perkins et al., 12). Ozone has also been show to effectively decolorize pure azo dye solutions (Sato et al., 13) with the products identified by GC and LC/MS. Some absorbents have been shown to be capable of removing specific types of dyes (Michelsen et al., 14). Many of these studies have been conducted with pure dye solutions. To date, only limited testing has been completed on actual waste streams.

Chlorine, while a powerful oxidant, can produce more toxic oxidation products. Chlorine dioxide, in reactions with substituted phenolic compounds, has also been shown to increase toxicity. In the same study, both permanganate and Fenton's reagent decreased the toxicity of the wastewater (Vella and Munder, 15).

FENTON'S REAGENT CHEMISTRY

Fenton's reagent is the combination of ferrous iron and hydrogen peroxide. The initiating reaction is the reduction of hydrogen peroxide to an hydroxide ion and an hydroxyl radical with the corresponding oxidation of ferrous iron to the ferric form as shown in the following equation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$$
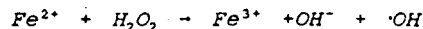
As with ozone in a basic solution, hydroxyl radicals and superoxy radicals are the main oxidizing species of Fenton's reagent. The oxidation of organics is accomplished by a free radical chain reaction mechanism similar to that involved in ozonation decomposition reactions.

The complete mechanism by which hydrogen peroxide and iron oxidize organics has only been postulated for simple compounds. A complete mechanism of Fenton's reagent oxidation of benzene in the presence of molecular oxygen has been proposed (Kunai et al., 20). A number of other articles on mechanisms have been published in the *Chemical Oxidation Technology for the Nineties* edited by Eckenfelder, Bower and Roth at Vanderbilt University (2).

OZONE CHEMISTRY

Ozone (O_3) is an allotrope of oxygen created by passing an air or oxygen gas stream through a coronal discharge. The corona creates singlet oxygen atoms which react with molecular oxygen to form O_3. Gaseous ozone concentrations of 1-3% are possible using air feed and 2-6% using pure oxygen. The concentration of ozone in the gas stream depends upon the coronal energy, gas flow rate, gas stream humidity, and temperature of the gas and generator (Rice and Netzer, 19).

It is a very powerful oxidant that is rather selective and reacts well with unsaturated bonds. The mechanism of the reaction has been discussed by Morrison and Boyd (16), Yamamoto (17), Matsui et al. (18), Sato et al. (13), and Rice and Netzer (19).

In summary, only a very limited number of research efforts have been conducted using either Fenton's Reagent or ozone for treating actual textile dye wastes.

DYE BATHS STUDIED

The dye bath concentrate discharges chosen for study came from the following batch dyeing operations:

1. A cotton reactive azo and disazo navy mix, labeled Navy 106, of predominantly Remazol Black GFA (Reactive Black 5), Remazol Red RB (Reactive Red 198), and Remazol Golden Yellow RNL used for jet dyeing the cotton of cotton/polyester knit blends after the polyester was dyed. The bath typically contained 10-12% NaCl.
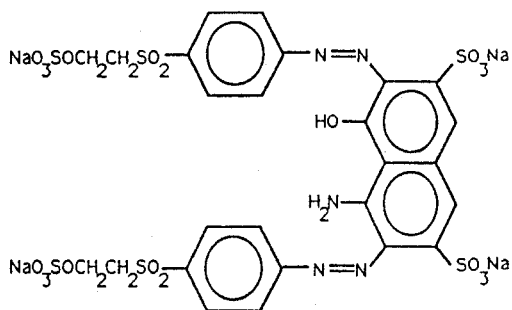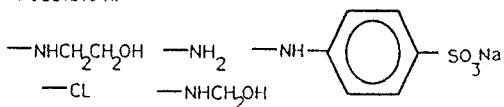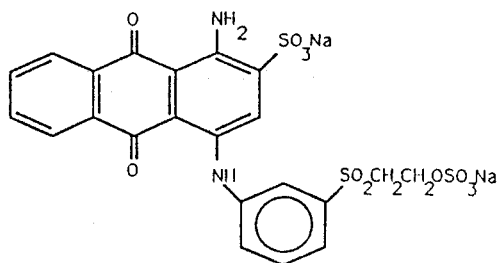

Reactive Black 5

Remazol Red RB

Possible X:

—NHCH₂CH₂OH   —NH₂   —NH—⟨⟩—SO₃Na
—CL   —NHCH₂OH
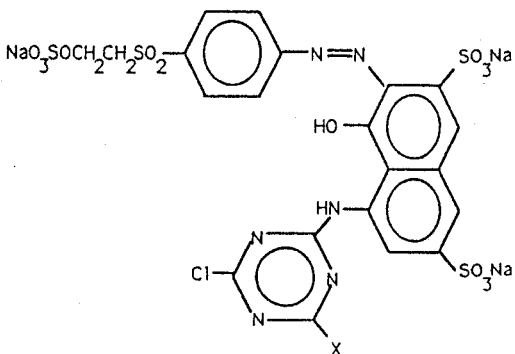
2. A cotton reactive anthraquinone blue mix, labeled Bright Blue 147, of Remazol Brilliant Blue R Special (Reactive Blue 19) used for jet dyeing the cotton of cotton/polyester knit blends before the polyester was dyed. The bath typically contained 10-12% NaCl.


Remazol Brilliant Blue R

3. A cotton reactive phthalocyanine and azo copper complex blue mix, labeled as Mediterranean 128, of predominantly Remazol Turquoise RP (Reactive Blue 21), Remazol Red RB (Reactive Red 198), and Remazol Brilliant Blue BB used for jet dyeing 100% cotton jersey. The copper content of the solid phthalocyanine Remazol Turquoise RP is 1.3% and 2.7% for the solid azo complex Remazol Brilliant Blue BB. The bath typically contained 10-12% NaCl.
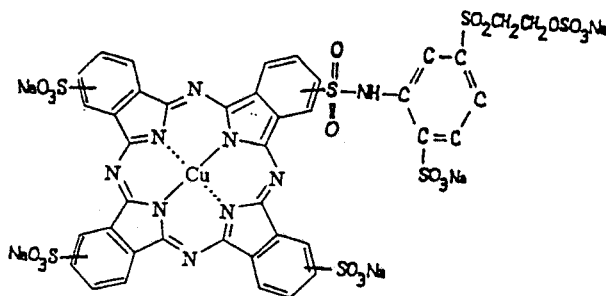

4. A cotton reactive azo copper complex purple mix, labeled Purple 120, of predominantly Remazol Brilliant Violet 5R (Reactive Violet 5) and Remazol Blue R2R used for jet dyeing 100% cotton jersey. The copper content of the solid azo complex Remazol Brilliant Violet 5R is 4.5% and 2.7% for the solid azo complex Remazol Blue R2R. The bath typically contained 10-12% NaCl.
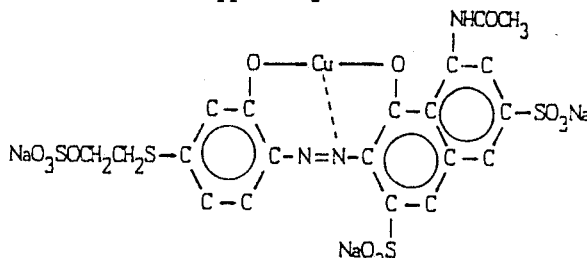
5. A nylon acid black mix of Nylon Fast Black BW, a proprietary blend of three dyes used in jig or Burlington dyers. At least one of the dyes is an azo chromium complex that gave the solid mix a chromium content of 3%.

137

6. A nylon acid red mix of predominantly Acid Red 114, a disazo dye, used in jig of Burlington dye machines.
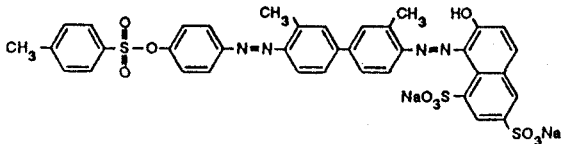
7. A cotton reactive Navy 106 (same as 1.) used in cold pad/batch dyeing. Samples for evaluation were taken from the most concentrated section of slack washers. Sodium silicate was used in the formulation.

PROCEDURE

Fenton's reactions were conducted primarily at 5, 10, or 20 to 1 weight ratios of H_2O_2 to ferrous ion. For each experimental point a predetermined amount of ferrous sulfate (hydrated form) was added to the actual dye concentrate after first adjusting the pH. Then, a known amount of H_2O_2 was added to provide the desired conditions. Typically within one hour or less the color removal had stabilized. The reaction products were then filtered through a Whatman GF/C 1.2 μm glass microfibre filters. The filtrate was analyzed for iron and residual metals such as copper and chromium, using a Perkin-Elmer 703 Atomic Absorption Spectrophotometer (A.A.) and the dissolved organic carbon (DOC) was measured using a Shimadzu TOC-5000 analyzer. For color measurements, the percent transmittances were measured at 590, 540, and 438 nm. Munsel values were calculated using a ninth ordered equation to arrive at the final ADMI color number. For selected runs the filter solids were dried and weighed to determine the total suspended solids (TSS).

The laboratory ozonation tests were conducted using a 4 inch inside diameter by 40 inch high glass contact tower containing no packing. Three liters of dye concentrate were tested during batch ozonations. Recirculation of the dye concentrate from the bottom of the contactor provided mixing and means for sampling. Ozone was sparged up through the contactor on a once through basis. Additional information on procedures and testing has been provided by Powell et al. (1, 3).

RESULTS AND DISCUSSION

Fenton's Reagent. The results of a series of tests using Fenton's reagent for removal of color (ADMI) and DOC from the previously identified dye bath waste concentrates are shown in Figures 1 through 19. Also, shown on these figures are the amount of ferrous ion added before hydrogen peroxide. The iron remaining in the filtrate after precipitation at low pH and an isolated total suspended solids (TSS) value are shown in several figures. Finally, for the copper containing

dyes, the metals remaining in the filtrate measured.

Figures 1 and 2 show results from Fenton's reagent treatment of a Navy 106 jet dye bath effluent, a mix of azo and disazo reactive dyes. These results can be compared with Figures 3 and 4 for treating Bright Blue 14 typical reactive anthraquinone dye mixture. These results point out the effectiveness of destroying color in a concentrated, low DOC bath, such as Navy 106 (Fig. 1), compared to the organic laden anthraquinone dye (Fig. 3 Note also the somewhat decreased level of T formed with the Navy 106, mostly because of reduced level of oxidation required for col removal. In the cotton-polyester blend dye the cotton is jet-dyed second for Navy 106, first in the case of the Bright Blue 147. Thus, less DOC is found in the effluent fro dyeing the cotton with Navy 106. Interestingly, the rates of DOC removal fro the filtrates into the filtered solids, as function of Fenton's reagent used, are abou the same for each.

The treatment with Fenton's reagent of a typical, very stable, copper phthalocyanine (Figs. 5 and 6) can be compared to treatmen a copper-complexed azo dye (Figs. 7 and 8). Decolorizing the stable, copper phthalocyar dye (Fig. 5), that contained initially 870 of DOC (Fig. 6), required 3000 ppm H_2O_2. Decolorizing the copper-complexed azo dye required 180 ppm H_2O_2 (Fig. 7) for a bath containing only 60 ppm DOC. Another sample the Purple 120 spent bath required 800 ppm for decolorization. Possibly, the sample u to generate Figures 7 and 8 was the first w instead of the spent dye bath. In any case the high DOC occurred as a result of dyeing 100% cotton jersey using organic auxiliarie and the residual spinning waxes. The difficulty in decolorizing an aqueous solut containing only the copper phthalocyanine Reactive Blue 21 is shown in Figures 9 and Figures 11 and 12 provide the results for copper-complexed Remazol Brilliant Violet 5 liquid dye (Reactive Violet 5). These two solutions of "pure" dyes were made to approximately 40% of the dye bath strength, since a fixation of 60% was assumed. The Reactive Blue 21 took about 2,000 ppm H_2O_2(I 9), well above the 800 ppm needed for decolorizing Reactive Violet 5 (Fig. 11). high initial DOC of the Turquoise RP (250 p was well above the 77 ppm DOC for the Viole 5R. This higher DOC could be the reason additional Fenton's reagent was needed. Furthermore, as seen in Figures 6, 8, 10 an 12, the copper washed through the filter an appeared in the filtrate. Thus, after oxidation, the copper was not significantly retained as part of the dye structure which from the 90% decrease in filtrate DOC, precipitated in the solids (TSS formation) low pH.

Three separate trials were made with the sa laboratory-prepared Turquoise RP solution. reaction at a 10 to 1 peroxide to ferrous r with 18,000 ppm H_2O_2, followed by filtration
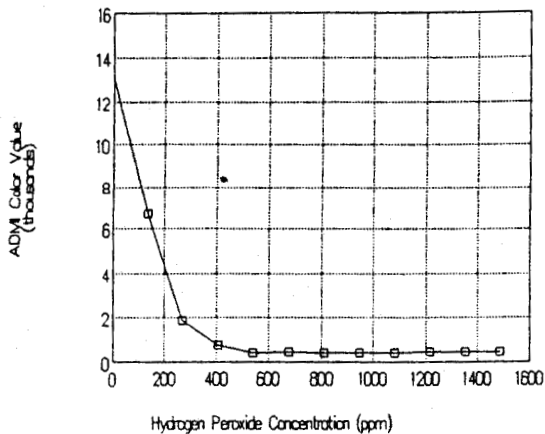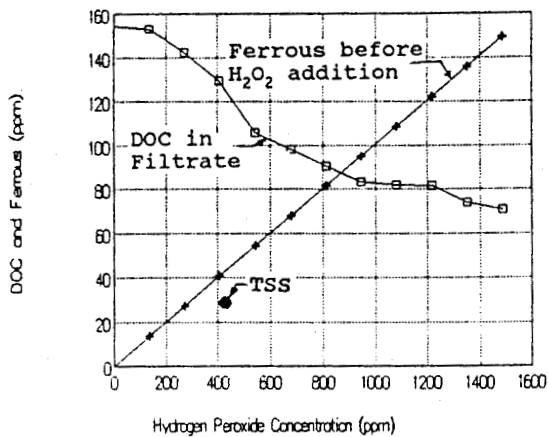
CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.2, T = 25C, color disappearance time = 1 hr.

FIG. 1 Decolorization of Navy 106 Jet dye bath waste using Fenton's Reagent oxidation.
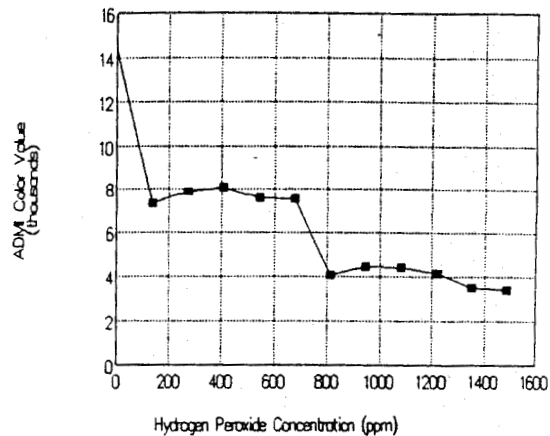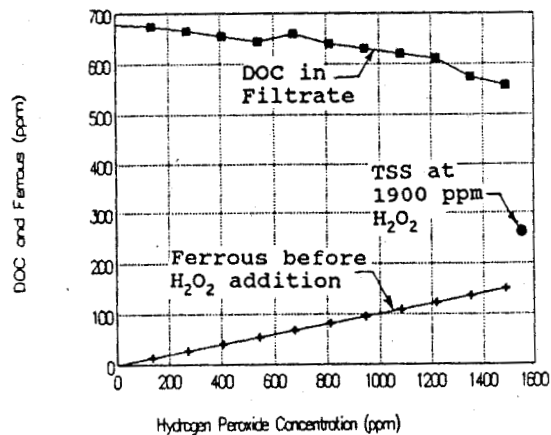

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH 3.3, T = 25C, color disappearance time = 1 hr.

FIG. 3. Decolorization of Bright Blue 147 (Reactive Blue) 19 jet dye bath waste concentrate using Fenton's Reagent oxidation.

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.2, T = 25C, color disappearance time = 1 hr.

FIG. 2. DOC and ferrous concentrations of Navy 106 jet dye bath waste concentrate treated using Fenton's Reagent oxidation and filtered at low pH.
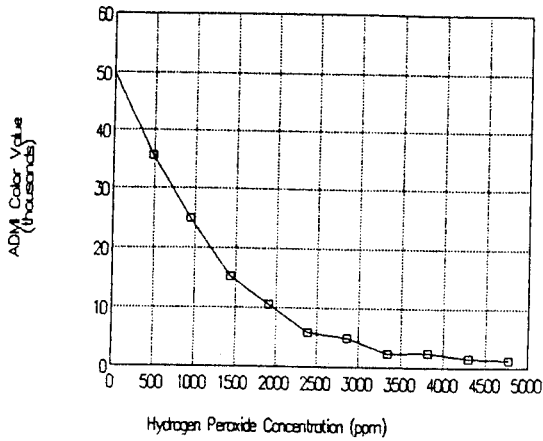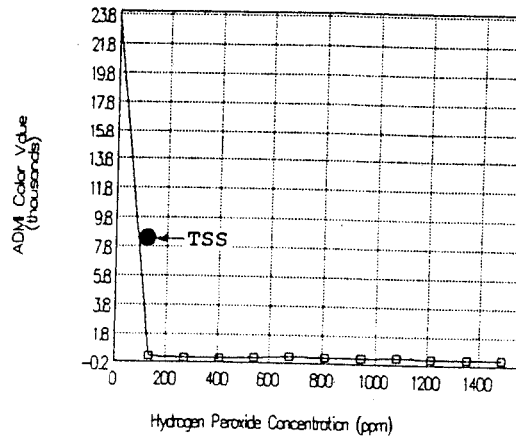

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.3, T = 25C, color disappearance time = 1 hr.

FIG. 4. DOC and ferrous concentrations of Bright Blue 147 (Reactive Blue 19) jet dye bath waste concentrate treated using Fenton's Reagent oxidation and filtered at low pH.
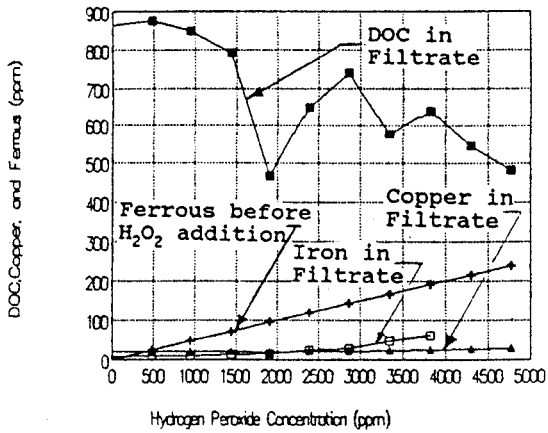
CONDITIONS: 20 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.7, T = 25C, color disappearance time = 1 hr.

FIG. 5. Decolorization of Mediterranean 128 (Reactive Blue 21) cotton jet dye (copper phthalocyanine) bath waste concentrate using Fenton's Reagent oxidation.
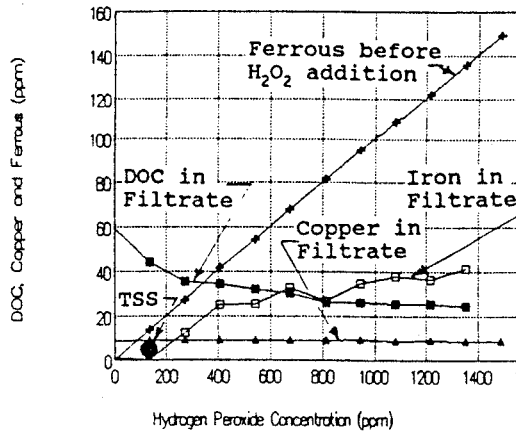
CONDITIONS: 10 to 1 hydrogen peroxide to weight ratio. pH = 3.2, T = 25C, disappearance time = 1 hr.

FIG. 7. Decolorization of Purple 120 (R Violet 5) jet dye (copper complex azo) bat using Fenton's Reagent oxidation.

CONDITIONS: 20 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.7, T = 25C, color disappearance time = 1 hr.

FIG. 6. DOC, copper and ferrous concentrations of Mediterranean 128 (Reactive Blue 21) cotton jet dye (copper phthalocyanine) bath concentrate treated using Fenton's Reagent oxidation and filtered at low pH.

CONDITIONS: 10 to 1 hydrogen peroxide to f weight ratio. pH = 3.2, T = 25C, disappearance time = 1 hr.

FIG. 8. DOC, copper and ferrous concentra Purple 120 (Reactive Violet 5) jet dye (azo complex) treated using Fenton's Reage filtered at low pH.

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.2, T = 80C, color disappearance time = .16 hr.

FIG. 9. Decolorization of pure Remazol Turquoise RP (Reactive Blue 21) as 877 ppm solution using Fenton's Reagent oxidation.

CONDITIONS: 20 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.2, T = 80C, color disappearance time = 0.10 hr.

FIG. 11. Decolorization of pure Remazol Violet 5R (Reactive Violet 5) as 896 ppm solution treated using Fenton's Reagent.

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.2, T = 80C, color disappearance time = .16 hr.

FIG. 10. DOC, ferrous and copper of pure Remazol Turquoise RP (Reactive Blue 21) as 877 ppm solution treated using Fenton's Reagent oxidation and filtered at low pH.
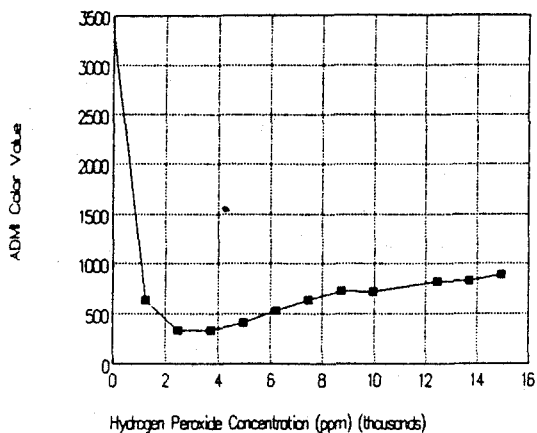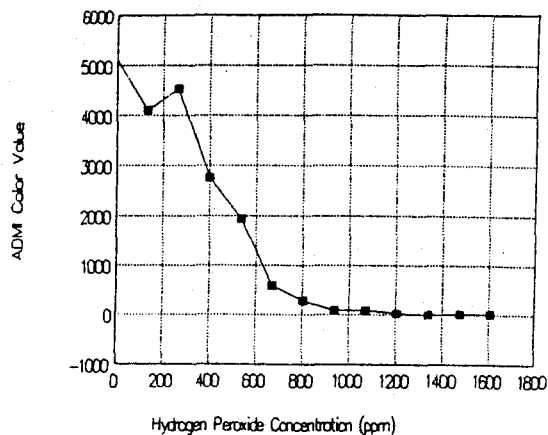
CONDITIONS: 20 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.2, T = 80C, color disappearance time = 0.10 hr.

FIG. 12. DOC, ferrous and copper of pure Remazol Violet 5R (Reactive Violet 5) as 986 ppm solution treated using Fenton's Reagent oxidation and filtered at low pH.

low pH, resulted in 18 ppm copper in the filtrate, which agrees with the Fe 10 extension. A second test using the same Fenton's reagent procedure followed by addition of NaOH to reach pH 10, and filtration, resulted in 0.3 ppm copper in the filtrate. A third test, the same as test two but with 400 ppm Ca(OH)$_2$ added before filtration resulted in a 0.14 ppm copper containing filtrate. We are investigating the leachability of copper from these sludges, although currently copper is not listed for analysis as part of the TCLP protocol.

Figures 13, 14 and 15 present the results of two laboratory trials on different bath concentrates of acid nylon dyeing using Nylon Fast Black BW - a chromium complex in an atmospheric jig or Burlington. Figures 13 and 15 both indicated that approximately 2,000 ppm H$_2$O$_2$ was necessary for decolorization. The DOC was high (Fig. 14), with typically 1500 ppm or more contributed by the acetic acid used for pH control. In one test, the level of DOC formed was much higher than that observed in previous testing, well above the amount of iron added as part of the Fenton's reagent. In addition, the DOC removal per amount of Fenton's reagent added was much higher for the Nylon Black BW (Fig. 14). The fate of chromium following reaction and the potential for its removal as sludge are being investigated.

Preliminary studies on the use of calcium hydroxide to aid in precipitating both metals and organic species following oxidation with Fenton's reagent indicated that rather large amounts of lime (about 500 ppm) were required to effect significant improvements. The next step was to adjust the pH with sodium hydroxide for maximum precipitation of the metal hydroxides. The results of adjusting the pH to 10.0, as suggested in references 21 and 22, and then adding calcium hydroxide are shown in Table I.

The tests on the Mediterranean bath containing the copper phthalocyanine dye, Reactive Blue 21, yielded new information. A color reduction of 143,000 to 2,580 ADMI color units made treatment with 5000 ppm hydrogen peroxide and 500 ppm ferrous ion at pH 3 appear to be a promising approach to the color and metal problem. Unfortunately, simply increasing the pH of the Fenton treated solution to pH 10 with sodium hydroxide brought back the turquoise color and yielded an ADMI color value of 75,400. Plainly, the phthalocyanine chromophore had not been completely destroyed as had previously been thought. However, the very high Fenton dosage of 50,000 ppm peroxide and 5,000 ppm ferrous ion yielded a solution that measured 14,600 ADMI after the pH was elevated to 10. This indicates that most of the phthalocyanine groups were destroyed. Addition of lime after 50,000 ppm peroxide increased the TSS and decreased the copper in solution by 88%.

The purple jet dye bath with an ADMI value of 76,000 required only 1200 ppm peroxide and 121 ppm ferrous ion to produce about 99% color

reduction. Upon increasing the pH to 10 the color was further reduced by 24% and the copper in solution was reduced by 95%. Addition of lime after raising the pH yielded negligible benefit in removing the copper and color from solution.

The nylon acid black spent bath with an ADMI of 21,500 required 3000 ppm peroxide and 300 ppm ferrous ion to effect an 80% color removal. Increasing the pH to 10 doubled the color which was only slightly lowered by addition of lime.

Figures 16 through 19 show the results of two studies in which nylon red was treated with Fenton's reagent. The 4500 ppm (Fig. 16) versus 2800 ppm H$_2$O$_2$ (Fig. 18) difference for color removal is unclear, except that these represent samples taken from different baths. The DOC removal per Fenton's reagent added and 4500 ppm TSS at 4700 ppm H$_2$O$_2$ added at a 10 to peroxide to ferrous weight ratio were the highest observed. Sludge formation is a concern.

Thiourea Dioxide. For comparison, we investigated briefly chemical reduction with thiourea dioxide for removal of color from nylon black and nylon red dye bath effluents. Note, the amount of thiourea dioxide for decolorization of the black was 3,000 ppm (Fig. 20) versus 2000 ppm H$_2$O$_2$ (Figs. 13 and 15). For the nylon red, 3000 ppm thiourea dioxide (Fig. 14) was also needed versus 2800 to 4700 ppm H$_2$O$_2$ (Figs. 16 and 18). At $2.00 per lb for thiourea dioxide versus $1.00 per lb for H$_2O_2$, one would tend to favor H$_2$O$_2$ although sludge formation must be considered. In addition, some reductive processes can at times create effluents unfavorable for subsequent aerobic treatment (McCurdy et al., 4; Loyd et al., 5).

Ozonation. Figures 22, 23 and 24 are earlier results by Powell et al. (1, 3) for treating Navy 106 jet effluent with ozone. The color and DOC removal were followed through oxidation, dilution, and aerobic treatment in sequencing batch reactor (SBR). These results first show that ozone can be effective at eliminating color from the navy jet (Fig. 22) but that color removal can be more effective using 1000 ppm H$_2$O$_2$ (H$_2$O$_2$/Fe^{++} = 10/1) versus 60 ppm ozone - the basis for these comparisons. The Fenton's reagent further removed greater quantities of DOC in the sludges (decantation). However, if H$_2$O$_2$ costs $1.00 per lb and ozone (total operating plus capital cost) is $2.00-4.00 per lb then Fenton's reagent looks promising, but sludges are formed in the Fenton's reaction. With dye waste containing more DOC, the choices are less clear.

Oxidative Decolorization. In order to compare the color removal efficiency of the oxidants for the three waste streams from navy jet, bright blue jet, and navy pad dyeing reported earlier by Powell et al. (1, 3), the color removed as a function of oxidant mass (either ozone or hydrogen peroxide) was calculated for each waste stream as shown in Fig. 25. These calculations roughly correspond to the slope of the color versus oxidant concentration curves
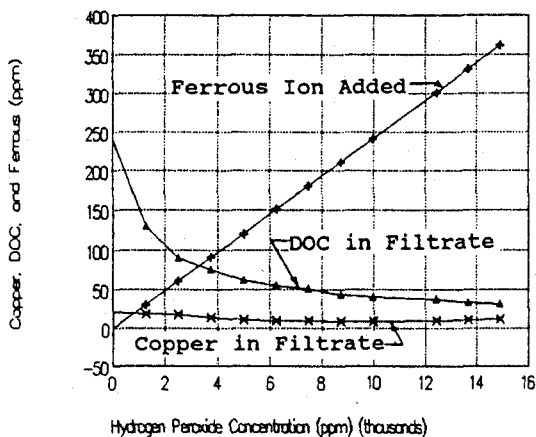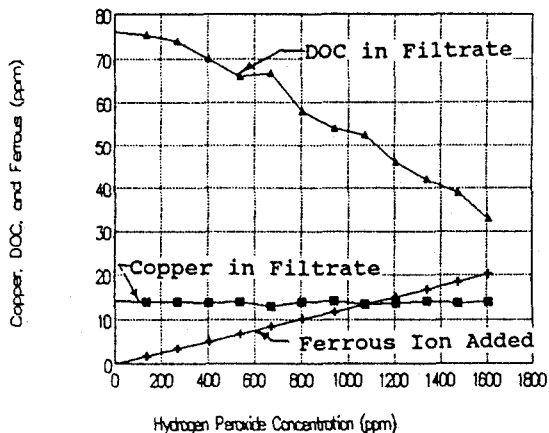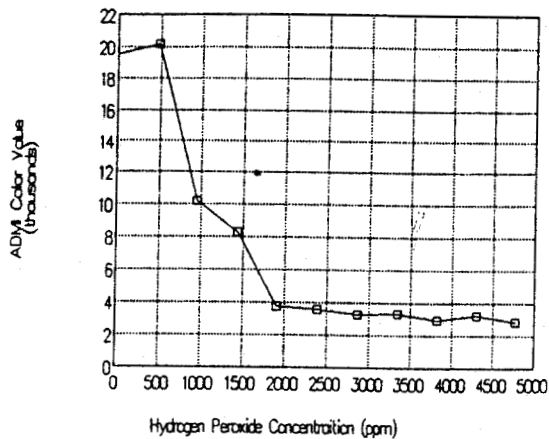
CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.9, T = 100C, color disappearance time = 0.5 hr.

FIG. 13. Decolorization of Nylon Fast Black BW dye (chromium azo complex) bath waste concentrate using Fenton's Reagent oxidation.
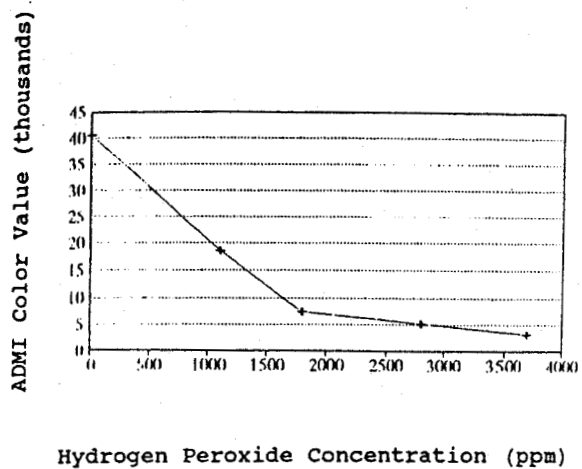
CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 2.7, T = 80C, color disappearance time + 0.5 hr, ADMI measured at 30X dilution.

FIG. 15. Decolorization of Nylon Fast Black BW dye (chromium azo complex) bath waste concentrate using Fenton's Reagent oxidation.

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 3.9, T = 100C, color disappearance time = .5 hr.

FIG. 14. DOC and ferrous concentrations of Nylon Black BW (chromium azo complex) bath waste concentrate treated using Fenton's Reagent oxidation and filtration at low pH.
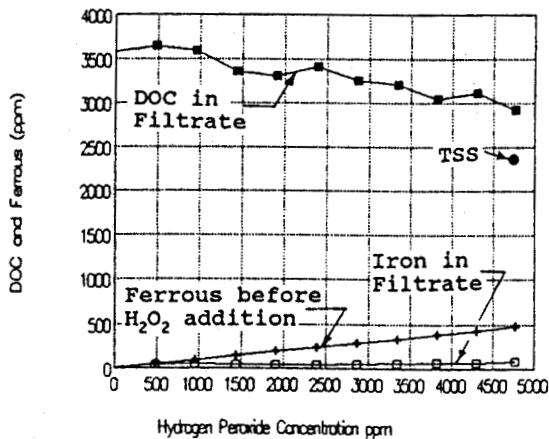

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 4.o, T = 100C, color disappearance time = .5 hr.

FIG. 16. Decolorization of Nylon Red dye (Nylon Red 114 [disazo] and Red B2B [azo] bath waste concentrate using Fenton's Reagent oxidation.

CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 4.0, T = 100C, color disappearance time = .5 hr.

FIG. 17. DOC and ferrous concentrations of Nylon Red Dye (Nylon Red 114 [disazo] and Red B2B [azo] bath waste concentrate using Fenton's Reagent oxidation and filtered at low pH.
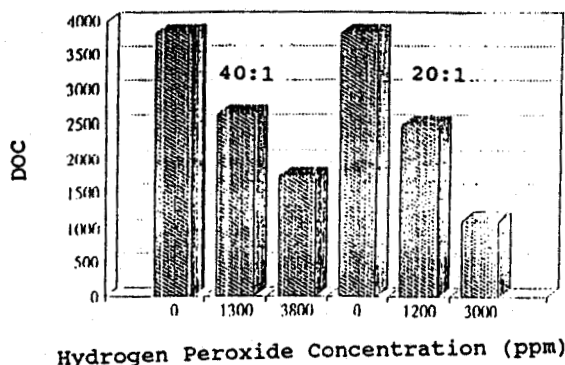
CONDITIONS: 40 to 1 and 20 to 1 H_2O_2 to ferr weight ratio. pH = 2.4, T = 80C, c disappearance time = .33 to 0.5 hr.

FIG. 19. DOC concentrations of Nylon Red (Nylon Red 114 [disazo] and Red B2B [azo]) b waste concentrates treated using Fenton's Reag oxidation and filtered at low pH.

Hydrogen Peroxide Concentration (ppm)
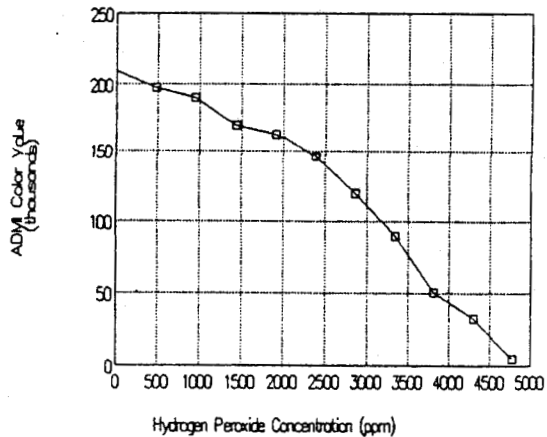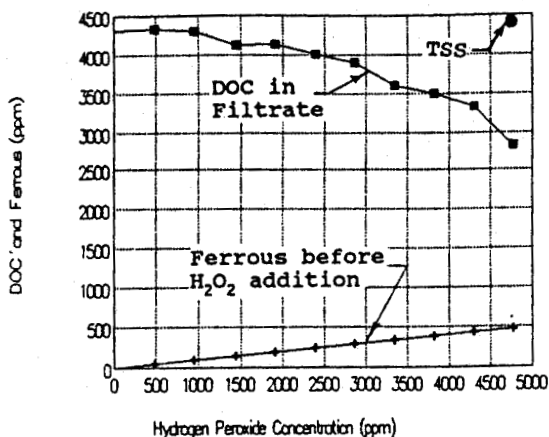

Thiourea Dioxide Concentration (ppm)
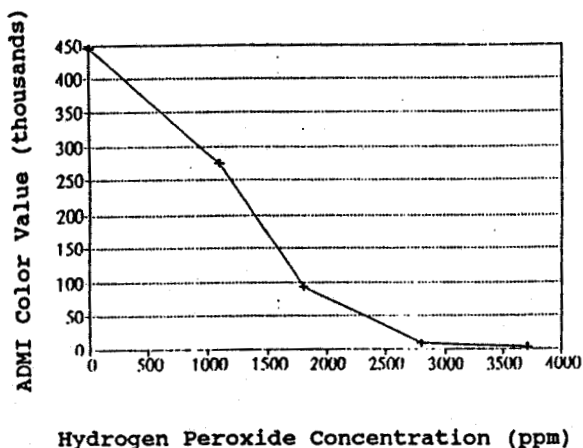
CONDITIONS: 10 to 1 hydrogen peroxide to ferrous weight ratio. pH = 4.5, T = 80C, color disappearance time = 0.5 hr administered at 30 to 1 dilution.

FIG. 18. Decolorization of Nylon Red dye (Nylon Red 114 [disazo] and Red B2B [azo] bath waste concentrate using Fenton's Reagent oxidation.

CONDITIONS: pH = 3.8, T = 89C, col disappearance time = 0.05 to 0.33 hr, AD measured at 30X dilution.

FIG. 20. Decolorization of Nylon Fast Black (chromium azo complex) bath waste concentra using thiourea dioxide reduction.
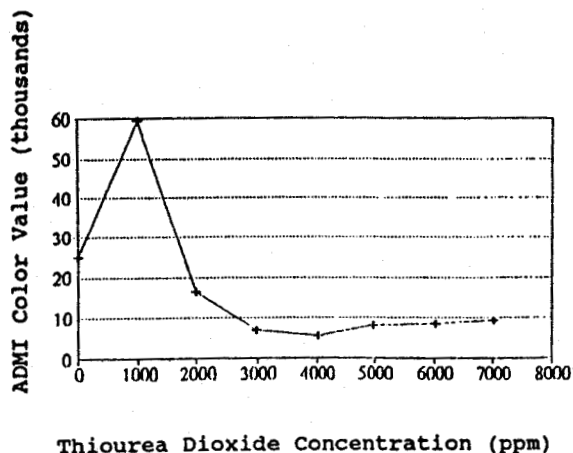
ADMI Color Value (thousands)

Thiourea Dioxide Concentration (ppm)

ADMI Color Value (Thousands)

Dyewash · Treated Dyewash · Reactor Influent · Reactor Effluent

CONDITIONS: pH = 7.5, T = 90C, color disappearance time = 0.10 to 0.33 hr, ADMI measured at 30X dilution.

FIG. 21. Decolorization of Nylon Red dye (Nylon Red 114 [disazo] and Red B28 [azo] bath waste concentrate using thiourea dioxide reduction.

CONDITIONS: ADMI measured at 25X dilution. Reactor influent is mixture of treated dyewash and primary effluent (1:9). SBRs have 2-day retention time. Results are average of six days.

FIG. 23. Effect of oxidation schemes on the removal of color from Navy jet dye waste in bioreactors.

ADMI Color Value (Thousands)

Ozone Reacted (ppm)

—— Pure Dye Soln.,pH 10   —□— pH 10   —■— pH 3

Dissolved Organic Carbon (ppm)

Untreated   High pH O3   Low pH O3   Fenton's

Dyewash · Following Oxidation · Reactor Influent · Reactor Effluent

CONDITIONS: ADMI measured at 25X dilution.

FIG. 22. Decolorization of Navy 106 jet dye bath waste concentrate using ozonation.
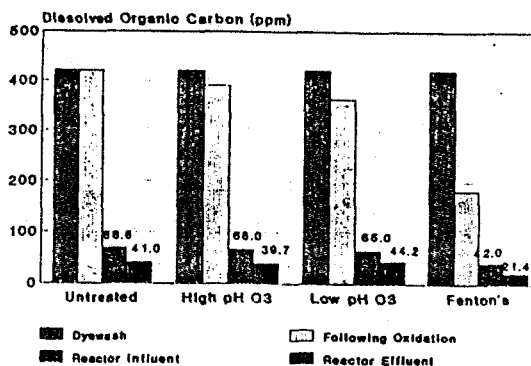
CONDITIONS: Reactor influent is mixture of treated dyewash and primary effluent (1:9). SBRs have 2-day retention time. Results average of six days.

FIG. 24. Effect of oxidation schemes on the removal of DOC from Navy jet dye waste in bioreactors.

ADMI Color Decrease per ppm O3 (or H2O2)

Legend: High pH O3, Low pH O3, Fenton's Reagent

Navy Slack — DOC: 175 ppm, Dye DOC: 15 ppm
Navy Jet — DOC: 326 ppm, Dye DOC: 225 ppm
Brilliant Blue Jet — DOC: 600 ppm, Dye DOC: 120 ppm

CONDITIONS: ADMI color value adjusted by dilution to the 0.85 power. Navy Slack and Brilliant Blue Jet were diluted 5X. Navy Jet was diluted 25X.

FIG. 25. Color removal efficiency from dye waste streams.

Table I: pH Adjustment and Lime Precipitation Following Reaction of Fenton's Reagent (1:10 ferrous:peroxide ratio) with Dye Baths 3, 4, and 5 Containing Metal Complexes

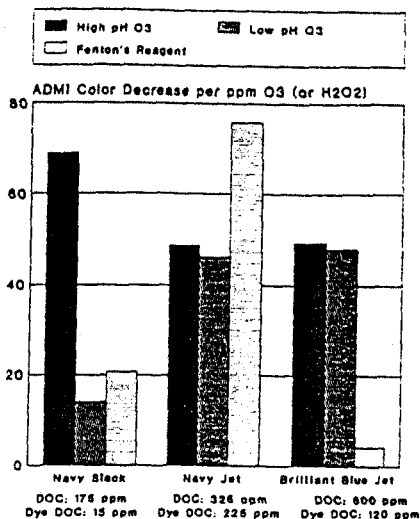| ID	Description	Ca(OH)$_2$ (ppm)	ADMI	Cu (ppm)	TSS (ppm)	Cu in TSS (ppm)
P	Purple 120 spent dye bath	0	76,000	41.4	0	0
P1	P + 1200 ppm H$_2$O$_2$, pH 2.6	0	820	42.0	2,100	0
P2	P1 at pH 10.0	0	631	2.7	6,400	39.3
P3	P2 + Ca(OH)$_2$	50	616	2.2	6,400	39.8
P4	P2 + Ca(OH)$_2$	200	509	2.0	6,600	40.0
M	Mediterranean 128 spent bath	0	143,000	57.0	0	0
M1	M + 5000 ppm H$_2$O$_2$, pH 2.2	0	2,580	27.8	3,300	29.2
M2	M1 at pH 10.0	0	75,400	37.6	9,700	19.4
M3	M2 + Ca(OH)$_2$	200	82,600	35.8	8,900	21.2
M4	M2 + Ca(OH)$_2$	600	78,400	33.6	9,400	23.4
MK1	M + 3000 ppm H$_2$O$_2$, pH 2.2	0	12,700	36.5	18,000	20.5
MK2	MK1 at pH 10.0	0	80,400	42.2	18,000	14.8
MK3	MK2 + Ca(OH)$_2$	4,000	90,000	31.5	---	25.5
ML1	M + 50,000 ppm H$_2$O$_2$, pH 2.2	0	2,820	48.7	33,000	8.3
ML2	ML1 at pH 10.0	0	14,600	6.0	21,000	51.0
ML3	ML2 + Ca(OH)$_2$	200	14,600	6.1	24,000	50.9
B	Nylon acid black spent bath	0	21,500	---	0	---
B1	B + 3000 ppm H$_2$O$_2$, pH 2.8	0	4,200	---	1,600	---
B2	B1 at pH 10.0	0	8,180	---	1,500	---
B3	B2 + Ca(OH)$_2$	100	7,420	---	1,400	---
B4	B2 + Ca(OH)$_2$	400	6,970	---	1,800	---

given, for example, on Fig. 22. For comparison of color values at different dilutions, it has been shown that the dilution ratio should be raised to the 0.85 power (Netzer and Miyamoto, 21) prior to multiplication to determine the ADMI color value. This is because the color value measurement is not linear with dilution. The decolorization efficiency calculated was roughly equivalent for all six ozonation experiments on all three wastewater streams, varying from approximately 50-70 ADMI color units per ppm of ozone. The only exception was ozonation of the navy slack wash water at low pH. The decolorization efficiency of the Fenton's reagent experiments, however, varied from 4 to almost 70 ADMI units per ppm of peroxide.

If, however, one compared the mass of oxidant required to decolorize the solutions to approximately 70% of the initial color value (regardless of the initial color value) to the initial DOC of the solution, as shown in Table II, the results were quite different. The mass of ozone required to achieve 70% color removal ranged from 0.11-1.76 ppm per mass of initial DOC. These data indicate that the amount of ozone required to remove 70% of the color from a given stream did not depend upon the initial level of dissolved organics. The hydrogen peroxide requirements per mass of initial DOC, however, were much closer, from a low of 0.86 to a high of about 1.25 ppm peroxide per ppm of initial carbon. This indicated that peroxide requirements for decolorization of the streams showed a positive correlation with DOC and not with the initial color. Pure dye experiments showed a similar correlation. The pure dye solution containing approximately the same dye concentrations as the navy slack washer effluent was decolorized with much less peroxide than the actual waste stream, though almost as much ozone was needed (Powell et al., 1). The pure brilliant blue dye solution Fenton's reagent trials confirmed this as well since much less peroxide was necessary for decolorization than the actual waste stream. Powell et al. (1) observed the difference in the ozonation of the pure dye solution and the actual waste stream was not nearly so pronounced. Clearly the elimination of the noncolored organic materials from waste streams greatly affected the peroxide oxidation, but not the ozonation. Approximately twice as much hydrogen peroxide was needed per mass of dissolved carbon in the waste stream to decolorize the wastewaters to their lowest attainable levels, both for actual waste streams and pure dye solutions.

It has been shown (Saunders et al., 22) that ozonation reactions occur more quickly than the diffusion of the gas into the liquid phase, meaning the kinetics are gas-transfer limiting. This means that predictions concerning the efficiency with which waste streams may be decolorized with ozone will depend on the characteristics of the dyes and other organic materials and salts present. Dye streams containing significant amounts of organics other than dyes might be decolorized by selective oxidation of the dyes, though the

presence of organics that can effectively compete with the dyes for the interface will require more ozone to effect reasonable color levels. Predictions concerning the use of ozone on waste streams might depend heavily on the chemical nature of any organics which could compete for the interface or the surface properties due to such solutes as inorganic salts. Laboratory tests may be the only reliable way to determine the possible effectiveness of ozone as a means of decolorization.

Fenton's reaction involved the same nonspecific oxidizer as the high pH ozone, hydroxyl radicals, but was a single phase reaction, so the surface-active properties of dyes could not affect their oxidation rate. Another important difference in the way in which oxidation via ozone and peroxide was performed lies in the time span over which the oxidants were added. Whereas the ozonation was performed in a semi-batch manner, with ozone continuously added over a period of time, the Fenton's reagent trials were all conducted as a true batch. The initially high peroxide concentration may account for the non-selective manner in which the oxidation occurred. Ozone was added slowly, relative to peroxide, and the oxidant concentration remained low over the course of the reaction. This gave the more reactive species a competitive advantage. This hypothesis is borne out by the fact that the DOC loading of the stream was the primary parameter for the amount of hydrogen peroxide required. Because of the non-selective manner in which Fenton's reagent oxidized the wastewaters, decolorization of actual waste streams would be most effective for streams in which dyestuffs constituted a large fraction of the total DOC. Further experimentation would be necessary to determine if selectivity could be increased by the slow addition of hydrogen peroxide to the reaction vessel.

In order to optimize the use of Fenton's reagent industrially, the elimination of organic material prior to reaction is desirable. The dye waste streams would then be more like the pure dye solutions which required much less oxidant to decolorize. The use of organic acids such as acetic acid for pH adjustment would necessitate the use of much more peroxide for the decolorization of the dyebath. Segregating the dye baths for reaction would also be advisable, since mixing with scouring streams, etc. would introduce additional organics.

It has been suggested that with high concentrations of chloride ions, the potential exists for oxidation of these ions to molecular chlorine (Walton, 23). Chlorine would then become the oxidizing species for the organics and the production of chlorinated organics is possible. Further work should include testing for chlorinated organics and toxic compounds.

Biological Testing. Biological testing following ozonation and Fenton's reaction with samples of navy jet, bright blue jet, and navy pad wash water was completed. However, as

Table II: Oxidant Requirements to Effect 70% Color Removal in Comparison to the Initial DOC

Dye Waste Stream	Oxidation Method Employed	Initial Dye Waste Stream DOC (ppm)	Oxidant Dosage (ppm)	Oxidant Mass per Mass of Carbon
Navy Slack Washer Effluent	High pH O_3	175	44	0.25
	Low pH O_3	175	224	1.28
	Fenton's Reagent	175	150	0.86
Navy Jet-dye Bath	High pH O_3	325	560	1.72
	Low pH O_3	325	560	1.72
	Fenton's reagent	325	350	1.08
Brilliant Blue Jet-dye Bath	High pH O_3	800	85	0.11
	Low pH O_3	800	85	0.11
	Fenton's reagent	800	1000	1.25

Table III: Bioreactor DOC Removal Comparison and Calculated Contribution of Added Primary Effluent to the Bioreactor Influent DOC

Wastewater Stream	Treatment	Influent DOC (ppm)	Influent DOC Contributed by Primary Effluent (ppm)	Effluent DOC (ppm)	Influent DOC-Effluent DOC (ppm)
Navy slack washer effluent	None	198.5	5.8	112.8	85.7
	High pH O_3	201.3	5.8	104.4	96.9
	Low pH O_3	170.9	5.8	101.5	69.4
	Fenton's Reagent	105.9	5.8	132.7 (99.3)	-26.8 (6.6)
Navy jet-dye bath	None	68.6	20.7	41.0	27.6
	High pH O_3	66.0	20.7	39.7	26.3
	Low pH O_3	65.0	20.7	44.2	20.8
	Fenton's Reagent	42.0	20.7	21.4	20.6
Brilliant Blue jet-dye bath	None	104.9	20.7	69.0	35.9
	High pH O_3	107.2	20.7	63.0	44.2
	Low pH O_3	106.1	20.7	58.6	47.5
	Fenton's Reagent	84.3	20.7	53.2	31.1

discussed by Powell (3), the results of biological testing on the three streams showed that the oxidative breakdown products did not inhibit biodegradation and should not hamper the performance of an activated-sludge system. However, very small changes in the color were noted with the exception of the dilution of the streams. The DOC removal in the bioreactors was not enhanced by either of the oxidation schemes. Use of Fenton's reagent reduced the influent DOC values but less DOC was subsequently removed. Toxicity of the control and treated waste streams was not determined.

A material balance was calculated to determine the DOC contribution to the bioreactor influents from primary effluent and is shown in Table III. The fraction of DOC removed due to the primary effluent (assuming that it was completely degraded) was calculated. The DOC loss in the navy jet-dye bath reactors was nearly equal to the primary effluent contribution. The parenthetic values presented for Fenton's reagent oxidation of the navy slack washer effluent were calculated from the last two days of testing where the solids were more carefully removed from the feed. They represent an estimate of the steady-state value without the influence of solids.

The control and ozonated-feed reactors had DOC removal beyond the contribution of the biological material, implying that the dye wastes were not inhibitory and, in fact, partially degraded. In the Fenton's reagent reactors for all three dye wastes and the ozone (low pH) navy jet-dye bioreactors, the DOC removal was very close to the expected biological contribution. Dilution partially with water rather than primary effluent, particularly in the jet dyebath streams, would lower the biological DOC contribution and would allow for more accurate determination of the biodegradation of the waste streams.

Hydraulic steady-state should have occurred at the seventh day of the run since the hydraulic retention time was two days ($1-(1/2)^7 = .98$ or 98% of the final value). The color values were quite constant and steady-state seemed to have been reached. The exception was the color of the streams oxidized with Fenton's reagent. The solids resulting from the reaction were allowed to settle and decanted rather than being filtered and, subsequently, some solids were able to enter the bioreactors. Solids not completely removed prior to mixing with primary effluent caused some of the yellow-orange color typical of ferric solution to return and raised the color value of the effluent. This caused much more variability from day to day in the color for those streams. The coefficient of variation (standard deviation divided by the mean), or COV, of the peroxide treated streams were 42%, 25%, and 15% for reactors fed the Fenton's reagent oxidized navy slack washwater, navy jet-dye effluent, and brilliant blue jet-dye effluent, respectively. The COVs of all of the other streams were 6% or lower.

The solids from Fenton's reaction caused great variability in the DOC, as well, particularly

in the reactor fed navy slack washer effluent oxidized with Fenton's reagent where the COV for the DOC was 34%. If the solids were not carefully removed prior to addition to biological reactors, some of the organics were released into solution, causing the large variations in DOC witnessed. In order to insure accurate values for effluent DOC, measurements were made for an additional two days.

CONCLUSIONS

1. Fenton's reagent looks promising for treating relatively pure jet-dye concentrates. However, auxiliaries including acetic acid and carry-over organics from knitting and/or scouring operations resulting in high DOC will decrease the effectiveness of Fenton's reagent

2. Ozonation, which seems to selectively oxidize the dyes, is preferred over Fenton's reagent for wastewaters containing significant amounts of noncolored organic matter. However, capital commitment, operating costs, and safety/health considerations limit acceptability.

3. Pretreatment by oxidation with ozone and Fenton's reagent did not inhibit aerobic biodegradation of navy jet, bright blue jet, and navy slack wash water. Ozone treated samples yielded better DOC removal than the Fenton treated ones.

4. Treatment of copper phthalocyanine and azo complexed dyes with Fenton's reagent frees the copper at low pH, but can be removed by precipitation as copper hydroxide by increasing the pH to 10. Increasing the pH of phthalocyanine dyes treated with minimal amounts of Fenton's reagent that removed most of the color brings back a large portion of the color indicating that the chromophore was not destroyed.

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