

The Removal of Color and DOC From Segregated Dye Waste
Streams Using Ozone and Fenton's Reagent Followed By
Biotreatment

by

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(Abstract)

The decolorization of reactive dye-containing waste streams using oxidizing chemicals and the determination of the effect of the oxidizing agents on the subsequent biotreatment of the streams was investigated. Three oxidizing schemes were chosen for study: molecular ozone, base-promoted ozonation, and Fenton's reagent (Fe^{2+} and H_2O_2). The ADMI color value of the solutions was used as the primary parameter for color comparison and dissolved organic carbon (DOC) removal was the measure of the effect of biodegradation.

Three different waste streams from a textile dyeing facility were chosen: a Navy slack washer effluent from a pad-dyeing operation, a Navy dyebath effluent from a dyejet, and a Brilliant Blue dyejet effluent. Pure dye solutions were oxidized as well to determine the effect of interfering species in the waste streams.

The results demonstrated that base-promoted ozonation was more effective than molecular ozone for the decolorization of the Navy slack washer effluent. In both cases the ADMI color

value could be decreased by 82% but almost half as much ozone was necessary for the high pH trials. The high pH ozonation proved more effective for the Navy jet-dye effluent, as well, achieving a much lower color value with less ozone. Greater decolorization (96%) of the Navy jet-dye effluent was achieved by Fenton's reagent than for either of the ozonation schemes. Ozonation of the Brilliant Blue jet-dye bath showed no dependence on pH and the color value of the solution was reduced could be 63%.

The results indicate that the dyes were selectively oxidized by ozonation and the amount of ozone required for decolorization depended mainly the initial color of the dye waste stream. The amount of hydrogen peroxide required for Fenton's reagent oxidation depended on the initial DOC of the dye waste stream.

Oxidation of the wastewater streams proved to neither enhance nor hinder the operation of the biological reactors. The color removals by biological activity were minimal for both control and experimental reactors. Dissolved carbon removal was not enhanced by oxidative pretreatment.

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1.0 Introduction

Researchers in the textile industry in the U. S. and worldwide have been investigating the fate of the dyes in the wastewater effluents which leave their plants for some time (Miyamoto and Tram, 1979). These dye-containing effluents eventually find their way into natural waterways. Dyes are unsightly and have proven to be toxic to certain microbes present in natural waters (Michaels and Lewis, 1985).

These colored effluents arise during the dyeing of all types of textile products: natural fibers such as cotton and wool, as well as man-made fibers such as polyester and nylon. The use of natural fibers is currently on the rise: cotton consumption has increased 4-5% per year since 1980. During the same period of time, the use of fiber-reactive dyes has increased 15% per year and are the choice for dyeing 27% of the cellulosic (i.e., cotton) fibers worldwide (Wagner, 1991). These dyes are the focus of this study.

When using fiber-reactive dyes, typically 10-25% of the dye which is charged to a dyebath remains in the dyebath following the dyeing procedure and are discharged in the wastewater. These dyes are very water-soluble and difficult to treat by conventional activated-sludge treatment facilities (Pagga and Brown, 1986). They are also, by design, very

resistant to oxidation and degradation due to light. Because of this, unless specific remediation steps are undertaken, a significant amount of dye is discharged in the water from wastewater treatment plants.

Different types of waste streams arise at textile dyeing plants depending on how the fabric is dyed. Cotton fabric dyeing (which give rise to the waste streams of this study) is accomplished in different ways. In pad-dyeing, the dyes and auxiliaries (consisting of surfactants, defoamers, and caustic) are applied to the cloth and allowed to react with the cloth for an extended period of time (approximately 12 hours). The dyed fabric is then washed to remove any unreacted dyes (Bright, 1991).

The fabric can also be dyed in jet machines in which the fabric and dye solution (liquor) are circulated at elevated temperatures (greater than 200 deg C.) for a relatively short period of time (less than 2 hours). Large amounts of inorganic salts (typically NaCl) are added to the liquor (approx. 10% solution) in order to increase the fraction of the dye which attaches to the cloth, termed fixation. The fixation rate depends upon the type of dye used and the temperature and pH at which the dyeing is performed. The spent liquor at the end of the process is very concentrated with dyes and other chemicals. After the dye bath or liquor is drained, the jet is refilled with water several times to

wash the cloth. These rinses also contain significant quantities of dye (Hehlen, 1991).

Streams from both processes, pad- and jet-dye, were chosen for treatment as indicative of textile plant waste streams. The chosen streams contained dyes that were believed to cause particularly high color levels at the local wastewater treatment plant. The first objective was to study the streams to determine which characteristics could affect their treatment. The main parameters analyzed were color, amount of organic chemicals in the stream (measured as dissolved organic carbon, or DOC), the type of dyes, and the fraction of DOC contributed by dyestuffs and auxiliary organics. Other parameters measured were pH and salt content.

After characterizing the waste streams, a suitable method for decolorizing was investigated. The oxidizing agents chosen for study were ozone and hydrogen peroxide (catalyzed with ferrous iron). The decolorization effectiveness of both of these oxidants was then determined for the pad- and jet-dye waste streams.

Finally, the subsequent biodegradability of the waste streams was determined. Because textile plants typically discharge their effluents into municipal wastewater facilities, any biologically-inhibitory effects of treatment would be detrimental. Conversely, the potential for increased biodegradability would mean even cleaner water returned to the

natural source. Therefore, the activity of a typical activated-sludge facility on these streams was simulated in the laboratory.

2.0 Literature Review

2.1 Textile Dyes

All dyes have a chromophore or light-absorbing portion which gives them their characteristic color. The light absorption is accomplished by synthesizing large molecular-weight molecules consisting of alternating single and double bonds, or conjugated species, which are electronically excited by the addition of light in the visible range. Typical dye chromophores are azo-linked aromatics, anthraquinones, and metal-complexed species, involving Fe, Cr, or Cu, for example (such as heme units which occur in biological systems). Various functional groups (e.g. -NH_2 , -OH) may be substituted on the molecule thereby altering the light absorption characteristics, and hence the color of the dye, as well as changing the solubility properties of the dyes (Giles, 1974).

Reactive dyes contain a functional group which can react with the fiber to form covalent linkages. One type of reactive moiety forms a vinyl-sulfone in the presence of base. The vinyl-sulfone group may then react with the nucleophilic groups of cotton or wool fibers (such as -OH , NH_2 , or -SH) forming a covalent bond. The vinyl-sulfone form of the dye may also be hydrolyzed by water which renders the dye molecule incapable of bonding to the cloth (Giles, 1974).

Both the hydrolyzed and vinyl-sulfone form of one dye

were identified in a textile wastewater. The hydrolyzed form of the dye could not be found following activated-sludge treatment, however. The vinyl-sulfone form of the dye is particularly stable in pure water. Researchers have estimated the half-life of the vinyl-sulfone form of one dye to be 46 years, though in the presence of anaerobic-sediment the half-life dropped to 2.5 days (Weber *et al.*, 1990).

2.2 Treatment Options

Many different schemes for treating colored waste streams have been investigated. Chemical reduction (or anaerobic treatment) will decolorize azo dyes by reducing the azo linkage (-N=N-) between the aromatic rings but these treated discharges are not easily biodegraded (McCurdy *et al.*, 1991). In addition, aromatic amines, reduction products of azo dyes, have been suspected to cause cancer (Eberhard *et al.*, 1990). 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.*, 1978). The biotreatment of a Disperse dye (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.*, 1990). 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. The adsorption of the amines was not considered (Brown and Laboureur, 1983).

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.*, 1979) and has been shown to decolorize a wide variety of dyes including reactive azo dyes (Gregor, 1992). 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.*, 1980). Ozone has also been shown to effectively decolorize pure azo dye solutions (Sato *et al.*, 1974) with the products identified by GC and GC-MS. Some absorbants have been shown to be capable of removing specific types of dyes (Michelsen *et al.*, 1991). Many of these studies have been conducted on 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 oxidation of substituted phenolic compounds resulted in increasing toxicity with increased levels of oxidation. In the same study, both permanganate and Fenton's reagent decreased the toxicity of the wastewater (Vella and Munder, 1991).

2.3 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, 1982). It is a very powerful oxidant that is rather selective and reacts well with unsaturated bonds. The mechanism of the reaction is postulated to be an electrophilic addition to the pi-bonded atoms creating an ozonide which reacts with water to cleave the molecule between the two atoms, forming aldehydes (or ketones) and carboxylic acids as shown in Figure 1, and is not capable of complete mineralization of organics to carbon dioxide and water (Morrison and Boyd, 1983). Ozonation products which confirm this mechanism have been identified by many different researchers. Several 2- and 4-carbon acids and aldehydes, as well as, formic acid and carbon dioxide have

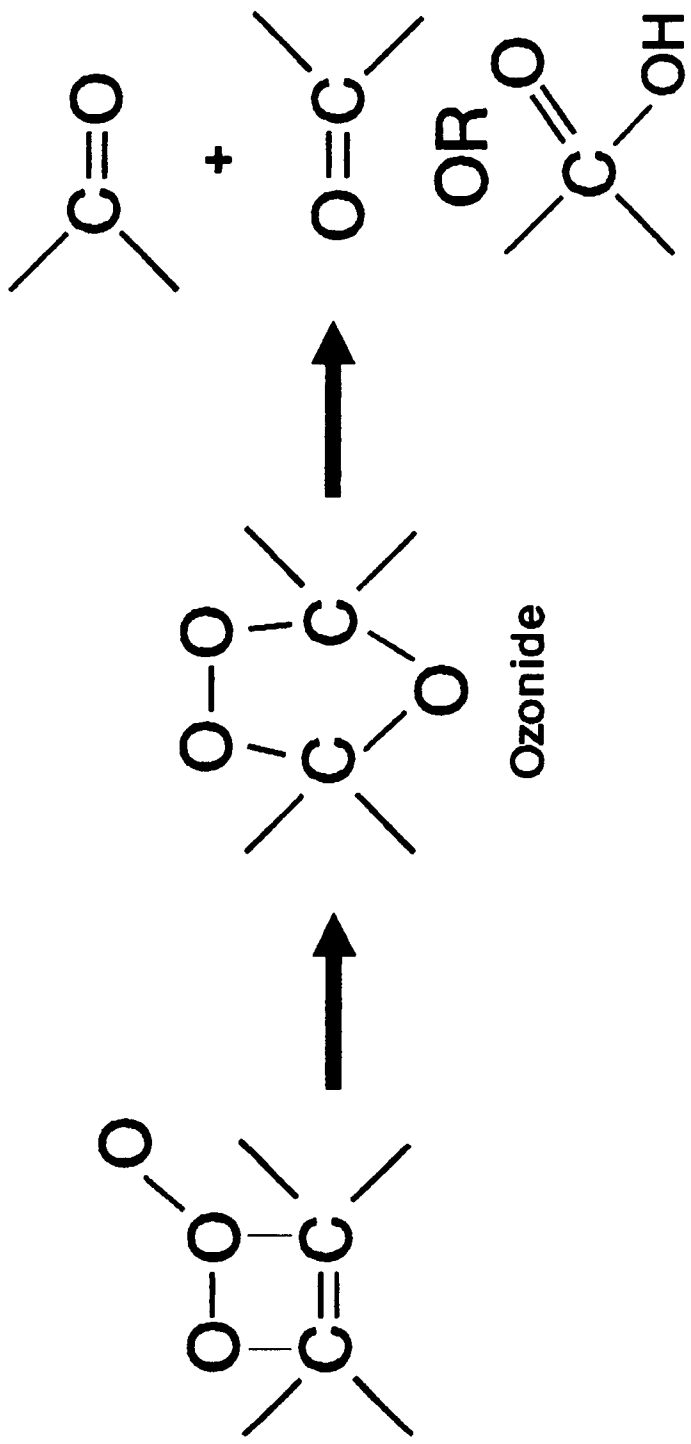


Figure 1: Direct Ozone Reaction Mechanism

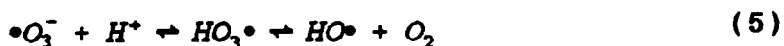
(Equation 1)

been identified in the aqueous ozonation of phenol (Yamamoto *et al.*, 1979). The molecular ozonation mechanism alone does not adequately account for the formation of carbon dioxide, however, which is likely formed due to radical reactions.

The aqueous ozonation of an azo dye, 4-phenylazo-1-naphthol, in high pH solution has been investigated (Matsui *et al.*, 1984). The products identified were nitrogen gas, phenol, and 1,4-naphthoquinone. This information led to a proposed mechanism whereby the ozone molecule attacked the azo compound at the carbon-nitrogen bond (which has pi-bond character). The possible decomposition of ozone was not considered in the reaction mechanism. Other researchers (Sato *et al.*, 1974) have identified products from the ozonation of several different substituted azo dyes. Oxalic (a 4 - carbon diacid) and glyoxylic (2-carbon diacid) acids were formed as well as nitrate ion.

In the presence of ultraviolet light, catalytic amounts of peroxide, or hydroxide ions, dissolved ozone decomposes to form hydroxyl and superoxy radicals. The decomposition of ozone by hydroxide ions is believed to occur according to a chain reaction mechanism (Staehelin and Hoigne, 1985) in which hydroxide ions initially cause the ozone to decompose. Further ozone decomposition reactions can occur with more hydroxide ions or by reaction with free-radicals formed during

the course of the reaction. These reactions are believed to occur as follows:



The two mechanisms by which ozone can react, directly with a substrate (Equation 1, Figure 1) or decomposition to hydroxyl and superoxy radicals (Equations 2-8), are always in competition when ozonation is carried out in the aqueous phase. The critical pH at which one begins to dominate the other depends on many factors such as radical scavengers and promoters and the rate at which molecular ozone reacts with the given substrate.

The hydroxyl radicals are capable of complete degradation of the organics to carbon dioxide and water. In practice, however, ozonation reactions are not typically allowed to continue until complete mineralization occurs. Hydroxyl radical reactions are fairly non-selective and rapid; oxidation rates can be so high that the reaction rate is

controlled by the rate of diffusion of the oxidants and intermediates (Rice and Netzer, 1982).

Radical promoters, such as formic acid, methanol, or aromatic compounds, react with hydroxyl radicals and molecular oxygen to form superoxy radicals (Equations 7 and 8) which are very reactive with organics and molecular ozone, accelerating the decomposition of dissolved molecular ozone (Equation 4). Radical scavengers, such as bicarbonate (Equation 9) and carbonate ions or alkyl groups, present in the treated water will react with the hydroxyl radicals but do not produce chain-propagating, radical species. Substrates which react very slowly with molecular ozone will allow the decomposition reaction to compete even at low pH (low OH^- concentration). Thus, the effects of different dissolved species upon the decomposition rate of molecular ozone can be determined by the lifetime of ozone in an aqueous solution of the substrate: shorter half-life values correspond to increased decomposition rate. The half-life of ozone in aqueous solution reportedly decreases with the addition of aromatic compounds which react very slowly with molecular ozone but act as radical promoters. The half-life of aqueous ozone decreased from 21,000 seconds to only 30 seconds by the addition of 5 mg/l benzene at pH 4. The radical reaction is therefore favored in the presence of aromatics even in low pH solutions. Conversely, the lifetime of molecular ozone in aqueous solution was increased by 3 to

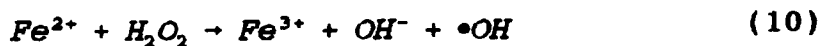
7 times by the addition of 170 mg/l bicarbonate presumably due to the scavenging of hydroxyl radicals (Hoigne and Bader, 1976).

As the reaction mechanism shows, molecular oxygen is a by-product of the reactions, and can re-enter the chain reaction with certain substrates (e.g. aromatics or formic acid). Because ozone is generated from molecular oxygen, it is always abundantly available during ozonation reactions. The amount of molecular oxygen entering the chain reaction has not been measured, however.

A multistage treatment system has been suggested to eliminate the effect of radical scavengers on ozonation treatment of dye waste. The system involves lowering the pH of the wastewater following ozonation and sparging to remove dissolved CO₂ and partially oxidized organics. The pH is then again raised and ozonation resumed (Rakoczi, 1991).

2.4 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 equation 10:



As with the ozone decomposition by base, hydroxyl radicals

and superoxy radicals are the main oxidizing species of Fenton's reagent. The oxidation of organics is accomplished by a 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.*, 1986). Using O^{18} gaseous oxygen as a blanket for the reaction, it was shown that molecular oxygen reacted with the organic radical intermediates to form organic superperoxy radicals which further oxidized the species as shown in Equation 8. This uptake of oxygen increased with increasing partial pressure of O_2 until the partial pressure of 0.4 atm was reached. The study showed that 20% of the phenol formed contains labelled oxygen and all of the benzoquinone formed contained O^{18} . This confirmed that the only way in which benzoquinone formed was by reaction of the aromatic radical with molecular oxygen. The exclusion of molecular oxygen from hydroxyl radical reactions would severely limit the efficiency of the oxidant (such as hydrogen peroxide) and would lead to a different product distribution.

2.5 Biological Oxidation

Chemical oxidation has been shown to enhance the

biodegradation of recalcitrant organics. It was found that oxidation of pentachlorophenol (PCP) using Fenton's reagent enhanced the subsequent performance of an activated-sludge system (Carberry and Benzing, 1991). Similar findings have been published for the ozonation of 3 different compounds. Paranitroaniline, polyethylene glycol, and anthraquinone-2-sulfonic acid, all of which are not biodegradable, were ozonated and the solutions fed to rotating disk biological contactors. Following ozonation the bioreactors achieved 35%, 68%, and 26% dissolved carbon removal, respectively, for the three substrates. Control reactors which were fed untreated substrates were unable to degrade any of the available carbon (Langlais *et al.*, 1989).

Textile dyes have been shown to be very resistant to aerobic biological activity, though a large number of dyes have been shown to exhibit no inhibition of aerobic wastewater bacteria. Of over 200 dyes tested, approximately 10% showed inhibitory effects (Brown *et al.*, 1981). Color removal of 10-40% in activated-sludge systems has been noted for certain dyes. Because the color change was independent of contact time and accompanied little oxygen uptake, it is hypothesized that the color change is primarily due to adsorption on the biological matter (Weeter and Hodgson, 1977; Pagga and Brown, 1986).

The aerobic biodegradability of pure dye solutions following treatment with chlorine and ozone has been determined. No increase or hinderance in biological oxidation was noted by the study. A slight decrease in toxicity was noted following pretreatment by both oxidants, however (Perkins *et al.*, 1980).

Based on this review of the available literature it was determined that oxidation would be investigated as a pretreatment for removing color due to the potentially for enhancing biodegradation. Because previous research had focused on pure dye solutions, the effectiveness of pretreatment on actual waste streams was investigated.

3.0 Experimental Design

3.1 Waste Stream Characterization

The first objective was to characterize the waste streams used in the study. The properties of the streams depended upon how the waste stream was generated. The dyeing steps which result in the waste streams studied are shown schematically in Figure 2. At the plant which provided the waste streams, when dyeing cotton/polyester blends a navy color, the polyester is dyed first in a pressurized jet machine, then the fabric can be washed, dried, and the cotton pad-dyed. This results in a Navy slack washer discharge. The wet cotton/polyester can alternately be jet-dyed to color the cotton in the same machine. The Navy jet-dye bath was the second stream chosen for treatment. In dyeing cotton/polyester a blue shade in a jet machine at this plant, the cotton is dyed prior to the polyester. This jet-dye bath was also chosen for analysis and is referred to as the Brilliant Blue jet-dye effluent. Because the order in which the dyeing occurs is opposite that of the other streams chosen (as Figure 2 shows), the spent jet-dyebath may still contain considerable residual contaminants from prior knitting. Thus three different waste streams were obtained for treatment: one stream was an effluent from a slack washer and the other two were jet dyebaths.

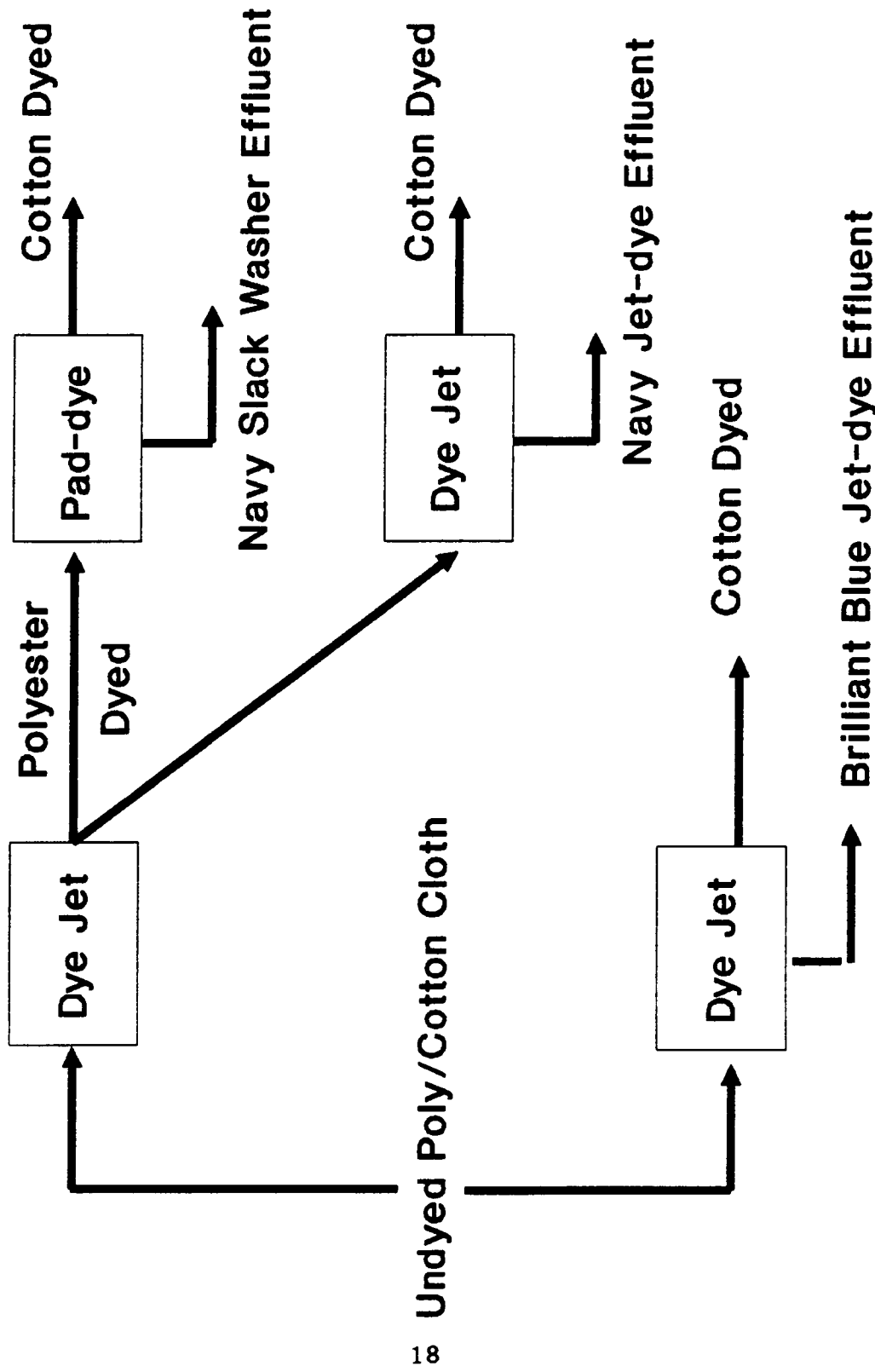
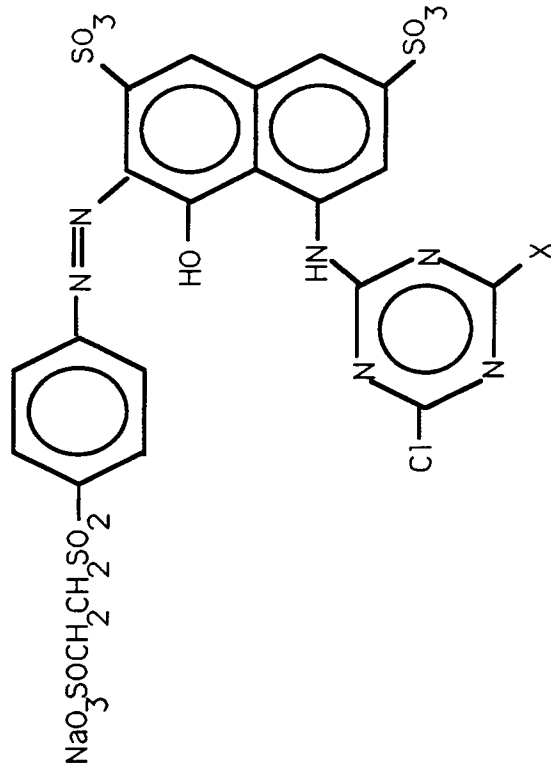
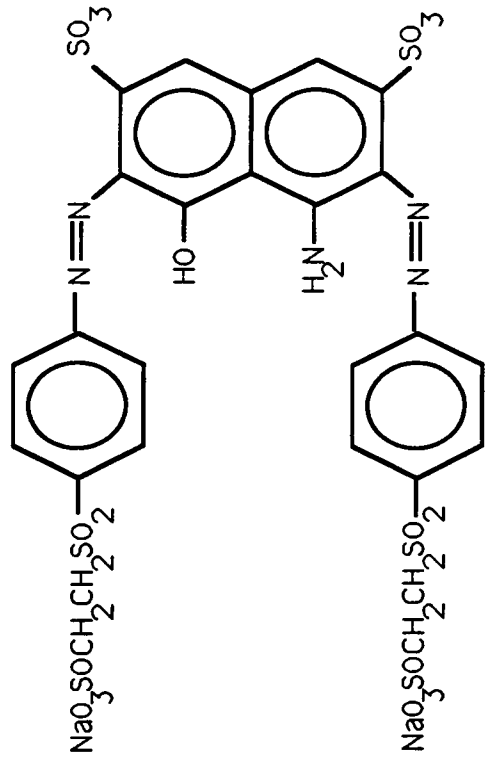


Figure 2: Schematic of Dyeing Operations

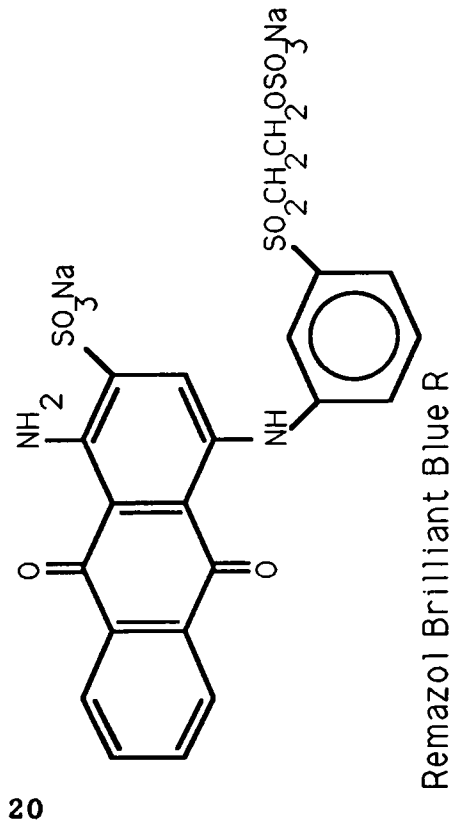
The three dyes used in the dye formulation for both the Navy pad-dye (which results in a slack washer discharge) and the Navy jet-dye formulation are Reactive Black 5, Remazol Red RB, and Remazol Yellow 3RA. The sole dye used in the formulation of the Brilliant Blue jet-dye bath is Remazol Brilliant Blue R, an anthraquinone dye. The known structures of Reactive Black 5 and Remazol Brilliant Blue R, as well as the hypothesized structure of Remazol Red RB (Reife, 1991), are shown in Figure 3. The structure of Remazol Yellow 3RA is not published.

Once the choices of dye streams to treat and potential oxidants were made, the design of the tests began. Textile dyes are sold in a mixture with salts and trace organics, such as carriers, to assist fixation. Because of this and the fact that minute chemical changes in the dyes will greatly alter their HPLC elution times, accurate measurements of dye concentration have not been possible to this point. In order to determine the amount of dye in the waste streams, therefore, solutions of pure dye with approximately the same color were to be constructed and the amount of dissolved carbon in these solutions was compared to that in the actual waste streams.

Because the color before and after oxidation was the prime parameter of the study, a method of quantitating the color of a solution was needed. The American Dye



Reactive Black 5



Possible X:

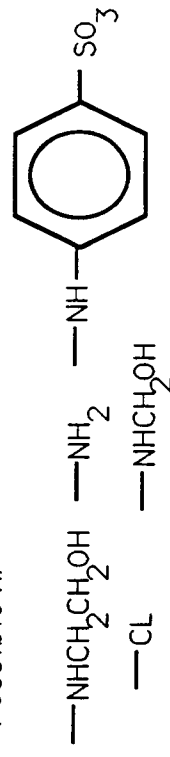


Figure 3: Dye Structures

(Structure of Remazol Red RB hypothesized by Reife, 1992)

Manufacturers Institute (ADMI) color method was chosen because of its wide use industrially. This method is based upon the measurement of light transmittance at three different wavelengths and is discussed at length in Appendix A.

3.2 Oxidation Experiments

All three waste streams were reacted with ozone at two different pHs, approximately 11 and 3. The effectiveness of the treatments was determined by the ADMI color removal as a function of oxidant dose. Limited testing was also performed on pure dye solutions to determine the effects of the other organics which make up the waste streams as possible promoters or inhibitors of the oxidation of the dyes.

Ozone was the first oxidant to be tested. Ozonation trials were initially attempted using a packed column with the waste stream being fed continuously from the top and ozone from the bottom which would most closely resemble an industrial process. The ozone dosage applied per unit volume of liquid depended on the ozone mass flow rate and the hydraulic retention time of the dye waste in the column. The hydraulic retention time in the contactor depended on a constant feed rate, and liquid volume within the reactor. Due to large amounts of foam which occurred in the packed column and difficulties in keeping the retention time constant, this method was abandoned. Instead, a semi-batch method was used in which a reactor column was filled with a known volume of

liquid to be treated and the ozone was bubbled through it at a constant rate for all of the experiments. No packing was used in any of the runs to prevent the occurrence of large amounts of foam.

For the oxidation of the waste streams using Fenton's reagent, both ferrous iron and hydrogen peroxide concentrations were considered as operational parameters. Studies of oxidation via Fenton's reagent usually express these concentrations as a ratio of hydrogen peroxide to iron. Therefore, several different peroxide concentrations were investigated and the ratio of iron added was varied for each peroxide concentration. The effects of temperature and free oxygen were not investigated. Once again, maximum ADMI color removal was the goal of the experiments and the DOC was measured as well.

All of the Fenton's trials were conducted in a batch manner. The iron and hydrogen peroxide were added at the beginning of the reaction and allowed to react at constant temperature until no further reaction could be seen. As with the ozonation studies, pure dye solutions were oxidized in the same manner as the actual wastewater streams.

3.3 Biological Reactors

Biological reactors were then constructed to determine the effect of chemical oxidation as a pretreatment on the operation of an activated-sludge facility. The influent and

effluent color was measured to determine if oxidation would affect biological color removal.

Dissolved carbon measurements of the influent and effluent were also made to measure the biodegradability of the organics in the waste stream following chemical oxidation. Biodegradability was said to be enhanced if the effluent dissolved carbon levels are lower following chemical oxidation. The reactors were operated as sequential-batch reactors (SBRs) by holding the liquid level in the containers constant at 2 liters and replacing half of the reactor volume every day with fresh feed resulting in a 2-day hydraulic retention time. Though activated-sludge systems typically used shorter times, this was the shortest retention time which could feasibly be used in a laboratory SBR. The dye streams were mixed with effluent from the local wastewater treatment plant to provide the necessary nutrients for the biomass.

4.0 Materials and Methods

4.1 Laboratory Chemicals

The reagents used in analysis and for reaction are shown in Table 1. All reagents were used as supplied with no further purification. The auxiliary chemicals which are known to be present in the wastewater samples collected from the textile plant cannot be disclosed due to the confidential nature of the formulations.

4.2 Analytical Procedures

Ozone measurement was performed using indigo trisulfonate solutions in a bubble chamber. The air feed rate was first confirmed using water displacement into an inverted graduated cylinder. The ozone feed concentration was then found by splitting the feed stream and bubbling through acidic (below pH 4) indigo solution (approximately 65 mg/L). The split air volume was also measured by water displacement. The initial and final absorbance of the indigo solution was measured on the spectrophotometer at 600 nm (Bader and Hoigne, 1981). The concentration of dissolved ozone in the bubble chamber was found according to the formula:

$$[O_3]_g = [O_3]_l * V_l O_{WR} V_g \left(\frac{mg}{l} \right) \quad (11)$$

The concentration of ozone in the gas stream was then calculated according to:

Table 1: Laboratory Reagents Used During Experimentation.

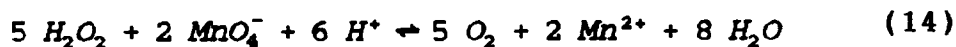
Chemical	Supplier	Purity (%)
Air, CO ₂ Free	Airco	
Ferric Sulfate	Fisher	unknown
Ferrous Sulfate, 7H ₂ O	Mallinkrodt	100.2%
Hydrogen Peroxide	Rose's	3%
Phosphoric Acid	Fisher	85%
Potassium Hydrogen Phthalate	Fisher	99.98%
Potassium Indigotrisulfonate	Aldrich	unknown
Potassium Iodide	Fisher	99.5%
Potassium Permanganate	Allied Chem.	98+
Reactive Black 5	Aldrich	55%
Remazol Brilliant Blue R	Aldrich	50%
Remazol Red RB	Hoescht	unknown
Sodium Bicarbonate	Fisher	99.96
Sodium Hydroxide, Solid	Fisher	98.2%
Sodium Phosphate, monobasic	Aldrich	98+
Sulfuric Acid	Fisher	98%

$$[O_3]_g = \frac{[O_3]_l * V_l}{V_g} \left(\frac{mg}{l} \right) \quad (12)$$

The ozone feed rate to the reactor column was then the product of the gas concentration (from Equation 11) and the air flow rate. This measurement was repeated during ozonation trials to determine the efficiency of the column in the transfer of ozone to the liquid phase. The average feed rate was 17.5 mg/minute and the average rate exiting the column was 3.5 mg/minute, therefore the average rate of ozone dosed to the aqueous phase was 14 mg/minute which results in a column efficiency of 80%. Ozone dosage in the reactor was then calculated as:

$$O_3 \text{ dose} \left(\frac{mg}{l} \right) = \frac{O_3 \text{ rate} \left(\frac{mg}{min} \right) * \text{Time} (min)}{Vol_{\text{Reactor}} (l)} \quad (13)$$

To accurately determine the concentration of the hydrogen peroxide prior to use, 5 ml of concentrated sulfuric acid was added to 25 ml of peroxide solution and the solution was titrated with 0.255M potassium permanganate solution until the color persisted. As shown in Equation 13, the stoichiometry is 5 moles peroxide to 2 moles permanganate (Fischer, 1961).



All samples taken during oxidation trials were stored in

clean, airtight, glass sample vials and refrigerated until analyzed. The samples were analyzed within 24 hours of collection. Duplicate samples were obtained at least once per run to insure that the amount of sampling error was not significant.

ADMI color value determination was performed according to Standard Methods for the Examination of Water and Wastewater (17th ed., 1989) no. 2120 D. using a Bausch and Lomb Spectronic 20 spectrophotometer with a 1 cm path length. In order to be able to measure the highly-colored solutions, it was necessary to dilute each sample. All samples from the Navy slack washer effluent treated by any of the oxidants were diluted 5X with distilled water following treatment and prior to analysis. Samples from the Navy jet-dye wastewater and the Brilliant Blue jet-dye wastewater were diluted 25X and 5X, respectively. The wavelengths measured were 590, 540 and 438 nm. Tristimulus values were determined using a ninth-ordered curve-fit equation to arrive at the final color number. Further information about ADMI color value is given in Appendix A.

Carbon analysis was performed using a Shimadzu TOC-5000 Total Organic Carbon Analyzer. Total carbon is measured by injection of a sample (typically 13 microliters) into a 680 deg C furnace with platinum catalysts. A CO₂-free air streams acts as a carrier gas and the sample is combusted and the

carbon dioxide formed is measured via an infrared detector. To determine the DOC, the Inorganic carbon (IC) is also measured and subtracted from the Total carbon. Inorganic carbon analysis is accomplished by injecting the sample into a 25% phosphoric acid solution into which the carrier gas is flowing causing the IC to bubble out of solution as CO₂. The carbon dioxide is measured by the same detector. For each analysis, whether TC or IC, a repeat sample injection was automatically performed and if the measured difference between the repeat injections is greater than 2% of the mean value then additional sample injections are performed until a consistent reading is reached. Inorganic Carbon standard solutions, sodium bicarbonate, as well as Total Carbon standard solutions, potassium bipthalate, both at a concentration of 200 ppm were measured on the instrument prior to analysis and after every 20 samples to insure accuracy. Blanks (distilled water) and duplicate samples were performed with equal frequency.

Biological feed and effluent samples were stored and analyzed in the same manner as the oxidation samples in glass 25 mL sample vials and stored in the refrigerator. For color analysis, however, dilution was not necessary and was not performed on any of the samples. The samples were analyzed within 24 hours of collection.

4.3 Pure Dye Solutions

For comparison, solutions of pure dye were mixed in the laboratory. The parent form of the dyes was used without chemical treatment. The first pure dye solution was constructed with approximately the same color as the Navy slack washer effluent. The maximum absorbance for the two predominant dyes, Reactive Black 5 and Remazol Red RB, occurs at 590 nm and 540 nm, respectively. Though due to slight shade differences and lack of auxiliaries the color values were not exactly equivalent. Pure dye solutions similar to the other two streams were constructed for comparison, as well. The DOC of the dye solutions was measured for estimation of dye content of the actual waste streams. These same solutions were used for limited oxidation trials, as well.

4.4 Ozonation

The ozone generator used was built by Pollution Control Industries. Compressed air from house lines was fed through a gas drying unit filled with calcium sulphate which is reported to provide a dewpoint of -73 deg C. An air flowrate of 4 liters/minute and 62 volts (AC) was used on the ozone generator for all runs. The contact tower was constructed of 4 inch i.d. glass and was filled with 3 liters of sample, equivalent to a height of approximately 2.5 meters. A peristaltic pump circulated the dyewash from the bottom of the contactor to the top at a flowrate of approximately 0.5

liters/minute and a tap on the circulation line was used for sample collection. Figure 4 shows schematically the ozonation reactor setup. The ozone dosage, therefore, depended simply on the time of application of ozone and the total volume of liquid in the reactor; parameters which were easily controlled.

The pH decreased over the course of the high pH trials to approximately neutral pH. Adjustment back to pH 11 did not increase the decolorization rate, therefore the experiments were conducted without pH control.

Dye solutions were prepared for ozonation by first lowering the pH below 4 using concentrated sulfuric acid and sparging using house air to remove any dissolved carbon dioxide, or inorganic carbon (IC). Because pad-dye formulations (such as result in the Navy slack washer wastewater) contain large amounts of sodium silicate, precipitation can occur upon acidification, therefore the supernatant was decanted if any silicates formed. The pH was then adjusted to the desired level using solid sodium hydroxide. Low pH trials were left at the sparging pH (approximately 3) and the high pH trials were all conducted above pH 10.5. The starting IC level was adjusted using sodium carbonate/bicarbonate solution. High pH ozonation of the pure dye solutions of the same color as the Navy slack washer discharge and Navy jet-dye effluent were also performed

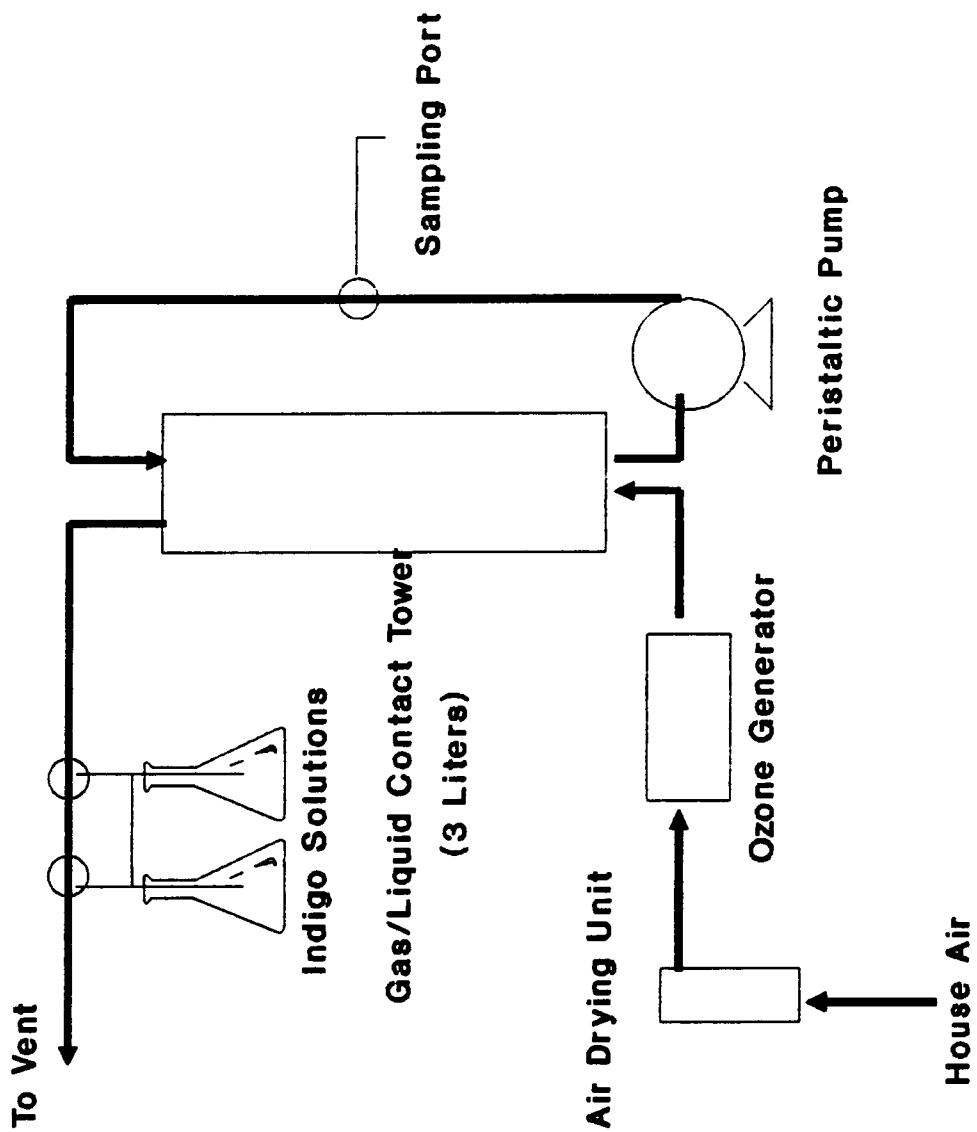


Figure 4: Schematic of Ozonation Apparatus

in the same manner as the actual dye waste streams.

Ozonation runs were allowed to continue until the dyewash color was no longer changing noticeably. Samples of 25 mL volume were removed from the sample port at periodic intervals and the time noted on a prepared data sheet.

4.5 Fenton's Reagent

The dye effluent wastewaters to be oxidized were adjusted to pH 3.0 +/- 0.1 using concentrated sulfuric acid. Samples of 200 ml were then heated to 60 deg C in beakers. The ferrous sulfate solution was added via pipet and allowed to mix for several seconds and the hydrogen peroxide was then added. Hydrogen peroxide solutions of 3% concentration and ferrous sulfate stock solutions of 386 ppm Fe and 772 ppm Fe were used for addition to the dye samples. All of the trials were performed batch-wise and not by continuous addition of reactants and removal of samples as the ozonation trials were. The solutions were constantly stirred using a magnetic stirrer at constant temperature (60 deg. C) for 30 minutes, by which time no visible change occurred in any of the reactions. Following reaction, 25ml samples were taken and refrigerated. Any solids formed were allowed to settle and the supernatant decanted for ADMI color and DOC analysis.

4.6 Bioreactor Operation

Plastic bottles of approximately 3 liter capacity were obtained locally along with aquarium air pumps. The

bioreactors were approximately 0.15 meters in diameter, 0.35 meters in height and constructed of high-density polyethylene. Agitation of the biomass was provided solely by the aerators which used 1 inch airstones. The aeration was cutoff for 1 hour every day to allow the suspended solids to settle and 1 liter was drained from the reactors and 1 liter of feed solution was added to yield a hydraulic retention time of 2 days. Samples of the supernatant removed from the reactors were filtered and refrigerated for color and DOC analysis. The reactors were operated until steady-state readings were confirmed for both the color and TOC of the effluents. No definite sludge age was controlled, rather the suspended solids were allowed to accumulate over the course of the experiment. The initial sludges for all of the reactors were taken from the wastewater treatment plant in Martinsville, Virginia which receives approximately 75% textile wastewater.

Effluent from the primary settling basin of the Blacksburg-VPI&SU wastewater treatment plant was obtained periodically for use in mixing feed solutions for the biological reactors and were stored in a refrigerator. These effluents have very little color upon filtration and have 20-30 ppm filtered DOC.

Table 2 summarizes the feed conditions of all of the bioreactors. The primary effluent was added at a ratio of 1 part to 3 parts slack washer solution. One control reactor

was fed untreated Navy slack washer solution in the mix whereas in the experimental reactors, treated slack washer solution was used: one each for the high and low pH ozonation and Fenton's reagent. The high salt content of the jet-dye baths necessitated that they be diluted to a greater extent than the slack washer effluent before addition to the bioreactors. For this reason, the feed was mixed 1 part dye bath (untreated for the control reactor) with 9 parts primary effluent. As Table 2 shows, the total feed rate for all of the bioreactors was 1 liter/day. The pH of all treated and untreated dye waste streams was adjusted to approximately 7.5 prior to mixing with the primary effluent. All twelve bioreactors were run concurrently.

Table 2: Bioreactor Operating Conditions

Waste Stream	Treatment	Feed rate (ml/day) Dye wash:primary effluent
Navy Slack Washer Effluent	None	750:250
	High pH O ₃ (75 ppm)	750:250
	Low pH O ₃ (150 ppm)	750:250
	H ₂ O ₂ /Fe ²⁺ (400/40 ppm)	750:250
Navy Jet-dye Effluent	None	100:900
	High pH O ₃ (300 ppm)	100:900
	Low pH O ₃ (600 ppm)	100:900
	H ₂ O ₂ /Fe ²⁺ (1000/75 ppm)	100:900
Brilliant Blue Jet-dye Effluent	None	100:900
	High pH O ₃ (150 ppm)	100:900
	Low pH O ₃ (150 ppm)	100:900
	H ₂ O ₂ /Fe ²⁺ (1500/150 ppm)	100:900

5.0 Results and Discussion

5.1 Wastewater Stream Characterization

The general characteristics of the different dye streams are summarized in Table 3. The contribution of dye to the DOC of the waste streams was estimated by constructing solutions of dye obtained from the manufacturer with approximately the same color as the Navy slack washer effluent. The DOC of the stream was 150-200 ppm carbon and it was estimated that only approximately 10% of that was due to dyestuffs. The stream also contained high concentrations of silicates which precipitated when the pH was decreased to below 5. The initial pH of the stream varied between 10.5-11.5.

By contrast, the Navy jet-dye bath had a higher dissolved carbon concentration and a larger fraction of that was dye. The DOC was measured at 250-400 ppm carbon and it has been estimated that 65+% of the DOC was due to dyes (primarily Reactive Black 5). About 10% of the stream, by weight, was salt. The pH of the stream was very high, approximately 12, and carbonates were present in high concentrations which bubbled out of solution as CO₂ when the pH was lowered to acidic levels.

The Brilliant Blue jet-dye bath contained only the single anthraquinone dye at an approximate concentration of 125 ppm Carbon. Many other organics were present at higher

Table 3: Dye Streams Characteristics

Type of stream	ADMI Color	DOC (ppm)	Approx. Dye DOC (ppm)	pH
COTTON Navy Slack Washer Effluent	5800	150-200	14	10.5-11.5
Blue/COTTON Navy Jet-dye Bath	63000	250-400	223	12-12.5
COTTON/POOR Brilliant Blue Jet-dye Bath	7500	800-850	125	12-12.5

concentrations, though. The DOC was close to 800 ppm carbon and only about 15% of that was due to the dye. The salt concentration was as high as the other jet-dye bath, approximately 10%, and the inorganic carbon concentration and pH were similar, as well.

5.2 Decolorization Using Ozone

Ozone effectively decolorized the Navy slack washer wastewater at both high and low pH. As shown in Figure 5, though, the pH at which ozonation was performed had a significant impact on the amount of ozone required. Much more ozone was needed for the low pH trial than for the oxidation at high pH to achieve similar color removals. Oxidation of the pure dye solution with ozone at high pH required almost as much as for the actual stream, as shown on Figure 5, despite having a much lower DOC. The high pH runs which began with differing levels of IC all decolorized equally.

The color of the Navy jet-dye wastewater disappeared at roughly the same rate at either pH, despite the slight difference in starting color. This is shown graphically in Figure 6. The high pH run was slightly superior in this and later ozonation trials. In contrast to the Navy slack washwater, the pure dye solution decolorized much more rapidly than did the actual stream at high pH (refer again to Figure 6). Although the DOC difference between the actual dye wastewater and the pure dye solution was not great, the pure

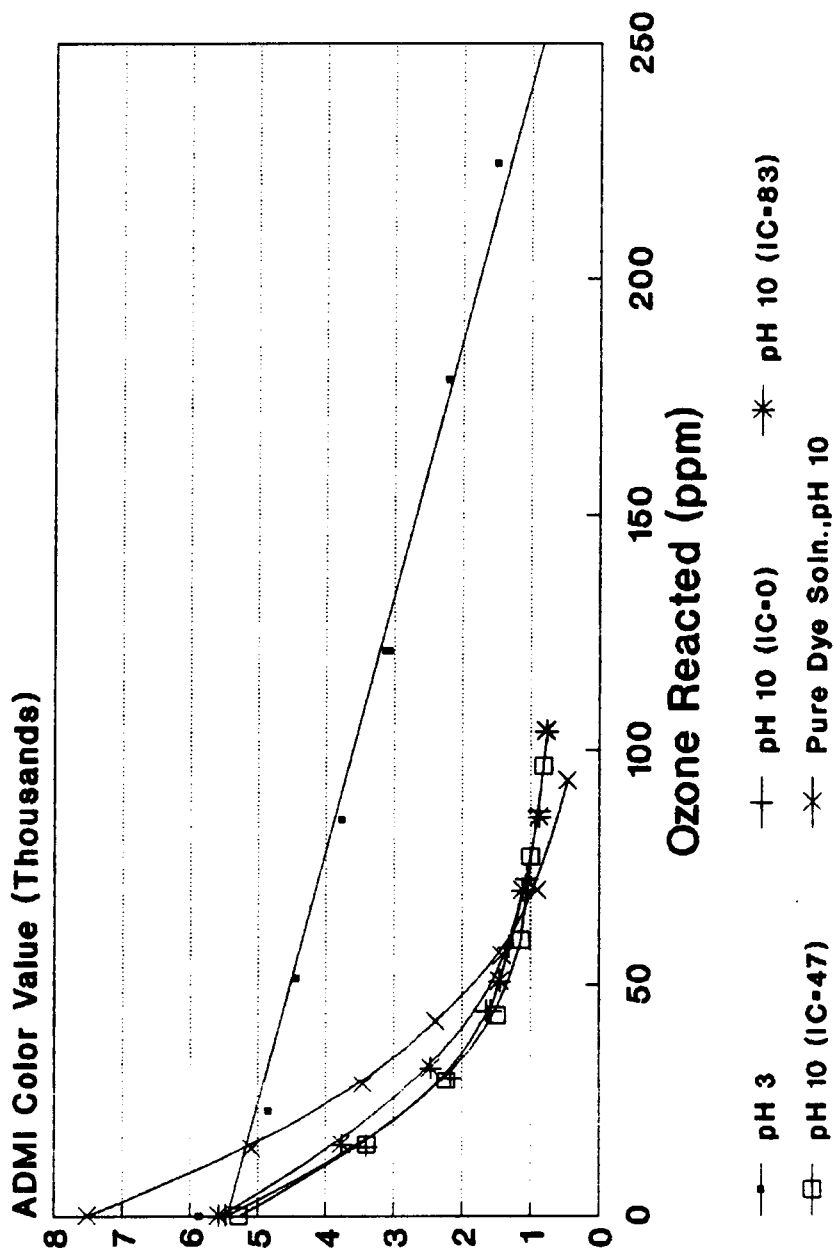


Figure 5: Results of Ozonation on the Decolorization of Navy Slack Washer Effluent and a Pure Dye Solution
 (IC is inorganic carbon concentration (ppm). ADM Color measured at 5X dilution)

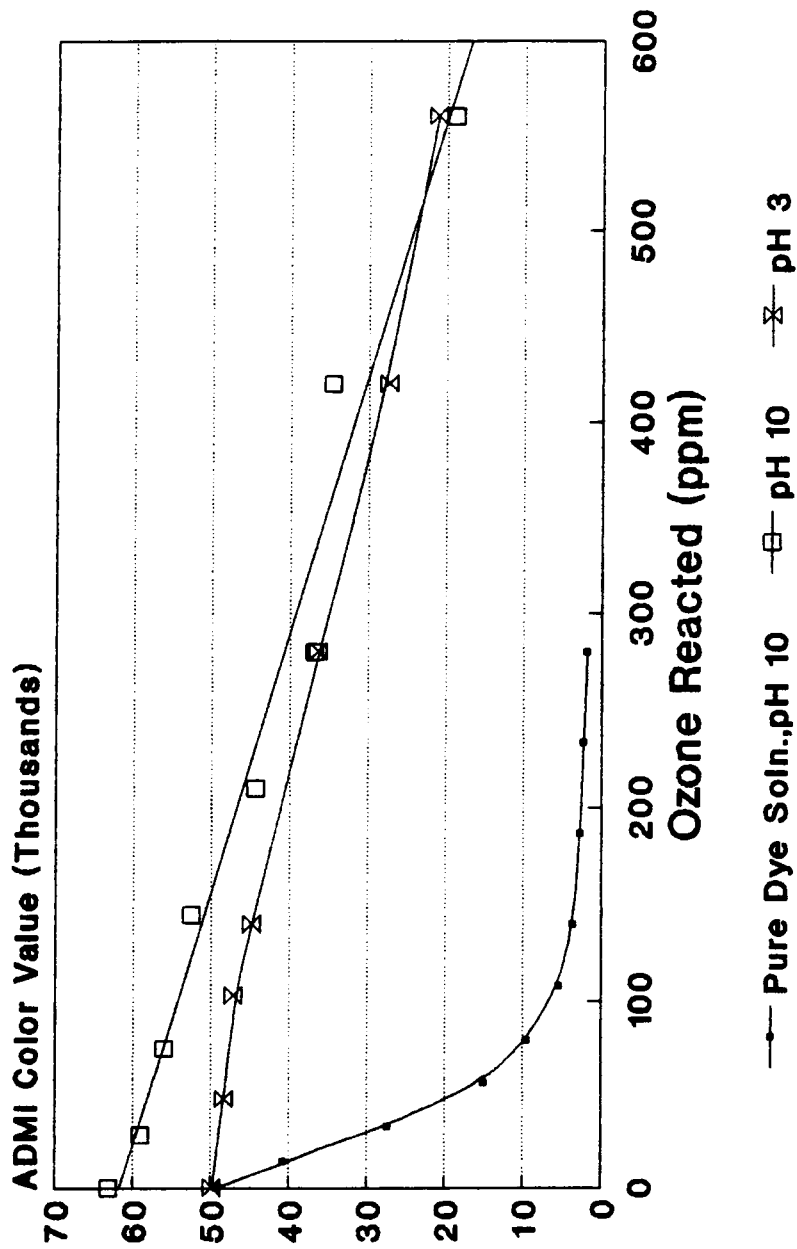


Figure 6: Results of Ozonation on the Decolorization of Navy Jet-dye Waste and a Pure Dye Solution
 (ADMi measured at 25X dilution)

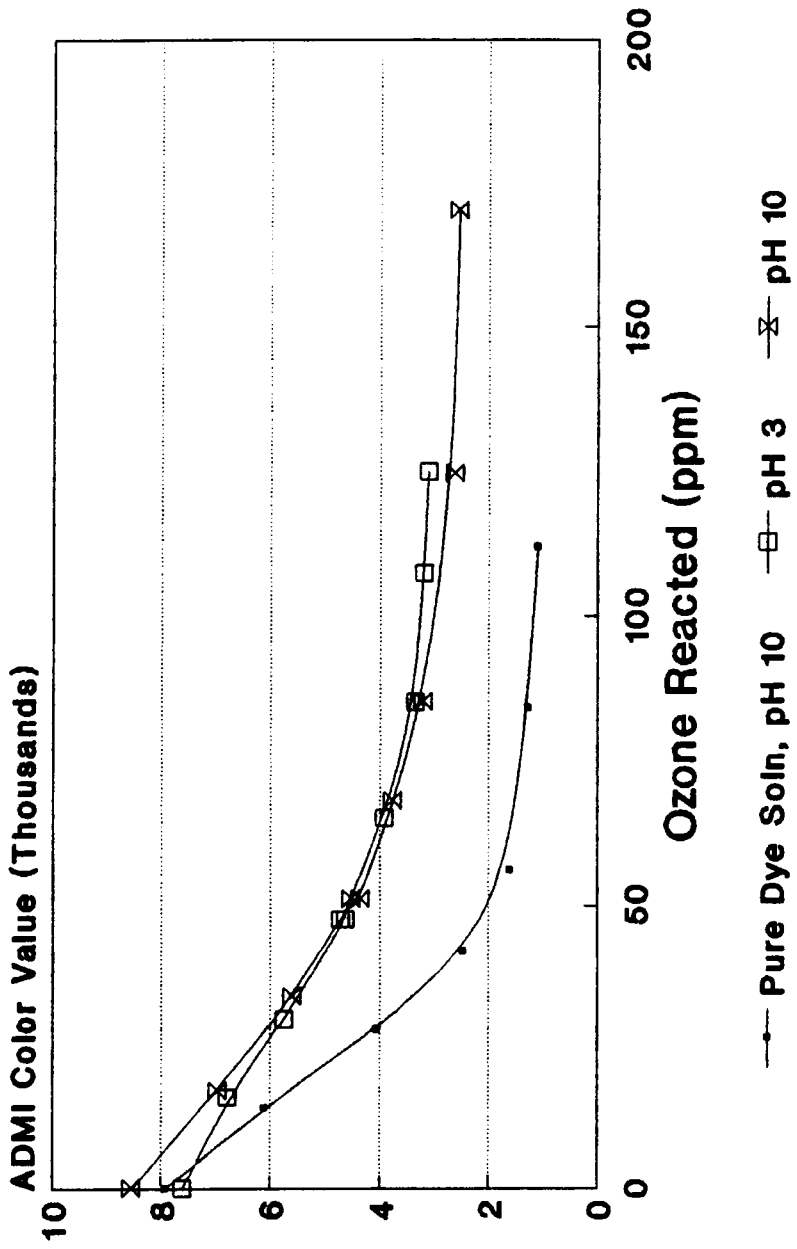


Figure 7: Results of Ozonation on the Decolorization of Brilliant Blue Jet-dye Waste and a Pure Dye Solution
 (ADMi measured at 5X dilution)

dye solution did not contain the enormous amount of salt that was added to the jet-dye bath.

The results of ozonation of the Brilliant Blue jet-dye bath are shown on Figure 7. The color loss in the high pH run was slightly better, though like the Navy jet-dye wastewater, the difference was minimal. The amount of ozone required was not great considering the much higher DOC of this stream. The decolorization reached a minimum value (approximately 75% color loss) with 125 ppm ozone. As in the ozonation of the Navy Jet-dye effluent, the pure dye solution required less ozone to decolorize, though the difference was not as pronounced.

5.3 Decolorization Using Fenton's Reagent

As Figure 8 shows, the final color achieved by Fenton's reagent oxidation of Navy slack washer effluent depended on both the hydrogen peroxide and ferrous iron concentration. Control experiments displayed on Figure 8, showed that neither hydrogen peroxide nor ferrous iron alone decolorized the solutions appreciably. At peroxide concentrations above about 300 ppm, little color difference could be seen between the different ratios of ferrous iron added. Much less hydrogen peroxide was necessary for the pure dye solution than required for the actual wastewater stream, whereas in the high pH ozonation of the Navy slack washer wastewater a roughly equivalent amount of oxidant was needed for the pure dye

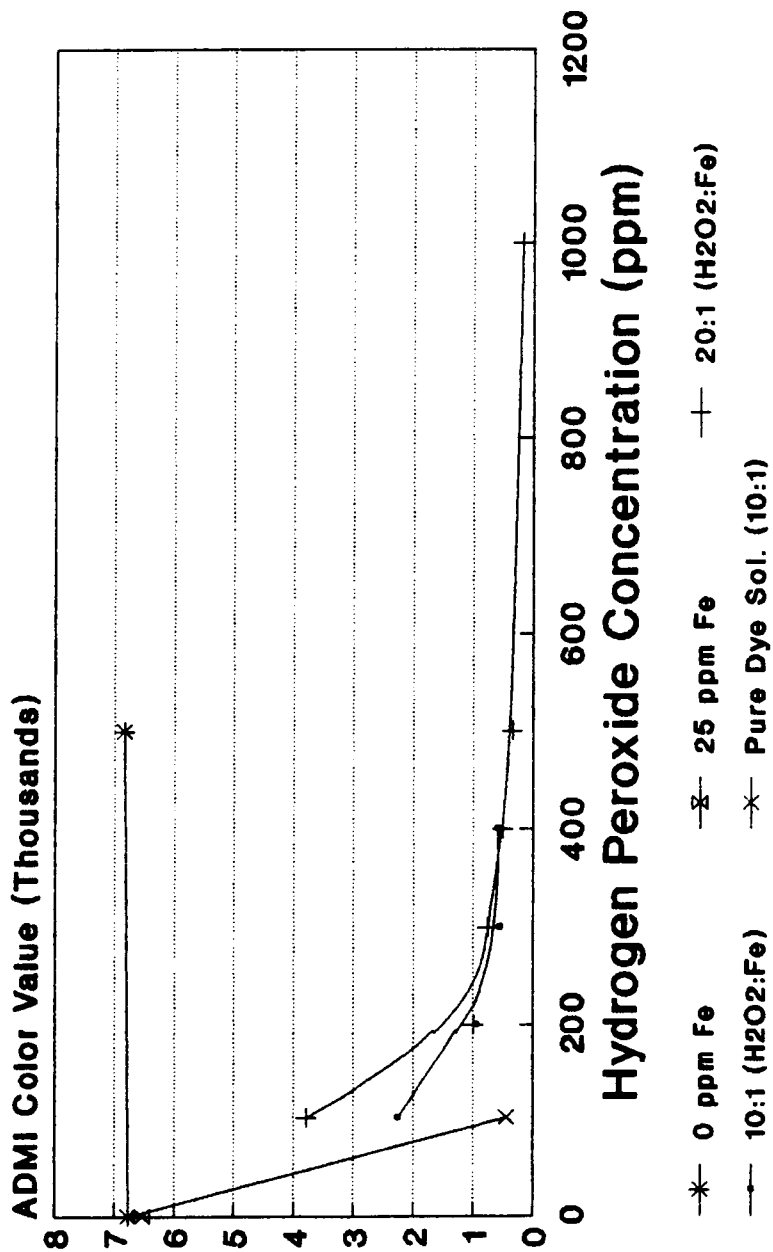


Figure 8: Results of Fenton's Reagent Oxidation on the Decolorization of Navy Slack Washer Effluent and a Pure Dye Solution
 (ADM I measured at 5X dilution)

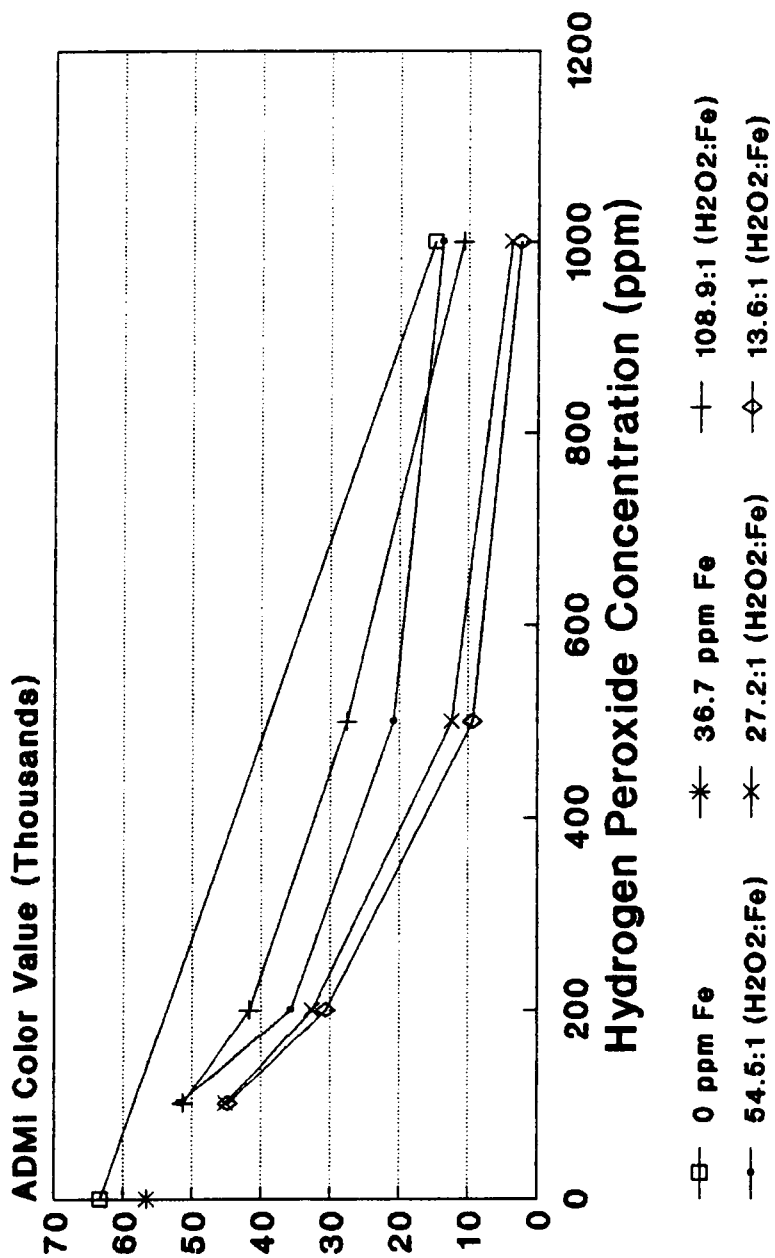


Figure 9: Results of Fenton's Reagent Oxidation on the Decolorization of Navy Jet-dye Waste
 (ADM I measured at 25X dilution)

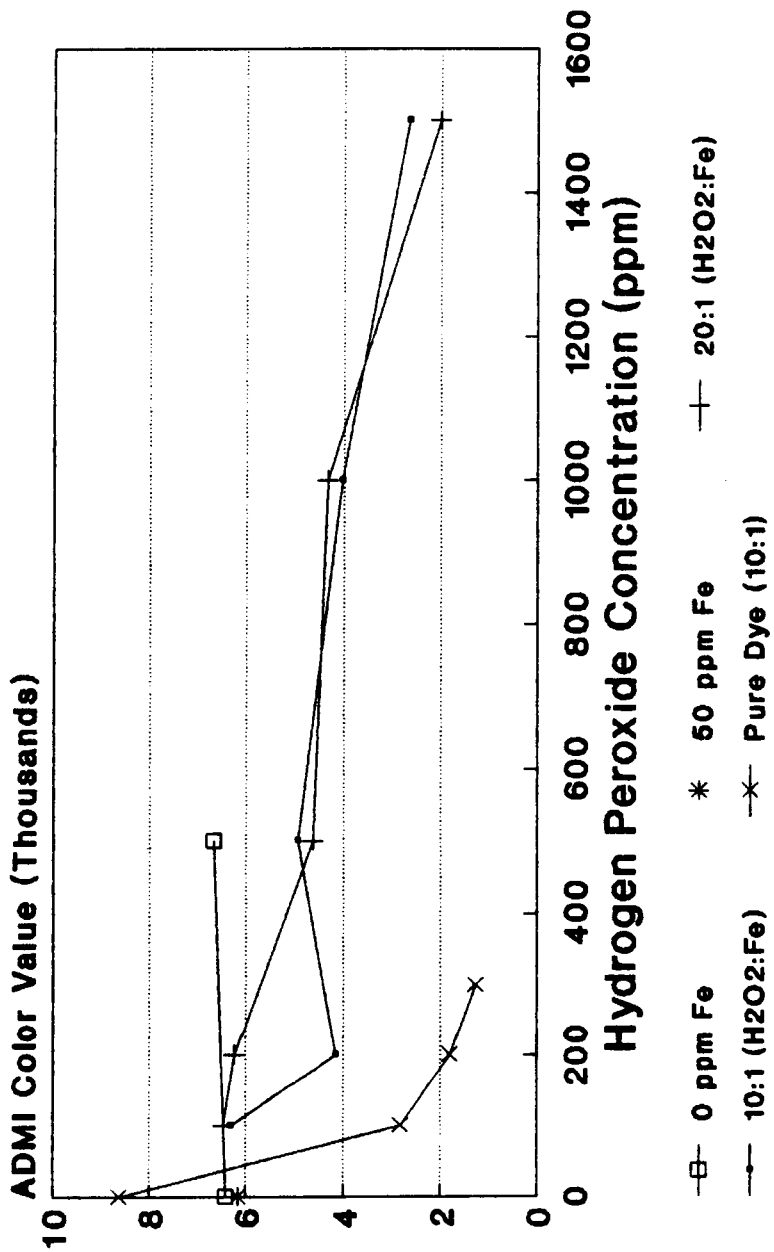


Figure 10: Results of Fenton's Reagent Oxidation on the Decolorization of Brilliant Blue Jet-dye Waste
 (ADM I measured at 5X dilution)

solution.

Twice as much peroxide was needed to decolorize the Navy jet-dye wastewater than was necessary for decolorization of the Navy slack washer effluent though the color was many times higher. As Figure 9 shows, the ratio of peroxide to ferric iron affected the color removal: lower ratios (higher iron concentrations) had lower final color values. A control experiment with peroxide alone lowered the color of the wastewater from above 60,000 to 15,000.

Ferric iron (Fe^{3+}) added following the oxidation of the wastewater further reduced the color in the Navy jet-dye bath. In this experiment, 1000 ppm peroxide was reacted with ferrous iron at 54.5:1 ratio and an equivalent amount of ferric iron (in the form of ferric chloride) was added after 30 minutes. The final color value was 4570, whereas the color value of the trial prior to addition the ferric iron was 13710.

The results for the Brilliant Blue jet-dye effluent are shown on Figure 10. By contrast with the ozonation experiments, more hydrogen peroxide was needed to remove an equal amount of color from the Brilliant Blue stream than for the two navy streams. No correlation between iron concentration and final color can be seen. As shown on Figure 10, neither of the control experiments, hydrogen peroxide alone nor ferrous iron alone, decolorized the dye wastewater appreciably. Oxidation of the pure dye solution required much

less peroxide than the actual waste stream to achieve low color levels.

5.4 Discussion of Oxidative Decolorization

In order to compare the color removal efficiency of the oxidants on the three waste streams, the color removed as a function of oxidant mass (either ozone or hydrogen peroxide) was calculated for each waste stream as shown in Figure 11. These calculations roughly correspond to the slope of the color versus oxidant concentration curves given in Figures 5-10. 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, 1975) prior to multiplication to determine the ADMI color value as shown in Appendix A. This is because the color value measurement is not linear with dilution. The decolorization efficiency calculated was roughly equivalent for the ozonation experiments on all three wastewater streams: varying from approximately 50-70 ADMI color units per ppm of ozone. The only exception was the low pH ozonation of the Navy slack wash water. 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 4, the results

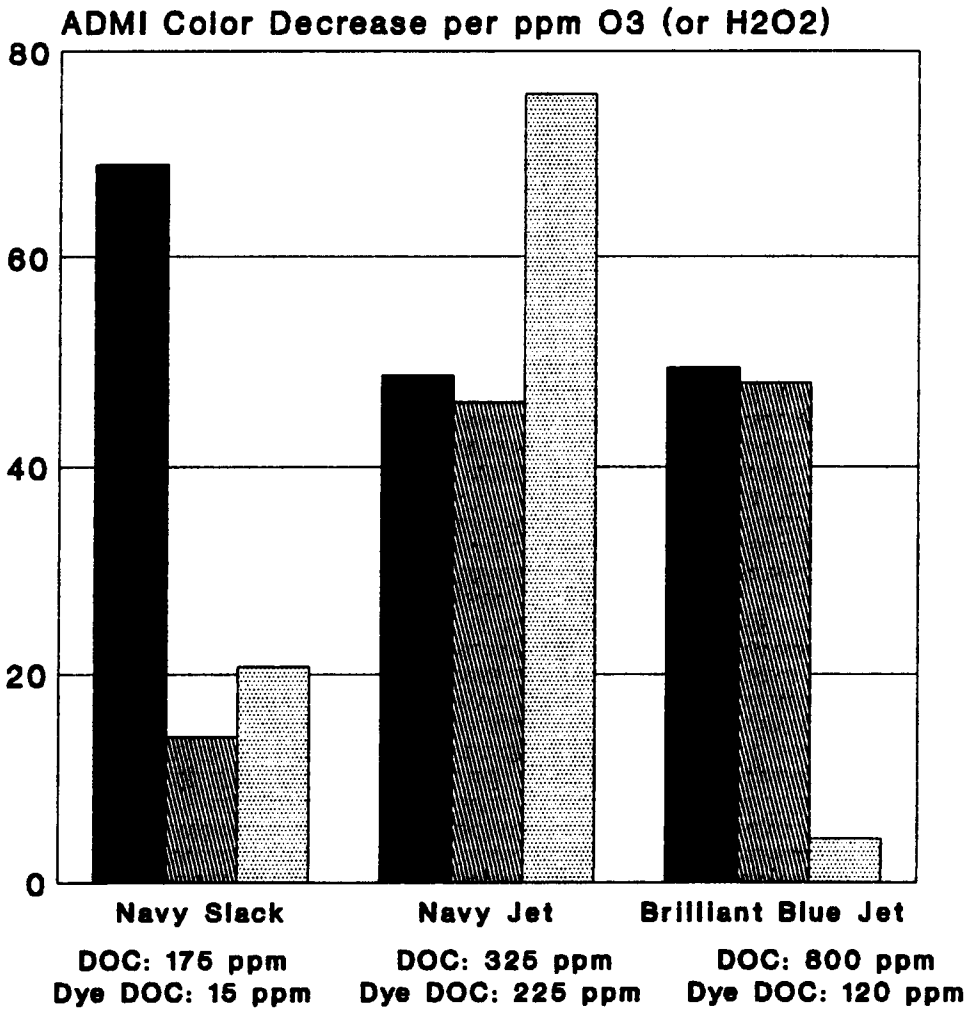
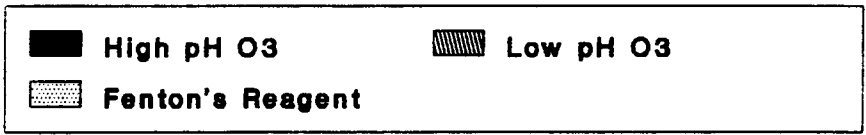


Figure 11: Color Removal Efficiency From Dye Waste Streams

(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.)

**Table 4: 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

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 (Figure 8) than the actual waste stream, though almost as much ozone was needed (Figure 5). 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 as shown on Figure 10, though 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 non-colored organic materials from these waste streams greatly affected the peroxide oxidation, but not the ozonation. Approximately twice as much mass of 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.*, 1983) that ozonation reactions occur more quickly than the diffusion of the gas into the liquid phase meaning the kinetics are gas-transfer limiting. This is particularly true of free-radical reactions which have very high reaction rate constants. Competition between the possible substrates in the streams for the interfacial area would then determine the efficiency with which they were oxidized. This may explain the results obtained in our trials. The ozonation requirements for decolorization were related to the dye concentration rather than total amount of dissolved organics (measured as DOC). If the dyes were able to compete favorably for the interfacial area, then they could be selectively oxidized. Lowering the pH might also alter the interfacial characteristics of the non-colored organics in the wastewater and thereby competing with the dyes.

Aromatics such as benzene and toluene are known to accelerate the decomposition of ozone in aqueous solution even in very acidic conditions as outlined in Chapter 2 making the free-radical mechanism predominant. High pH conditions would still accelerate the process which is seen by the experimental results. Salts, conversely, retard the chain-reaction

mechanism by scavenging radicals and the presence of such a large quantity in the Navy jet-dye bath could be the cause of the difference in oxidation rates between the pure and actual dye streams. Experiments using pure dye solution and varying salt concentrations would confirm this hypothesis. The addition of surfactants to the pure dye solutions would affect the surface properties and therefore the kinetics if they were determined by such surface interactions.

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.

Dissolved CO_2 in the form of carbonates and bicarbonates is known to be a radical scavenger. For this reason, the high

pH trials on the Navy slack washer effluent were begun with different levels of dissolved inorganic carbon as shown in Figure 5. However, no difference in color removal could be seen in the three different trials. The reason for this may be the rate with which hydroxyl radicals react with the dyes could be much higher than the scavenging rate of IC. Higher IC concentrations might provide further insight.

Reaction via Fenton's reagent involved the same non-specific 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 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.

Much lower final color values were attained using iron and peroxide. This could be due in part to the complexing of organics with the ferric iron following reaction. As mentioned previously, a trial on the Navy jet-dye effluent with ferric iron added after oxidation via Fenton's reagent lowered the color from 13710 to 4570. This is close to the final color value of 3751 which was obtained by oxidation using the same amount of iron in the ferrous form at the initiation of the reaction. This confirmed that complexing of organics is responsible for part of the color removal.

The DOC of the wastewater streams was also lowered using Fenton's reagent, but it appeared not entirely by oxidation to CO_2 . Higher initial iron concentrations lowered the final DOC value implying that the DOC removed is bound up in the solids which precipitate. The added ferric iron experiment also confirmed this fact as additional DOC was removed. In addition, if the solids were added to the biological reactors, the effluent DOC values were higher than the influent implying that the solids contained significant DOC. Because these

solids contained organics, the suitability of these sludges for landfill application should be tested.

The effect of atmospheric oxygen was not controlled in the Fenton's reagent experiments. As the literature states, molecular oxygen reacts with free-radical intermediates. Sparging with oxygen or air could increase the oxidating efficiency of Fenton's reagent thereby requiring less hydrogen peroxide. Many questions would have to be answered concerning the optimal temperature. Higher temperatures, which should increase reaction rates, will lower the solubility of oxygen in water. Addition of the peroxide slowly, rather than all at once, might also improve efficiency by keeping the radical concentration lower and thereby decreasing the further oxidation of breakdown products and auxiliaries with lower hydroxyl oxidation rate constants.

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 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, 1992). 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.

5.5 Biological Testing Results

Figures 12-17 summarize the results of biological action on the streams. As shown on Figures 12-14, very little color change resulted from the influent to the effluent of the biological reactors. Comparison of the color data by a t-test showed that only the untreated reactors and the high pH ozone reactors had significant differences between the influent and effluent mean values. Ozonation pretreatment resulted in final effluent color values of about half the untreated value for all three streams. Fenton's reagent gave much lower final color values, particularly for the Navy slack washwater and the Navy jet-dye bath, where the effluent color values were approximately 20% and 4%, respectively, of the control values.

The DOC data for the bioreactors are summarized in Figures 15-17. Ozonation pretreatment at either high or low pH caused no significant drop in the DOC in any of the streams. The DOC of the solutions were reduced with Fenton's reagent, though, making the bioreactor influents resulting from that treatment the lowest of all the conditions. In

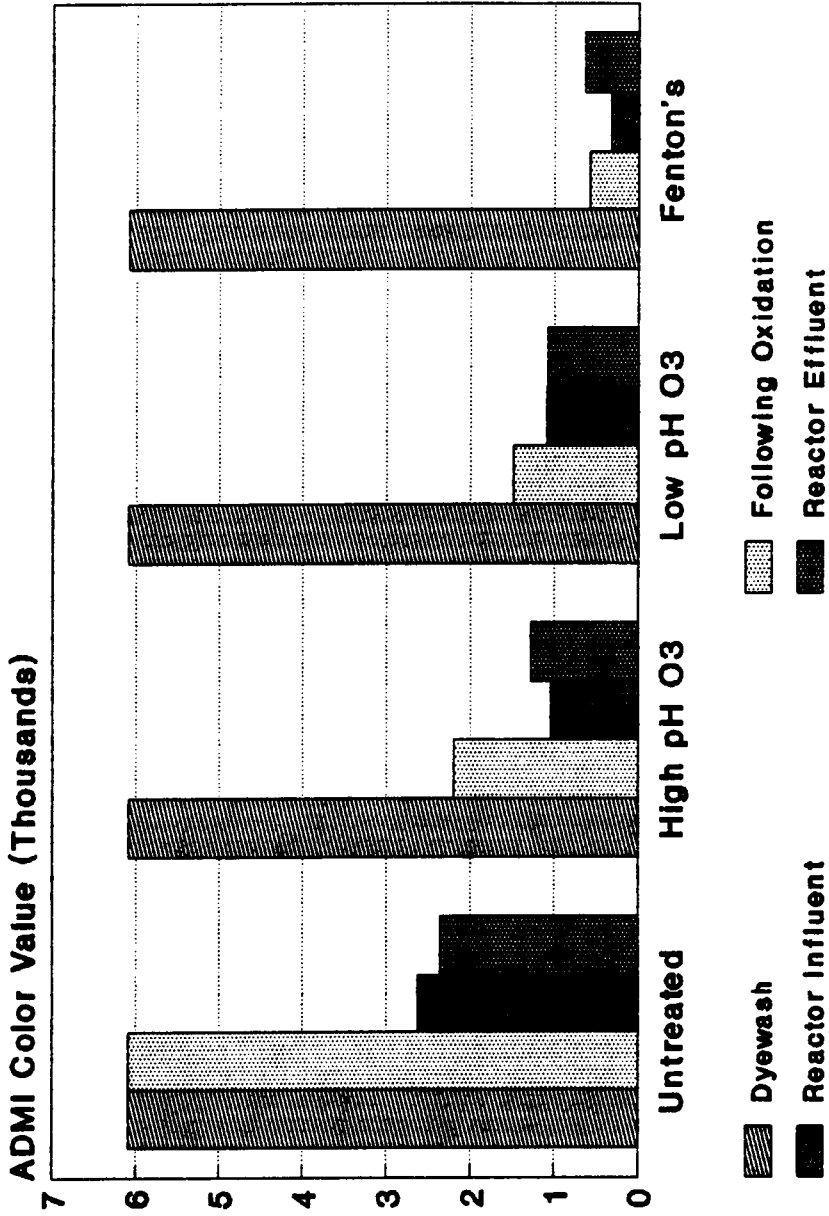


Figure 12: Effect of Oxidation Schemes on the Removal of Color From Navy Slack Washer Effluent in Bioreactors

(ADM I measured at 5X dilution. Reactor influent is mixture of treated dyewash and primary effluent (3:1). SBRs have 2-day retention time. Results are average of six days.)

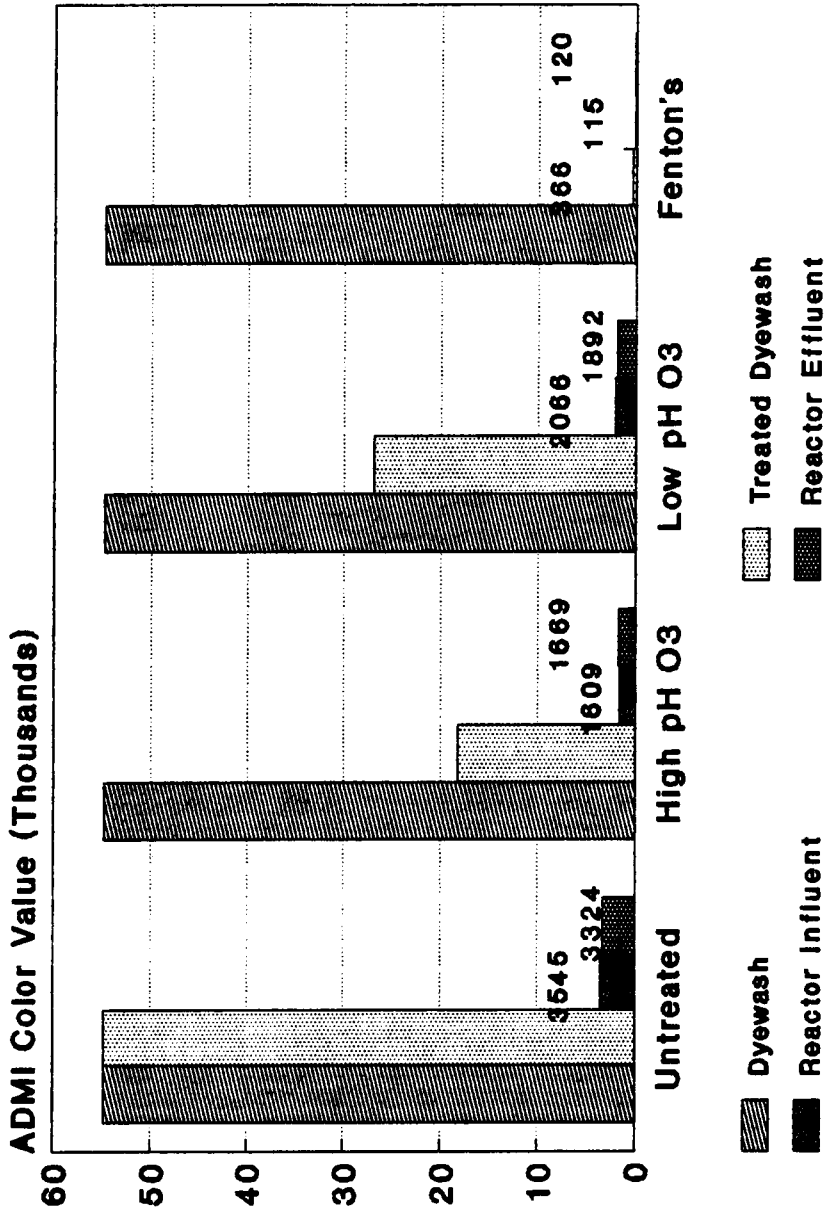


Figure 13: Effect of Oxidation Schemes on the Removal of Color From Navy Jet-dye Waste in Bioreactors

(ADM I 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.)

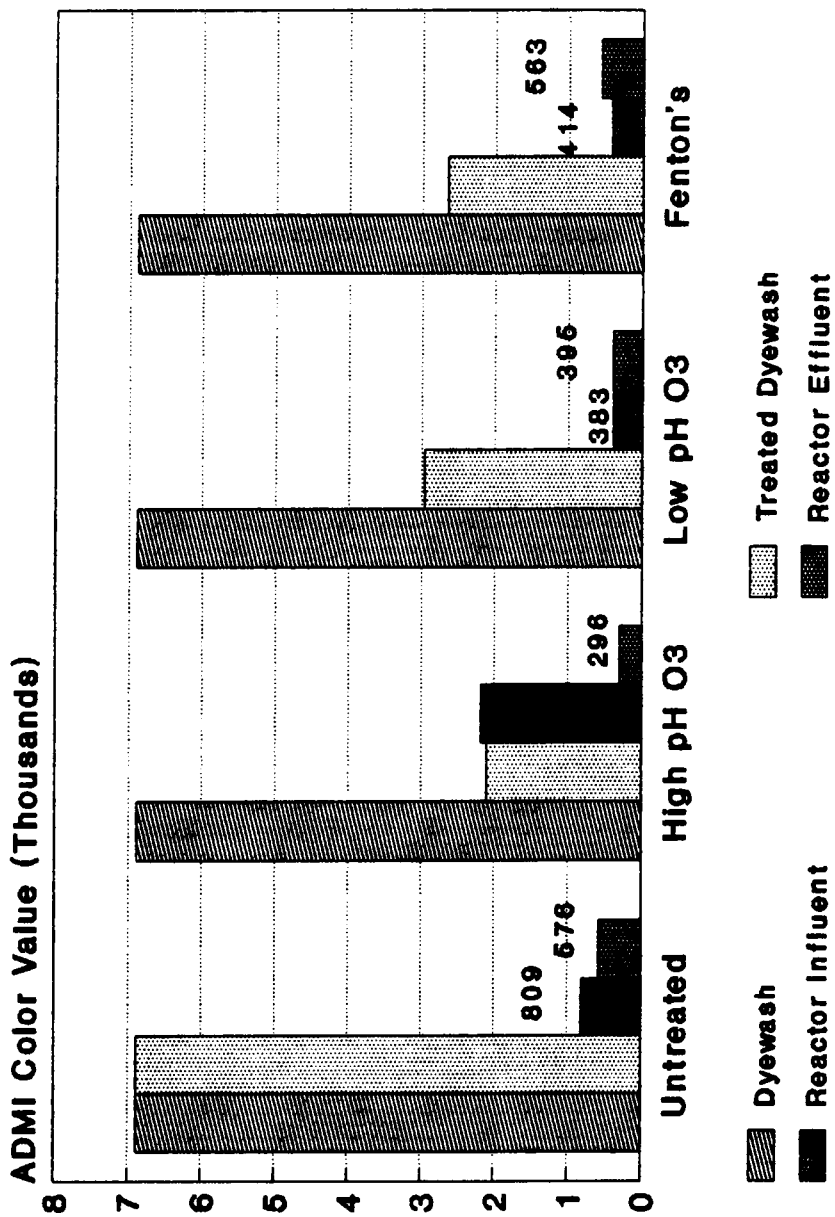


Figure 14: Effect of Oxidation Schemes on the Removal of Color From Brilliant Blue Jet-dye Waste in Bioreactors

(ADM I measured at 5X 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.)

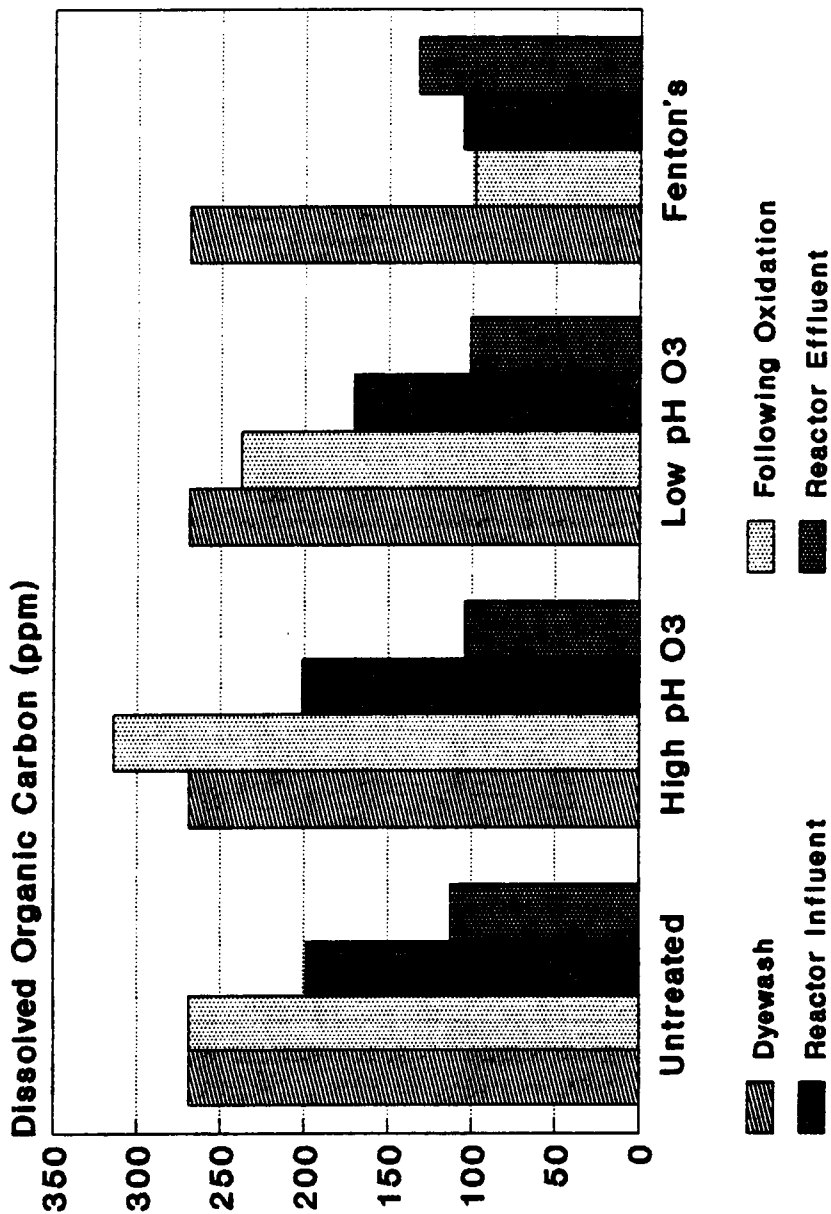


Figure 15: Effect of Oxidation Schemes on the Removal of DOC From Navy Slack Washer Effluent in Bioreactors

(Reactor influent is mixture of treated dyewash and primary effluent (3:1). SBRs have 2-day retention time. Results are average of six days.)

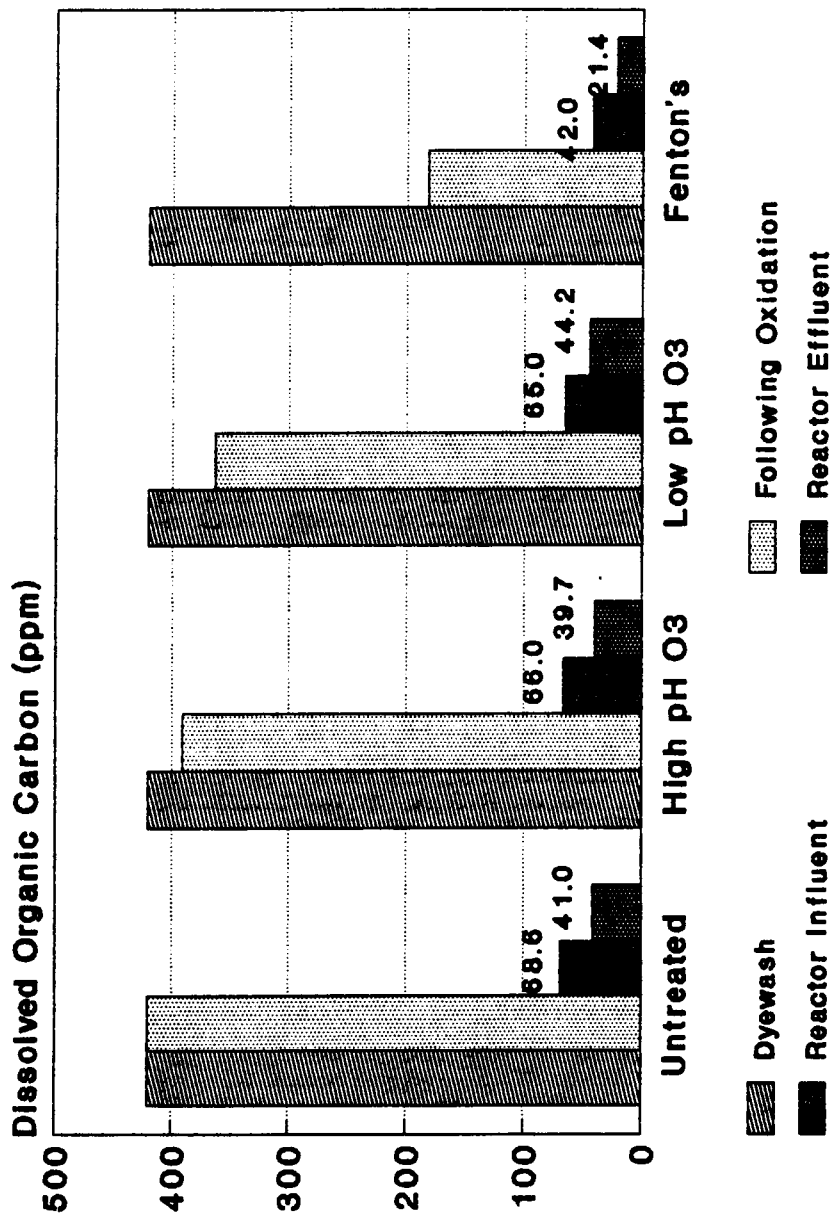


Figure 16: Effect of Oxidation Schemes on the Removal of DOC From Navy Jet-dye Waste in Bioreactors

(Reactor influent is mixture of treated dyewash and primary effluent (1:9). SBRs have 2-day retention time. Results average of six days.)

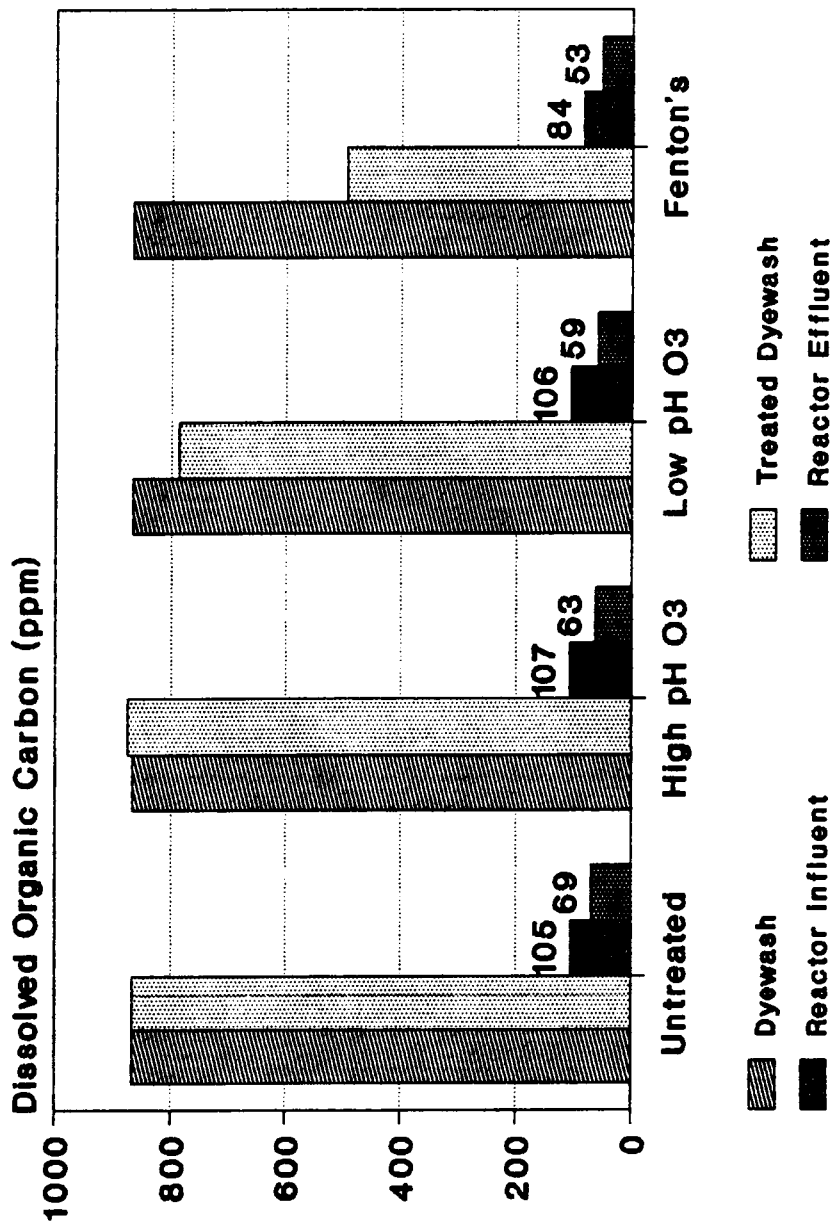


Figure 17: Effect of Oxidation Schemes on the Removal of DOC From Brilliant Blue Jet-dye Waste in Bioreactors

(Reactor influent is mixture of treated dyewash and primary effluent (1:9). SBRs have 2-day retention time. Results average of six days.)

general, the effluent DOC was also lowest for the Fenton trials, though the amount of carbon removed in the bioreactors was less for those streams. Due to the high variance of the effluent data for the Fenton's reagent oxidized Navy slack washer effluent bioreactor, the difference in the influent and effluent DOC were not statistically significant.

All of the bioreactors were begun with equivalent amounts of biomass from the same acclimated culture. The final suspended solids measurements revealed that not all of the reactors ended with the same amount of biomass. The bioreactors fed Navy slack washwater effluent untreated and treated by ozonation at either condition contained more suspended solids than the other reactors. Much of this was likely due to silicate formation and precipitation though the volatile portion of the suspended solids was not measured. No such accumulation was noted in the bioreactor fed Navy slack washwater treated by Fenton's reagent where the solids formed following acidification and oxidation were decanted. The average suspended solids concentration for the other reactors was about 1200 ppm. Some biofilm accumulation was noted on the sides of the reactors but their mass was not measured.

5.6 Discussion of Biological Testing

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. Very little 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 5. 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 are 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 low pH ozone Navy jet-dye bioreactors, the DOC removal was very close to the expected biological

Table 5: 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

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 occur at the seventh day of the run since the hydraulic retention time was two days ($(1/2)^7 = .98$ or 98% of the final value). The color values were quite constant and steady-state seemed to have been reached. The exception is 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 are 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.

5.7 Recommended Conditions for Decolorization

The Navy slack washer effluent could be most effectively decolorized with Fenton's reagent, though the reduction of the auxiliary organics would further reduce the oxidant requirements. A peroxide concentration of 300 ppm and 15 ppm ferrous iron (20:1 ratio) would result in an ADMI color value of approximately 600 and approximately 40% DOC reduction. Because of the large quantity of wastewater that would have to be treated, lower iron concentrations should be used in order to reduce the total amount of solids produced.

The Navy jet-dye effluent should also be decolorized using Fenton's reagent. The hydrogen peroxide concentration needed would be 1000 ppm with a 30:1 ratio of peroxide to iron. The resulting color would be below 1000 with approximately 35% DOC removal.

The third waste stream investigated could be more effectively decolorized using ozone. This was because the

high DOC concentration of the streams required a large amount of hydrogen peroxide to oxidize. An ozone dose of 125 ppm at pH 10 or above would result in a final color value of about 2500 with little DOC removal. However, if the fabric were scoured or the polyester dyed prior to the cotton dyeing, the DOC of the dyebath would be reduced making oxidation via Fenton's reagent viable.

6.0 Conclusions

1. Ozonation at basic pH (approximately 10.5) proved to be much more effective than at acidic pH (approximately 3) for decolorizing the Navy slack washer discharge and slightly more effective for the Navy jet-dye bath and the Brilliant Blue jet-dye bath.

2. Fenton's reagent decreased the ADMI color to very low levels (below 1000 for the Navy jet-dye effluent) and was dependent on the initial DOC of the waste stream. Trials with a peroxide to iron ratio of 10 or 20 to 1 resulted in the lowest color values. Lower iron concentrations (20:1) produce fewer solids.

3. Ozonation, which seems to selectively oxidize the dyes, would be preferred over Fenton's reagent for wastewater streams which contain significant amounts of non-colored organic matter. Relatively pure streams (most of the organics being dyestuffs), such as the Navy jet-dye effluent, could be effectively decolorized by hydrogen peroxide.

4. DOC removal was in biological reactors was not enhanced or hindered by the oxidative schemes employed. No change in the

color was noted in the biotreatment. The oxidized waste streams created appear to pose no potential hazard for an activated-sludge wastewater treatment plant.

7.0 Recommendations

1. To increase the oxidative decolorization efficiency of Fenton's reagent, auxiliary organics should be reduced as much as possible. The dyebath components should be investigated to determine their effect on oxidation by ozone and hydrogen peroxide.
2. Sparging with air or oxygen should be investigated as a potential method of increasing the efficiency of Fenton's reagent.
3. Slow addition of the hydrogen peroxide should be investigated to determine if the dyes may be selectively oxidized.
4. The decolorized waste streams and reaction solids should be further analyzed. While no hindrance to microbial activity was noted, the toxicity or mutagenicity was not investigated. The Fenton's reaction solids should be tested for landfill leachability, as well.
5. Oxidative decolorization with different added salts (besides NaCl) should be attempted to determine whether

chlorine is produced during oxidation.

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Appendix A: ADMI Color Calculation

Because the treatment of colored solutions may create other intermediate color bodies, simply measuring the concentrations of the dyes does not accurately represent the color of the resulting solution. Color values used for comparison of treatment schemes were determined according to the American Dye Manufacturers Institute (ADMI) method. The method is based on the measurement of 3 different wavelengths, 590 nm, 540 nm, and 438 nm. Tristimulus values are then calculated based on the transmittance at these wavelengths which relate the measured color to a position in color-space. Color space is widely used to compare shades in the textile industry and is defined as a 3-dimensional field in which the axes are labelled L, A, and B. The L axis is a measurement of how light or dark a shade is. The A axis gives the red-green position and B, the yellow-blue. The pure solvent matrix (distilled water in our samples) provides the reference point (0,0,0). The color value is then calculated as a magnitude or distance from the reference point in color space. Munsell values based on the tristimulus values can be determined from published charts, or as in this study, a curve-fit equation can be used to calculate them. If the sample is too dark to obtain an accurate transmittance value (lower than 10%) then the sample must be diluted. The result is then multiplied by the factor by which the sample was diluted (e.g. if diluted

10:1, then the color value of the diluted sample is multiplied by 10 to determine the ADMI color value of the original solution).

A spreadsheet was used for color calculations which required that only the transmittance values and the dilution ratio be entered. The cell formulae which were contained in the spreadsheet are shown:

A1: '590 %T

B1: '540 %T

C1: '438 %T

D1: +C1*0.1899 + A1*0.791

E1: @SQRT(D1/98.06)

F1: @ABS((30.646*E1) + (-97.172*E1^2) + (292.949*E1^3) + (-608.85*E1^4) + (870.83*E1^5) + (-840.79*E1^6) + (521.73*E1^7) + (-187.64*E1^8) + (29.73*E1^9) - 1.5324)

G1: +B1

H1: @SQRT(G1/100)

I1: @ABS((30.646*H1) + (-97.172*H1^2) + (292.949*H1^3) + (-608.85*H1^4) + (870.83*H1^5) + (-840.79*H1^6) + (521.73*H1^7) + (-187.64*H1^8) + (29.73*H1^9) - 1.5324)

J1: +C1*1.1835

K1: @SQRT(J1/118.11)

L1: @ABS((30.646*K1) + (-97.172*K1^2) + (292.949*K1^3) + (-608.85*K1^4) + (870.83*K1^5) + (-840.79*K1^6) + (521.73*K1^7) + (-187.64*K1^8) + (29.73*K1^9) - 1.5324)

$$M1: \quad @SQRT((0.23*(9.902-I1))^2 + ((9.904-9.902) - (F1-I1))^2 + (0.4*((9.902-9.91) - (I1-L1)))^2)$$

$$N1: 1272 (F_{ave})$$

$$O1: 5 \text{ (Dilution Ratio)}$$

$$P1: +M1*N1*O1$$

The cells which compute the Munsell values, F1, I1, and L1, are ninth-order equations which agree very well with published Munsell value charts. Cell N1 is a factor which depends on the spectrophotometer in use. Cell P1 is the ADMI color value resulting from the calculations.

In practice, however, the ADMI calculation is not quite linear with respect to dilution. For example, a sample which has been diluted by a factor of five will not give a color value one-fifth of the original sample. Researchers have (Netzer, 1975) found that more accurate comparisons could be made if the dilution factor were raised to the 0.85 power prior to multiplication.

$$ADMI - Color_{diluted\ sample} * Dilution^{0.85}$$

Appendix B: Oxidation and Bioreactor Data Tables

Table II.1: Low pH Ozonation Data for Navy Slack Washer Effluent

Sample ID	Time (min)	Ozone Dose (ppm)	590 %T	540 %T	438 %T	ADMI Color
0	0.00	0.00	39.5	37.6	52.7	5856
1	3.17	22.17	46.1	45	58.9	4842
2	7.33	51.33	51	48.8	61	4433
3	12.17	85.17	60.2	55.7	63.5	3764
4A	17.25	120.75	71.8	64.9	67.2	3061
4B	17.25	120.75	70.9	64	66.5	3126
5	25.50	178.50	84	76.4	72.5	2208
6	32.03	224.23	88.1	83.1	76.5	1494

Table II.2: High pH Ozonation Data for Navy Slack Washer Effluent

Sample ID	Reaction Time (min)	Dosage (ppm)	590 %T	540 %T	438 %T	ADMI Color
1	0.00	0.00	41.1	40.9	58	5470
2	3.00	14.48	58.2	56	62.8	3401
3	6.17	29.77	72.1	68.9	68.1	2162
4A	9.17	44.27	82.5	78.4	72.4	1646
4B	9.17	44.27	84.5	80.2	73.6	1580
5	12.00	57.93	89.2	85.3	78	1312
6	15.00	72.41	92.4	89.5	82.1	1053
7	18.00	86.90	94	91.6	85	884

Table II.3: High pH Ozonation Data for Navy Slack Washer Effluent with Initial Inorganic Carbon Level of 83 ppm.

Sample ID	Time (min)	Dosage (ppm)	ADMI Color
1	0	0	5573.815
2	3.083	14.88345	3766
3	6.583	31.78	2455.368
4	10.5	50.68966	1446.328
5	14.5	70	1117.45
6	17.75	85.68966	872.0095
7a	21.5	103.7931	769.8538
7b	21.5	103.7931	763.1536

Table II.4: High pH Ozonation Data for Navy Slack Washer Effluent with Initial IC Level of 47 ppm.

Sample ID	Time (min)	Dosage (ppm)	ADMI Color
1	0	0	5274
2	3.083	14.88345	3396
3	6	28.96552	2232
4	9	43.44828	1487
5a	12.3	59.37931	1133
5b	12.3	59.37931	1145
6	16	77.24138	1000
7	20	96.55172	814

Table II.5: Low pH Ozonation Data for the Brilliant Blue Jet-dye Bath

Sample ID	Time (min)	Dosage (ppm)	590 %T	540 %T	438 %T	ADMI
904-1	0	0	24.9	28.5	53.9	7605
904-2	3.1667	15.83	30.4	32.2	53.6	6778
904-3	6	30	36	37	53.5	5753
904-4a	9.5	47.5	43.3	43.1	53	4626
904-4b	9.5	47.5	42.2	42.1	51.8	4711
904-5	13	65	49.5	48	52.5	3919
904-6	17	85	57.2	54	52.8	3343
904-7	21.5	107.5	63	58	51.7	3194
904-8	25	125	68	62	52	3115

Table II.6: High pH Ozonation Data for Brilliant Blue Jet-dye Effluent

Sample ID	Time (min)	Dosage (ppm)	590 %T	540 %T	438 %T	ADMI Color
905-1	0	0	16.8	24.5	53.8	8547
906-2	3	17	23.1	31	53	6956
905-3	6	34	30.9	38	53.1	5597
905-4a	9	51	38.9	45	53.5	4517
905-4b	9	51	40.5	46.3	55	4353
905-5	12	68	46.1	50.3	54.5	3758
905-6	15	85	52.9	55.7	55.1	3201
905-8	22	124.67	65.4	64	56.5	2615
905-9	30	170	76.3	71	59	2549

Table II.7: High pH Ozonation Data for Navy Jet-dye Effluent

Sample ID	Time (min)	Dosage (ppm)	590 %T	540 %T	438 %T	ADMI Color
1002-1	0	0	22.7	18.7	57.5	63098
1002-3	6	28	32	23.8	59	59057
1002-5	16	74.667	44.1	30.1	60.2	56013
1002-6	31	144.67	56.9	38.2	65.1	52560
1002-7	45	210	65.1	46.5	69.3	44377
1002-8	60	280	71	53.6	72	36872
1002-10	90	420	81	61.4	77.9	34556
1002-12	120	560	86	74	81.9	18897

Table II.8: High pH Ozonation Data for Pure Dye Solution of Approximate Navy Jet-dye Effluent Color

Sample ID	Time (min)	Dose (ppm)	590 %T	540 %T	438 %T	ADMI Color
1010-1	0	0	30	26.9	60.7	49266
1010-2	3	14	35.8	33.5	63.5	40683
1010-3	7	32.67	50.1	47.5	68.4	27293
1010-4	12	56	69.1	65.6	75.2	14960
1010-5	17	79.33	81.3	77	80.2	9523
1010-6	23	107.3	88.9	85.7	83.3	5339
1010-7	30	140	94.4	92	87.8	3550
1010-8	40	186.7	97.2	95.9	91.3	2668
1010-9	50	233.3	98.7	97.7	93.5	2242
1010-10	60	280	99	98.2	94.7	1848

Table II.9: Low pH Ozonation Data for Navy Jet-dye Effluent

Sample ID	Time (min)	Dosage (ppm)	590 %T	540 %T	438 %T	ADMI Color
0201-1	0	0	29.9	26	58.2	49847
0201-2	10	46.67	40.5	30.6	56.9	48307
0201-3	22	102.7	49.7	35.3	57.4	47120
0201-4	30	140	54	38.5	58.4	44756
0201-5	60	280	64	48	62.2	36385
0201-6	90	420	71.9	57.8	67	27342
0210-7	120	560	77.1	64.9	70.3	21170

Table II.10: High pH Ozonation and Fenton's Reagent Data for Pure Dye Solution of Approximately Navy Slack Washer Effluent Color

Sample ID	Time (min)	Ozone (ppm)	H ₂ O ₂ /Fe (ppm/ppm)	590 %T	540 %T	438 %T	ADMI Color
1	0	0		43.5	40.5	72.2	7513
2	3	14		59.6	54.9	76	5094
3	6	28		72	66.8	79.9	3460
4	9	42		82.5	76.9	84	2385
5	12	56		89	85	88.1	1420
6	15	70		92.9	89.9	90.7	904
7	20	93.3		97.1	95.1	94.2	468
Fenton			100/10	98.5	98	93.9	444

Table II.11: Fenton's Reagent Data for Navy Slack Washer Effluent

Sample ID	H ₂ O ₂ (ppm)	Fe (ppm)	590 %T	540 %T	438 %T	ADMI Color
1110-1	0	0	40.5	35.1	50.9	6775
1110-2	500	0	39.9	34.7	50.9	6835
1110-3	0	25	42.3	36.7	51.8	6530
1110-5	100	5	65.7	57.4	57.9	3777
1110-6	200	10	93	91.3	83.5	994.3
1110-7	500	25	98	98.1	95.3	343.6
1110-8	1000	50	100	99.9	98.2	181.4
1110-9	100	10	87	82.3	92.9	2261
1110-10	200	20	92.4	90.5	83.5	950.6
1110-11	300	30	96.3	95.2	90.5	563.7
1110-12	400	40	96	94.9	90.1	583
1110-13	300	15	94.4	92.6	86.8	761.2
1110-14	400	20	96.2	95	91	509.6

Table II.12: Fenton's Reagent Data for Navy Jet-dye Wastewater

Sample ID	H2O2 (ppm)	Fe (ppm)	590 %T	540 %T	438 %T	ADMI Color
1	100	0.92	43.1	28.5	47.3	51354
2	200	1.84	57.2	40.2	53.1	41710
3	500	4.59	67.6	53.7	59.3	27567
4	1000	9.18	85.7	78	74.9	10745
5	100	1.84	43	28	46	51880
6	200	3.67	55.5	41.8	52.4	35724
7	500	9.18	74.4	62.2	63.1	20786
8	1000	18.36	83.5	73.8	70.7	13711
9	100	3.67	47.6	33.1	48.4	45156
10	200	7.35	60.8	46.1	52.6	32603
11	500	18.36	81.6	73.5	69.7	12328
12	1000	36.73	96.3	94.3	88	3751
13	100	7.35	47	33.1	49.1	44804
14	200	14.69	60.3	47.4	55.6	30603
15	500	36.73	89	81.8	75.1	9291
16	1000	73.45	98.2	97.1	92.7	2406
C1	0	0	21.3	17	52.3	63341
C2	1000	0	80.5	71.2	72	14868
C3	0	36.73	28.5	22	53.5	56547
C4	1000	36.73	94.9	91.7	85.3	4571

Table II.13: Fenton's Reagent Data for Brilliant Blue Jet-dye Wastewater

Sample ID	H ₂ O ₂ (ppm)	Fe (ppm)	590 %T	540 %T	438 %T	ADMI Color
1117-1	0	0	28.3	35.6	58.9	6415
1117-2	500	0	27	34	58.1	6669
1117-3	0	50	29.5	36.3	57.6	6157
1117-4	100	10	29	34.7	55.9	6311
1117-5	200	20	44	45	50.5	4153
1117-6	500	50	67.9	54	43	4936
1117-7	1000	100	82.9	74.1	48.5	4025
1117-8	100	5	27.9	34.4	56.9	6472
1117-9	200	10	29.5	35.1	56	6235
1117-10	500	25	67.8	55	44.8	4632
1117-11	1000	50	76.9	68.6	43.5	4324

Table II.14: High pH Ozonation Data for Pure Reactive Blue 19 Solution of Approximate Brilliant Blue Jet-dye Effluent Color

Sample ID	Ozonation Time (min)	Dosage (ppm)	590 %T	540 %T	438 %T	ADMI Color
0224-1	0	0	24.1	43.3	85	7935
0224-2	3	14	35	52	80.1	6117
0224-3	6	28	50.1	62.4	77	4052
0224-4	9	42	64.1	71	76.1	2465
0224-5	12	56	74.9	77.7	76.1	1602
0224-6	18	84	87	85.9	77.8	1272
0224-7	24	112	92.3	89.9	81.7	1090

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