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116

**CHEMICAL REDUCTION AND OXIDATION COMBINED WITH
BIODEGRADATION FOR THE TREATMENT
OF A TEXTILE DYE WASTEWATER**

by

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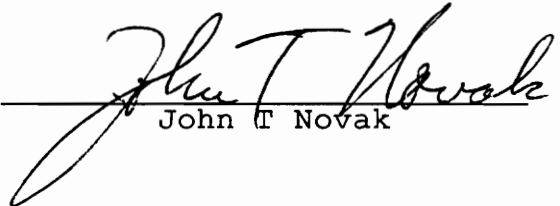
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ENVIRONMENTAL ENGINEERING

Approved:


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(ABSTRACT)

Pretreatment of the textile dye wastewater was accomplished using reducing agents. The reducing agents studied were sodium hydrosulfite, thiourea dioxide, and sodium borohydride. Preliminary tests were conducted using just the reducing agents. Although there was color reduction, the reduced wastewater was inhibitory to biological degradation. Additional tests were conducted with sodium hydrosulfite. These included reduction followed by pH adjustment, nutrient addition, pH adjustment and nutrient addition, and lime addition. These tests were also successful in reducing the color but were not biologically degradable.

Reduction of the dye wastewater followed by oxidation, however, provided positive results (color reduction and biodegradation). A series of reduction/oxidation experiments on the textile wastewater were performed: treatment of 17 percent, 33 percent, 67 percent, and 100 percent of the textile wastewater stream. The wastewater is

composed of 75 percent textile and 25 percent municipal wastewater. For the 17, 33, and 67 percent of the textile wastewater pretreated with reduction/oxidation, untreated textile and municipal wastewater were added before transfer into sequencing batch reactors for biological treatment. For the 100 percent textile wastewater stream, the initial, untreated parameters were: 2650 American Dye Manufactures Institute (ADMI) color; 780 mg/L COD; 211 mg/L TOC; and 182 mg/L BOD. The reduction/oxidation pretreatment followed by biological treatment resulted in effluent values of 615 ADMI color (77 percent reduction), 310 mg/L COD (60 percent reduction), 82 mg/L TOC (61 percent reduction), and 62 mg/L BOD (66 percent reduction).

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Dedicated to
Wallace Shepard
and
Gib McCurdy

TABLE OF CONTENTS

	Page
Abstract.....	ii
Acknowledgements.....	iv
List of Tables.....	viii
List of Figures.....	x
Introduction.....	1
Objectives.....	5
Literature Review.....	7
Types of Azo Dyestuffs.....	9
Acid Dyestuffs.....	9
Basic Dyestuffs.....	10
Direct Dyestuffs.....	10
Disperse Dyestuffs.....	10
Fiber Reactive Dyestuffs.....	11
Vat Dyestuffs.....	13
Chemistry of Azo Dyestuffs.....	13
Chemistry of Reactive Azo Dyestuffs.....	14
Wastewater Treatment of Azo Dyestuffs.....	15
Biological Treatment of Azo Dyestuffs.....	17
Aerobic Biological Treatment of Azo Dyestuffs.....	17
Anaerobic Biological Treatment of Azo Dyestuffs.....	19
Chemical Treatment of Azo Dyestuffs.....	21
Chemical Reduction of Azo Dyestuffs.....	21
Chemical Oxidation of Azo Dyestuffs.....	23
Chemical Precipitation of Azo Dyestuffs.....	25
Physical Treatment of Azo Dyestuffs.....	26
Carbon Adsorption of Azo Dyestuffs.....	27
Filtration of Azo Dyestuffs.....	28
Transformation of Azo Dyestuffs.....	28
Hydrolysis of Azo Dyestuffs.....	29
Photolysis of Azo Dyestuffs.....	29
Transportation Processes of Azo Dyestuffs.....	31
Transportation Between Water/Air.....	32
Transportation Between Water/Soil and Water/Biota.....	33
Toxicity of Azo Dyestuffs.....	36

Methods and Materials.....	39
Chemical Pretreatment of Navy 106.....	39
Sodium Hydrosulfite.....	42
Chemical Reduction with pH Adjustment...	43
Chemical Reduction with	
Nutrient Addition.....	43
Chemical Reduction with Nutrient Addition	
and pH Adjustment.....	44
Chemical Reduction with Lime Addition...	44
Chemical Reduction Followed by	
Oxidation.....	44
Thiourea Dioxide.....	45
Sodium Borohydride.....	46
Biological Treatment of Navy 106.....	47
Analytical Procedures.....	51
Results and Discussion.....	57
Acclimation of SBR A and B.....	57
Preliminary Tests.....	65
Reduction with Sodium Hydrosulfite and	
Oxidation with Hydrogen Peroxide.....	69
17 % Textile Dye Wastewater Pretreated.....	69
33 % Textile Dye Wastewater Pretreated.....	73
67 % Textile Dye Wastewater Pretreated.....	81
100 % Textile Dye Wastewater Pretreated.....	84
Comparison of the Reduction-Oxidation	
Studies.....	92
Toxicity.....	114
BOD-Toxicity Test.....	114
Heavy Metal Analysis.....	118
Additional Tests.....	121
Cost Comparison.....	123
Conclusions.....	127
Summary of Results.....	127
Conclusions.....	127
Recommendations.....	129
References.....	132
Appendix A. ADMI Color Measurement Procedure.....	139
Appendix B. Chromaticity Graph.....	143

Appendix C. Preliminary Test Data.....	146
C-1. Reduction with Hydrosulfite	147
C-2. Reduction with Thiourea Dioxide	150
C-3. Reduction with Sodium Borohydride	152
C-4. Reduction with Hydrosulfite with pH Adjustment	154
C-5. Reduction with Hydrosulfite with Nutrient Addition	156
C-6. Reduction with Hydrosulfite with pH Adjustment and Nutrient Addition	158
C-7. Reduction with Hydrosulfite with Lime Addition	160
C-8. Oxidation with Hydrogen Peroxide	162
Appendix D. Hydrosulfite Reduction with Hydrogen Peroxide Oxidation	164
D-1. 17 % Textile Dye Wastewater Pretreated	165
D-2. 33 % Textile Dye Wastewater Pretreated	168
D-3. 67 % Textile Dye Wastewater Pretreated	171
D-4. 100 % Textile Dye Wastewater Pretreated	174
Appendix E. ADMI Color vs Reducing Agent Concentration.....	177
Vita.....	181

LIST OF TABLES

Table	Page
1. Acclimation Data for Each Treatment Step.....	59
2. Effluent Data during Acclimation of SBR A and B...	64
3. SBR Influent and Effluent Color and TOC Values for the Preliminary Tests.....	67
4. Wastewater Characteristics for 17% Pretreatment of the Textile Dye Wastewater.....	71
5. Effluent Data for 17% Pretreatment of the Textile Dye Wastewater.....	72
6. Wastewater Characteristics for 33% Pretreatment of the Textile Dye Wastewater.....	77
7. Effluent Data for 33% Pretreatment of the Textile Dye Wastewater.....	78
8. Wastewater Characteristics for 67% Pretreatment of the Textile Dye Wastewater.....	82
9. Effluent Data for 67% Pretreatment of the Textile Dye Wastewater.....	83
10. Wastewater Characteristics for 100% Pretreatment of the Textile Dye Wastewater.....	88
11. Effluent Data for 100% Pretreatment of the Textile Dye Wastewater.....	89
12. Food/Microorganism Ratios for the Reduction/Oxidation Tests.....	95
13. Growth Yield Values for the Reduction/Oxidation Tests.....	96
14. BOD-Toxicity Test: Color, COD, TOC, and BOD Data.	116
15. Concentrations of Chromium, Cobalt, and Copper in the Textile Dye Wastewater for each Treatment Process Step.....	120

16. Chemical Costs for the Reducing and Oxidizing Agents Used in the Pretreatment of the Textile Dye Wastewater..... 124

LIST OF FIGURES

Figure	Page
1. Schematic of the Degradation of Azo Dyestuffs.....	16
2. Schematic for the Treatment of Navy 106.....	40
3. The Five Operating Periods of the SBR.....	48
4. Relationship Between Reactors for Color Removal During Acclimation of SBR A and B.....	60
5. Relationship Between Reactors for COD Removal During Acclimation of SBR A and B.....	61
6. Relationship Between Reactors for TOC Removal During Acclimation of SBR A and B.....	62
7. Relationship Between Reactors for BOD Removal During Acclimation of SBR A and B.....	63
8. Relationship Between Test (17% Pretreated) and Control Reactor Performance for Color Removal.....	74
9. Relationship Between Test (17% Pretreated) and Control Reactor Performance for TOC Removal.....	75
10. Relationship Between Test (33% Pretreated) and Control Reactor Performance for Color Removal.....	79
11. Relationship Between Test (33% Pretreated) and Control Reactor Performance for TOC Removal.....	80
12. Relationship Between Test (67% Pretreated) and Control Reactor Performance for Color Removal.....	85
13. Relationship Between Test (67% Pretreated) and Control Reactor Performance for TOC Removal.....	86
14. Relationship Between Test (100% Pretreated) and Control Reactor Performance for Color Removal.....	90
15. Relationship Between Test (100% Pretreated) and Control Reactor Performance for TOC Removal.....	91
16. Reduction/Oxidation Color Trend Comparison Between 17, 33, 67, and 100 % Pretreatment of the Textile Dye Wastewater.....	97

17.	Reduction/Oxidation COD Trend Comparison Between 17, 33, 67, and 100 % Pretreatment of the Textile Dye Wastewater.....	99
18.	Reduction/Oxidation TOC Trend Comparison Between 17, 33, 67, and 100 % Pretreatment of the Textile Dye Wastewater.....	100
19.	Reduction/Oxidation BOD Trend Comparison Between the 17, 33, 67, and 100 % Pretreatment of the Textile Dye Wastewater.....	101
20.	Reduction/Oxidation Color Trend Comparison Between each Treatment Process Step.....	103
21.	Reduction/Oxidation COD Trend Comparison Between each Treatment Process Step.....	105
22.	Reduction/Oxidation TOC Trend Comparison Between each Treatment Process Step.....	106
23.	Reduction/Oxidation BOD Trend Comparison Between each Treatment Process Step.....	107
24.	Percent Remaining of Color, COD, TOC, and BOD for 17, 33, 67, and 100% Pretreatment of the Textile Dye Wastewater.....	109
25.	Biological Percent Removals of Color, COD, TOC, and BOD for 17, 33, 67, and 100% Pretreatment of the Textile Dye Wastewater.....	110
26.	The pH Trend for 17, 33, 67, and 100% Pretreatment of the Textile Dye Wastewater.....	112
27.	Redox Potential Trend for 17, 33, 67, and 100% Pretreatment of the Textile Dye Wastewater.....	113
28.	COD, TOC, and BOD Trend during BOD-Toxicity Test.	117
29.	Color Trend during the BOD-Toxicity Test.....	119
30.	Chemical Cost Comparison between Reduction- Oxidation Pretreatment Chemicals.....	125

INTRODUCTION

Approximately 800 U.S. mills or plants engage in some sort of dyeing process (Alspaugh, 1973). Consumer demand for brightly colored textile goods has continued since the development of the first dye. This demand has caused the textile industry to develop new types of fibers and fabrics, new types of dyes to color these new fibers, new colors that are brighter and last longer than previous colors, and new improved methods of dye application.

These new parameters, especially the new dyes, which impart a color to textile wastewater, are of particular importance from a wastewater treatment view point. The new dyes must yield a color that is bright, and last throughout the lifetime of the fabric. The stability of the dye refers to the ability of the dye to maintain its structure and color and not break down with time and exposure to sunlight, water, soap, soil, and a variety of other parameters. Therefore, when a new dye is made that is stable under all of these conditions, it becomes more difficult to treat the dye in wastewater.

Because of the developments of new fabrics, new dyes, and new methods of dyeing, textile wastewater

characteristics are very diverse from one mill to the next. The wastewater characteristics can also be highly variable within the same mill, on a day-to-day or even hour-to-hour basis. The most pronounced variations include the type of dye in the wastewater and the color of the wastewater. The colored substances, which are the dyes, impart only a small fraction of the total organic load in the wastewater, but color is readily apparent (McKay, 1980). To the public colored water is toxic, polluted water and must be treated to remove the color.

The treatment alternatives applicable to the removal of color from textile mill wastewaters are also variable. A certain treatment scheme may be sufficient for one textile mill or even one type of dye, but not for another mills or types of dyes. The removal of dyes (color) is therefore a challenge to both the textile industry and the wastewater treatment facilities that must treat these wastewaters. According to Alspaugh (1973), no one specific treatment process can handle the removal of color from all textile wastewaters; therefore, each wastewater has a "tailored solution requiring a combination of methods."

Samples for this research were collected from a textile mill located in Virginia. This textile mill will be referred to as the Mill for simplicity. The Mill produces approximately 1.2 million pounds of dyed cotton-polyester

jogging suits per week. The cotton fabric is dyed by batch, pad dyeing processes and is dyed with reactive dyes. The cotton dye wastewater constitutes approximately 70 percent of the total wastewater flow. Polyester fabric is dyed using Theis, pressure-jet, dyeing machines and is dyed with disperse dyes. The polyester dye wastewater stream constitutes approximately 30 percent of the total wastewater flow. The wastewater from these processes is combined and discharged to a Publicly Owned Treatment Works (POTW) located near the Mill. The wastewater flow of the Mill is 3 million gallons per day (MGD).

One other textile mill discharges wastewater to this same POTW. The approximate composition of the combined wastewater influent to the POTW, wastewater from the two textile mills plus the municipal wastewater, is three-fourths textile wastewater and one-fourth municipal wastewater. Total wastewater flow to the POTW is 7 MGD. The POTW treatment system is comprised of extended aeration and aerobic sludge digestion.

The POTW has been successful at removing such wastewater parameters as biochemical oxygen demand (BOD) and total suspended solids (TSS), but not at removing the color (Anon, 1990a). The river, which receives the treated effluent from the POTW, serves as a water source for a city downstream from the POTW. Since the color is not readily

removed by the conventional methods of treatment used by the POTW, the colored river water creates water treatment problems for the city downstream. However, the river water has been tested and found to contain no harmful chemicals (Anon, 1990a). Therefore this problem was deemed to be an aesthetic problem and not a toxicity problem.

The reactive azo dye wastewater stream used in this research was chosen because treatment plant officials stated that, "the treatment plant had no trouble treating the textile wastewater until the mills began using the reactive dyes." The reactive dye wastewater stream from the textile mill used in this research is approximately 70 percent of the total wastewater stream. The Navy 106 dye wastewater stream comprises approximately 15 percent of the total wastewater stream, which correlates to approximately 22 percent of the reactive dye wastewater stream (Anon, 1990b)

Recently, state and federal agencies have been considering new color standards for textile wastewater discharged from treatment facilities (Tincher, 1989). The Virginia State Water Control Board (VSWCB), in conjunction with the United States Environmental Protection Agency (EPA), is requiring color, as measured in American Dye Manufacturers Institute (ADMI) color units, to be reduced. This requirement calls for the color to be reduced from 800

ADMI to 300 ADMI by January 1990, to 250 ADMI by 1991, and to 200 ADMI by January 1992 (Anon, 1991).

The POTW is currently adding quaternary amine polymers to remove the color, which is generally achieving an effluent color of less than 250 ADMI (Anon, 1991a). The cost of the polymers are distributed between the textile plants that discharge to the POTW. The polymer costs are approximately \$1000.00 per day to treat the 7 MGD going through the POTW (Anon, 1991). The choice of treatment method, or methods, to be used in color removal may not necessarily be governed by cost only (Gardiner and Borne, 1978). The choice may be of what will remove the color for a specific textile wastewater, since, according to McKay (1980), there is no universal, economical treatment scheme for the removal of color.

Objectives

The new requirements to remove color may take the form of pretreatment standards to be implemented by the industry prior to discharge to a POTW (Anon, 1990a; Tincher, 1989). Therefore, this research was conducted to fulfill two major objectives:

- (1) Development of a chemical pretreatment technique to remove the color of one specific textile mill wastewater effluent. The results from this research can be used by that specific textile mill to pretreat their wastewater prior to discharge to a municipal treatment facility.

- (2) Biologically treat the wastewater after chemical pretreatment to simulate the municipal treatment of the wastewater. This simulated treatment will show how chemical pretreatment would effect the biological treatment at the municipal wastewater treatment plant.

The wastewater stream studied was limited to the wash water from cotton fabric dyed with Navy 106. The wash water can be estimated to contain up to 25 percent of the dye due to low application efficiency (Weber et al., 1990). The Navy 106 dye is actually a mixture of three reactive dyes; Remazol black, Remazol red, and Remazol yellow, all of which are reactive azo dyes (Anon, 1990b).

LITERATURE REVIEW

The colorant industry can be divided into two major and very broad categories; pigments and dyestuffs. Pigments are water-insoluble substances, inorganic or organic, used to color various types of fabric. Dyestuffs are water-soluble and water-dispersible organic substances also used to color various types of fabric. Pigments will not be discussed further. Dyestuffs are a large and important group of industrial chemicals. The world production of dyestuffs in 1978 was estimated at 640,000 tons, and production of dyestuffs in the United States in 1980 was estimated to be approximately 122,500 tons (Baughman and Perenich, 1988a).

The levels of aqueous and airborne discharges of dyestuffs, as individual dye types or in the total combined emission, are low as compared with the discharges from other industries (Brown, 1987). The airborne discharges will not be covered because the discharges of dyestuffs are almost entirely in the aqueous phase. Aqueous phase discharges occur during the course of dyestuff manufacturing operations and during dyehouse processing operations. The actual concentrations of dyestuffs in these aqueous discharges are usually quite low; however, only a small amount of a

dyestuff is required to color water (Brown, 1987). The removal of the color is probably the single most perplexing problem in the treatment of textile wastewater (Beszedits et al., 1980). The degradability of textile wastewater is variable, usually poor and erratic, and the combination of many types of dyes often creates a gray, green or black colored wastewater (US EPA, 1974).

Dyes can be classified in many different ways. Two more common classifications are by dye structure and by method of dye application to the fiber. The dye structures include, but are not limited to azo, anthraquinone, benzodifuranone, polycyclic aromatic carbonyl, indigoid, polymethane, phthalocyanine, quinophthalone, sulfur, nitro or nitroso, and metal complexed. The methods of application include, but are not limited to acid, basic, direct, disperse, fiber-reactive (reactive), and vat. However, azo compounds are found in nearly every dye classification based on method of application (Anliker, 1979).

This section will cover the relevant literature that has been published on the chemistry, wastewater treatment of textile mill effluents, and on the removal of color from wastewater. Several types of dyes will be discussed, but the emphasis will be placed on the azo group of dyes, and specifically on reactive azo dyes.

Types of Azo Dyestuffs

The various types of azo dyes that will be briefly discussed are acid, basic, direct, disperse, fiber reactive, and vat. Each type will be briefly discussed; however, the focus will be on the fiber reactive azo dyes. A compilation of several sources was used to describe each type of dyestuff. These references are: Abrahart, 1977; Cooper, 1978; Jones, 1973; Lewis, 1989; Rys and Zollinger, 1972; Venkataraman, 1970; Venkataraman, 1977; and Waring and Hallas, 1990.

Acid Dyestuffs

Acid dyes are an anionic, water soluble dye used to primarily dye wool, but are also used to dye silk, nylon, acrylic, and leather. Acid dyes are seldomly used to dye cotton. Acid dyes are normally applied from a dye liquor containing sulfuric, formic, or acetic acid to increase the solubility of the dye. These dyestuffs contain one or more SO_3Na or SOH group. Though acid dyes have various structures, nearly all of the acid yellow, orange, red, brown, and black are azo dyes. The acid violets, blues, and greens are anthraquinone, and triphenylmethanes.

Basic Dyestuffs

Basic dyes are a cationic, water soluble dye used mainly for dyeing acrylic and wool. They contain ammonium, sulfonium, or oxonium salt groups. The affinity for the fabric is created by addition of acetic acid. Basic dyes come from the azo, anthraquinone, diphenylmethane, phenoxazine, and phenothiazine structures. These dyes are usually quite large, larger than the other types of dyes, and have a brilliant hue to them.

Direct Dyestuffs

Direct dyes are an anionic, water soluble dye used to color cotton. They are closely related to acid dyes, but have a high affinity for cellulose in the presence of sodium chloride and sodium sulfate. Nearly all direct dyes are azo, but there are a few dioxazines and phthalocyanines. The most numerous acid dyestuffs contain two azo linkages within the dye molecule (i.e. disazo dyestuffs).

Disperse Dyestuffs

Disperse dyes are a water insoluble dye used to color man-made fibers, cellulose acetate and polyester. Nearly

all are azo or anthroquinone. Disperse dyes will have one or more NH_2 or NR_1R_2 groups attached, where R_1 and R_2 are $\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{CH}_2\text{CN}$, or similar groups designed to balance the hydrophobic and hydrophilic character of the dye. They do not contain any sulfonic groups.

Fiber Reactive Dyestuffs

Fiber reactive dyes are an anionic water soluble dye. Reactive dyes were first developed in 1955. They combine ease of application with very high levels of wet fastness, and are superior to, but more costly than, the direct dyes used frequently for cotton dyeing. These dyes have an attached reactive group that is capable of forming a covalent bond between the carbon of the reactive group and an oxygen, nitrogen, or sulfur of the hydroxy, amino, or mercapto group of the fiber. The covalent bond that is formed is much stronger than the other types of bonds (ionic, hydrogen, and Van der Waals) that other dyes are capable of forming (Abrahart, 1977). The covalent bond increases the fastness of the dye. Fastness is the resistance of the dye to fading. Therefore, the dye is stable when exposed to light, perspiration, atmospheric gases, washing, alkalis, acids, and most other environmental

conditions. Thus, the fiber reactive dye is difficult to degrade.

Fiber reactive dyes are used in the dyeing of cotton and wool. All reactive dyes are sulfonated, i.e. they contain one or more SO_3Na or SOH_3 group. They are divided nearly equally between the azo and anthroquinone structures with the reactive group being chlorotriazines, vinylsulfones, and chloropyrimidines.

Wastewater containing reactive azo dyes have high salt concentrations associated with them. The salt helps to drive the dye from the water to the cotton during the dyeing process and is incorporated into the wastewater.

Concentrated aqueous, alkali dyebath solutions at an elevated temperature also force the dye to the cellulose (cotton) rather than the water. The fixation rate for reactive dyes varies from 50 to 90 percent. Other fixation rates reported are from 20 to 95 percent. They have an almost unrestricted shade range. Because of the wide range of colors available, the United States places more emphasis on the reactive dyes and less on the direct, sulfur, and vat dyes.

Vat Dyestuffs

Vat dyes are water insoluble dyes used in the dyeing of cotton. An affinity for cotton is obtained by mixing the dye with sodium hydroxide and dithionite, and subsequent oxidation to form the original dye on the fiber. These dyes are mainly anthraquinone.

Chemistry of Azo Dyestuffs

Azo dyes are a specific type of dyestuff based on the structure of the dye. For textile mill dyeing and finishing operations, the azo group of dyes account for approximately 60 to 70 percent of the total dyestuffs manufactured and used (Richardson, 1988). This amounts to more than 50,000 aromatic azo compounds (Anliker, 1979). Therefore, this type of dye is environmentally important.

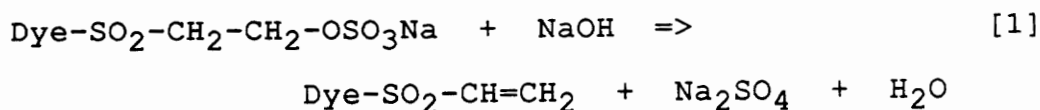
The azo type of dye is characterized as having at least one azo linkage, nitrogen to nitrogen double bond ($N = N$) in a large and usually complex chemical structure. Some azo dyes have more than one azo linkage. Dyes with two azo linkages are referred to as disazo, and dyes with three are referred to as trisazo. The nitrogens that are double bonded together are also attached to some type of aromatic compound or some type of substituent group. These

substituent groups (-OH, -SO₃, etc.) may also be attached to some type of aromatic compound. The type and number of substituent groups that are attached to the nitrogens and the aromatic compounds determine the color that is seen. Almost every color, red, yellow, blue, violet, brown, and black, can be produced using azo dyes. However, green is not typically derived from azo dyes.

Chemistry of Reactive Azo Dyestuffs

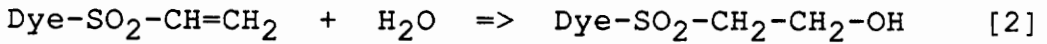
For the Remozal dyes, the vinyl sulfone group is the reactive group (Abraham, 1977). The active vinyl sulfone group of the reactive azo dye is generated by heating under alkaline conditions during the dyeing process (Beech, 1970; Flege, 1970).

The formation of the active vinyl sulfone group is shown below (Abraham, 1977; Flege, 1970):



The active vinyl sulfone group is the double bonded carbon of the product. During dyeing, the sulfone group partitions itself between the cellulose of the cotton and the water of

the dyebath (Flege, 1970). The reaction of the sulfone group with water yields a hydroxyethylene sulfone group attached to the dye molecule as shown below (Flege, 1970):



These dyes are deactivated and will not react with the cotton to form any covalent bonds. They may, however, diffuse into the fabric. These dyes are removed from the fabric by washing (Beech, 1970). Approximately 25 percent of the dye may be "washed out" after dyeing and discharged in the wastewater effluent. This wash water may also contain some non-bonded active reactive dye that may be toxic (Weber et al., 1990).

Wastewater Treatment of Azo Dyestuffs

This section will describe the treatability of textile wastewater. The treatment of textile effluents consists of one or more of the following treatment processes; biological, chemical, and physical. The transformation and transport of a compound may also be an important process in the degradation of that compound. A schematic showing the general degradation routes of azo dyes is shown in Figure 1.

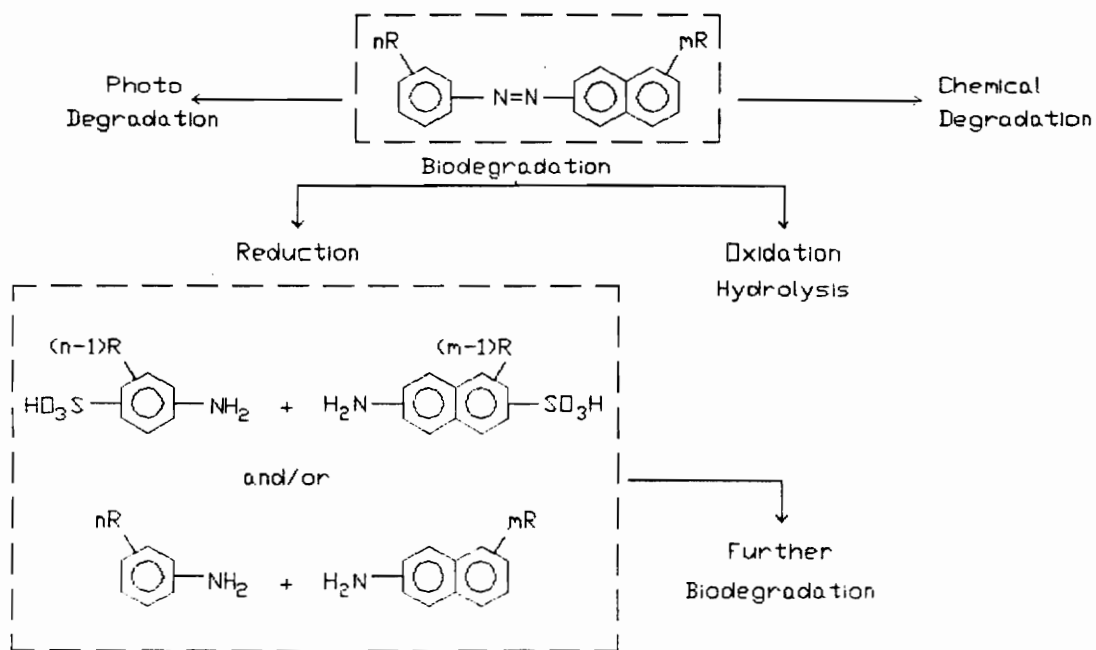


Figure 1. Schematic of the degradation of azo dyestuffs.
(Source Anliker, 1979)

Biological Treatment of Azo Dyestuffs

The biological treatment of azo dyes can be accomplished in either an aerobic or anaerobic environment.

Aerobic Biological Treatment of Azo Dyestuffs.

Aerobic biological treatment consists of degradation of a substance in the presence of oxygen. At a wastewater treatment plant this usually includes some sort of activated sludge system. From a study conducted on several types of dye wastewaters (acid, basic, direct, disperse, fiber reactive, and vat), aerobic biological treatment was found to be effective in the removal of biochemical oxygen demand (BOD) and total organic carbon (TOC), but was ineffective in color removal (Horning, 1977).

One of the problems with industrial wastewater, such as textile dye wastewater, is that it is usually nutrient deficient (Eckenfelder, 1989). The nutrients, nitrogen and phosphorus, can be provided by the mixing of the textile wastewater with municipal wastewater (Eckenfelder, 1989; Beszedits et al., 1980; Ghosh et al., 1978; Porter, 1970). This would indicate that the dyes will not significantly interfere with the operation of an aerobic biological

treatment system. However, the treatment of dye wastewater is complicated by the great variety of materials contained within the wastewater from dyeing operations (Weeter and Hodgson, 1977).

The biodegradation of some types of azo dyes have been studied using the activated sludge from typical wastewater treatment plants. It has been reported that up to 90 percent color removal in an activated sludge system can occur; however, the mechanism for this unusually high removal rate was not investigated (Horning, 1975). Typically azo dyes are not aerobically biodegradable. According to Pagga and Brown (1986), the biodegradation of the azo dyes cannot be expected to occur in an aerobic environment. But the degradation of azo dyes can be expected to occur in an anaerobic environment (Brown and Laboureur, 1983a). Dyes containing more than one azo linkage are even less likely to be degraded (Brown and Laboureur, 1983a) According to Porter (1973), acid dyes may or may not be removed by aerobic biological treatment. In general, it appears that dyestuffs cannot be aerobically biodegraded due to their rather large and complex chemical structure.

The aerobic degradation of dyestuffs may be enhanced, however. The addition of hydrogen peroxide has been successful for some cases, but not enough is known to say if

it will work in all cases (Alspaugh, 1973). More recently, peroxide has been more extensively used as an enhancer to improve the poor performance of wastewater treatment plants (Eul et al., 1990).

Another important characteristic of dyestuffs contributing to their stability during aerobic treatment is that the dyes are required to be very stable under normal environmental conditions (Pagga and Brown, 1986). These environmental conditions are atmospheric conditions, an aerobic environment. However, relatively few results are available from studies conducted to determine the removal and degradation of dyes in aerobic bacterial systems (Anliker and Moser, 1987).

A possible source of trouble in the aerobic treatment of dyes is foaming. In aerobic biological systems, foaming is common in the treatment of textile wastewater. The extent of foaming is related to the solids concentration, more foam is produced at a low solids concentration (Shriver and Daugue, 1978). Shriver and Daugue (1978) state that foaming should not interfere with the treatment process.

Anaerobic Biological Treatment of Azo Dyestuffs.

Anaerobic biological treatment consists of degradation of a substance in the absence of oxygen. The biodegradation

under anaerobic conditions has been studied more extensively. Under anaerobic conditions, azo dyes can be reduced microbially by living cells or by cellular extracts to their original aromatic derivatives (Richardson, 1988). The reductive cleavage of the azo bond, a nitrogen to nitrogen double bond, splits the azo dye molecule into its major intermediate amine components. These intermediates are usually some type of substituted naphthalene and aniline (Brown and Laboureur, 1983a). These resulting aromatic amines are highly toxic and possibly carcinogenic. Thus, the degradation products created from splitting the azo bridge are more noxious environmental compounds than the parent azo dye compound (Richardson, 1983).

Most of the azo dyes contain substituted amino naphthalenes with one or more -OH groups and usually one or more -SO₃ groups (Haag and Mill, 1987). These lipophilic aromatic amines are formed under anaerobic conditions, and thus, are not anaerobically biodegradable (Brown and Hamburger, 1987). However, they are, in general, aerobically biodegradable to some extent (Brown, 1987). A problem arises from the presence of the substituted groups. The sulphonated aromatic amines are not aerobically biodegradable and ortho-substitution interferes with the biodegradation of substituted anilines (Brown and Hamburger, 1987).

Since biological treatment alone does not appear to be able to degrade dyes, a more effective treatment scheme may be physical or chemical treatment or a combination of physicochemical with biological treatment (McKay, 1979; Dohanyos et al., 1978; Porter, 1970; Ghosh et al., 1978). However, some degree of biological treatment is almost always required to reduce biodegradable matter in the wastewater (Gardiner & Borne, 1978).

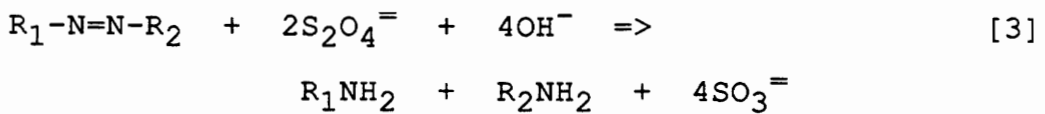
Chemical Treatment of Azo Dyestuffs

The chemical treatment processes used in the treatment of azo dyes involve the reduction and/or oxidation of the dye compound, and chemical precipitation.

Chemical Reduction of Azo Dyestuffs.

Reduction is the breaking apart of the dye molecule to produce colorless or near colorless products by the addition of reducing chemicals. This reduction of the dye molecule occurs in an anaerobic environment. These reactions can be microbially mediated, as discussed under the biological treatment section above, or chemically mediated. The end result is the same. When azo dye compounds are chemically reduced, the result is the regeneration of the aromatic

amines from which the dyes were originally manufactured (Venkataraman, 1977; Weber and Wolfe, 1987). For azo dyes, reduction is a feasible method to remove color from a wastewater (Gubser, 1979; Park and Shore, 1984). The reaction equation of hydrosulfite with azo dyes is given by (Wasmuth et al., 1965):



However, the actual identification of the reduction products is difficult to accomplish due to the variety, nature, and often poor stability of those products (Venkataraman, 1977). Types of chemical reducing agents that can be used to decolorize textile wastewater containing reactive dyestuffs include; hydrosulfite, bisulfite, sulfite, thiourea dioxide, and borohydride. As a general rule, hydrosulfites will decolorize any dye with a Chemical Index (CI) number of 40,999 or less and will most likely decolorize dyes with CI numbers of 42,000 to 44535 (Barton, 1962). Reducing agent dosages range from 135 ppm to 1800 ppm, depending on the type of reducing agent, the type and concentration of dyes, and the degree of treatment desired (Asahi, 1976). Also, some dyes are known to be oxidized after reduction, thus re-colorizing the wastewater (Baughman and Perenich, 1988a;

Gubser, 1979). Types of dyes that will re-colorize include anthraquinone, triarylmethane, azine, and some others (Barton, 1962). These chemical alterations can occur with the parent compound or with the degradation products, but require the presence of one or more reducing agents.

Chemical Oxidation of Azo Dyestuffs.

Dye molecules can be broken apart to yield colorless or near colorless products by the addition of oxidizing chemicals. These reactions can be microbially mediated, as discussed under the biological treatment section above, or can be chemically mediated. The end result is the same. When azo dye compounds are chemically oxidized, the result is the formation of aromatic nitroso- or nitro- compounds (Venkataraman, 1977; Weber and Wolfe, 1987). Types of oxidizing agents include; ozone, chlorine, hypochlorite, and hydrogen peroxide. Ozone was found to be effective in decolorizing reactive and basic dyes, but not for disperse dyes (Horning, 1977; Park and Shore, 1984). Park and Shore (1984) state that oxidation is a main method of decolorization for all classes of soluble dyes. Chlorine oxidizes dyes to colorless products with up to 99 percent color removal for reactive and direct dyes (Beszedits et al., 1980). However, neither calcium hypochlorite nor

hydrogen peroxide were effective in color removal for the reactive and direct dyes (Beszedits et al., 1980). Ozone is a much more powerful oxidant than chlorine, but is usually too expensive and inefficiently created to utilize.

These chemical alterations can occur with the parent compound or with the degradation products, but require the presence of one or more oxidizing agents. A powerful peracid, potassium persulfate in sulfuric acid, is required to accomplish total oxidation of aromatic amines to nitros (Rinehart, 1973). However, hydrogen peroxide is capable of oxidizing aromatic amines to amine oxides (RNOH) or to quinones (double bonded oxygen to a carbon in the aromatic ring (Rinehart, 1973)).

A disadvantage of using chlorine as an oxidant is that non-degradable chlorinated compounds (chlorinated aromatics) may be created (Gardiner and Borne, 1978). If biphenyl carriers are used in the dyeing process, polychlorobiphenyls (PCBs) are likely to be formed (Perkins et al., 1980). Chlorination of an azo dye wastewater had complete color removal, but created a number of chlorinated compounds (Gardiner and Borne, 1978). However, chlorination prior to biological treatment does not generally appear to have any adverse effects on performance (Perkins et al., 1980). Chlorine and peroxide have varying success depending on the dye being treated (Brower et al., 1986). Not all dyes

respond similarly to ozone (Beszedits, 1980; Day, 1973). Some may be permanently, or temporarily decolorized, where as others may not be affected by ozone at all. However, ozone is effective at decolorizing reactive dyes, with the attack point being the azo linkage (Beszedits, 1980).

Chemical Precipitation of Azo Dyestuffs.

Weeter and Hodgson (1977) reported that color is removed to a limited degree (approximately 5 to 30 percent) by the activated sludge process, but is significantly removed by coagulation. Several chemicals can be used to precipitate the dyes from the wastewater. These chemicals include alum, iron salts, lime, polyelectrolytes (cationic and anionic polymers), and quaternary ammonium polymers (Porter, 1977; McKay, 1979; Woldman, 1974).

According to McKay (1979), the most popular coagulant is lime. Lime combined with iron salts or alum may be more effective over a wider range of dyes than any one coagulant alone (Park and Shore, 1984). Depending on the type of dye in the wastewater the typical lime dosages range from 100 ppm to 1200 ppm; alum dosages range from 140 ppm to 2000 ppm; and iron salt dosages range from 500 ppm to 700 ppm (Brower et al., 1986; Horning, 1977; and Rodman, 1971). Other reported lime dosages are from 300 ppm to 600 ppm for

between 75 and 90 percent color removal (Beszedits et al., 1980). However, coagulation is not effective in the removal of soluble dyestuffs (Beszedits et al., 1980), and therefore is not effective for all types of dyes. To determine if coagulation is a feasible method for color removal of a specific textile wastewater, testing should be conducted on the specific textile wastewater streams and individual dyes (Brower et al., 1986).

Chemical precipitation of azo dyes is a valid treatment technique for some wastewaters, but creates large quantities of sludge. This sludge problem creates an additional expense that can be quite high for the industry or the treatment facility. Other disadvantages include the specialized testing that must be done to determine the most effective dose and the need for skilled technicians to assure that proper chemicals are added in the correct dosages (Jones, 1973; McKay, 1979).

Physical Treatment of Azo Dyestuffs

The major physical treatment processes for the removal of dyes are carbon adsorption and filtration.

Carbon Adsorption of Azo Dyestuffs.

Carbon adsorption of dyes is a feasible treatment technique for the removal of color. Powder Activated Carbon (PAC) is effective in the removal of reactive, acid, metal complexed, and basic dyes, but is not effective in the removal of vat or dispersed dyes, with typical dosages ranging from 200 ppm to 900 ppm (Beszedits et al., 1980; Horning, 1977). Activated carbon may remove some of the color in textile wastewater, but in general, is more efficient in removing soluble dyes than insoluble dyes (Day, 1973; Porter, 1977). The adsorption of dyes is dependent on the type of dye, dye chemistry and structure, type and structure of adsorbent, solution pH, and salinity (Dohanyos et al., 1978). The removability of dyes increases with increased dye size and number of azo groups attached. Also, the presence of hydroxide groups increase the removability, whereas the presence of sulfo groups will decrease the removability (Dohanyos et al., 1978).

Disadvantages of carbon adsorption are the high costs associated with the carbon, its reactivation, and replacing the 10 % carbon lost during regeneration (Gardiner and Borne, 1978). The treatment costs for activated carbon range from \$0.02 to \$0.05 per 1000 gallons with regeneration

costs ranging from \$0.01 to \$0.10 per pound of carbon (Adams, 1976).

Filtration of Azo Dyestuffs.

Filtration of textile wastewaters can be accomplished using sand filters or membrane filters such as reverse osmosis utilizing synthetic resins. Filtration of textile dye wastewater is not expected to be very effective in color removal because the large size of the dye molecules tend to clog the filters (Flege, 1970; McKay, 1979). Also, reverse osmosis concentrate must be disposed of by further treatment, such as evaporation or incineration (Park and Shore, 1984). Other disadvantages of the filtration methods include the high costs of the filters, and operation and maintenance of filtration systems (\$150 per million gallons (MG) treated for sand filtration; \$250 per MG for reverse osmosis) (Alspaugh, 1973; Gardiner and Borne, 1978).

Transformation of Azo Dyestuffs

Dyestuffs may also undergo degradation in the presence of water or sunlight. These transformation processes are hydrolysis and photolysis, and are not biologically, or

chemically mediated. However, they may occur naturally with enhancement by addition of chemicals.

Hydrolysis of Azo Dyestuffs.

Hydrolysis of azo dyes is the reaction of the azo dye with water, which frequently results in the formation of smaller hydrophilic molecules. The hydrolysis of azo dyes is not a significant transformation process for these compounds since the dyes are by nature either water-soluble or water-dispersible (Haag and Mill, 1987). The water-soluble dyes are already hydrolyzed and the water-dispersible dyes do not react with water.

Photolysis of Azo Dyestuffs.

Azo dyes can be subjected to either direct photolysis or indirect photolysis. Sunlight which causes the degradation of a compound by itself is one method of direct photolysis. Indirect photolysis is the degradation that is caused by the activation of sensitizers by direct sunlight. The photodegradation of azo dyes is accelerated in the presence of humic material (Haag and Mill, 1987). Both direct and indirect photolysis reactions are oxidation reactions.

The direct photolysis half-lives of most azo dyes are generally greater than 2000 hours (approximately 83 days) (Haag and Mill, 1987). This suggests that azo dyes are relatively stable in direct sunlight. This would be expected since the dyes are required to be stable under the conditions that the dyed fabric will exist in, sunlight. However, some dyes are more resistant to sunlight than others (Porter, 1973)

Indirect photolysis, as mentioned earlier, involves some type of sensitizer. These sensitizers cause oxidation reactions by singlet-oxygen or by oxy-radicals. In water systems these sensitizer are usually some type of humic material. The half-lives of most azo dyes by indirect photolysis are an order of magnitude lower than that of direct photolysis. Specific values cannot be given for the azo dye class as a whole because the half-lives are a function of the dissociation of the azo dyes (Haag and Mill, 1987). For this reason, the extent of ionization is the most important factor in determining indirect photolysis half-lives of azo dyes. This is due to the fact that the dissociated forms of azo dyes have a much shorter half-life than the protonated forms and the half-lives decrease with increasing pH. Therefore, The extent of dissociation is directly related to the pKa values of each azo dye. Most of the azo dyes have a pKa value greater than 9, with many

greater than 11 (Haag and Mill, 1987). Therefore, in the pH ranges found in the environment, generally pH 6 to 9, the dissociated form would be at a significantly less concentration than the protonated forms, thereby limiting the effectiveness of indirect photolysis.

If photolysis did occur, the azo linkage would be destroyed. This degradation would result in the formation of substituted aromatics similar to those from aerobic biodegradation and chemical oxidation. However, the formation of potentially carcinogenic aromatic amines is unlikely under these conditions since the aromatic amines that could be formed are highly susceptible to photolysis (Haag and Mill, 1987).

Transportation Processes Of Azo Dyestuffs

The transportation processes of azo dyes involve the tendency of the dye to move from one environmental compartment to another. These compartments are air, biological systems, water, and soil. Each pair will be briefly discussed as they pertain to azo dyes. As mentioned under the transformation section, transport mechanisms may be involved in the degradation of the dyes naturally or in wastewater treatment facilities.

Transportation Between Water/Air.

The movement of an azo compound between water and air is governed by the vapor pressure and water solubility of the azo dye. The vapor pressure of the azo dye determines how volatile that dye is. Volatilization is actually a type of partition coefficient between water and air, and is strongly dependent on the Henry's constant and the water solubility of the chemical.

Volatilization of an azo dye from water is possible if the dye is hydrophobic. An azo dye with a high Henry's constant will tend to volatilize. Whereas an azo dye with a low Henry's constant will tend to remain in solution. This azo dye would be termed non-volatile. Highly soluble dyes, such as the reactive azo dyes, will not volatilize. Insoluble dyes, such as disperse dyes, have solubilities ranging from 3×10^{-7} to 3×10^{-6} moles per liter (Baughman and Perenich, 1988b), and would be predicted to volatilize. However, according to Mackay and Leinonen (1975), the volatilization of the azo dyes is entirely vapor-phase controlled. Because the rate of volatilization is proportional to the Henry's constant for vapor-phase controlled compounds, the rate of volatilization of azo dyes will be very slow (Mackay and Leinonen, 1975). The Henry's constants for most azo dyes, even the water insoluble ones,

are relatively low (Mackay and Leinonen, 1975). Therefore, volatilization will not be an important transport pathway for the loss of azo dyes from aquatic systems.

Transportation Between Water/Soil and Water/Biota.

The movement of an azo compound between water and soil or biological systems is governed by the water-solubility, partition coefficient, and sorption characteristics of the dye. The solubility of azo dyes was discussed previously under the transportation between water/air section. The partition coefficient in this case refers to the octanol/water partition; i.e. the partitioning of material between a nonpolar and polar phase. This parameter is strongly influenced by the solubility of the compound. The final factor is sorption. Sorption refers to a compound's tendency to associate with inorganic or organic material.

It has been shown that the partition coefficient in octanol and water, represented by K_{ow} , is a useful indicator of the bioaccumulation tendency of organic dyestuffs (Anliker et al., 1981). The correspondence between octanol and lipid solubility is valid at even low solubilities, so measured solubilities of azo dyes in octanol are reasonably close to their solubility in lipids. Lipids are the main, if not the only, storage site for

lipophilic chemicals in fish (Anliker and Moser, 1987). Bioaccumulation would be predicted when K_{OW} values exceed 3. The range of K_{OW} for some azo dyes is from 3.4 to 4.2, which indicates the potential for greater than 1000-fold bioconcentration to occur (Baughman and Perenich, 1988b). However, the azo dyes in a study conducted by Anliker and Moser (1987) did not accumulate. Because of the large size of the chemical structure of azo dye compounds, the octanol/water partition coefficient may over predict dye bioconcentration (Baughman and Perenich, 1988b). The dye molecules are too large to bioconcentrate.

Many dyestuffs, by reason of their structure and required stability, may be expected to be removed by sorption (Brown, 1987). Azo dyes have been shown in laboratory experiments to sorb to the soft, granular, bacterial-rich material produced in the activated sludge process (Hitz et al., 1978). Therefore, some types of dyes would be expected to be removed by sorption onto the activated sludge of wastewater treatment plants. In a study of 20 dyes comprised of acid, direct and reactive dyes, Dohanyos et al (1978) found that dye sorption onto activated sludge followed the Freundlich Isotherm with K ranging from 0.31 to 0.80 and $1/n$ ranging from 0.65 to 0.88. Sorption of dyes onto inorganic solid is similar to sorption onto powder activated carbon adsorption in activated sludge (Dohanyos et

al., 1978). Therefore, inorganic solids in a river bed behave in a similar manner as the carbon, thus there could be some color removal by river sediment.

Sorption is inversely proportional to the water-solubility of the dye; high solubility will give a low sorption, and low solubility will give a high sorption. The sorption of various azo dyes is low for the highly water-soluble acid and reactive dyes, and high for the lower water-soluble direct, disperse, and basic dyes (Hitz et al., 1978).

Tincher (1988) conducted a study on the release of dyes from wastewater treatment sludge disposed of in a landfill. Known concentrations of dyes in solution were allowed to sorb onto the sludge. Sludges contaminated with azo dyestuffs did not release the dyestuff into leachate, when held under simulated landfill conditions (Tincher, 1988). The amine metabolites that are expected to occur as a result of anaerobic degradation were also not found in the leachate (Richardson, 1988). This suggests that the sorption of some types of azo dyes is very strong; therefore, dyes sorbed onto sludges of an activated sludge treatment system would be expected to remain on the sludge.

The azo dye compounds are characteristically nonvolatile, resistant to hydrolysis, and should not bioaccumulate in the lipid material of animals. Azo dyes,

however, do readily sorb onto sediments and other organic solids. However, this generality varies for different types of azo dyes; i.e. reactive azo dyes do hydrolyze, but do not sorb onto sediments.

Toxicity Of Azo Dyestuffs

It is not scientifically accurate to make the generalization that azo dye compounds are carcinogenic because compounds containing azo groups have been found to be carcinogenic in animal tests. A wide variety of azo compounds have been shown in long-term animal tests to be non-carcinogenic (Anliker, 1979).

Analysis of approximately 4500 different azo dyes, representing many different azo dye structures, was conducted by R. Anliker in 1979. This toxicity analysis was conducted using rats to determine an LD₅₀ value for each of the azo dyes studied. Of these 4500 different azo dyes studied, approximately 99 percent had an LD₅₀ greater than 250 mg/kg, with 83 percent having an LD₅₀ greater than 5000 mg/kg. This indicates that the azo dyes, as a group, are relatively non-toxic in doses that would be expected to occur in the environment. One percent of the azo dyes exhibited an LD₅₀ between 100 mg/kg and 250 mg/kg (Anliker, 1979).

From the above analysis, many types of azo dyes did not reveal any recognizable structure-toxicity relationship. However, the type and position of the substituent groups in the parent compound influenced the toxicity. In general, amino groups and cationic dissociation (basic dyes) increase toxicity (Walsh et al., 1980).

In general, acute toxic effects to aquatic species are found, if at all, at levels which are far in excess of anything that would be tolerated in terms of color in natural waterways (Brown, 1987). No long-term aquatic toxicity or bioconcentration in fish is expected from azo dyes because of the large size of the dye molecule (Baughman and Perenich, 1988b). There is unlikely to be a significant environmental risk caused by azo dye discharges at levels which are less than 1 percent of acute toxicity levels (Richardson, 1988). The majority of azo dyestuffs are not very toxic to fish. Of nearly 4500 dyes tested, 59 percent had an LC(50) greater than 100 mg/l, with only 2 percent having an LC(50) less than 1 mg/l. These more toxic azo dyestuffs include a number of different structural types, the largest number belonging to the basic dye class. One dye, CI Basic Violet 1, has an LC(50) of 0.05 mg/l (Richardson, 1988). Also, no inhibition is found at the 100 mg/l dose for bacterial respiration (Brown, 1987). Thus it is unlikely that the dyes will have an adverse

effect on water and soil bacteria at the very much lower levels that are likely to be present in rivers or soils.

However, an innocuous parent compound can be converted to a toxic intermediate. Such is the case of azo dyes (Howard et al., 1978). They degrade, as discussed previously, to form aromatic amines. These aromatic amines are either "proven or suspected to be carcinogenic" (Brown and Laboureur, 1983b). Problems could arise, however, by the formation of lipophilic aromatic amines. These aromatic amines are toxic (Anliker, 1979). Also, enzymatic cleavage of the azo group to form carcinogenic amines can occur in the "human gut" (Haag and Mill, 1987).

Highly toxic, readily degradable substances will cause less environmental damage than less toxic, more persistent chemicals (Howard et al., 1978). Since the azo dyes are reported as having a low toxicity, their degradation potential will determine the environmental effect they have. The toxicity and exposure to azo dyes is low, compared with that of other chemicals. Therefore, most dyes present no unreasonable environmental risk. However, caution should be used in assuming that dyestuffs belonging to a single broad class, such as the azo dyes, will necessarily have similar toxicological properties. The toxicity of each dye must be considered individually.

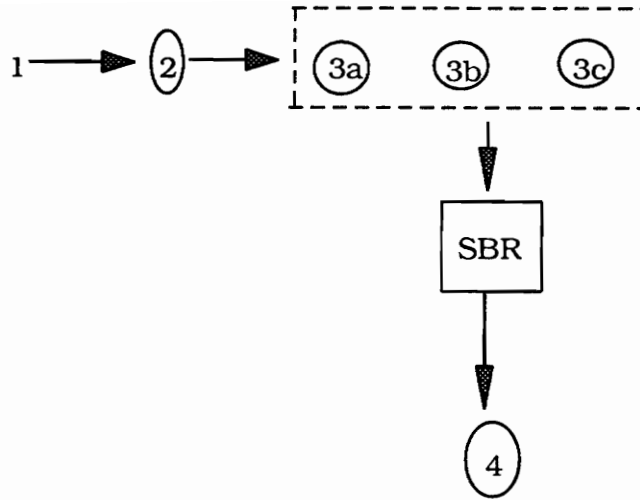
METHODS AND MATERIALS

The methods and materials used to perform the chemical pretreatment and biological treatment study on the Navy 106 textile dye wastewater stream are presented in this chapter, as well as the analytical procedures used to characterize the wastewater.

Chemical Pretreatment of Navy 106

Chemical reduction of the Navy 106 textile dye wastewater to remove the color was investigated as a pretreatment technique using three reducing agents; sodium hydrosulfite (also known as dithionite or hydro), thiourea dioxide (also known as amino iminomethane sulfinic acid), and sodium borohydride.

For each of the reducing agents, a portion of the textile wastewater was treated, mixed with untreated textile dye wastewater, mixed with municipal wastewater, and fed to the test reactor. Figure 2 shows the treatment process schematic of the Navy 106 textile dye wastewater. This schematic includes pretreatment and biological treatment.



- 1 -- Initial, untreated textile wastewater.
- 2 -- Addition of reducing agent to correct portion of textile wastewater.
- 3a -- Addition of other chemicals (i.e. sulfuric acid for pH adjustment, nutrients, lime, hydrogen peroxide), if conducted as part of the experiment.
- 3b -- Addition of correct un-pretreated portion of textile dye wastewater to pretreated portion of textile dye wastewater (if required).
- 3c -- Addition of municipal wastewater.
- SBR -- Batch biological treatment reactors.
- 4 -- Treated textile dye wastewater.

Figure 2. Schematic for the treatment of Navy 106.

Initially 17 percent of the textile dye wastewater was pretreated. The treated portion was increased from 17 percent to 33 percent to 67 percent to 100 percent of the textile dye wastewater in different trials. Only untreated textile dye wastewater mixed with municipal wastewater was treated in the control reactor. This control was used to quantify the impact of chemical pretreatment. As this study progressed, more textile dye wastewater was treated. The general procedure for the addition of the reducing agents (2 in Figure 2) was as follows:

1. Heat while stirring the portion of textile dye wastewater to be treated with the reducing agent to 65 degrees Celsius (C) (150 degrees Fahrenheit, F).
2. Turn off heat, but continue stirring, as reducing agent is added. Stop stirring after reducing agent is added and mixed (approximately 5 minutes for mixing).
3. Cool treated textile dye wastewater to 30 C (86 F) by placement of container in a cold water bath.

After the addition of the municipal wastewater, the temperature of the combined wastewater was approximately 25 C (77 F). The combined wastewater was then transferred to a sequencing batch reactor (SBR) for biological treatment.

Sodium Hydrosulfite

Sodium hydrosulfite (hydrosulfite or hydro) was obtained from Fisher Scientific in a powder form. Its chemical formula is $\text{Na}_2\text{S}_2\text{O}_4$ and its formula weight is 174.1 grams. The cost of hydro is \$0.62 per pound (Chemical Marketing Reporter, 1990).

The concentration of hydrosulfite mixed with the textile wastewater was determined using information from laboratory work conducted by Woodby (1990). For this study, a concentration of 225 ppm was chosen based on paired concentration and final color value data for hydrosulfite. Refer to Appendix E for the paired concentration and color value data. The hydrosulfite was added in the powder form and resulted in a visual change of color from purple-blue to yellow. The original purple-blue color did not return nor did the yellow change with time.

Other tests conducted in conjunction with hydro reduction were: pH adjustment, nutrient addition, nutrient addition and pH adjustment, lime addition, and chemical

oxidation. Each of these are discussed in the following sections.

Chemical Reduction with pH Adjustment.

After reduction with hydrosulfite, the pH was adjusted (point 3 in Figure 2). The total textile wastewater portion, treated and untreated, was adjusted to a pH of 7.5 using 2 Normal (N) sulfuric acid (H_2SO_4). Approximately 5 to 10 ml of the sulfuric acid was required to obtain a pH of 7.5. After pH adjustment, the municipal wastewater was added and the combined mixture was fed to the test SBR.

Chemical Reduction with Nutrient Addition.

After reduction with hydrosulfite, nutrients were added (point 3 in Figure 2). These nutrients included; phosphate, ammonium, potassium, magnesium, calcium, and ferric salt solutions. These salt solutions are the reagents added in the biochemical oxygen demand test and were prepared following the procedures outlined in Standard Methods. Approximately 1 ml of each salt solution per liter of reactor feed solution was added. After the nutrient addition, municipal wastewater was added and the combined mixture was fed to the test SBR.

Chemical Reduction with Nutrient Addition and pH Adjustment.

After reduction with hydrosulfite, nutrients were added with pH adjustment (point 3 in Figure 2). The same nutrients in the same quantity as described in the previous section were added. The pH adjustment was also conducted in the same manner as previously discussed. After both of these steps were accomplished, municipal wastewater was added and the combined mixture was fed to the test SBR.

Chemical Reduction with Lime Addition.

After reduction with hydrosulfite, lime (Ca(OH)_2) was added (point 3 in Figure 2). Lime is sometimes used for the removal of heavy metals. Since some reactive azo dyes are metal complexed, 100 ppm of lime was added. Municipal wastewater was then added and the combined mixture was fed to the test SBR.

Chemical Reduction Followed by Chemical Oxidation.

After reduction with hydrosulfite, hydrogen peroxide was added to only the treated portion of the textile dye

wastewater (point 3 in Figure 2). The concentration of hydrogen peroxide added was 150 ppm. This concentration was based on the volume of a 3 percent hydrogen peroxide solution required to raise the reduction/oxidation potential from -600 millivolts (reduced state after addition of hydrosulfite) to +350 millivolts (oxidized state) in the treatment of 17 percent of the textile dye wastewater. As the portion of treated textile dye wastewater increased, the concentration of peroxide was held constant. The untreated portion of textile dye wastewater was then added to the treated portion. Municipal wastewater was then added and the combined mixture was transferred to the test SBR.

Thiourea Dioxide

Thiourea dioxide was obtained from Eastman Kodak Company in powder form. Its chemical formula is $\text{NH}_2\text{CNHSO}_2\text{H}$ and its formula weight is 108.12 grams. The cost of thiourea dioxide is \$2.00 per pound (Chemical Marketing Reporter, 1990).

The concentration of thiourea dioxide mixed with the textile dye wastewater was determined using information from work conducted by Woodby (1990). For this study, a concentration of 225 ppm was chosen based on paired concentration and final color value data for thiourea

dioxide. Refer to Appendix E for the paired concentration and color value data. The thiourea dioxide was added in powder form and resulted in a visual change of color from purple-blue to yellow. The original purple-blue color did not return nor did the yellow change with time.

Sodium Borohydride

Sodium borohydride was obtained from Morton in liquid form, 12% sodium borohydride in a 40% sodium hydroxide solution. The chemical formula is NaBH_4 and it has a formula weight of 34.81 grams. The cost of borohydride is \$18.30 per pound for 3000 gallons of a 12% liquid (Chemical Marketing Reporter, 1990).

The concentration of sodium borohydride to be mixed with the textile dye wastewater was determined from work conducted by Woodby (1990). For this study, a concentration of 150 ppm was chosen based on paired concentration and final color value data for borohydride. Refer to Appendix E for the paired concentration and color value data. The sodium borohydride was added in the liquid form and resulted in a visual color change from purple-blue to a near clear solution. The original purple-blue color did not return nor did the near clear solution change with time.

Biological Treatment of Navy 106

The biological treatment of the Navy 106 textile dye wastewater stream was conducted to determine the biodegradability of the treated wastewater after the chemical pretreatment steps were performed. Biological treatment was selected since the effluent from the Mill is discharged to a municipal treatment plant that utilizes an extended aeration treatment process.

For a laboratory-scale biological treatment process, the sequencing batch reactor (SBR) was chosen. The SBR was chosen because the repetitions of experiments with the SBR comes close to simulating a continuous flow system, without the large space requirements (Irvine and Busch, 1979). The SBR is called a fill and draw activated sludge system (Arora et al., 1985).

The SBR has five basic sequential, repeating modes of operation; fill, react, settle, draw, and idle (Irvine and Busch, 1979; Irvine et al., 1979; Arora et al., 1985). During the fill period, the SBR is filled with the wastewater to be biologically treated. During the react period, the SBR is aerated to provide oxygen to the biomass in the reactor and to provide mixing of the wastewater to ensure efficient contact occurs between the biomass and the

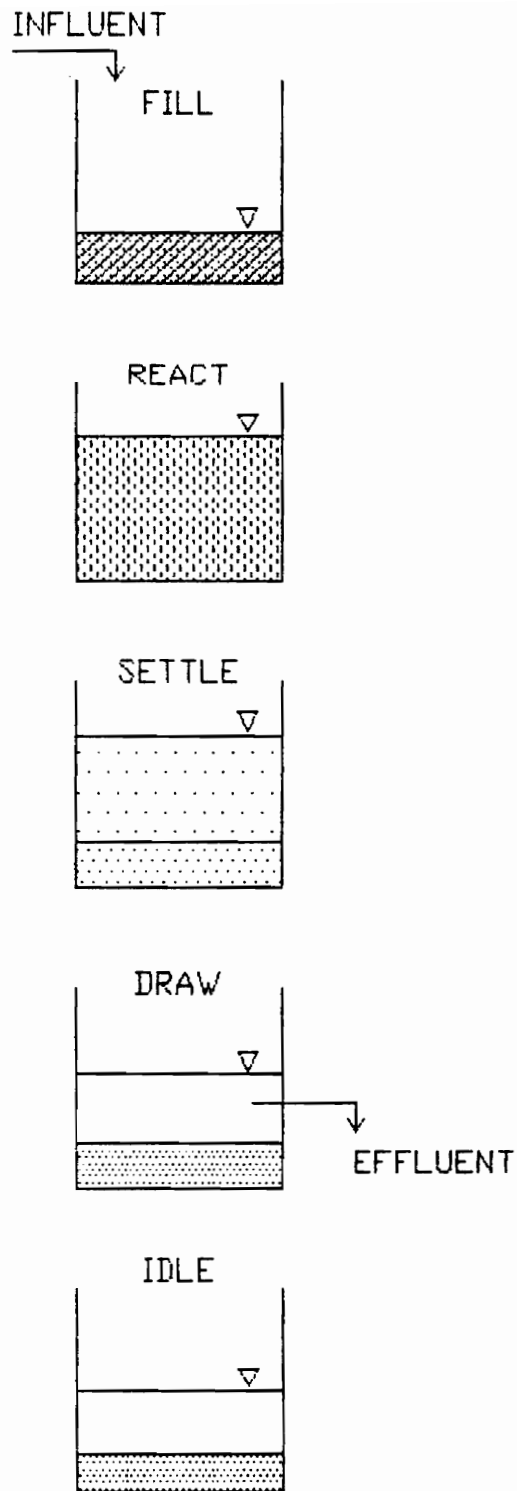


Figure 3. The five operating periods of the SBR. (Source: Irvine and Busch, 1979).

wastewater. During the settle period, no aeration or mixing occurs to allow the biomass to settle to the bottom the SBR, providing a solid/liquid separation, thus creating a treated supernatant to be drawn off. The draw period is the discharge of the treated effluent from the SBR. This is done in such a way as to not disturb the settled biomass. The idle period is the time between the draw period of one SBR run and the fill period of the next SBR run. A schematic showing each period is shown in Figure 3.

Two SBRs were used in this study and were designated reactors A and B. Reactor A was the test reactor and reactor B was the control reactor. Each of the reactors had a total volume of 10 liters, with 8 liters being used during testing. The reactors were initially seeded with mixed liquor taken from the extended aeration-activated sludge basin of the POTW which receives discharge from the Mill. The Navy 106 textile dye wastewater was transferred to the reactors, after being supplemented with municipal wastewater. The municipal wastewater was taken from the Blacksburg-Christiansburg-VPI Sewage Authority.

For this study, the feed was delivered to the reactors by carefully and slowly pouring the wastewater into the reactors to minimize aeration. During the react period, the reactors were aerated, through two 6 inch air diffuser stones per reactor, with lab supplied air. The air was

filtered to remove solid impurities and was regulated at a constant pressure of 20 psi. After the settle period, the supernatant was drawn off by gravity. To maintain a desired mixed liquor suspended solids (MLSS) of between 2000 mg/L and 2500 mg/L within each reactor, mixed liquor was periodically wasted. The amount wasted was calculated using a mass balance on the MLSS.

A daily feed of 4 liters of wastewater was used. This 4 liters consisted of 3 liters of Navy 106 textile dye wastewater and 1 liter of primary clarified municipal wastewater, which were combined before being transferred to reactors. These proportions correspond to those at the actual POTW.

The time period of each SBR phase were as follows. The fill period was 5 minutes, approximately 1 liter per minute. The react period was approximately 21 hours. The settle period was 1 hour (60 minutes). The draw period was 0.5 hours (30 minutes), approximately 8 liters per hour (0.14 liters per minute). The idle period was approximately 1 hour (60 minutes). The total time of each run was 24 hours. These times were constant for each test performed.

Analytical Procedures

The wastewater parameters analyzed included: chemical oxygen demand (COD), total organic carbon (TOC), five day biochemical oxygen demand (BOD), total suspended solids (TSS), color at the treated pH and color at a pH of 7.6 (in American Dye Manufacturers Instituted units, ADMI), pH, and reduction/oxidation potential (redox). During the biological treatment of the textile wastewater, mixed liquor suspended solids (MLSS) and temperature were measured in addition to the parameters previously mentioned. One adsorption test was performed. The textile wastewater was analyzed once for heavy metals (chromium, cobalt, and copper) before and after chemical pretreatment and after biological treatment by Grender (1990). Nutrients (Total Kjeldahl Nitrogen, TKN and Total Phosphorus, TP) were measured only once in the biological effluent. Since municipal wastewater was being mixed with the textile wastewater prior to biological treatment, it was assumed to supply the nutrient (nitrogen and phosphorus) requirements.

The conventional tests for color measurement are not applicable to textile wastewaters. The ADMI method gives results that are independent of hue; i.e., water containing blue, red or yellow and of equal visual appearance regarding depth and intensity will have the same ADMI color value

(Clapham, 1973; ADMI, 1973; Balmforth and Rice, 1976). The normal APHA method of color measurement gives misleading results for waters not colored reddish-yellow (Clapham, 1973; ADMI, 1973). For highly colored textile wastewaters, it is more important for the color measurement to be related to the "visual perception" and not the concentration of the color bodies, since the identity of the colored bodies in this type of wastewater is usually unknown and difficult to determine (ADMI, 1973).

Wastewater testing procedures were performed in accordance with the procedures outlined in Standard Methods for the Examination of Water and Wastewater (1990). Specifics of and exceptions to the standard procedure are provided below:

1. The COD was determined using the closed reflux, titrimetric method, section 508 B of Standard Methods. A sample size of 5 ml was placed into 20 mm x 150 mm culture tubes. The digestion period was 2 hours
2. The TOC was analyzed using a Dohrmann DC-80 total organic carbon analyzer. Samples were allowed to attain room temperature, if they had been stored in a refrigerator. Samples were acidified and

diffused to remove inorganic carbon and injected into the TOC Analyzer in a 20 ug/l syringe.

3. Biochemical Oxygen Demand was measured in accordance with section 507 of Standard Methods. The BOD test was conducted in a constant temperature room (temperature 20 C) and in the dark. Individual BOD samples were seeded with settled mixed liquor taken from the SBR. Seeded blanks were also used.

4. The color was measured using the ADMI Tristimulus Filter (Tentative) Method, section 204 D of Standard Methods. Specifically the alternate method (section 204 D 4) utilizing a spectrophotometer was used. A Bausch and Lomb Spectronic 20 spectrophotometer with a 1 cm path length was used to measure transmittance of the samples. The selected wavelengths used in measuring the color were 590 nanometers (nm) for T1, 540 nm for T2, and 438 nm for T3. Distilled water blanks were used for 100 percent transmittance. For the spectrophotometer used, a calibration curve was developed using a range of known platinum-cobalt color standards, yielding a

calibration factor was 1343. The calibration procedure and curve as well as a detailed procedure for the ADMI method of color measurement is outlined in Appendix A. The reader is referred to Appendix B for a brief explanation of color theory and a chromaticity graph.

5. Total suspended solids were measured in accordance to section 209 C of Standard Methods. Samples were taken before and after chemical pretreatment and after biological treatment. A measured amount of sample was pipetted onto a 7 cm glass-fiber filter and dried at 105 C for 1 hour. Samples were placed in a desiccator and allowed to cool to room temperature before weighing.
6. Mixed liquor suspended solids were measured similarly to TSS, except samples were taken from the SBR during the react phase.
7. The pH was measured using a Corning pH Meter 220. The pH meter was calibrated with pH 7 and pH 10 buffers before each sample was measured.

8. The redox potential was measured using a standard redox electrode attached to the Corning pH meter 220. The meter was calibrated following the procedure outlined in Thermochemical redox equilibria of ZoBell's solution (Nordstrom, 1977). The following temperature dependent potential equation was used to calibrate the meter:

$$E(\text{volts}) = 0.43028 - [2.5157 \times 10^{-3}(t - 25)] - [3.7979 \times 10^{-6}(t - 25)^2] \quad [4]$$

After the temperature of the wastewater was determined and the instrument calibrated for that temperature, the redox potential of the wastewater could be read in millivolts.

9. Total Phosphorus (TP) was measured in accordance with section 424 F of Standard Methods. The ascorbic acid method had to be corrected as outlined in the procedure due to the color of the treated effluent. A Beckman DU-6 spectrophotometer was used to measure the adsorbance at a wavelength of 880 nm.

10. Total Kjeldahl Nitrogen (TKN) was measured in accordance with section 420 A of Standard Methods. A sample size of 100 mL was used in this test. Following distillation, TKN was determined titrimetrically.
11. A combination heating/magnetic stirring plate was used to heat and/or stir samples.
12. A Mettler H54 scale was used to weigh samples.
13. An adsorption test was performed using sludge taken from the test SBR. A measured amount of waste sludge was placed into 250 mL beakers filled with 200 mL of untreated Navy 106 wastewater to obtain an MLSS concentration of approximately 2000 mg/L. Color was measured before the sludge was placed in the beakers. Color was also measured after mixing the sludge and wastewater together for 45 minutes.

RESULTS AND DISCUSSION

The results of chemically pretreating textile dye wastewater from the Mill and the biological treatment of the pretreated wastewater are presented in this chapter. This chapter is organized in the chronological order that each pretreatment/biological treatment test were performed. Also, the results of a BOD-Toxicity test on the pretreated textile wastewater are presented. Although completed early in the research, the BOD-Toxicity test results are presented near the end of this section, after the pretreatment-biological treatment alternatives are discussed. Additional wastewater characteristic test results are discussed after the pretreatment-biological treatment alternatives. The first section covers the acclimation of the SBRs to the Navy 106 textile dye wastewater from the Mill. The last section provides a limited cost comparison.

Acclimation of SBR A and B

Before any testing of chemical pretreatment methods for the removal of color, two SBRs (A and B) were acclimated to the Navy 106 textile dye wastewater from the Mill. Each reactor contained mixed liquor from the aeration basins of

the POTW which receives wastewater from the Mill. This biomass was acclimated to the Navy 106 dye wastewater over a period of four weeks. During this time frame, the amount of Navy 106 dye wastewater was increased from 12.5 percent of the combined influent to 75 percent. The remaining 25 percent of combined influent consisted of primary clarified wastewater from the Blacksburg-Christiansburg-VPI Wastewater Treatment Facility.

The performance of the reactors during the fifth week is shown Table 1. Figure 4 shows the relationship between each reactor's performance and color removal for each treatment step (note that since no pretreatment was conducted during acclimation, the pretreatment step data were the same as the initial step data). Figure 5 shows this relationship for COD, Figure 6 for TOC, and Figure 7 for BOD for each treatment process step. Table 2 shows each reactor's effluent data. Each reactor's performance was similar regarding effluent color (SBR A, 1440 ADMI; SBR B, 1430 ADMI), effluent COD (SBR A, 300 mg/L; SBR B, 315 mg/L), effluent TOC (SBR A, 169 mg/L; SBR B, 172 mg/L), and effluent BOD (SBR A, 109 mg/L; SBR B, 113 mg/L). These correspond to total color removals of 52 percent (SBR A and SBR B), total COD removals of 63 percent (SBR A) and 61 percent (SBR B), total TOC removals of 50 percent (SBR A)

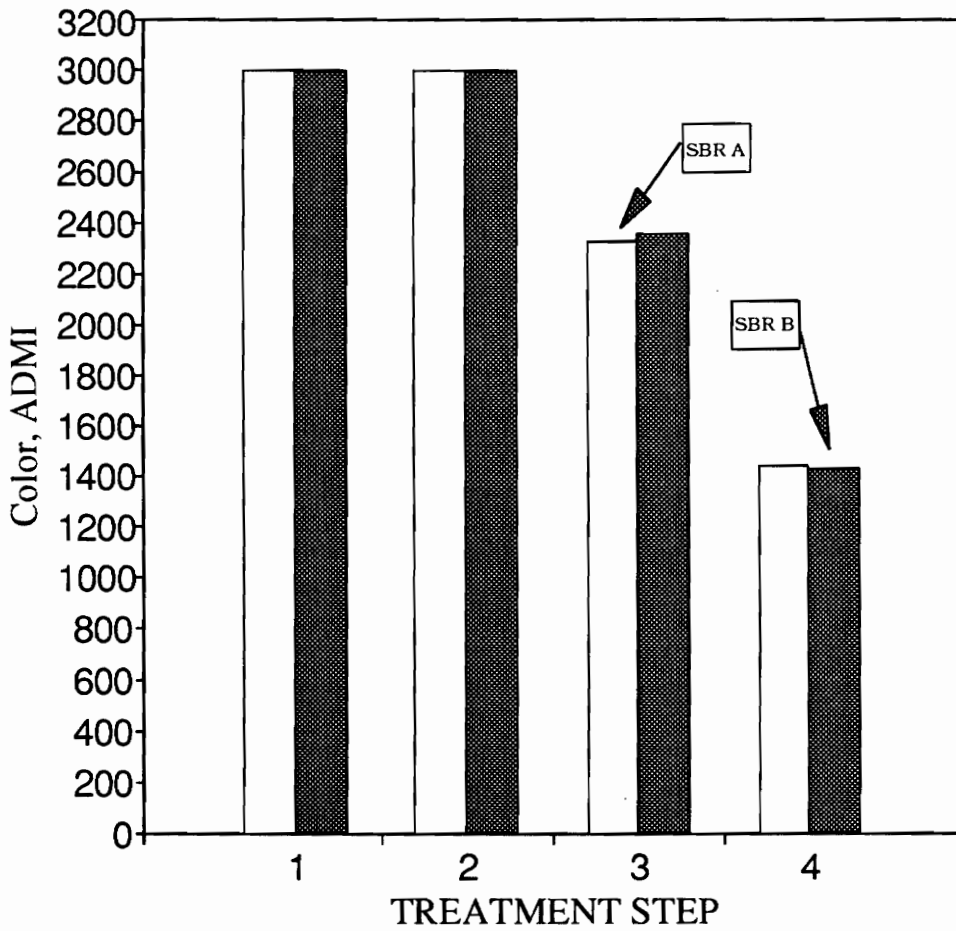
Table 1. Wastewater characteristics during acclimation of SBR A and B for each treatment process step.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER OXIDATION AND MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
SBR A				
COLOR (1)	3000	3000	2325	1440
COD mg/L	850	850	809	300
TOC mg/L	335	335	302	169
BOD mg/L	192	192	173	109
TSS mg/L	15	15	25	73
COLOR (2)	3200	3200	2450	1565
pH	10.3	10.3	9.7	9.1
REDOX mV	-----	-----	-----	-----
SBR B				
COLOR (1)	3000	3000	2350	1430
COD mg/L	853	853	815	315
TOC mg/L	340	340	310	172
BOD mg/L	201	201	181	113
TSS mg/L	10	10	23	68
COLOR (2)	3200	3200	2500	1555
pH	10.2	10.2	9.8	9
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

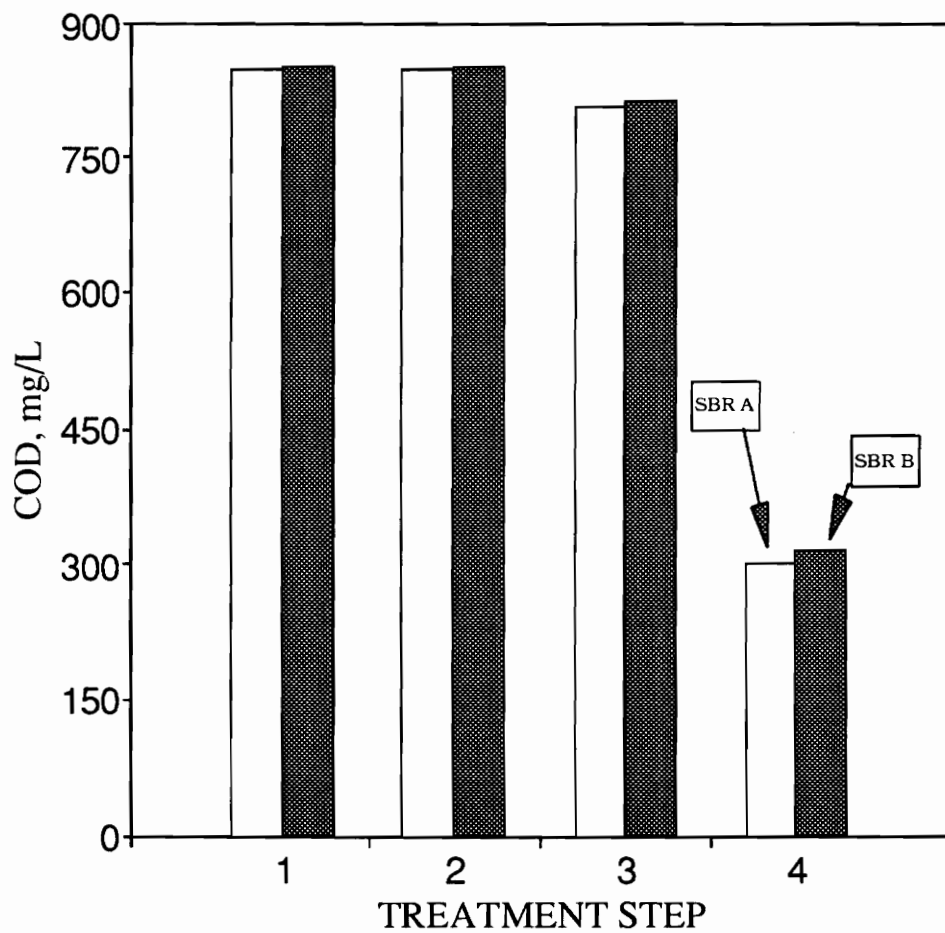
2 = ADMI color at normal sample pH.

WW = WASTEWATER



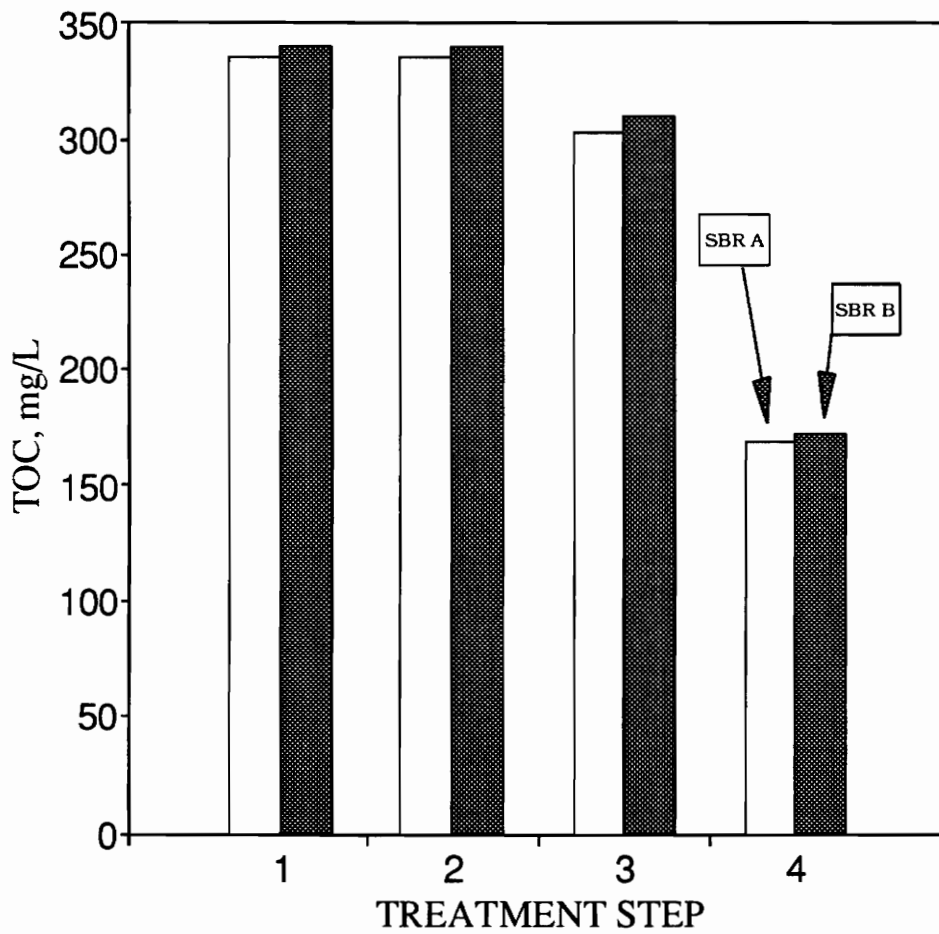
- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 4. Relationship between reactors for color removal during acclimation of SBR A and B.



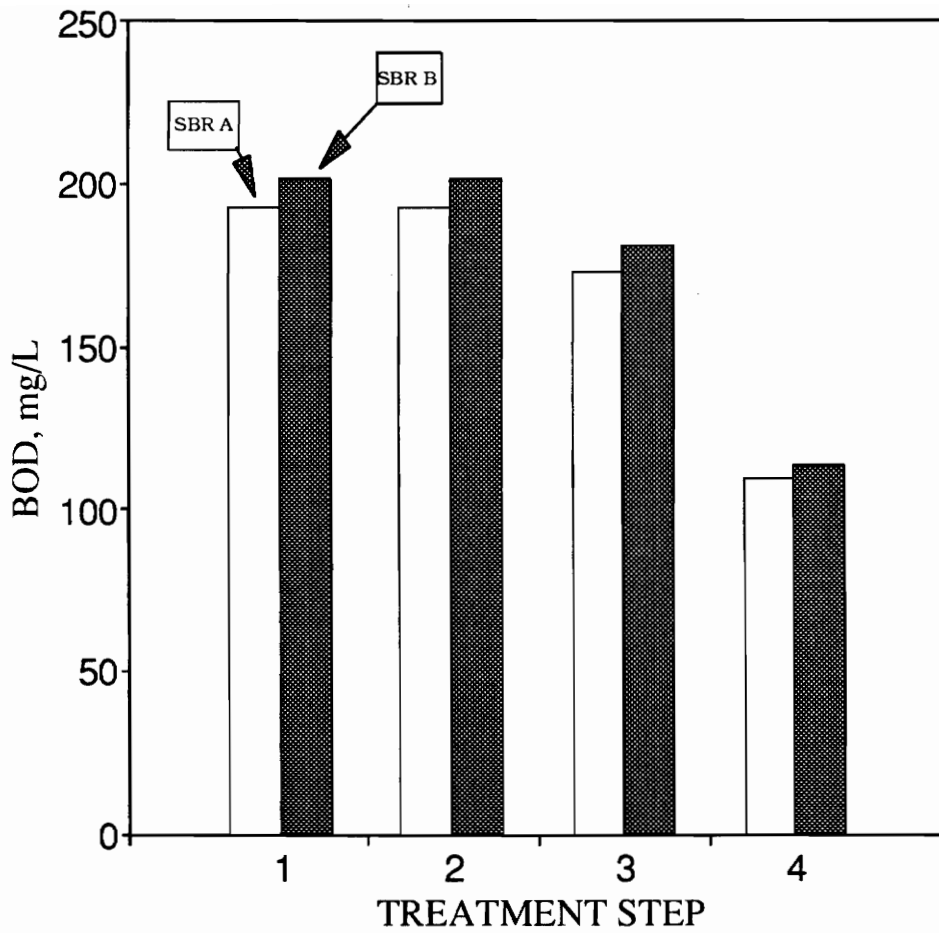
- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 5. Relationship between reactors for COD removal during acclimation of SBR A and B.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 6. Relationship between reactors for TOC removal during acclimation of SBR A and B.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 7. Relationship between reactors for BOD removal during acclimation of SBR A and B.

Table 2. Effluent data during acclimation of SBR A and B.

SBR	PARAMETER	EFFLUENT		REMOVALS		MLSS mg/L
		MEAN	RANGE	TOTAL	BIOL	
SBR A	COLOR (1)	1440	1405 - 1470	52	38	2250
SBR B		1430	1405 - 1450	52	39	2150
SBR A	COD mg/L	300	285 - 320	65	63	2250
SBR B		315	310 - 350	63	61	2150
SBR A	TOC mg/L	169	157 - 173	50	44	2250
SBR B		172	155 - 175	49	45	2150
SBR A	BOD mg/L	109	95 - 117	43	37	2250
SBR B		113	100 - 120	44	38	2150

1 = ADMI color at pH 7.6.

and 49 percent (SBR B), and total BOD removals of 43 percent (SBR A) and 44 percent (SBR B). However, there was an increase in TSS. The influent TSS was small, ranging from 10 to 25 mg/L. For the one hour settling period chosen for this study, effluent TSS ranged from 65 to 85 mg/L. A longer settling period may give lower effluent TSS values. Since the reactors were performing similarly, testing of the pretreatment methods was initiated. The test SBR was designated SBR A and the control SBR was designated SBR B.

Preliminary Tests

In this section, the preliminary tests that were conducted will be discussed. These preliminary tests were performed with hydrosulfite, thiourea, borohydride, hydrosulfite with pH adjustment, hydrosulfite with nutrient addition, hydrosulfite with pH adjustment and nutrient addition, hydrosulfite with lime addition, and hydrogen peroxide alone. All but one of the tests were successful in removing the color from the textile wastewater; however, only one was successfully biologically treated. None of these tests were successful in both. A successful test must satisfy:

- (1) Reduction in the level of color.
- (2) Reduction in the biodegradable matter.

Table 3 shows the SBR influent and effluent values for color and TOC of the tests that failed. The reader is referred to Appendix C for more complete data on these tests. A typical control SBR influent and effluent values are also given in Table 3. From these data, there was little change in the color or TOC during biological treatment in the SBR for all of the preliminary tests except for pretreatment with peroxide alone. The removals of color, COD, TOC, and BOD for all but peroxide pretreatment were less than 11 percent (less than 6 percent in most cases for TOC and BOD). However, biological removals for the corresponding controls were greater than 30 percent. Most of the color reduction was achieved by the reducing agents. However, the controls (biological treatment only, no chemical pretreatment) exhibited greater than 45 percent total color removal.

These results show that reduction as a pretreatment step of the Mill's textile wastewater removed some color (approximately 30 percent removal for 17 percent pretreatment of the textile wastewater), but also created a non-aerobically biodegradable wastewater. Thus, reduction is a feasible method for color removal as stated by Gubser (1979), Barton (1962), and Park and Shore (1984). However, the reduced wastewater contained compounds that were not biodegradable or contained compounds (unreacted reducing agent or reduction by-products) that were inhibitory or

Table 3. SBR influent and effluent color and TOC values for the preliminary tests.

Pretreatment Trial	Percent Textile Pretreated	Color		TOC	
		Inf	Eff	Inf	Eff
		ADMI		mg/L	
Control	0	1570	1045	247	168
Hydrosulfite	100	190	185	204	200
	17	1435	1365	269	265
Thiourea	17	1020	955	210	208
Borohydride	17	850	815	111	110
Hydrosulfite with pH adj.	17	1910	1850	266	260
Hydrosulfite with nutrient addition	17	1000	960	128	122
Hydrosulfite with pH adj and nutrient addition	17	1025	1000	126	122
Hydrosulfite with lime addition	17	1890	1835	277	270
Peroxide	100	2090	1720	174	120

Inf = SBR influent

Eff = SBR effluent

toxic to the aerobic bacteria. Recall that the splitting of an azo compound results in the formation of aromatic amines (naphthalene and aniline) that are toxic (Brown and Laboureur, 1983a; Richardson, 1983). These conditions resulted in little or no degradation of the biodegradable matter in the wastewater.

Different reducing agents (with different chemical properties), pH adjustment, nutrient addition, a combination of pH adjustment and nutrient addition, or lime addition did not overcome these intolerances to create a wastewater susceptible to aerobic biodegradation. Therefore, these pretreatment techniques were not feasible for treatment of the wastewater.

Pretreatment with hydrogen peroxide alone did not enhance the biological degradation of the textile wastewater. Peroxide addition to enhance biodegradation has been reported by Alspaugh (1973). Addition of 150 ppm of hydrogen peroxide achieved biological COD removal of 28 percent, TOC removal of 31 percent, and BOD removal of 24 percent and achieved 20 percent biological color removal. However, the control achieved biological color removal of 26 percent, COD removal of 47 percent, TOC removal of 48 percent, and BOD removal of 53 percent. No color was removed in the pretreatment step. The performance of the test reactor was below that of the control. These results

show that the addition of hydrogen peroxide did not enhance the removal of color, COD, TOC, or BOD. Therefore, pretreatment with hydrogen peroxide alone at a concentration of 150 ppm was not a feasible method for color removal. This supports work conducted by Beszedits et al (1980), where peroxide was found to be ineffective in the removal of color from a wastewater containing reactive dyes.

Reduction with Sodium Hydrosulfite and Oxidation with Hydrogen Peroxide

The final pretreatment process studied was reduction followed by oxidation. It was believed that the oxidation of the untreated reducing agent and reduction by-products would create a wastewater more conducive to aerobic biodegradation.

17% Textile Dye Wastewater Pretreated

Due to the failure of the test reactor when subjected to all of the previous tests, pretreatment of 17 percent of the textile dye wastewater (12.5 percent of the combined wastewater stream) was conducted using a combination of reduction with hydrosulfite and oxidation with hydrogen peroxide (peroxide). It was believed that the pretreated

textile dye wastewater contained biologically noxious compounds which could be oxidized to more aerobically biodegradable by-products to create an environment better suited for aerobic biodegradation. Therefore, the pretreated textile wastewater with reduction followed by oxidation and the municipal wastewater were fed to the test reactor for biological treatment. Within one day the test reactor performance was better than the control reactor performance. This test was conducted over 7 days to determine if the performance would improve. However, the performance did not improve.

The wastewater characteristics for each process step that were measured during this test are shown in Table 4. The performance of the control reactor during this test is also shown in Table 4. Table 5 shows the effluent data (means and ranges) along with the biological and total percent removals for this test and the control. From these data, there was a reduction in color to 815 ADMI (60 percent total removal, 42 percent biological removal), and the COD, TOC, and BOD were also reduced to below control values. They were reduced to 150 mg/L COD (74 percent total removal, 70 percent biological removal), 82 mg/L TOC (48 percent total removal, 45 percent biological removal), and 53 mg/L BOD (52 percent total removal, 46 percent biological

Table 4. Wastewater characteristics for 17 % pretreatment of the textile dye wastewater.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER OXIDATION AND MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2050	1825	1400	815
COD mg/L	585	586	500	150
TOC mg/L	158	162	148	82
BOD mg/L	111	-----	98	53
TSS mg/L	23	-----	25	85
COLOR (2)	2170	1935	1480	865
pH	10.6	9.7	9.5	9
REDOX mV	+ 57	- 587	(+ 348)	+ 78
CONTROL REACTOR				
COLOR (1)	2050	2050	1570	1060
COD mg/L	575	575	494	205
TOC mg/L	158	158	150	104
BOD mg/L	115	115	100	65
TSS mg/L	25	25	30	90
COLOR (2)	2175	2175	1665	1125
pH	10.6	10.6	9.8	9.3
REDOX mV	+ 60	+ 60	+ 55	+ 70

1 = ADMI color at pH 7.6.
 2 = ADMI color at normal sample pH.
 () = REDOX potential after oxidation
 WW = wastewater

Table 5. Effluent data for 17 % pretreatment of the textile dye wastewater.

SBR	PARAMETER	EFFLUENT		REMOVALS		MLSS mg/L
		MEAN	RANGE	TOTAL	BIOL	
TEST	COLOR (1)	815	800 - 845	60	42	2100
CONTROL		1060	1020 - 1120	48	32	2200
TEST	COD mg/L	150	140 - 155	74	70	2100
CONTROL		205	200 - 210	64	59	2200
TEST	TOC mg/L	82	80 - 89	48	45	2100
CONTROL		105	100 - 115	34	31	2200
TEST	BOD mg/L	53	46 - 58	52	46	2100
CONTROL		65	54 - 78	43	35	2200

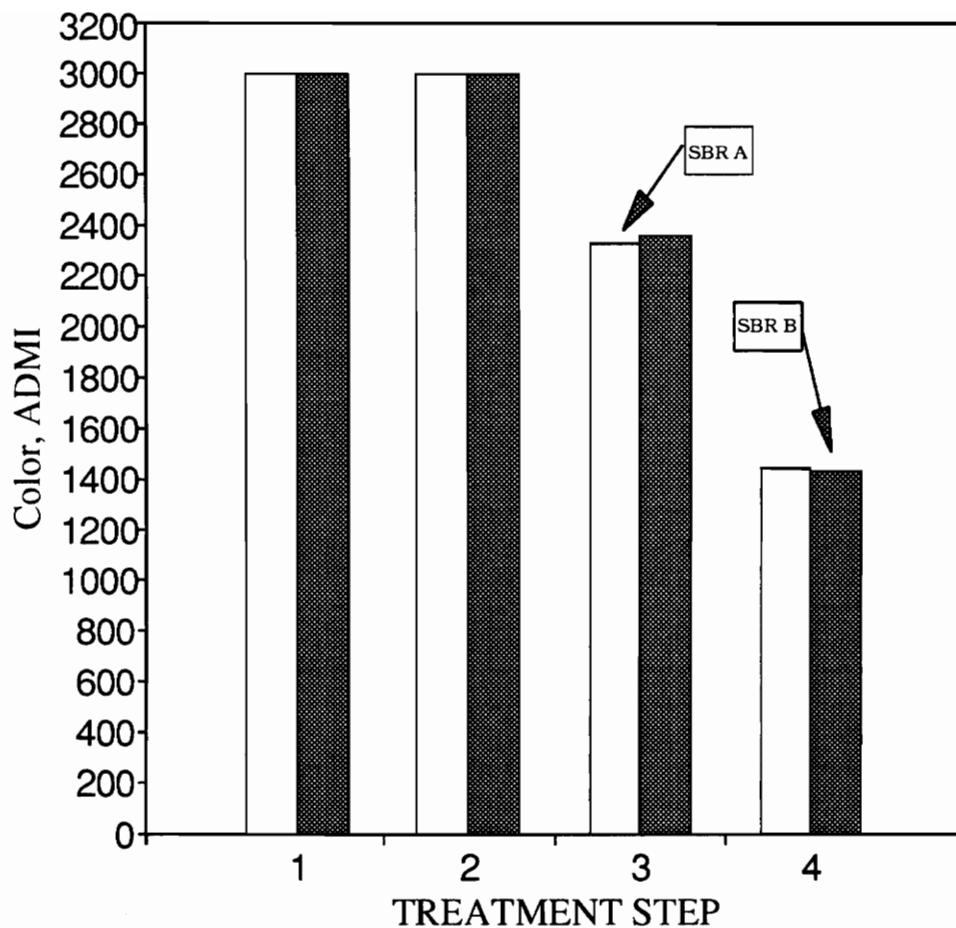
1 = ADMI color at pH 7.6.

removal). Control performance here was similar to the controls of the preliminary tests discussed earlier: 48 percent total color removal, 64 total COD removal, 34 total TOC removal, and 43 total BOD removal.

Figure 8 shows the relationship between the performance of the test and control reactor for color removal in each process step. Figure 9 shows this relationship for TOC. Refer to Appendix D for this relationship regarding COD and BOD. Removals achieved in the test reactor suggested the peroxide addition to the reduced wastewater created an oxidized environment allowing the biomass to degrade the wastewater aerobically, and possibly created less noxious by-products by converting aromatic amines to aromatic amine oxides or quinones.

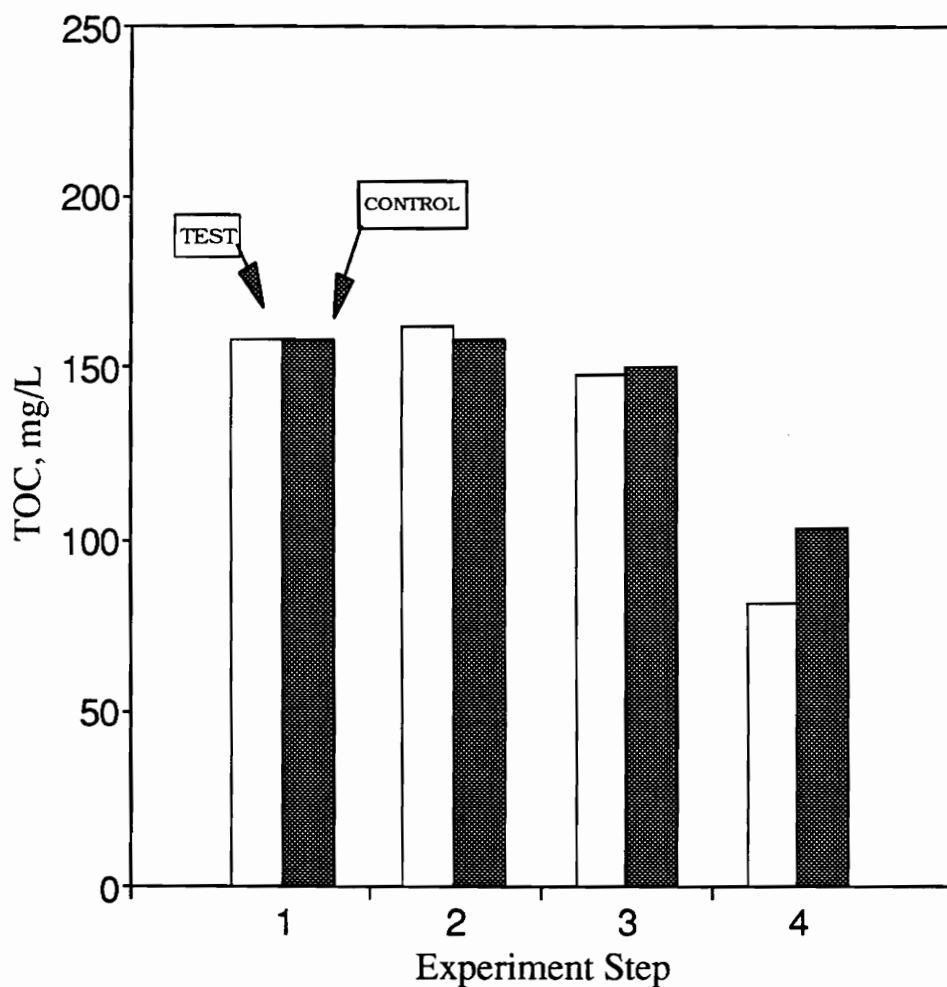
33% Textile Dye Wastewater Pretreated

Due to the success of reduction-oxidation on 17 percent of the textile dye wastewater, 33 percent of the textile dye wastewater was treated with hydrosulfite and hydrogen peroxide. The pretreated textile wastewater and municipal wastewater were transferred to the test reactor for biological treatment. Within one day the test reactor performance was better than the control reactor performance.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 8. Relationship between test (17 % pretreated) and control reactor performance for color removal.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 9. Relationship between test (17 % pretreated) and control reactor performance for TOC removal.

This test was conducted over 6 days to determine if the performance would improve. However, the performance did not improve.

Wastewater characteristics for each process step that were measured during this test are shown in Table 6. The performance of the control reactor during this test is also shown in Table 6. Table 7 shows the effluent data (means and ranges) along with the biological and total percent removals for this test and the control. These data shows there was a reduction in color to 950 ADMI (63 percent total removal, 39 percent biological removal), and the COD, TOC, and BOD were also reduced below control values. They were reduced to 415 mg/L COD (57 percent total removal, 47 percent biological removal), 133 mg/L TOC (49 percent total removal, 41 percent biological removal), and 74 mg/L BOD (61 percent total removal, 55 percent biological removal). Control performance in these tests were similar to the controls of the preliminary tests discussed earlier: 50 percent total color removal, 45 total COD removal, 35 total TOC removal, and 43 total BOD removal. Figure 10 shows the relationship between the performance of the test and control reactor for color removal in each process step. Figure 11 shows this relationship for TOC. Refer to Appendix D for

Table 6. Wastewater characteristics for 33 % pretreatment of the textile dye wastewater.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER OXIDATION AND MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2550	1950	1550	950
COD mg/L	955	957	780	415
TOC mg/L	259	263	225	133
BOD mg/L	191	-----	163	74
TSS mg/L	27	-----	30	75
COLOR (2)	2700	2060	1640	1000
pH	10.5	9.6	9.2	8.7
REDOX mV	+ 54	- 611	(+ 312)	+ 64
CONTROL REACTOR				
COLOR (1)	2550	-----	1990	1273
COD mg/L	960	-----	783	528
TOC mg/L	260	-----	226	168
BOD mg/L	185	-----	165	105
TSS mg/L	30	-----	33	
COLOR (2)	2710	-----	1730	1350
pH	10.4	-----	9.7	9.2
REDOX mV	+ 69	-----	+ 64	+ 75

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

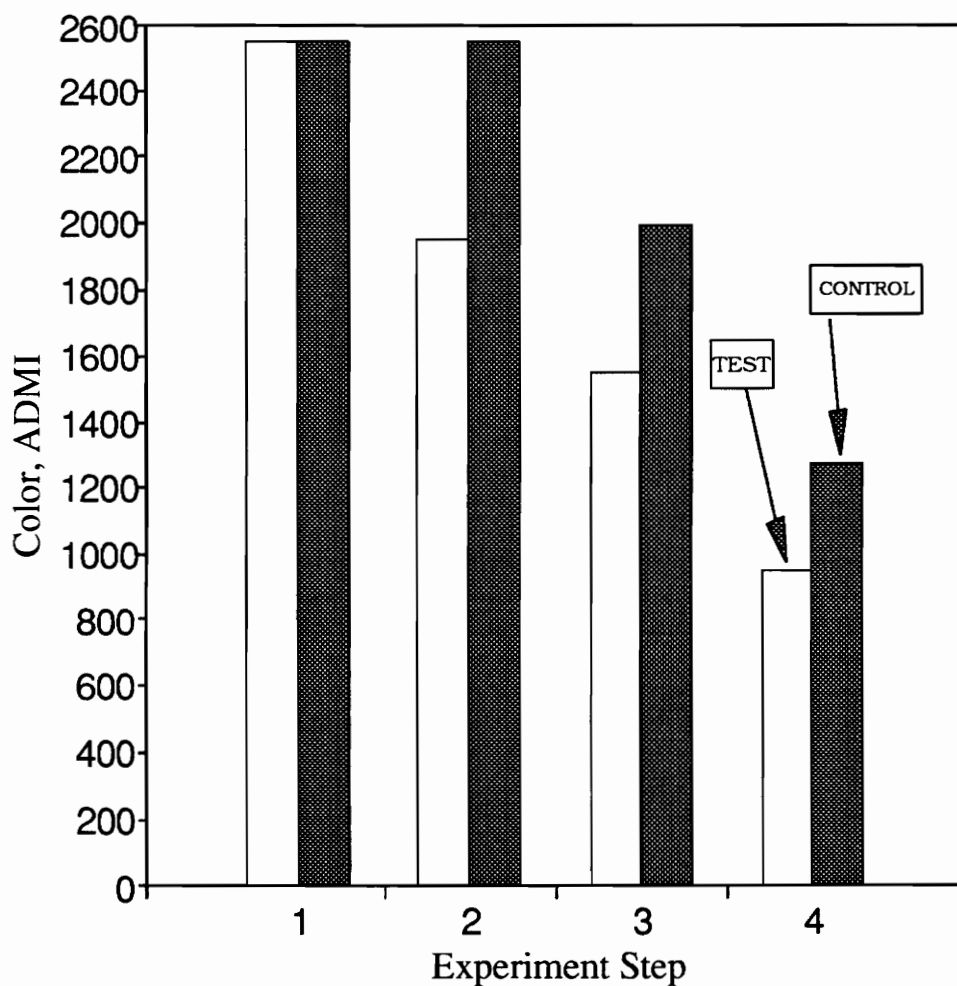
() = REDOX after oxidation

WW = Wastewater

Table 7. Effluent data for 33 % pretreatment of the textile dye wastewater.

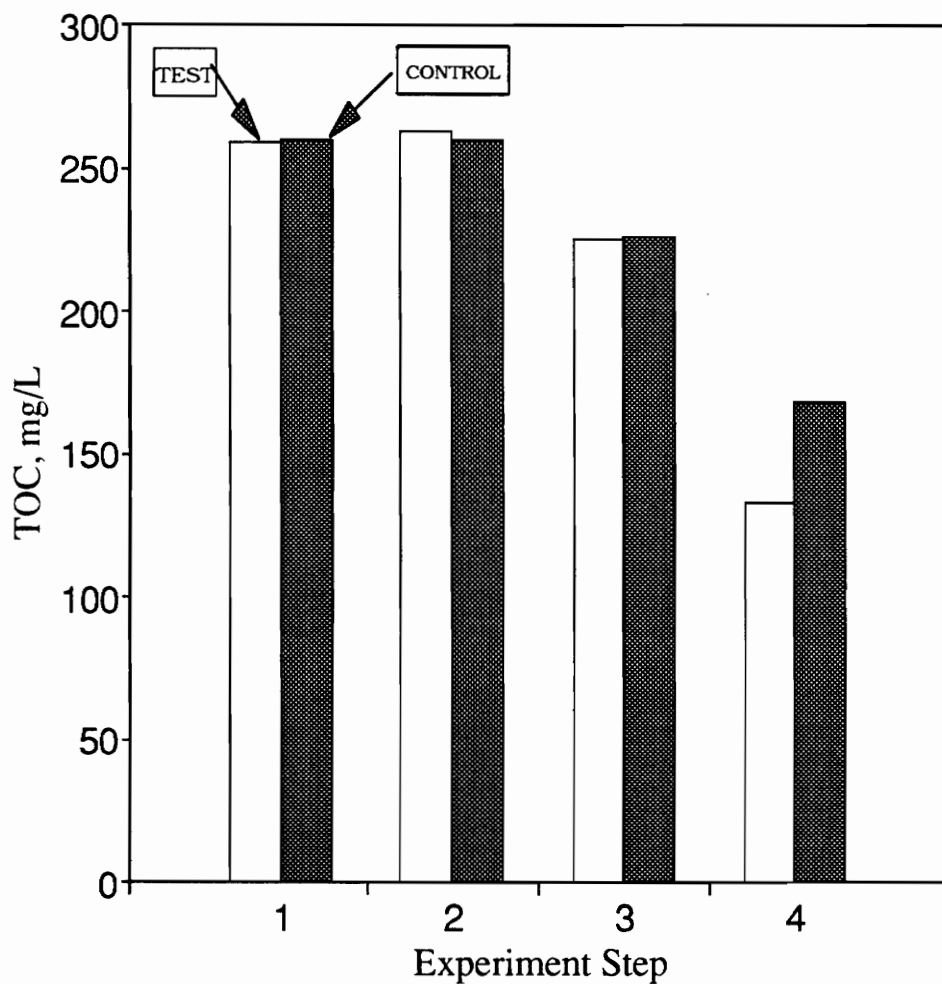
SBR	PARAMETER	EFFLUENT		REMOVALS		MLSS mg/L
		MEAN	RANGE	TOTAL	BIOL	
TEST	COLOR (1)	950	910 - 985	63	39	2250
CONTROL		1273	1234 - 1315	50	36	2100
TEST	COD mg/L	415	400 - 425	57	47	2250
CONTROL		528	500 - 587	45	33	2100
TEST	TOC mg/L	133	129 - 139	49	41	2250
CONTROL		168	165 - 174	35	26	2100
TEST	BOD mg/L	74	70 - 79	61	55	2250
CONTROL		105	87 - 116	43	36	2100

1 = ADMI color at pH 7.6.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 10. Relationship between test (33 % pretreated) and control reactor performance for color removal.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 11. Relationship between test (33 % pretreated) and control reactor performance for TOC removal.

this relationship regarding COD and BOD. Note a different initial, untreated textile wastewater batch was used for this and the subsequent tests than the reduction-oxidation test on 17 percent of the dye wastewater.

67% Textile Dye Wastewater Pretreated

Due to the success of pretreating 33 percent of the textile dye wastewater, 67 percent of the textile dye wastewater was treated using hydrosulfite and hydrogen peroxide. The pretreated textile wastewater and the municipal wastewater were transferred to the test reactor for biological treatment. Within one day the test reactor performance was again better than that of the control reactor. This test was also conducted over 6 days to determine if the performance would change, but it did not.

The wastewater characteristics for each process step that were measured during this test are shown in Table 8. The performance of the control reactor during this testing is also shown in Table 8. Table 9 shows the effluent data (means and ranges) along with the biological and total percent removals for this test and the control. These data indicate that there was a reduction in color to 750 ADMI (71 percent total removal, 29 percent biological removal), and that the COD, TOC, and BOD were also reduced below control

Table 8. Wastewater characteristics for 67 % pretreatment of the textile dye wastewater.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER OXIDATION AND MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2550	1450	1050	750
COD mg/L	850	854	780	365
TOC mg/L	252	251	215	106
BOD mg/L	187	-----	154	67
TSS mg/L	29	-----	30	80
COLOR (2)	2705	1530	1110	795
pH	10.4	9.6	9.3	8.9
REDOX mV	+ 79	- 523	(+ 289)	+ 67
CONTROL REACTOR				
COLOR (1)	2550	-----	2018	1298
COD mg/L	855	-----	798	520
TOC mg/L	260	-----	237	170
BOD mg/L	180	-----	160	111
TSS mg/L	30	-----	33	
COLOR (2)	2690	-----	2140	1376
pH	10.3	-----	9.8	9.1
REDOX mV	+ 73	-----	+ 63	+ 67

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

() = REDOX after oxidation

WW = Wastewater

Table 9. Effluent data for 67 % pretreatment of the textile dye wastewater.

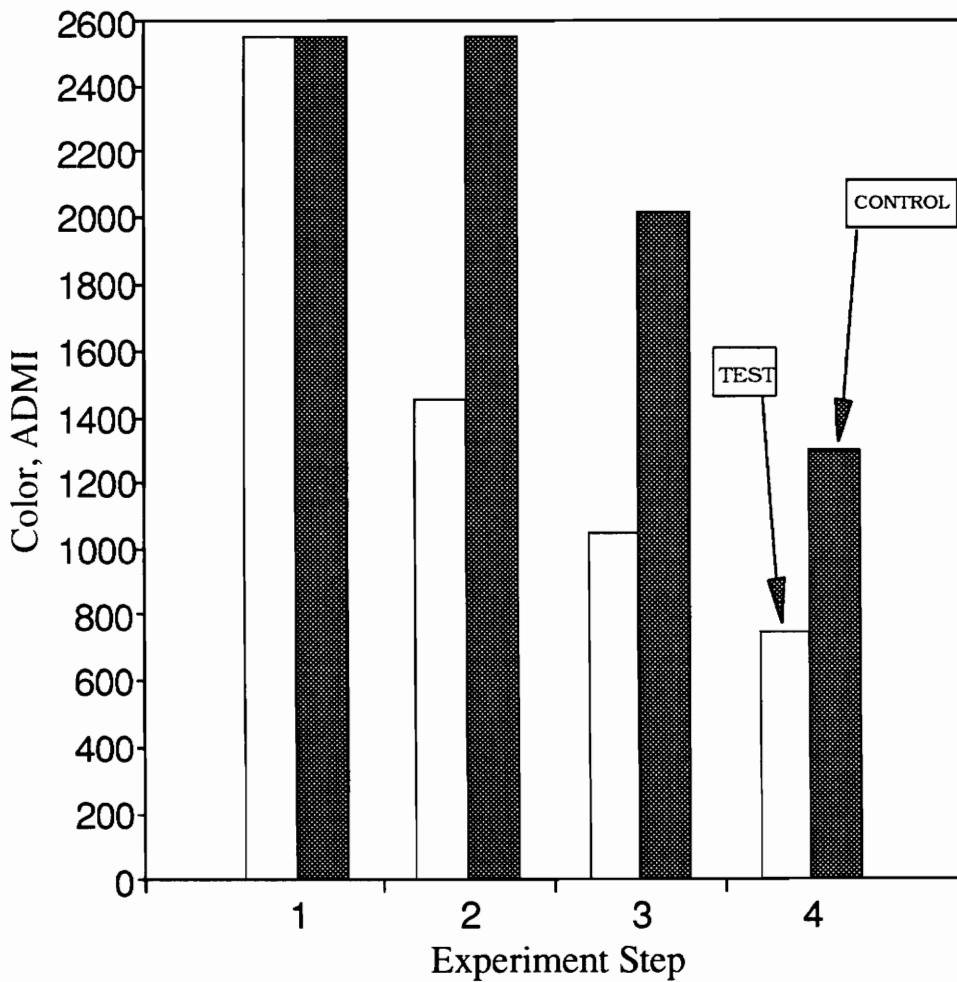
SBR	PARAMETER	EFFLUENT		REMOVALS		MLSS mg/L
		MEAN	RANGE	TOTAL	BIOL	
TEST	COLOR (1)	750	715 - 790	71	29	2150
CONTROL		1298	1276 - 1345	49	36	2000
TEST	COD mg/L	365	360 - 375	57	53	2150
CONTROL		520	496 - 547	39	35	2000
TEST	TOC mg/L	106	103 - 117	58	51	2150
CONTROL		170	167 - 178	35	28	2000
TEST	BOD mg/L	67	66 - 75	64	56	2150
CONTROL		111	100 - 125	38	31	2000

1 = ADMI color at pH 7.6.

values. The effluent levels were as follows: 365 mg/L COD (57 percent total removal, 53 percent biological removal), 106 mg/L TOC (58 percent total removal, 51 percent biological removal), and 67 mg/L BOD (64 percent total removal, 56 percent biological removal). The control characteristics were similar to the controls of the preliminary tests discussed earlier: 49 percent total color removal, 39 total COD removal, 35 total TOC removal, and 38 total BOD removal. Figure 12 shows the relationship between the performance of the test and control reactor for color removal in each process step. Figure 13 shows this relationship for TOC. Refer to Appendix D for this relationship regarding COD and BOD.

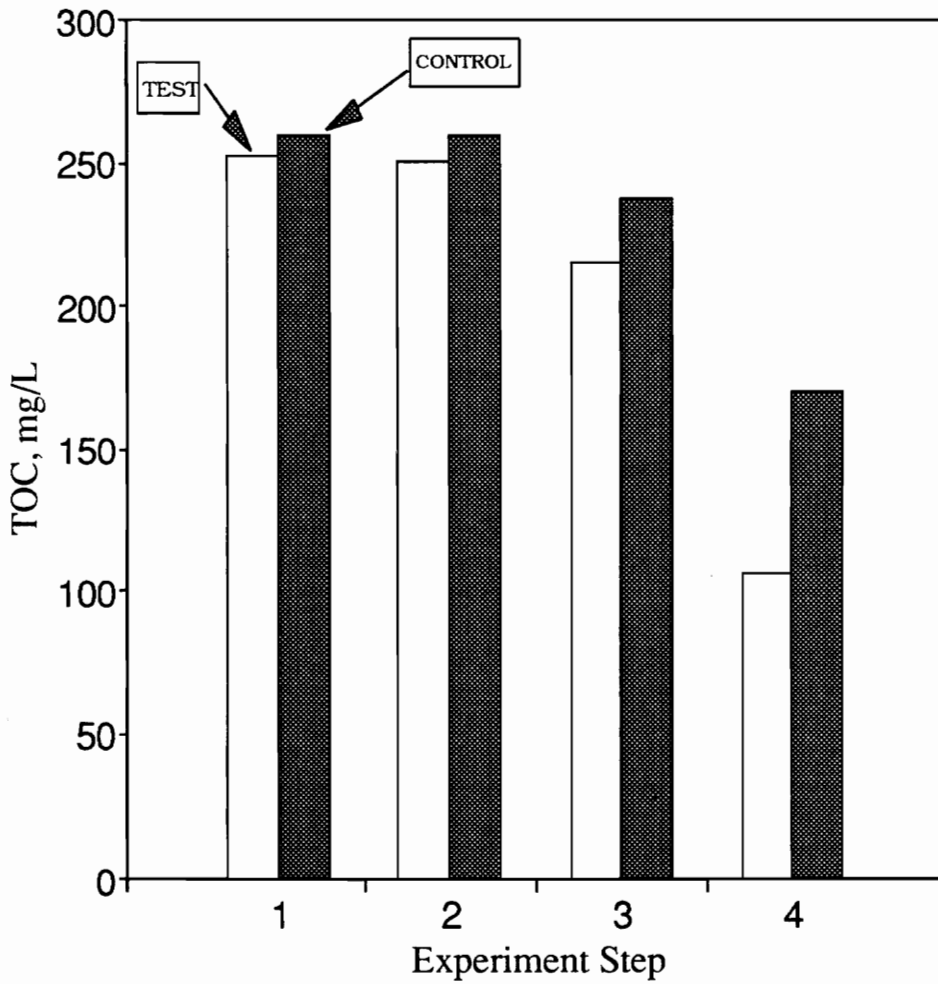
100% Textile Dye Wastewater Pretreated

Due to the success of pretreatment of 67 percent of the textile dye wastewater, 100 percent of the textile dye wastewater was treated with hydrosulfite and hydrogen peroxide. The pretreated textile wastewater and municipal wastewater were transferred to the test reactor for biological treatment. Within one day the test reactor performance was again better than the control reactor performance. This test was conducted over 9 days to



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 12. Relationship between test (67 % pretreated) and control reactor performance for color removal.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 13. Relationship between test (67 % pretreated) and control reactor performance for TOC removal.

determine if the performance would change, however it did not.

The wastewater characteristics for each process step that were measured during this test are shown in Table 10. The performance of the control reactor during this testing is also shown in Table 10 . Table 11 shows the effluent data (means and ranges) along with the percent removals for this test and the control. From this data, there was a reduction in color to 615 ADMI (77 percent total removal, 18 percent biological removal), and the COD, TOC, and BOD were also reduced below control values. COD, TOC, and BOD levels were reduced to 310 mg/L (60 percent total removal, 52 percent biological removal), 82 mg/L (61 percent total removal, 57 percent biological removal), and 62 mg/L (66 percent total removal, 59 percent biological removal), respectively. The control characteristics were similar to the controls of the preliminary tests discussed earlier: 48 percent total color removal, 43 total COD removal, 38 total TOC removal, and 50 total BOD removal. Note the batch textile wastewater used for this test. Figure 14 shows the relationship between the test and control reactor for color removal for each process step. Figure 15 shows this relationship for TOC. Refer to Appendix D for this relationship regarding COD and BOD.

Table 10. Wastewater characteristics for 100 % pretreatment of the textile dye wastewater.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER OXIDATION AND MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2650	1000	750	615
COD mg/L	780	783	650	310
TOC mg/L	211	212	189	82
BOD mg/L	182	----	152	62
TSS mg/L	24	----	25	75
COLOR (2)	2810	1070	800	650
pH	10.2	9.5	9.2	8.8
REDOX mV	+ 59	- 458	(+ 178)	+ 85
CONTROL REACTOR				
COLOR (1)	2650	----	2040	1370
COD mg/L	785	----	653	450
TOC mg/L	210	----	188	130
BOD mg/L	185	----	160	93
TSS mg/L	20	----	23	70
COLOR (2)	2800	----	2165	1455
pH	10.3	----	9.8	9
REDOX mV	+ 79	----	+ 66	+ 73

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

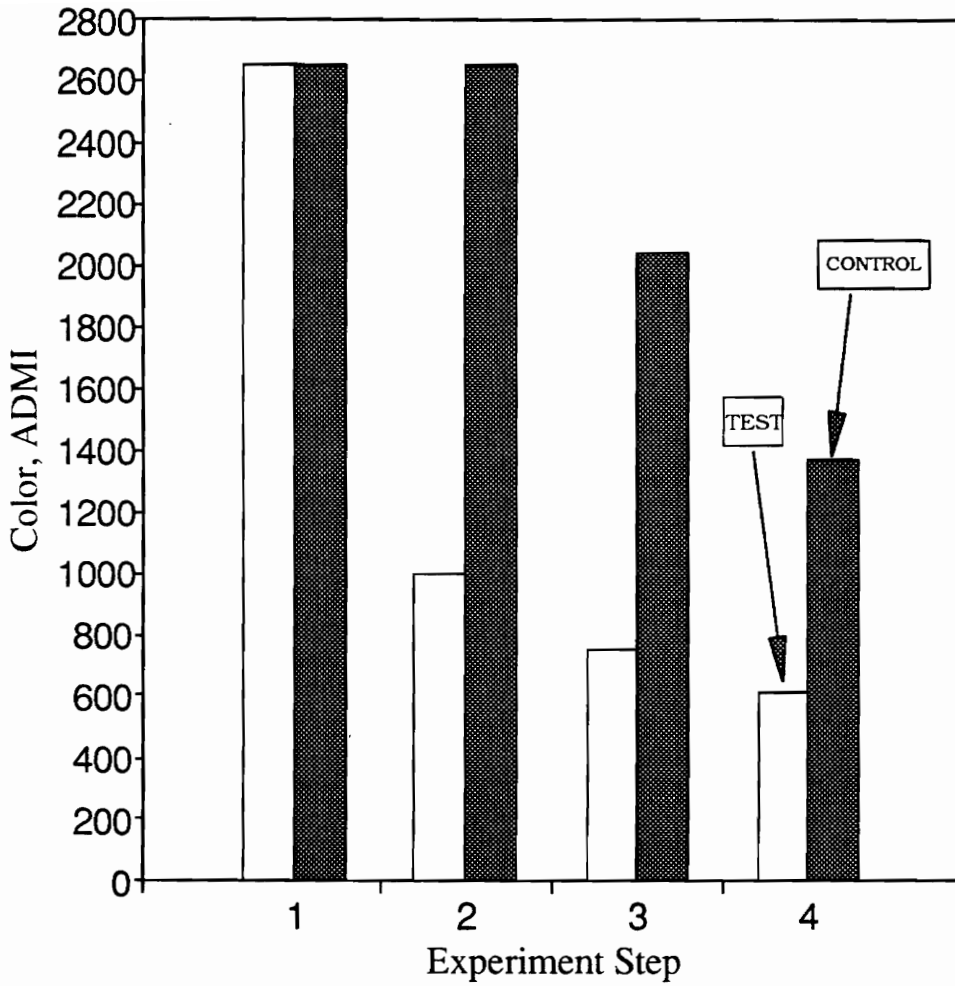
() = REDOX after oxidation

WW = Wastewater

Table 11. Effluent data for 100 % pretreatment of the textile dye wastewater.

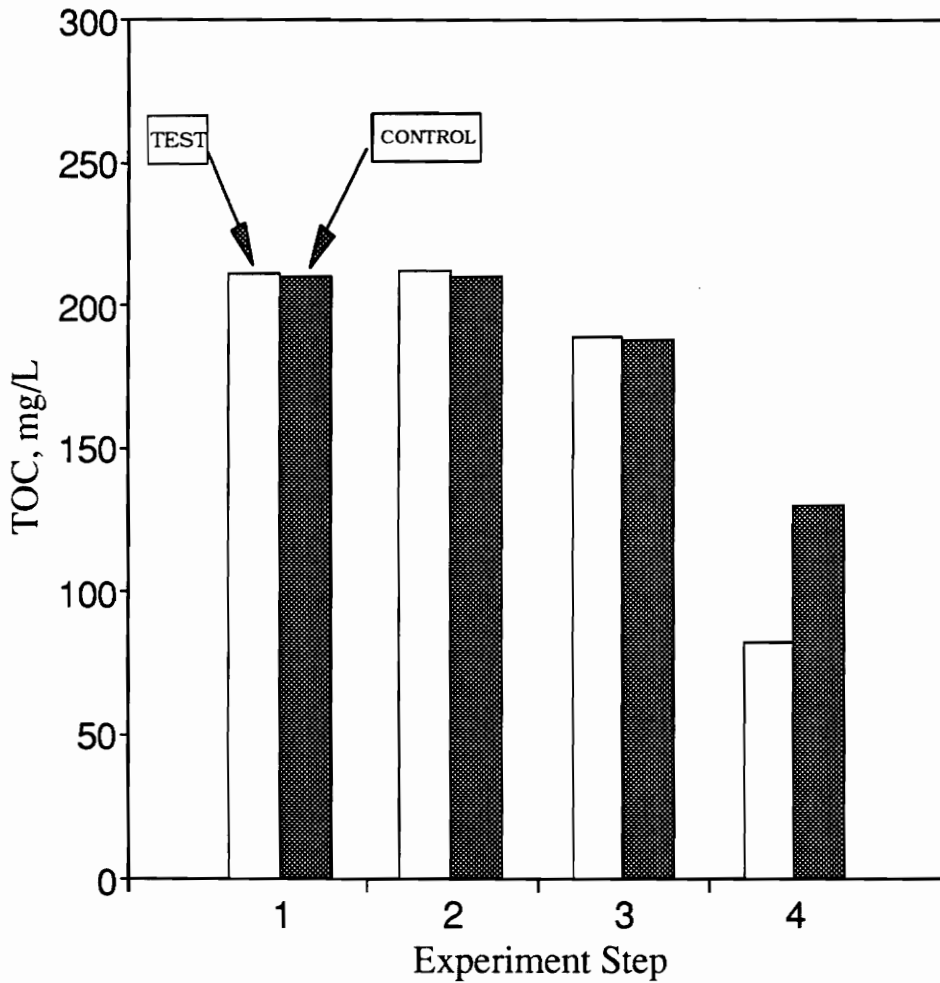
SBR	PARAMETER	EFFLUENT		REMOVALS		MLSS mg/L
		MEAN	RANGE	TOTAL	BIOL	
TEST	COLOR (1)	615	600 - 650	77	18	2050
CONTROL		1370	1326 - 1400	48	33	2350
TEST	COD mg/L	310	290 - 345	60	52	2050
CONTROL		450	413 - 487	43	31	2350
TEST	TOC mg/L	82	78 - 90	61	57	2050
CONTROL		130	125 - 137	38	31	2350
TEST	BOD mg/L	62	53 - 64	66	59	2050
CONTROL		93	84 - 100	50	42	2350

1 = ADMI color at pH 7.6.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 14. Relationship between test (100 % pretreated) and control reactor performance for color removal.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 15. Relationship between test (100 % pretreated) and control reactor performance for TOC removal.

These results show that a pretreatment combination of reduction and oxidation on the entire textile portion of the combined wastewater allowed for the biodegradation of the wastewater (reduction of COD from 780 mg/L to 310 mg/L, TOC from 211 mg/L to 82 mg/l, and BOD from 182 mg/L to 62 mg/L) and a large reduction in color from 2650 ADMI to 615 ADMI (77 percent removal).

Comparison of the Reduction-Oxidation Studies

Of the conditions considered, only reduction with hydrosulfite followed by oxidation with hydrogen peroxide was successful in aiding color removal and the biodegradation of organic matter. Since the reduction/oxidation tests were conducted in a step-wise series on the amount of textile wastewater pretreated, from 17 percent pretreated to 100 percent pretreated, a comparison of the data obtained from each experiment can be made. The SBR influent was comprised of 75 percent textile wastewater and 25 percent municipal wastewater.

Biological kinetic coefficients calculated for these tests were the Food-to-Microorganism ratio (F/M) and the observed growth yield coefficient (Y). The F/M ratio was calculated for each experiment and the controls. The F/M ratio is defined as the substrate loading applied per unit

of biomass (lb BOD per day per lb MLSS) (Benefield and Randall, 1980). Table 12 illustrates the MLSS level attained in each reactor (test and control), the BOD loading, and the corresponding F/M ratios. The F/M ratios for these tests ranged from 0.023 to 0.037 in the test reactor and from 0.023 to 0.040 in the control reactor. For a series of treatment tests conducted on a textile wastewater, Shriver and Daugue (1978) report F/M ratios ranging from 0.06 to 0.28, depending on the hydraulic residence time. For the Shriver and Daugue (1978) study, loading was held constant. For domestic wastewater, F/M ratios are typically from 0.2 to 0.7 (Eckenfelder, 1989). Low loading applies to reactors with an F/M less than 0.1 and high loading applies to reactors with an F/M greater than 0.8. Therefore, since the F/M ratios for these tests were less than 0.1, the reactors had a low loading. A decrease in the MLSS content would increase the F/M ratio, and could change the performance of the reactor. A decrease in the hydraulic residence time (HRT) would have similar results.

The observed growth yield (Y) attained at these loadings is shown in Table 13. Growth yield is defined as the increase in biomass per decrease in substrate (lb MLSS generated per lb BOD removed) (Benefield and Randall, 1980). For these tests, Y ranged from 0.16 to 0.35 for the tests

and from 0.18 to 0.33 for the controls. For a study conducted by Ghosh et al (1978), a yield coefficient of 0.52 was achieved, with an F/M ratio of 0.19. For municipal wastewater, yield coefficients are typically around 0.7 (Benefield and Randall, 1980). The change in MLSS was determined over a period of 3 days. The MLSS generated, as reported in Table 13, was calculated by averaging the MLSS generated over a 3 day period.

Figure 16 shows the color trend during each reduction-oxidation experiment. This figure shows the decline in the ADMI color value as a larger portion of the textile dye wastewater was pretreated. The tapering off of the 100 percent pretreated line around 600 ADMI suggested that there was a non-biodegradable, refractory component in the wastewater. However, this refractory component could be attributed to the fact that excess reducing agent was not used. The amount of hydrosulfite (225 ppm) chosen was based on the hope that biological treatment would remove the additional color remaining after pretreatment. Refer to Appendix E for the relation between reducing agent concentration and resulting color. Although for 100 % pretreatment of the textile dye wastewater only 18 % color removal was achieved during biological treatment, it is probable that a portion of the remaining color could be removed with a larger dose of hydrosulfite.

Table 12. Food/Microorganism ratios for the reduction/oxidation tests.

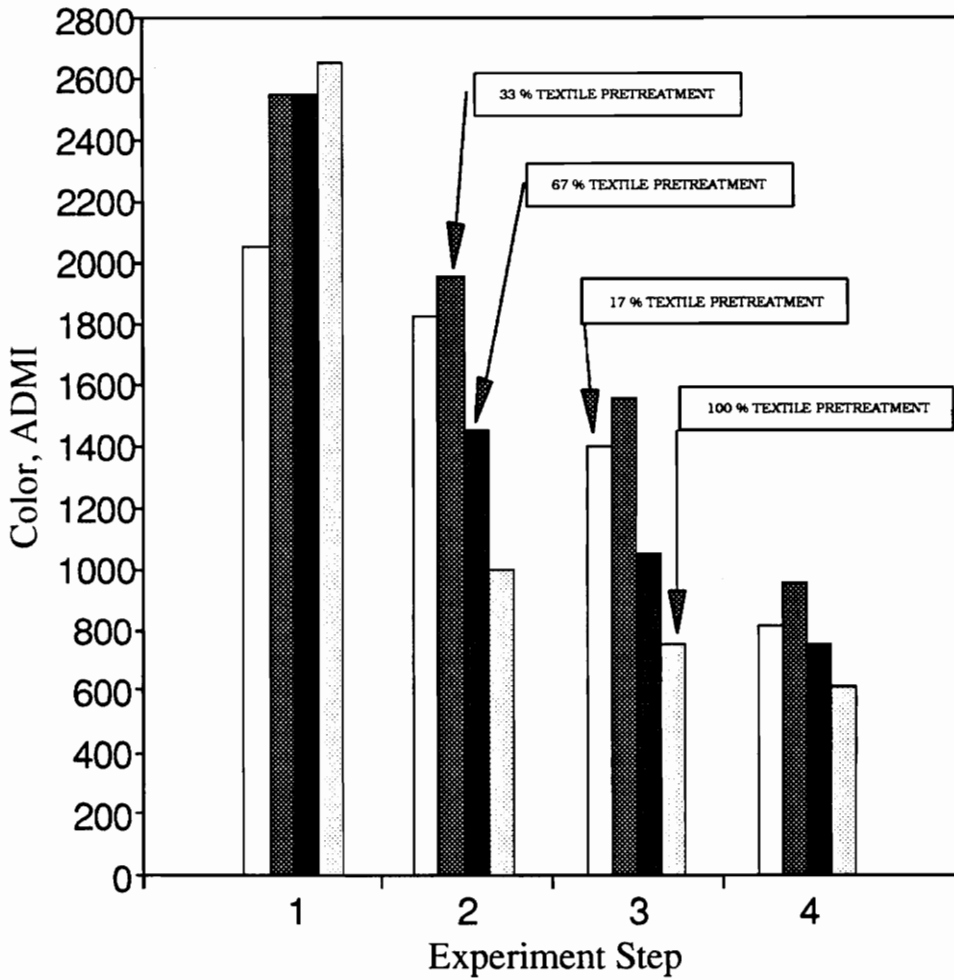
Percent Pretreated	Influent BOD mg/L	MLSS mg/L	F/M lb/day/lb	HRT days
17	98(100)	2100(2200)	0.023(0.023)	2
33	163(165)	2250(2100)	0.036(0.039)	2
67	154(160)	2150(2000)	0.036(0.040)	2
100	152(160)	2050(2350)	0.037(0.034)	2

() Control values

Table 13. Growth yield values for the reduction/oxidation tests.

Percent Pretreated	BOD Removal mg/L	MLSS Generated mg/L/day	Observed Growth Yield (Y) lb/d/lb
17	45(35)	11(10)	0.16(0.19)
33	89(89)	36(44)	0.27(0.33)
67	88(49)	34(23)	0.26(0.31)
100	90(67)	47(28)	0.35(0.28)

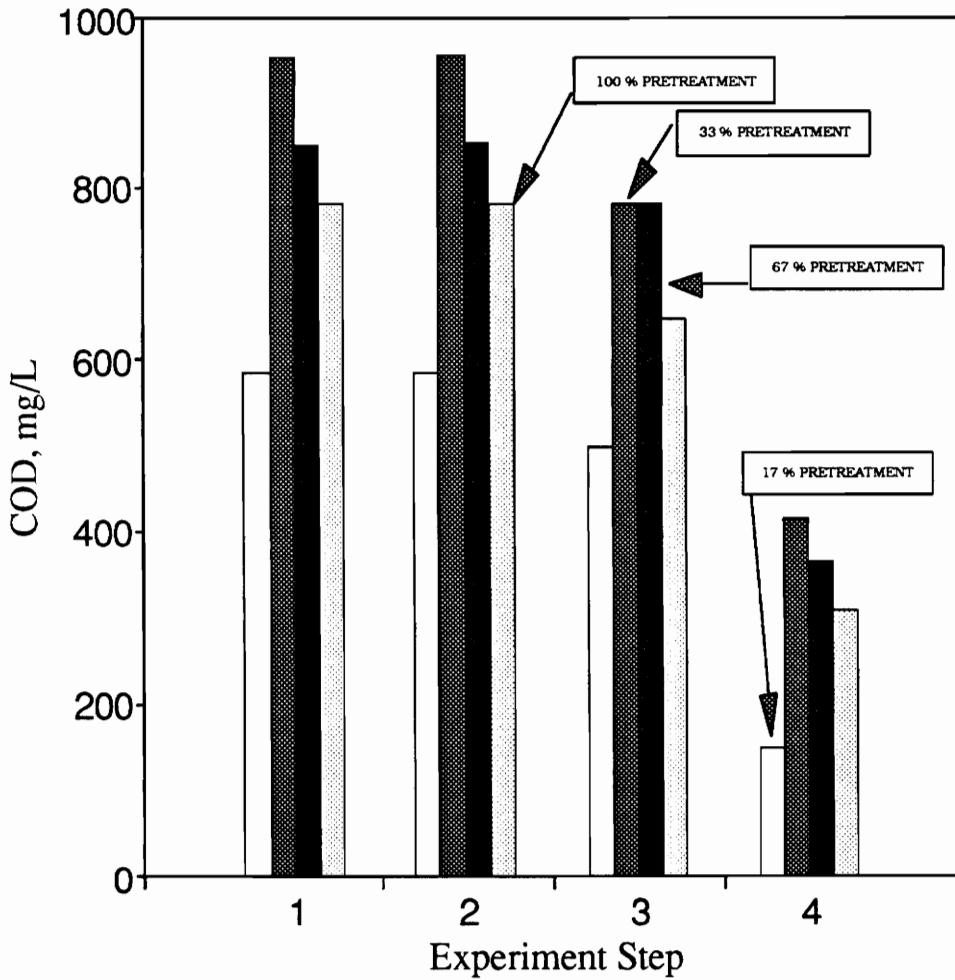
() Control values



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

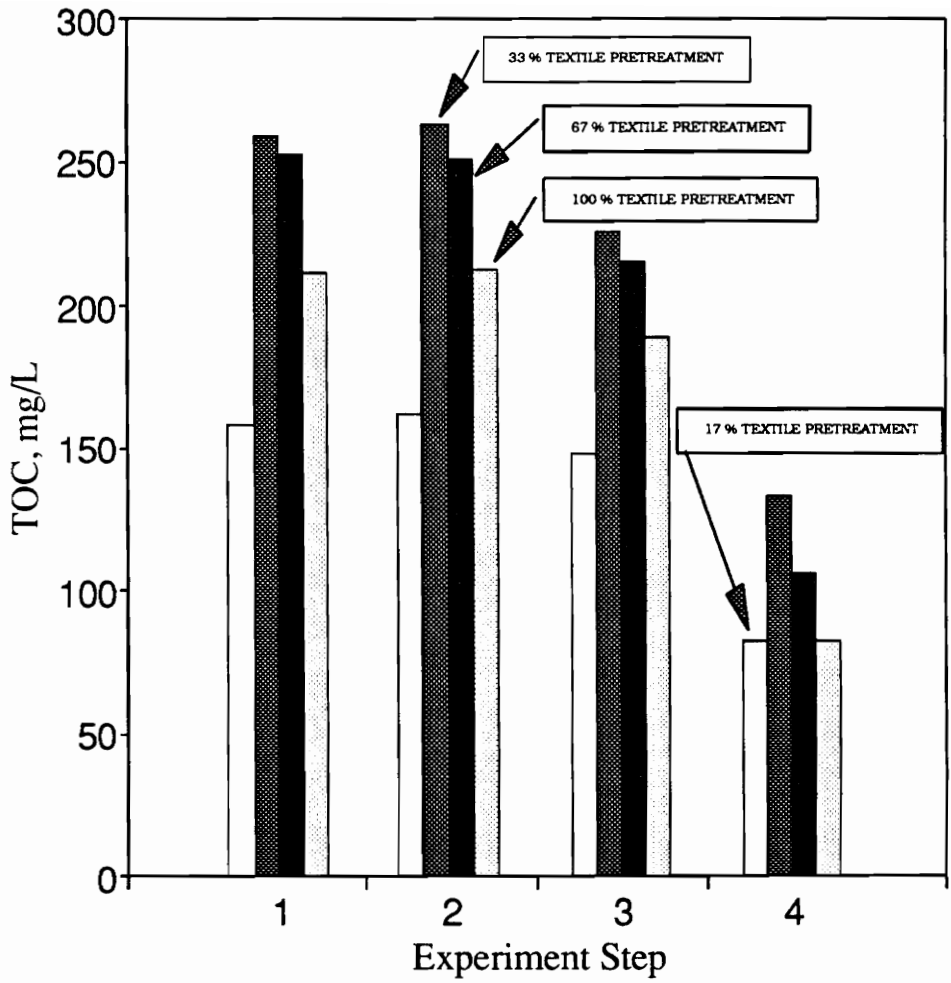
Figure 16. Reduction/oxidation color trend comparison between 17, 33, 67, and 100 % pretreatment of the textile dye wastewater.

Figure 17 shows the COD trend, Figure 18 the TOC trend, and Figure 19 the BOD trend during each (reduction-oxidation) experiment. These figures show that the COD, TOC, and BOD levels had a variation of less than 1 percent (usually the initial and after pretreatment steps had similar values) during the pretreatment process, a near constant change (approximately 15 percent COD and BOD reduction, and 12 percent TOC reduction due to dilution with municipal wastewater) prior to transfer to the SBR, and removals greater than 50 percent (for COD, TOC, and BOD) during biological treatment in the SBR. The role of oxidation after reduction was to create an environment more conducive to biological treatment, oxidize unreacted hydrosulfite, and may have oxidized potentially toxic aromatic amines to aromatic amine oxides or aromatic quinones, supporting conclusions from Rinehart (1973). Peroxide is capable of oxidizing aromatic amines to these latter compounds, but not typically to aromatic nitros (Rinehart, 1973). Recall from the preliminary tests section, hydrogen peroxide alone did not enhance biological treatment of untreated dye wastewater. The high effluent values (615 ADMI color, 310 mg/L COD, 82 mg/L TOC, and 62 mg/L BOD) obtained for the 100 percent pretreatment test suggested that refractory, non-biodegradable materials were present.



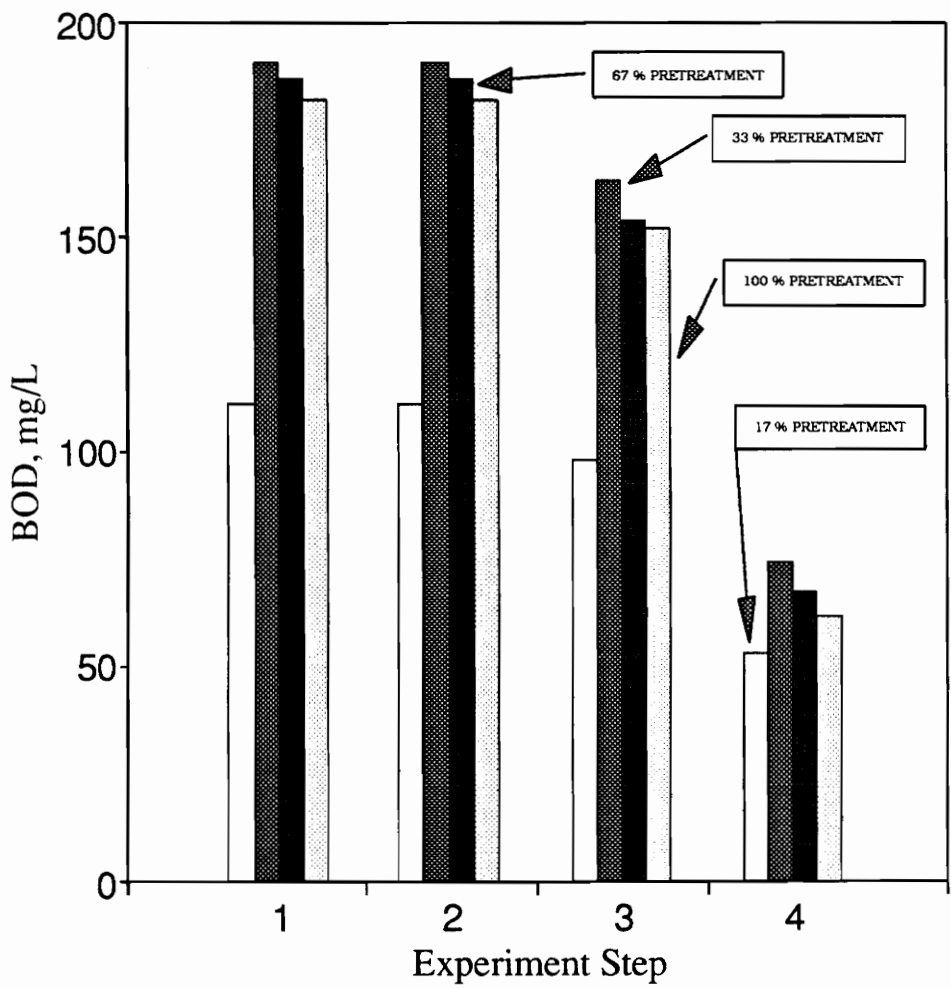
- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 17. Reduction/oxidation COD trend comparison between 17, 33, 67, and 100 % pretreatment of the textile dye wastewater.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 18. Reduction/oxidation TOC trend comparison between 17, 33, 67, and 100 % pretreatment of the textile dye wastewater.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 19. Reduction/oxidation BOD trend comparison between 17, 33, 67, and 100 % pretreatment of the textile dye wastewater.

Figure 20 shows the color trend after each experimental step. The gap between the untreated textile wastewater line and the pretreated textile wastewater line is the amount of color removed during pretreatment. The gap between the pretreated textile wastewater line and the biological influent line was due to dilution with municipal wastewater. The gap between the biological influent line and the biological effluent line is the amount of color removed during biological treatment.

Figure 20 shows that as the amount of color removed during pretreatment increased, the amount of color removed during biological treatment decreased. When 17 percent of the textile wastewater was pretreated, 11 percent of the color was removed by the reducing agent and the microbes removed 42 percent, whereas when 100 percent was pretreated, the reducing agent removed 62 percent and the microbes removed only 18 percent. This would be expected since there was a lower amount of color remaining for the microbes to degrade. Addition of the municipal wastewater diluted the color by 21 to 28 percent. This dilution was not actually removal of the color and was fairly constant, as expected, since a constant amount (25 percent of the total wastewater stream) of municipal wastewater was added during each experiment.

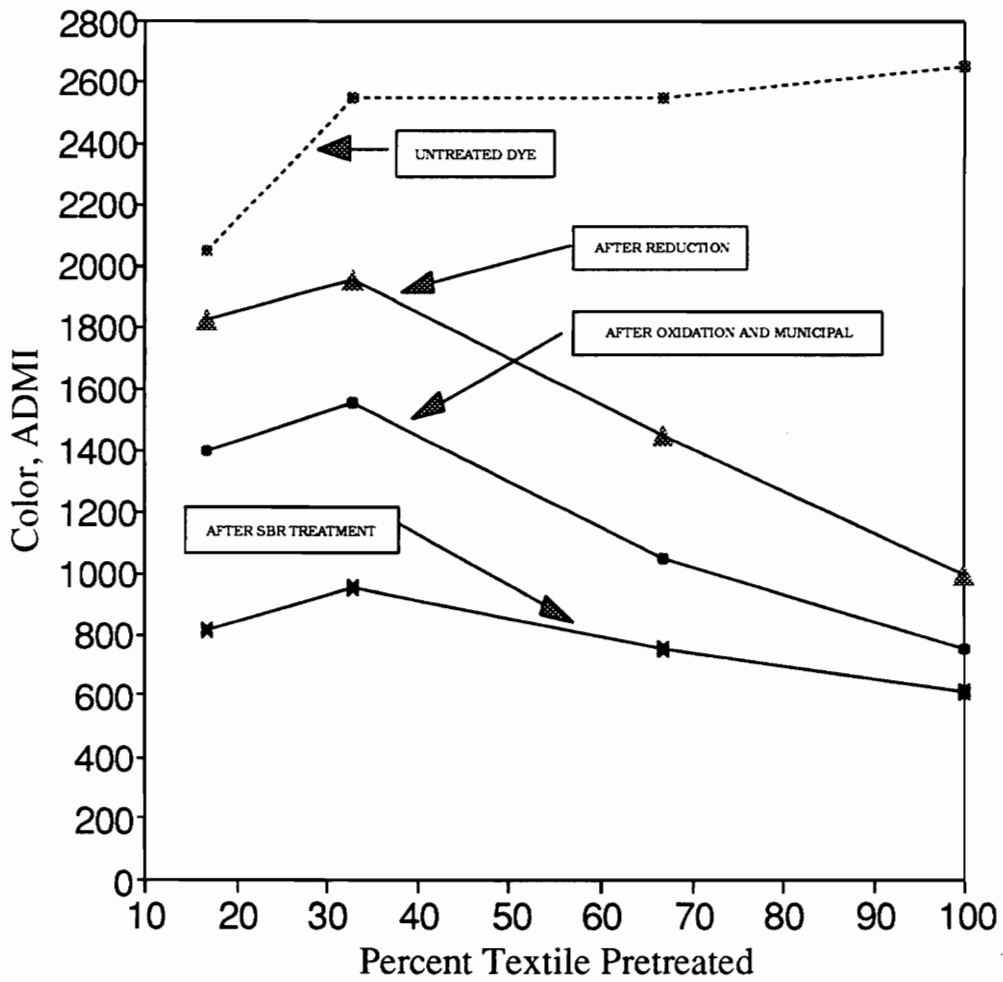


Figure 20. Reduction/oxidation color trend comparison between each treatment process step.

Figure 21 shows the COD values, Figure 22 the TOC values, and Figure 23 the BOD values after each experimental step. The peaks in each of these figures are attributed to the fact that between experiment 1 (17 percent pretreated) and experiment 2 (33 percent pretreated), a new batch of textile dye wastewater was obtained from the Mill. For experiment numbers 2, 3, and 4, these figures show a general decline in the level of COD, TOC, and BOD. This would be expected if pretreatment of a larger percentage of the textile dye wastewater resulted in a larger percentage of the wastewater being biodegradable.

Figure 24 shows the percent remaining of the four main parameters for each redox experiment. It was expected that as more textile wastewater was pretreated, the percent remaining would decrease. Total color removals were from 60 to 77 percent as more textile wastewater was pretreated. Total TOC removals were from 48 to 61 percent. Total BOD removals were from 52 to 66 percent. However, for each experiment (17, 33, 67, and 100 percent pretreatment of the textile wastewater), total COD removals were from 74 to 57 to 58 to 60 percent, respectively. This can be explained by a statement by Kelly et al. (1977); "The COD test does not give valid results for the large, stable, aromatic compounds used in the textile industry." Kelly et al (1977) also states that the COD test may give misleading or false

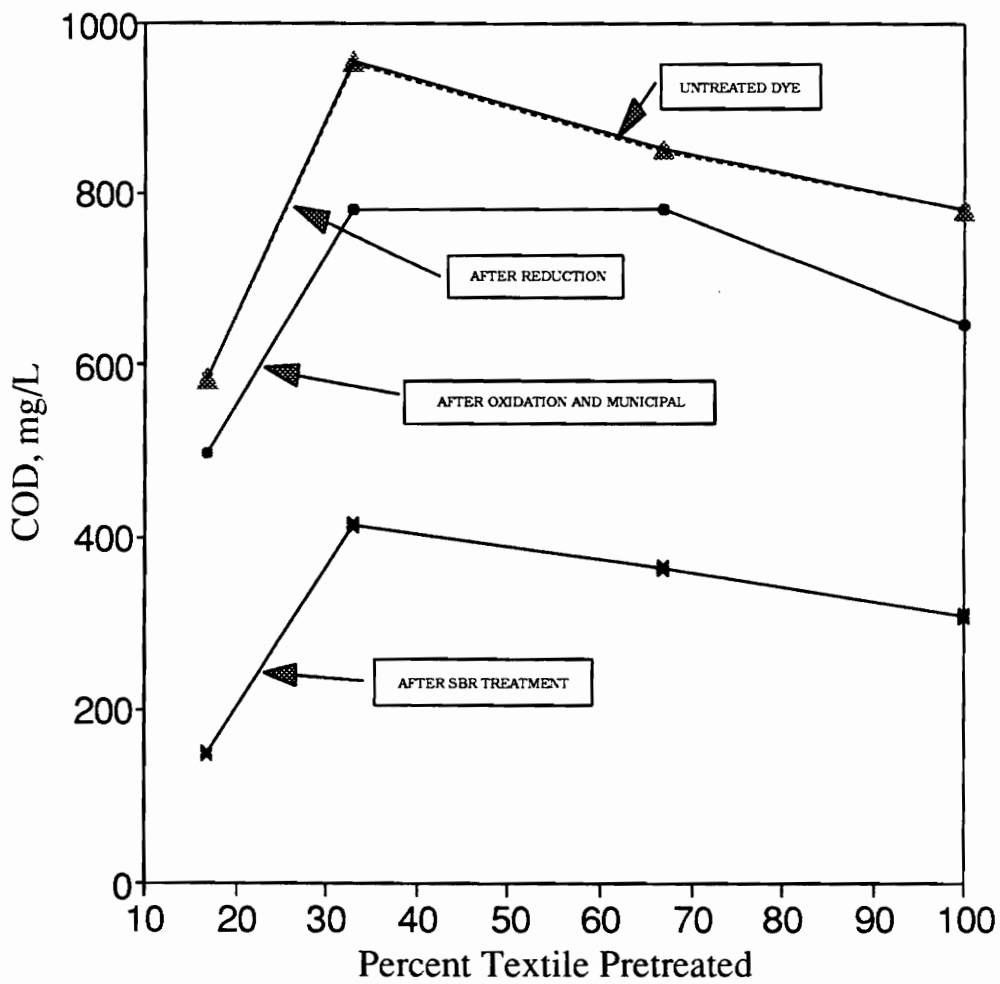


Figure 21. Reduction/oxidation COD trend comparison between each treatment process step.

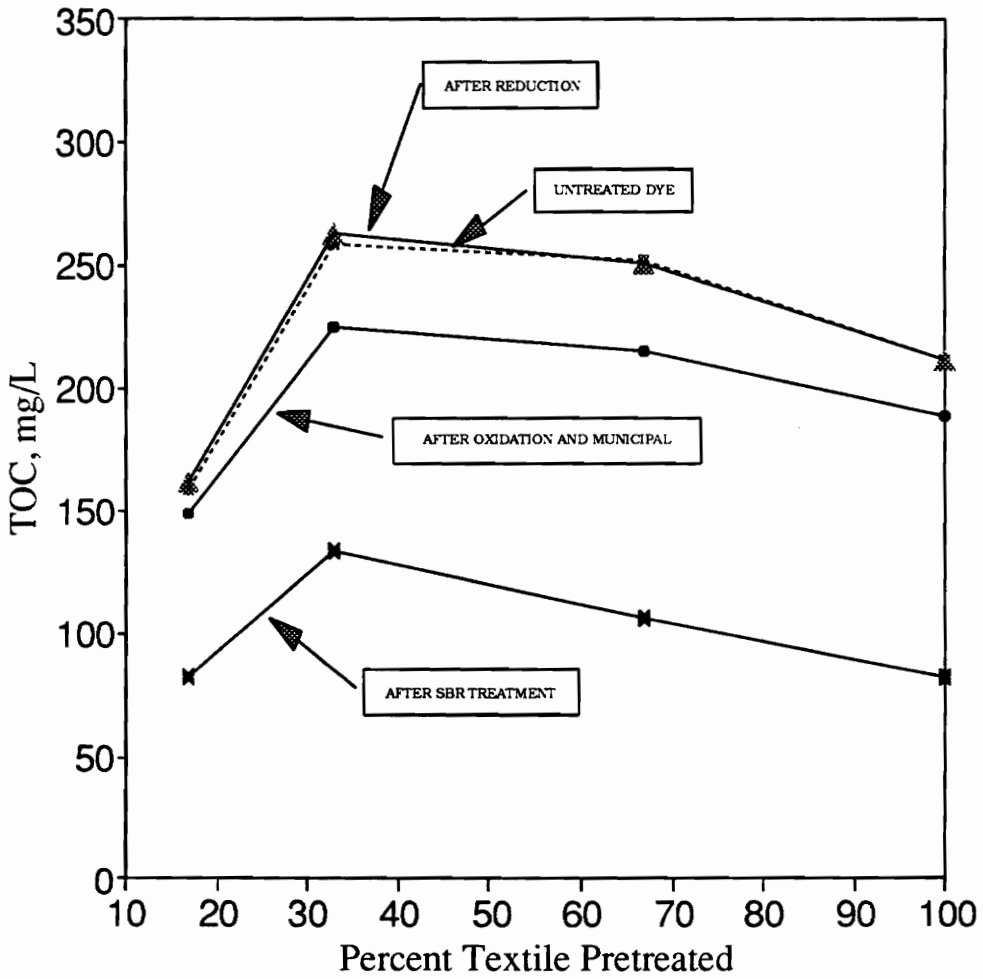


Figure 22. Reduction/oxidation TOC trend comparison between each treatment process step.

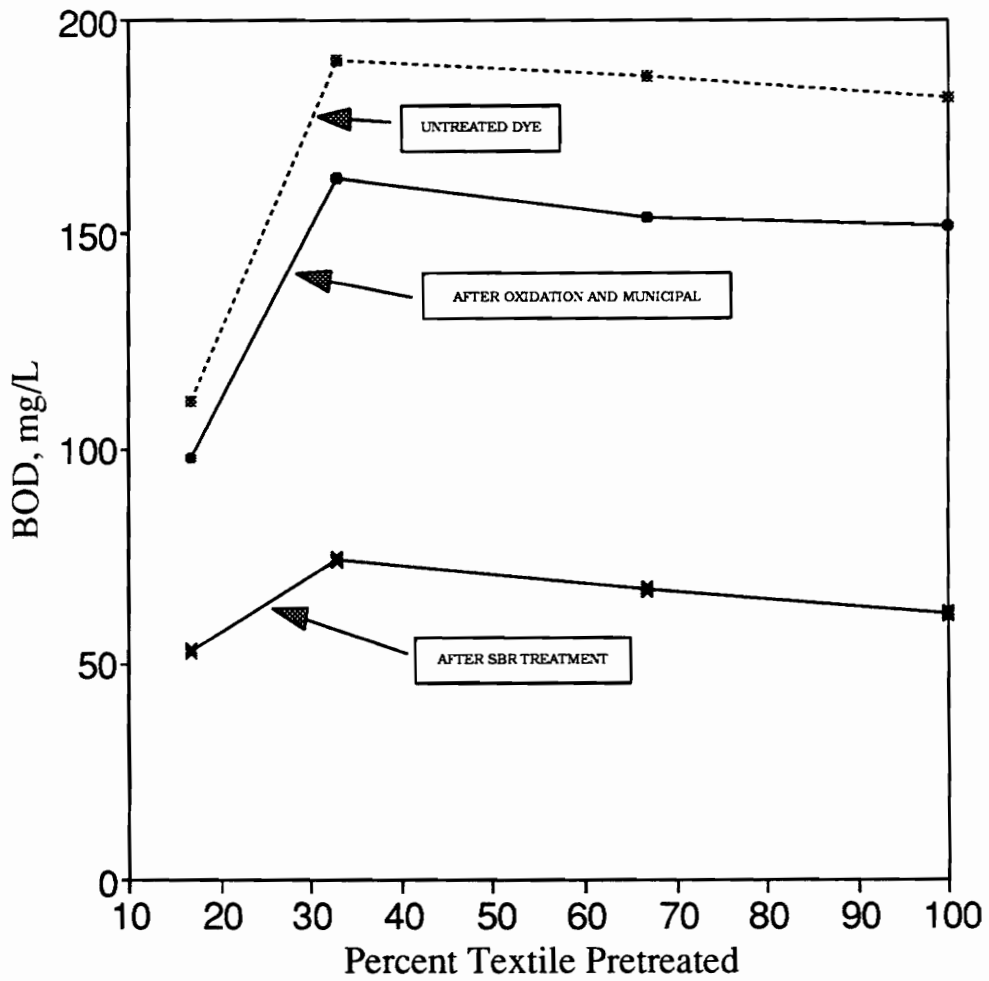


Figure 23. Reduction/oxidation BOD trend comparison between each treatment process step.

results for textile wastewaters. The dye molecules are sufficiently stable to resist oxidation by the dichromate solution used in the COD test. The removals of the latter experiments may be more indicative of the true COD since a greater percentage of the stable dye molecules would have been reduced to smaller intermediates that may be more dichromate oxidizable. However, the TOC test is also dependent on oxidizing the sample and the TOC is fairly well correlated with the COD as seen the Figure 17 and Figure 18. Therefore, the unexpected COD results may be due to a different batch of textile dye wastewater being used.

The total removals of the other parameters, color, TOC, and BOD, increased as the portion of textile wastewater pretreated was increased. These results would be expected of a properly working treatment system.

Figure 25 shows the biological removals of the four main parameters for each redox experiment. Again the COD removal decreased. The COD test reagent does not oxidize large, stable aromatic compounds, such as dye molecules. The TOC and BOD removals increased since a larger portion of the wastewater was more susceptible to biodegradation. The color removals during biological treatment decreased because there was less color remaining after the pretreatment step and there was a refractory, nonbiodegradable component.

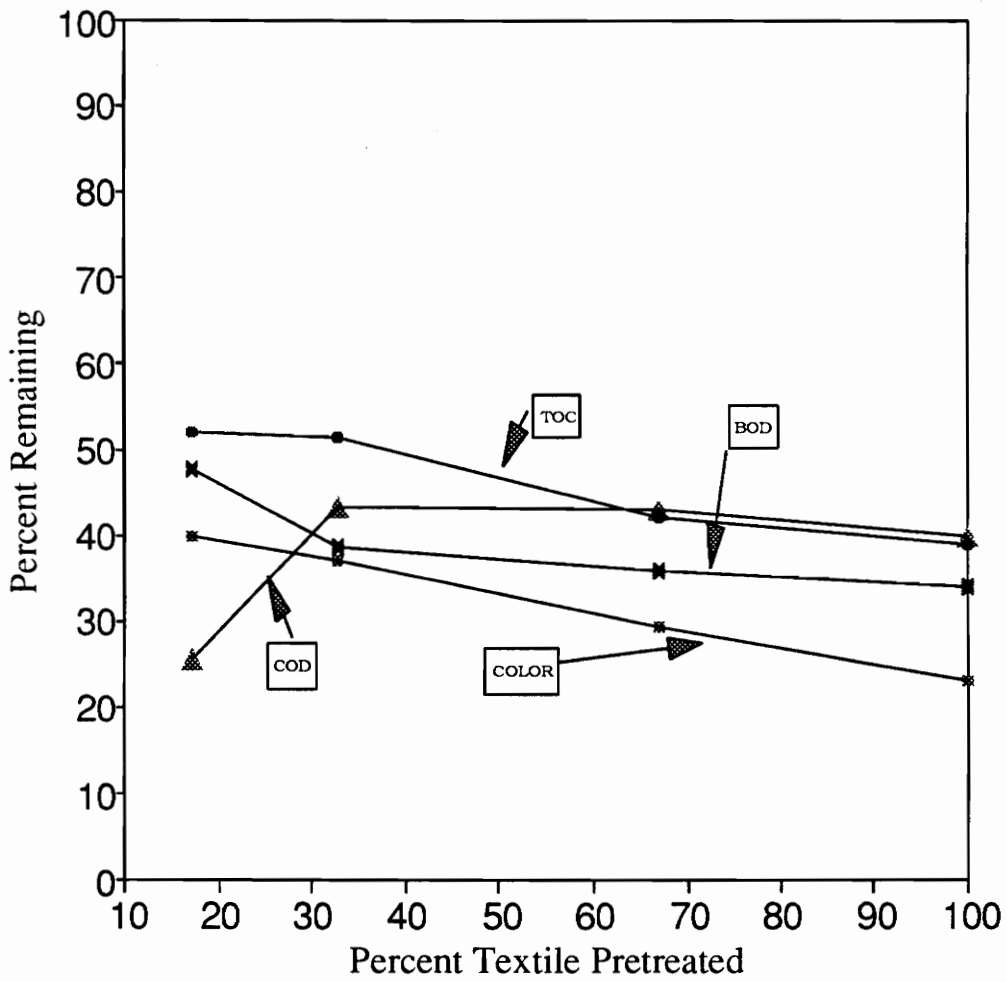


Figure 24. Percent remaining of color, COD, TOC, and BOD for 17, 33, 67, 100 % pretreatment of the textile dye wastewater.

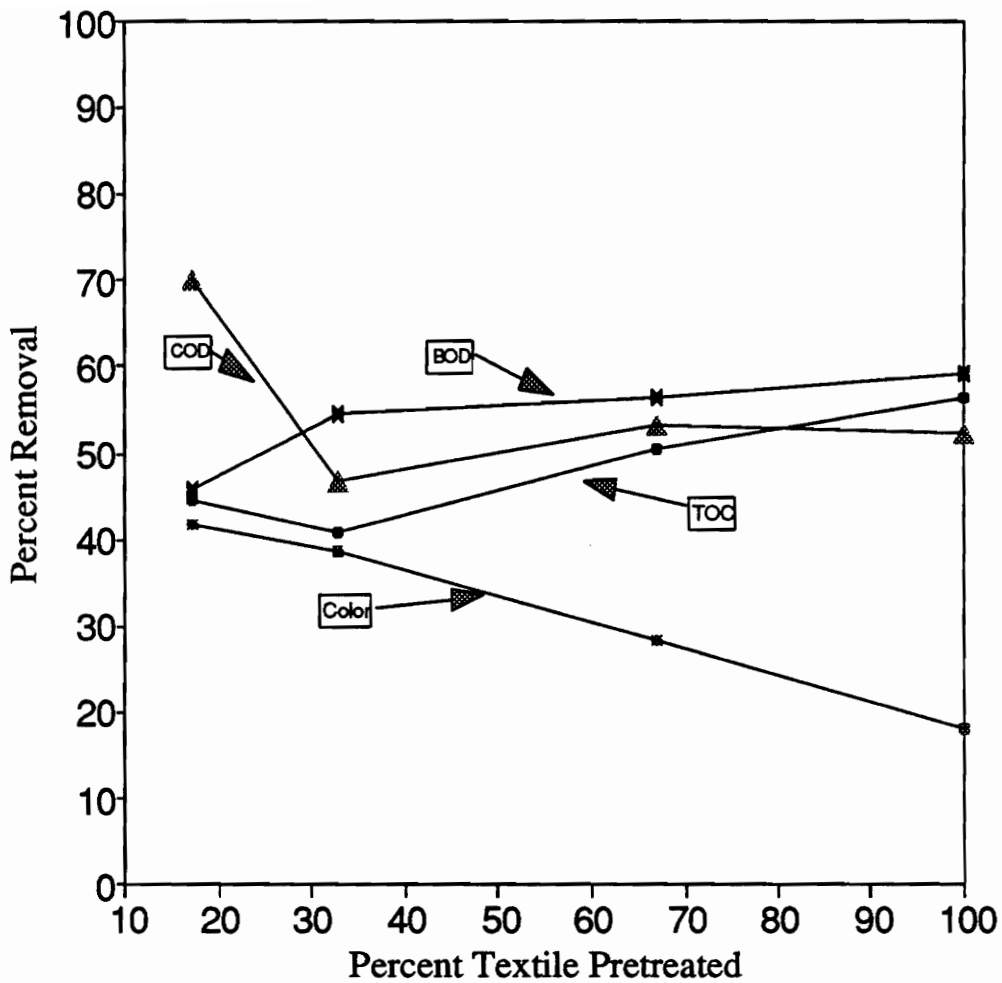
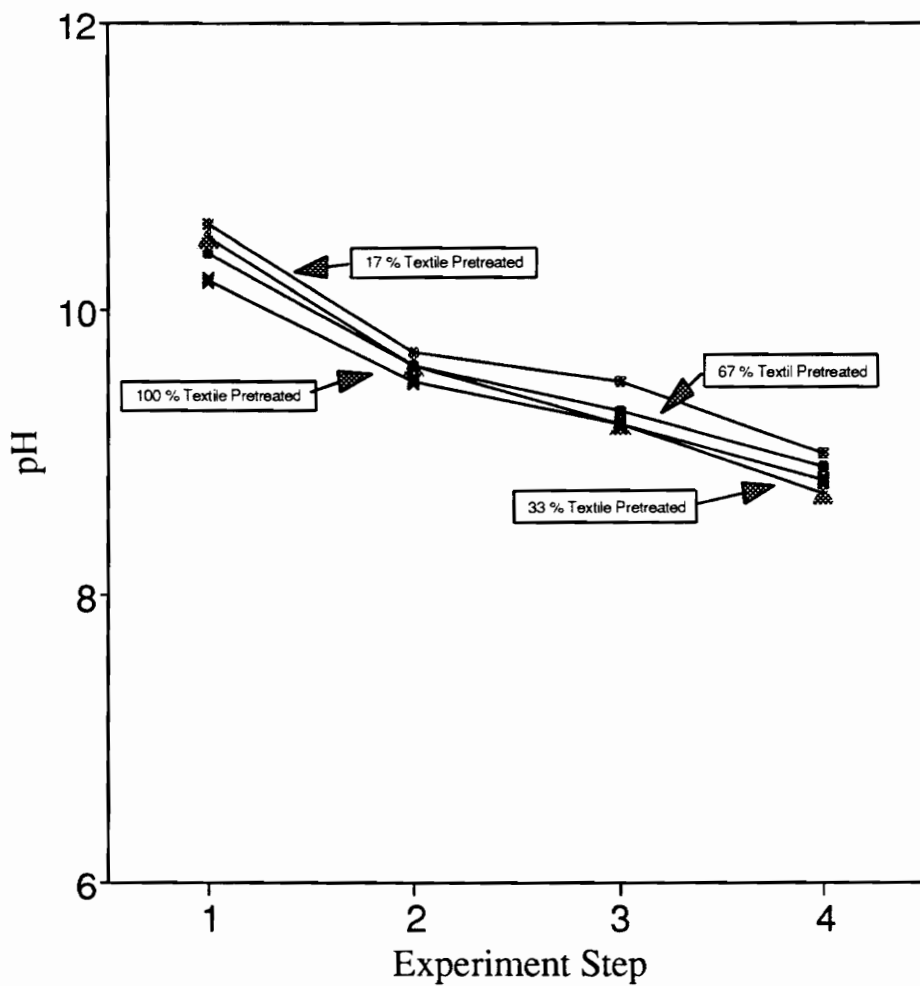


Figure 25. Biological percent removals of color, COD, TOC, and BOD for 17, 33, 67, 100 % pretreatment of the textile dye wastewater.

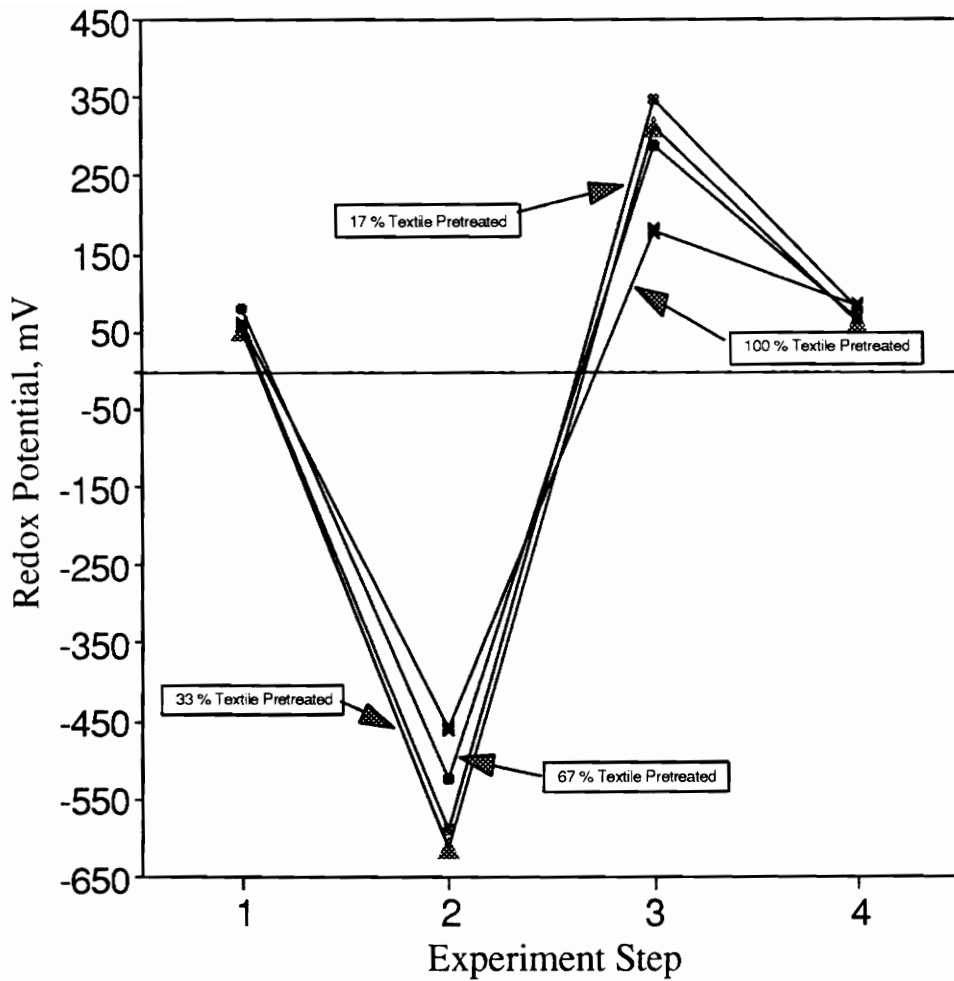
Figure 26 shows the trend of pH values after each experimental step. These results show that the pH decreased after each subsequent treatment step, but decreased little below pH 9. Although these experiments were marginally successful in treating this wastewater, the pH during the biological treatment step was relatively high with an average of pH 9.3. Generally, a pH from 6 to 9 is maintained for biological treatment; however, there are cases where activated sludge systems operate at a pH of greater than 10. Adjustments in the pH might enhance the biological treatment of the textile dye wastewater by changing the operational characteristics of reactor and by changing the speciation of the chemicals in the wastewater. The pH adjustment would result in a change in speciation that may change the toxicity of compounds within the wastewater.

Figure 27 shows the trend of the redox potential values after each experimental step. These results show that the untreated textile dye wastewater had a positive redox potential averaging +55 millivolts (mV). The pretreated portion of the textile dye wastewater, however, had a large negative redox potential, ranging from -458 mV to -611 mV. This would prevent aerobic biological activity and was one of the factors attributed to the failure of the preliminary experiments in which reduction was not combined with



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 26. The pH trend for 17, 33, 67, and 100 % pretreatment of the textile dye wastewater.



- 1 = Initial textile wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure 27. Redox potential trend for 17, 33, 67, and 100 % pretreatment of the textile dye wastewater.

oxidation. As shown in Figure 27, the redox after oxidation was positive, ranging from + 178 mV to +348 mV and was one of the reasons for the success of the reduction/oxidation pretreatment trials.

Toxicity

In this section, results from a toxicity test and from a heavy metal analysis of the textile dye wastewater will be presented.

BOD-Toxicity Test

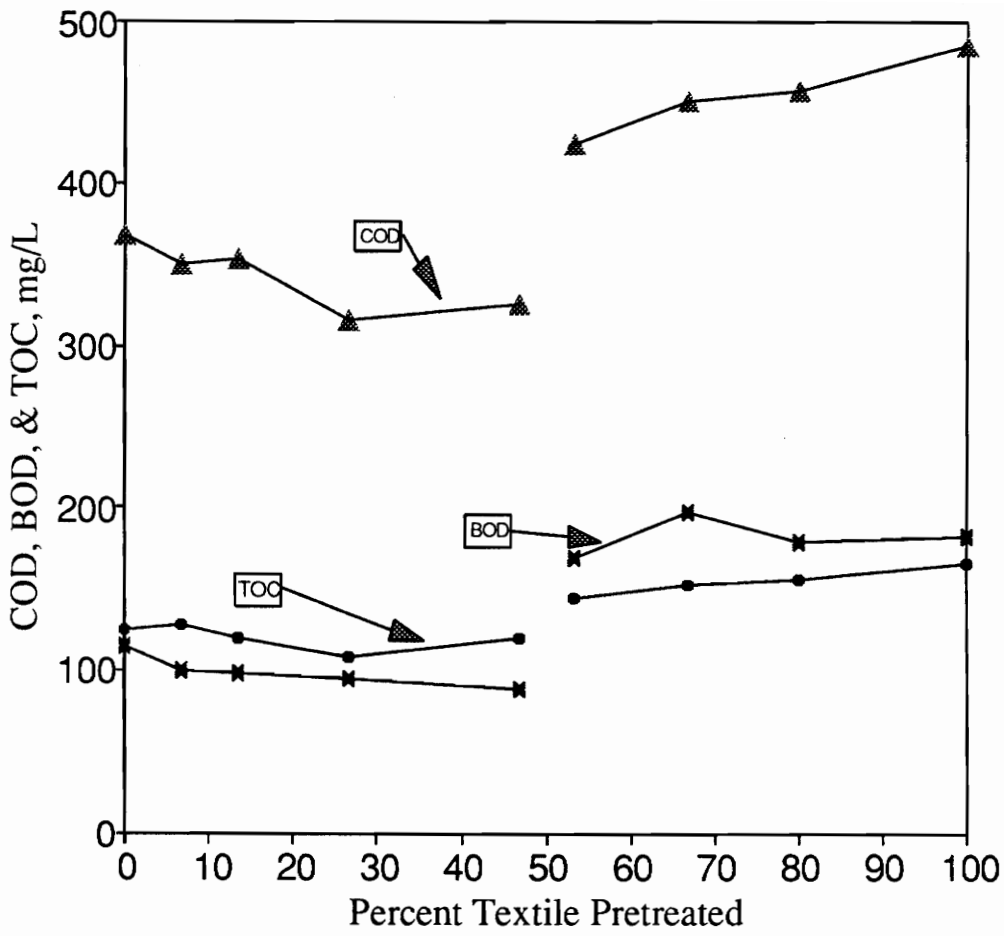
Because of the failure of the test SBR to effectively treat the hydrosulfite pretreated wastewater at the beginning of the research, the BOD test was used as a toxicity test. This toxicity test was conducted on what was the influent to the SBR (pretreated wastewater mixed with un-pretreated wastewater and municipal wastewater). The pretreatment was conducted with hydrosulfite only, no other pretreatment chemicals were added. It was conducted in the same manner as a normal five day BOD test. The results of the test, including color, COD, and TOC are shown in Table 14. Figure 28 shows the general trend of BOD, COD, and TOC. The COD ranged from 367 mg/L for zero percent pretreatment

to 485 mg/L for 100 percent pretreatment. The TOC ranged from 125 mg/L for zero percent pretreatment to 165 mg/L for 100 percent pretreatment. The BOD ranged from 114 mg/L for zero percent pretreatment to 182 mg/L for 100 percent pretreatment. An increase in BOD from 87 mg/L for 46.7 percent pretreatment to 169 mg/L for 53.3 percent pretreatment was observed. The reason for this increase may have been due to a larger portion of the wastewater being more biodegradable as more wastewater was pretreated or due to a variation in the test procedure. The test was conducted in two steps; zero to 46.7 percent pretreatment and 53.3 to 100 percent pretreatment. The TOC measurement was more precise and had less erratic results than the COD and BOD as shown in Figure 28. However, during the SBR testing of the hydrosulfite pretreated wastewater, there was no significant biological activity, suggesting toxic or inhibitory conditions.

One of the reasons why the BOD could be measured in the BOD test was due to dilution. For a range of BOD between 50 mg/L and 500 mg/L, only 5 mL or 10 mL of wastewater is added in the 300 mL BOD bottles. Therefore, there was at most 10 mL of wastewater in 290 mL of nutrient-rich dilution water suited for biological activity. This corresponds to a dilution of 1:29. In the reactor, however, there was at most a dilution of 3:8 (approximately 1:3). Therefore, if a

Table 14. BOD-Toxicity test color, COD, TOC, and BOD data.

Percent Textile Pretreated	Color ADMI	COD mg/L	BOD mg/L	TOC mg/L
0.0	2405	367	114	125
6.7	2236	350	99	127
13.3	2024	353	98	120
26.7	1838	315	95	107
46.7	1260	325	87	120
53.3	1054	425	169	144
67.0	764	451	196	153
80.0	648	458	178	155
100.0	620	485	182	165



(Break due to test being conducted in two parts)

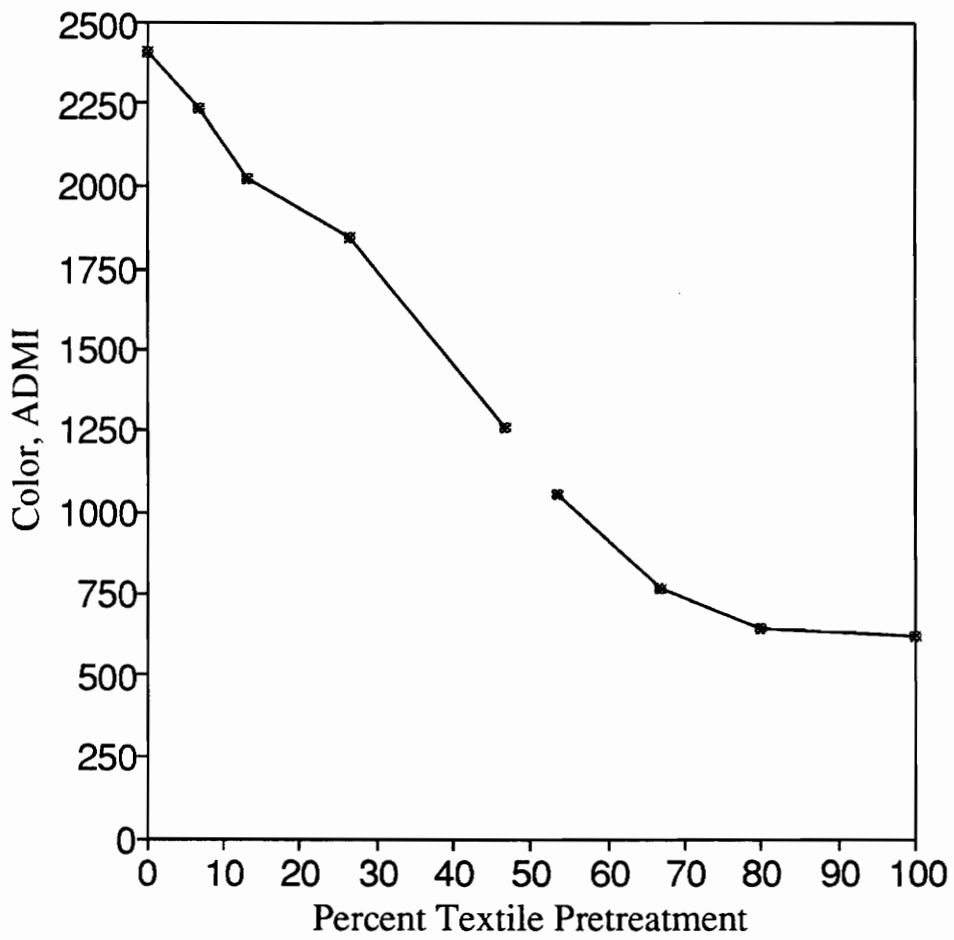
Figure 28. COD, TOC, and BOD trend during the BOD-Toxicity Test.

dilution of 1:29 could be achieved in biological treatment, reduction alone could be used to chemically remove the color from textile wastewater.

Figure 29 shows the general color trend for the BOD-Toxicity test. From Figure 29, the effluent color achieved for 100 percent pretreatment with hydrosulfite alone was greater than 600 ADMI, which suggested there was a refractory component for this particular wastewater. Recall from the reduction/oxidation section that for 100 percent pretreatment with hydrosulfite and peroxide, an effluent color of 615 ADMI was achieved.

Heavy Metal Analysis

Due to the failure of the preliminary reduction alone tests conducted early in the research and that dyes are often metal complexed, an analysis of several heavy metals was conducted. The heavy metals were analyzed at the untreated, pretreated, biological influent, and biological effluent treatment process steps. Chromium (Cr), cobalt (Co), and copper (Cu) concentrations were determined. In Table 15, the Co concentration was less than 1 ug/L, Cr was less than 8 ug/L, and Cu ranged from 7 ug/L to 50 ug/L. The 50 ug/L in the biological effluent was most likely due to buildup within the reactor. The POTW has concentrations of



(Break due to test being conducted in two parts)

Figure 29. Color trend during the BOD-Toxicity Test.

Table 15. Concentration of chromium, cobalt, and copper in the textile dye wastewater for each treatment process step.

Experiment Step	Chromium ug/L	Cobalt ug/L	Copper ug/L
Untreated dye	<DL	8	10
After reduction	1	4	7
After municipal wastewater addition	1	4	7
After Biological treatment	<DL	4	50
Level of Detection	1	0.5	1

Cr ranging from 40 ug/L to 75 ug/L and Cu ranging from 200 ug/L to 400 ug/L (Anon, 1991). The current Cu limits are 1 mg/L (1000 ug/L); however, Cu limits will be reduced to 31.5 ug/L in 1993 (Anon, 1991). Personnel at the POTW have indicated that copper removal will be a problem when the new limits go into effect. Copper is toxic to aerobic biological activity in concentrations greater than 1 mg/L and Cr (total chromium) is toxic in concentrations greater than 5 mg/L (Eckenfelder, 1980). Therefore, heavy metal toxicity was not a reason for the failure of the preliminary tests.

Additional Tests

Several tests were conducted in addition to those previously mentioned. These tests consisted of an adsorption test, an aeration test, and a test for nitrogen and phosphorus.

A simple adsorption test and aeration test was conducted on the textile wastewater stream to help determine the mechanism for color removal. The adsorption test was conducted over a pretreatment range from zero to 100 percent in 20 percent increments. This test was conducted on untreated textile wastewater, textile wastewater pretreated with hydrosulfite, and textile wastewater pretreated with

hydrosulfite and peroxide. The results from these tests indicated that there was less than 5 percent color removal that could be attributed to adsorption. This would be expected for a hydrolyzed azo dye, such as Navy 106.

A sample of untreated textile wastewater and pretreated textile wastewater was aerated for approximately 22 hours, corresponding to the aeration time during biological treatment in the SBR. These results showed there was less than 1 percent color removal that could be attributed to volatilization. This would also be expected of a hydrolyzed azo dye, such as Navy 106.

Also, TKN and TP tests were conducted on one effluent sample from the reduction-oxidation pretreatment experiments. The TKN was 3.2 mg/L and the TP was 0.2 mg/L. TKN is the combined concentration of ammonia and organic nitrogen and TP is the combined concentration of orthophosphate and organic phosphate. The availability of the nitrogen (NH_4^+) and phosphorus (PO_4^{3-}) was not determined. Therefore, although it appeared that nitrogen and phosphorus were not limiting, they may in fact be limiting.

Cost Comparison

A cost comparison was conducted between the reduction-oxidation pretreatment technique and the polymer, a quaternary amine) currently used at the POTW. This comparison included only the cost of the pretreatment chemicals and the polymer. The cost of the polymer was obtained from personnel at the POTW and the reduction-oxidation chemical costs were obtained from the Chemical Marketing Reporter (1990).

Although no testing was conducted using thiourea dioxide and hydrogen peroxide or sodium borohydride and hydrogen peroxide, it was assumed for this comparison that the same concentration of hydrogen peroxide from the hydrosulfite-hydrogen peroxide test would be used. The cost of each chemical is shown in Table 16. Figure 30 shows the costs for pretreating one million gallons of textile dye wastewater per day. The majority of the cost associated with reduction-oxidation is the cost of the reducing agent. Sodium borohydride is most-likely cost prohibitive to use. Thiourea is approximately twice as costly at \$2.00 per pound as hydrosulfite (\$0.62 per pound). The polymer costs \$1000 per day to treat 7 MGD. The cost of hydrosulfite-peroxide pretreatment is \$1600 per 1 MGD. Polymer addition is currently achieving a final color value of less than 250

ADMI (Anon, 1991), where as pretreatment with hydrosulfite-peroxide only achieved approximately 600 ADMI. Because the polymer is added to the 7 MGD entering the POTW, the reduction/oxidation tests were performed on only the Mill's wastewater, and that the Mill only produces 3 MGD of wastewater, a direct cost comparison cannot be made.

Table 16. Chemical costs for the reducing and oxidizing agents used in the pretreatment of the textile dye wastewater.

Pretreatment Chemical	Cost \$/lb	Conc. ppm	Cost of Peroxide \$/MGD	Total Chemical Cost \$/MGD
Oxidant:				
Peroxide	0.25	150	313	-----
Reductants:				
Hydrosulfite	0.62	225	313	1476
Thiourea	2.00	225	313	4066
Borohydride	18.30	150	313	23206

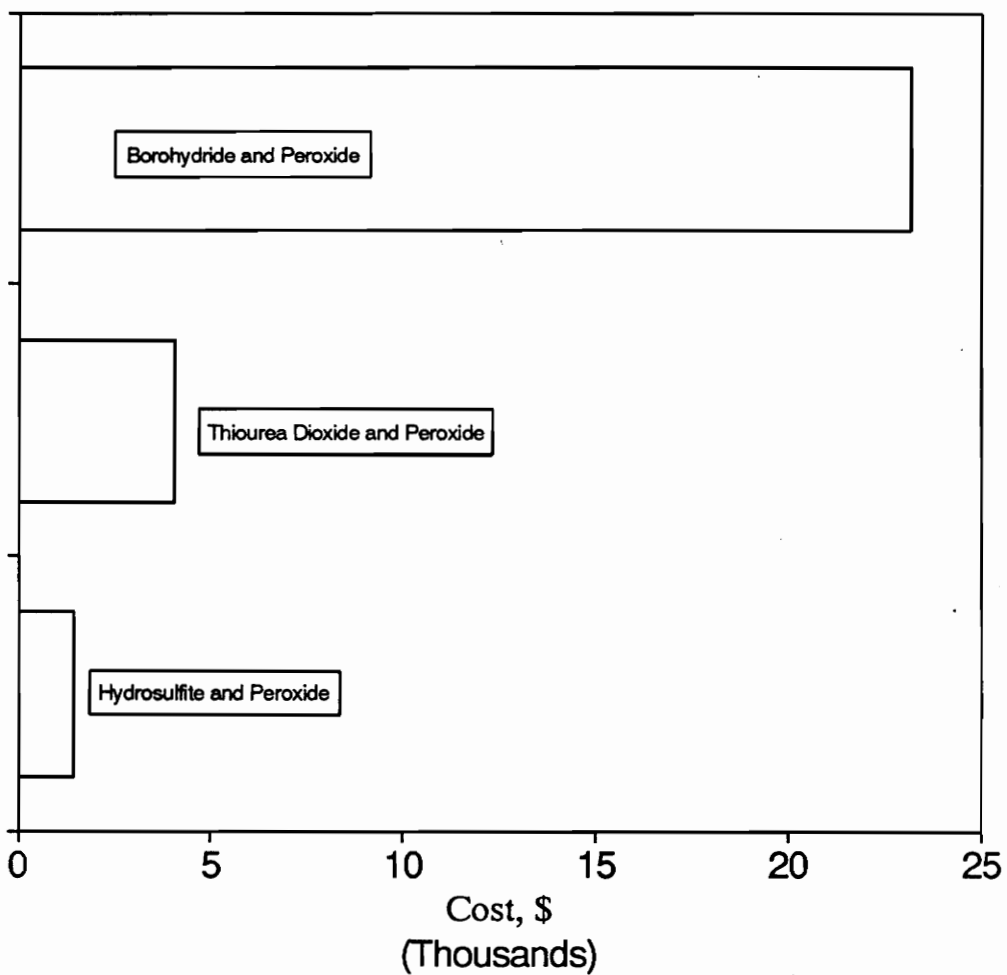


Figure 30. Chemical cost comparison between reduction-oxidation pretreatment chemicals.

CONCLUSIONS

Summary of Results

The focus of this research was to determine the feasibility of pretreating a textile dye wastewater with reducing agents prior to aerobic biological treatment. Therefore, the reduced wastewater had to be susceptible to aerobic biodegradation. Reduction with a variety of reducing agents was effective in color removal, but the resulting wastewater was not aerobically biologically treatable. However, reduction followed by oxidation as a pretreatment method was effective in color removal and biodegradability.

Conclusions

The following conclusions can be made regarding chemical pretreatment of the textile wastewater considered in this study with reducing agents:

1. The addition of hydrosulfite, thiourea dioxide, and sodium borohydride to the textile wastewater resulted

in a reduction in color that did not re-colorize upon exposure to air or addition of oxidizing agent.

2. Addition of reducing agents (hydrosulfite, thiourea, and borohydride) to the reactive azo dye wastewater achieved a color removal of 11 percent when pretreating 17 percent whereas hydrosulfite achieved 62 percent color removal when pretreating 100 percent of the textile dye wastewater.

The following conclusion can be made regarding biological treatment of the non-pretreated textile wastewater considered in this study:

3. There was a residual, non-biodegradable, refractory component associated with the untreated textile wastewater that limited the efficiency of total color, COD, BOD, and TOC removals to 48 %, 43 %, 38%, and 50 %, respectively.

The following conclusions can be made regarding chemical pretreatment of the textile wastewater considered in this study followed by biological treatment:

4. The reduction in color achieved by the addition of the reducing agents resulted in a biologically inhibitory environment possibly due to unreacted reducing agent, creation of a reduced environment, or reduction by-products.
5. The addition of 150 ppm hydrogen peroxide after the addition of 225 ppm hydrosulfite resulted in an oxidized environment conducive to aerobic biological treatment resulting in effluent values of 615 ADMI color, 310 mg/L COD , 82 mg/L TOC , and 62 mg/L BOD.
6. There appeared to be a residual, nonbiodegradable, refractory component associated with the textile wastewater that limited the total percent removals of color, COD, BOD, and TOC to 77 %, 60 %, 61 %, and 66 %, respectively.

Recommendations

The following are recommendation that can be made regarding chemical pretreatment of the textile wastewater followed by biological treatment.

1. More rigorous testing should be conducted to optimize the amount of hydrosulfite and hydrogen peroxide added to remove color from the textile wastewater, but still maintain aerobic biodegradability.
2. Testing should be conducted to determine if different reducing and oxidizing agent combinations are viable alternatives for the removal of color from reactive azo dye wastewater.
3. Testing should be conducted to explore the chemistry, concentration, and toxicity of compounds contained in the untreated textile wastewater, the by-products of reduction, the by-products of oxidation after reduction, and the compounds after aerobic biological treatment.
4. Testing should be conducted to determine if oxidation alone is a viable alternative for color removal of wastewater containing reactive azo dyes.
5. Testing should be conducted to determine if anaerobic biological treatment is a viable replacement of aerobic biological treatment, thus eliminating the need for an oxidizing agent.

6. Testing should be conducted utilizing other wastewater treatment alternatives, such as powder activated carbon and foam separation.

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APPENDIX A

ADMI COLOR MEASUREMENT PROCEDURE

Calibration of Instrument

1. Prepare color standards from stock APHA solution.
2. Using distilled water in the reference cell and the color standard in the sample cell, determine the percent transmittance at the following wavelengths:

$$T1 = 590 \text{ nm}, T2 = 540 \text{ nm}, T3 = 438 \text{ nm}.$$

3. Calculate the intermediate tristimulus value for each standard using the following equations:

$$\begin{aligned} \text{Red: } X_s &= (T3 * 0.1899) + (T1 * 0.791) \\ \text{Green: } Y_s &= T2 \\ \text{Blue: } Z_s &= (T3 * 1.1835) \end{aligned}$$

4. Convert the tristimulus values to corresponding Munsell values V_x , V_y , and V_z by use of a Munsell Table.
5. Calculate DE values for each standard using the following equation:

$$DE = \left[\left[0.23 * (V_{yc} - V_y) \right]^2 + \left[(V_{xs} - V_{yc}) - (V_x - V_y) \right]^2 + \left[0.4 * [(V_{yc} - V_{zc}) - (V_y - V_z)] \right]^2 \right]^{0.5}$$

where: V_{xc} , V_{yc} , V_{zc} are Munsell values for the distilled water blanks
 V_x , V_y , V_z are Munsell values for the sample

6. Calculate the calibration factor for each standard using the following equation:

$$F_n = (APHA)_n * b / (DE)_n$$

where: $(APHA)_n$ is the APHA color value for standard n
 $(DE)_n$ is the DE for standard n
 b is the cell path in cm

7. Average the calibration factors for each standard.

Sample Color Measurement

1. Adjust the pH of a sample to 7.6 using sulfuric acid or sodium hydroxide.
2. Filter the sample three times through a washed glass fiber filter.
3. Dilute sample to be within the color range calibrated for above, if necessary.
4. Using distilled water in the reference cell and the color standard in the sample cell, determine the percent transmittance at the following wavelengths:
T1 = 590 nm, T2 = 540 nm, T3 = 438 nm.
5. Calculate the intermediate tristimulus value for each standard using the following equations:
Red: $X_s = (T_3 * 0.1899) + (T_1 * 0.791)$
Green: $Y_s = T_2$
Blue: $Z_s = (T_3 * 1.1835)$
6. Convert the tristimulus values to corresponding Munsell values V_x , V_y , and V_z by use of a Munsell Table.
7. Calculate DE values for each standard using the following equation:
$$DE = \left[\left[0.23 * (V_{yc} - V_y) \right]^2 + \left[(V_{xs} - V_{yc}) - (V_x - V_y) \right]^2 + \left[0.4 * [(V_{yc} - V_{zc}) - (V_y - V_z)] \right]^2 \right]^{0.5}$$

where: V_{xc} , V_{yc} , V_{zc} are Munsell values for the distilled water blanks
 V_x , V_y , V_z are Munsell values for the sample
8. Calculate ADMI color value by the following equation or use plot of DE vs ADMI, such as Figure A-1:
 $ADMI = (F) * (DE) / b$
9. Repeat this procedure at the normal sample pH.
10. Report both color numbers and the corresponding pH.

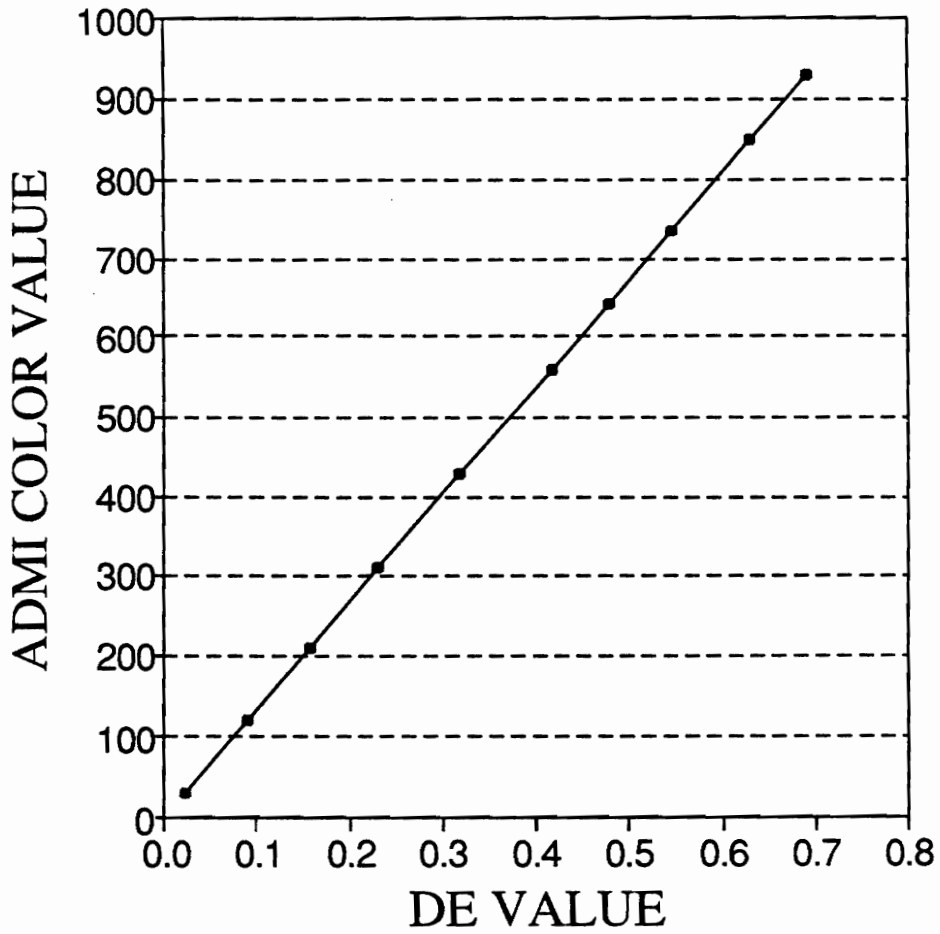


Figure A-1. Calibration curve: plot of DE vs ADMI.

APPENDIX B

CHROMATICITY GRAPH

The most frequently used color measurement system was developed by the CIE (International Congress on Color) as shown in Figure B-1 (Tannas, 1985). "This system is based upon three artificial primaries, X, Y, and Z, which are approximately equal to red, green, and blue, respectively...it is necessary to plot only two of these coefficients to characterize the color..." (Tannas, 1985). Since the graph bounds all visible colors, any three wavelengths from approximately 380 nm to 780 nm will specify any color within the triangle created by those three points.

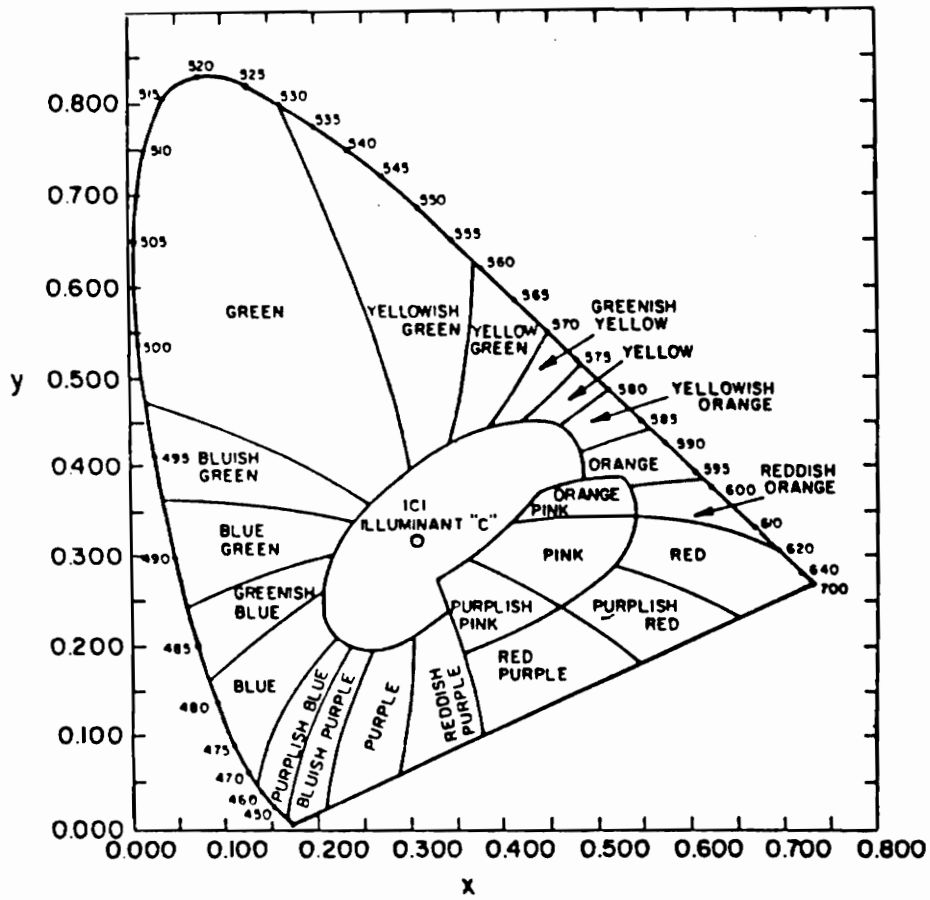


Figure B-1. Chromaticity Graph.

APPENDIX C

PRELIMINARY TEST DATA

APPENDIX C-1

REDUCTION WITH HYDROSULFITE

Table C-1a. Wastewater characteristics for 100 % pretreatment with hydrosulfite alone.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2950	235	190	185
COD mg/L	780	800	650	625
TOC mg/L	217	225	204	200
BOD mg/L	154	-----	145	143
TSS mg/L	27	-----	34	67
COLOR (2)	3130	250	200	200
pH	10.9	10.7	9.5	9.2
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	2950	-----	2230	1460
COD mg/L	800	-----	665	265
TOC mg/L	220	-----	214	132
BOD mg/L	150	-----	124	78
TSS mg/L	25	-----	32	67
COLOR (2)	3120	-----	2365	1545
pH	10.2	-----	9.9	9.1
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

WW = Wastewater

Table C-1b. Wastewater characteristics for 17 % pretreatment with hydrosulfite alone.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2000	1785	1435	1365
COD mg/L	865	880	710	630
TOC mg/L	280	284	269	265
BOD mg/L	179	179	165	160
TSS mg/L	27	-----	30	75
COLOR (2)	2120	1890	1520	1440
pH	10.8	10.6	9.5	9.3
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	2000	-----	1570	1045
COD mg/L	890	-----	715	335
TOC mg/L	279	-----	247	168
BOD mg/L	165	-----	158	100
TSS mg/L	34	-----	37	67
COLOR (2)	2100	-----	1500	1450
pH	10.4	-----	9.5	9.1
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

WW = Wastewater

APPENDIX C-2

REDUCTION WITH THIOUREA DIOXIDE

Table C-2. Wastewater characteristics for 17 % pretreatment with thiourea dioxide alone.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	1475	1310	1020	955
COD mg/L	645	650	575	535
TOC mg/L	232	235	210	208
BOD mg/L	126	-----	99	98
TSS mg/L	29	-----	30	80
COLOR (2)	1555	1380	1090	1010
pH	10.4	9.8	9.4	9.1
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	1475	-----	1090	725
COD mg/L	650	-----	634	260
TOC mg/L	225	-----	200	122
BOD mg/L	125	-----	110	66
TSS mg/L	30	-----	33	
COLOR (2)	1565	-----	1150	775
pH	10.3	-----	9.9	9.3
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

WW = Wastewater

APPENDIX C-3

REDUCTION WITH SODIUM BOROHYDRIDE

Table C-3. Wastewater characteristics for 17 % pretreatment with borohydride alone.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	1250	1115	850	815
COD mg/L	450	465	400	370
TOC mg/L	132	134	111	110
BOD mg/L	103	-----	98	97
TSS mg/L	24	-----	25	75
COLOR (2)	1325	1180	900	870
pH	10.3	9.6	9.3	9
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	1250	-----	945	625
COD mg/L	450	-----	410	180
TOC mg/L	122	-----	113	111
BOD mg/L	87	-----	80	79
TSS mg/L	20	-----	23	70
COLOR (2)	1315	-----	1000	666
pH	10.1	-----	9.8	9.1
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

WW =Wastewater

APPENDIX C-4

REDUCTION WITH HYDROSULFITE WITH pH ADJUSTMENT

Table C-4. Wastewater characteristics for 17 % pretreatment with hydrosulfite and pH adjustment.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2800	2465	1910	1850
COD mg/L	985	990	800	755
TOC mg/L	287	290	266	260
BOD mg/L	168	168	153	147
TSS mg/L	24	-----	25	75
COLOR (2)	2955	2610	2020	1965
pH	10.3	7.4	7.8	7.5
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	2800	-----	2185	1550
COD mg/L	990	-----	810	345
TOC mg/L	285	-----	270	153
BOD mg/L	165	-----	155	78
TSS mg/L	20	-----	23	70
COLOR (2)	2950	-----	1280	1660
pH	10.3	-----	9.8	9.1
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.
 2 = ADMI color at normal sample pH.
 WW = Wastewater

APPENDIX C-5

REDUCTION WITH HYDROSULFITE WITH NUTRIENT ADDITION

Table C-5. Wastewater characteristics for 17 % pretreatment with hydrosulfite and nutrient addition.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	1450	1265	1000	960
COD mg/L	575	580	510	485
TOC mg/L	146	150	128	125
BOD mg/L	122	122	103	100
TSS mg/L	24	-----	25	75
COLOR (2)	1550	1335	1050	1020
pH	10.4	9.7	9.2	8.9
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	1450	-----	1135	765
COD mg/L	560	-----	515	205
TOC mg/L	155	-----	142	93
BOD mg/L	132	-----	121	65
TSS mg/L	20	-----	23	70
COLOR (2)	1565	-----	1200	825
pH	10.3	-----	9.8	9.2
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.
 2 = ADMI color at normal sample pH.
 WW = Wastewater

APPENDIX C-6

**REDUCTION WITH HYDROSULFITE WITH pH ADJUSTMENT
AND NUTRIENT ADDITION**

Table C-6. Wastewater characteristics for 17 % pretreatment with hydrosulfite with pH adjustment and nutrient addition.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	1450	1280	1025	1000
COD mg/L	560	558	510	485
TOC mg/L	138	136	126	122
BOD mg/L	132	132	124	119
TSS mg/L	24	-----	25	75
COLOR (2)	1565	1386	1087	1035
pH	10.4	7.3	7.9	7.7
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	1450	-----	1105	760
COD mg/L	555	-----	513	205
TOC mg/L	134	-----	124	83
BOD mg/L	132	-----	121	59
TSS mg/L	20	-----	23	70
COLOR (2)	1540	-----	1175	800
pH	10.4	-----	9.9	9.2
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

WW = Wastewater

APPENDIX C-7

REDUCTION WITH HYDROSULFITE WITH LIME ADDITION

Table C-7. Wastewater characteristics for 17 % pretreatment with hydrosulfite and lime addition.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER REDUCTION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2800	2455	1890	1835
COD mg/L	990	993	800	715
TOC mg/L	287	290	277	270
BOD mg/L	194	194	179	175
TSS mg/L	24	-----	25	75
COLOR (2)	2960	2600	2000	1955
pH	10.4	9.9	9.6	9.4
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	2800	-----	1135	765
COD mg/L	985	-----	805	300
TOC mg/L	290	-----	266	164
BOD mg/L	188	-----	158	74
TSS mg/L	20	-----	23	70
COLOR (2)	2975	-----	1190	815
pH	10.3	-----	9.8	9.2
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

WW = Wastewater

APPENDIX C-8

OXIDATION WITH HYDROGEN PEROXIDE

Table C-8. Wastewater characteristics for 100 % pretreatment with hydrogen peroxide alone.

WASTEWATER PARAMETER	INITIAL TEXTILE	AFTER OXIDATION	AFTER MUNICIPAL WW ADDITION	AFTER SBR TREATMENT
TEST REACTOR				
COLOR (1)	2650	2650	2090	1720
COD mg/L	760	765	675	486
TOC mg/L	200	202	174	120
BOD mg/L	170	-----	145	110
TSS mg/L	24	-----	25	75
COLOR (2)	2800	2800	2000	1855
pH	10.2	9.6	9.3	9
REDOX mV	-----	-----	-----	-----
CONTROL REACTOR				
COLOR (1)	2660	-----	2100	1540
COD mg/L	785	-----	680	360
TOC mg/L	190	-----	176	92
BOD mg/L	178	-----	166	78
TSS mg/L	20	-----	23	70
COLOR (2)	2855	-----	2350	1670
pH	10.2	-----	9.5	9.1
REDOX mV	-----	-----	-----	-----

1 = ADMI color at pH 7.6.

2 = ADMI color at normal sample pH.

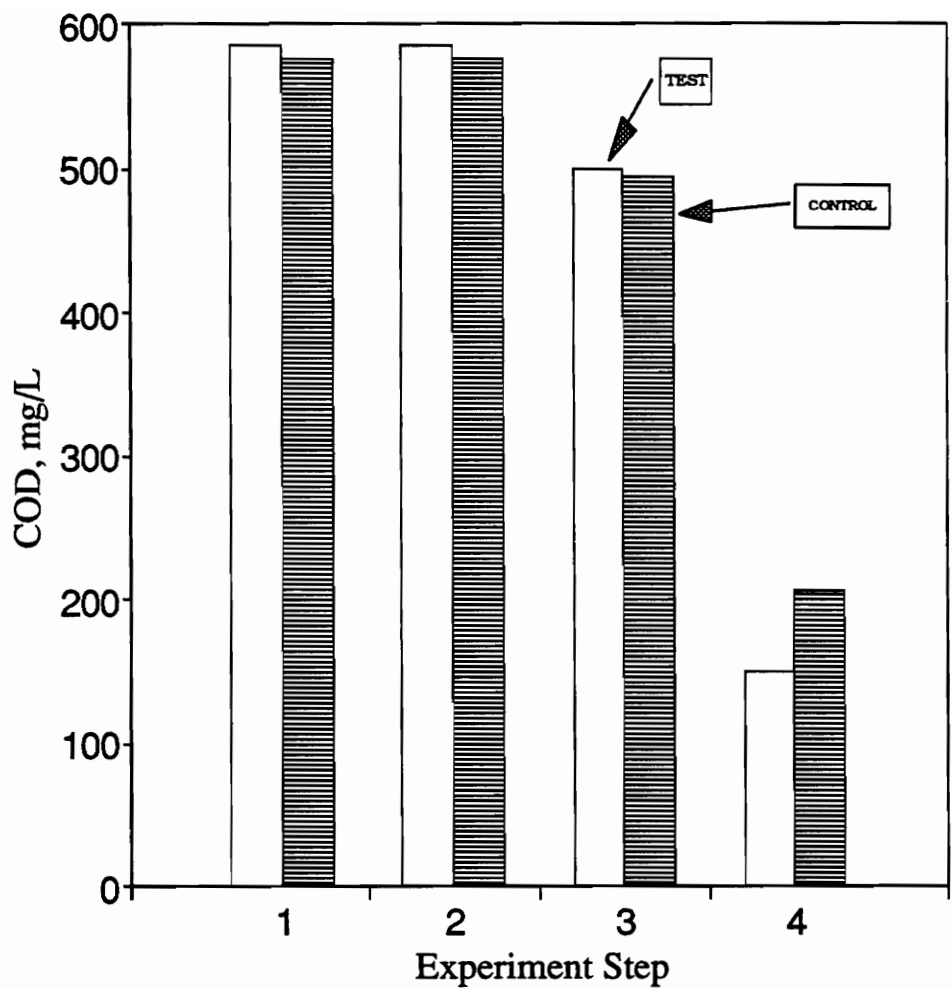
WW = Wastewater

APPENDIX D

HYDROSULFITE REDUCTION WITH HYDROGEN PEROXIDE OXIDATION

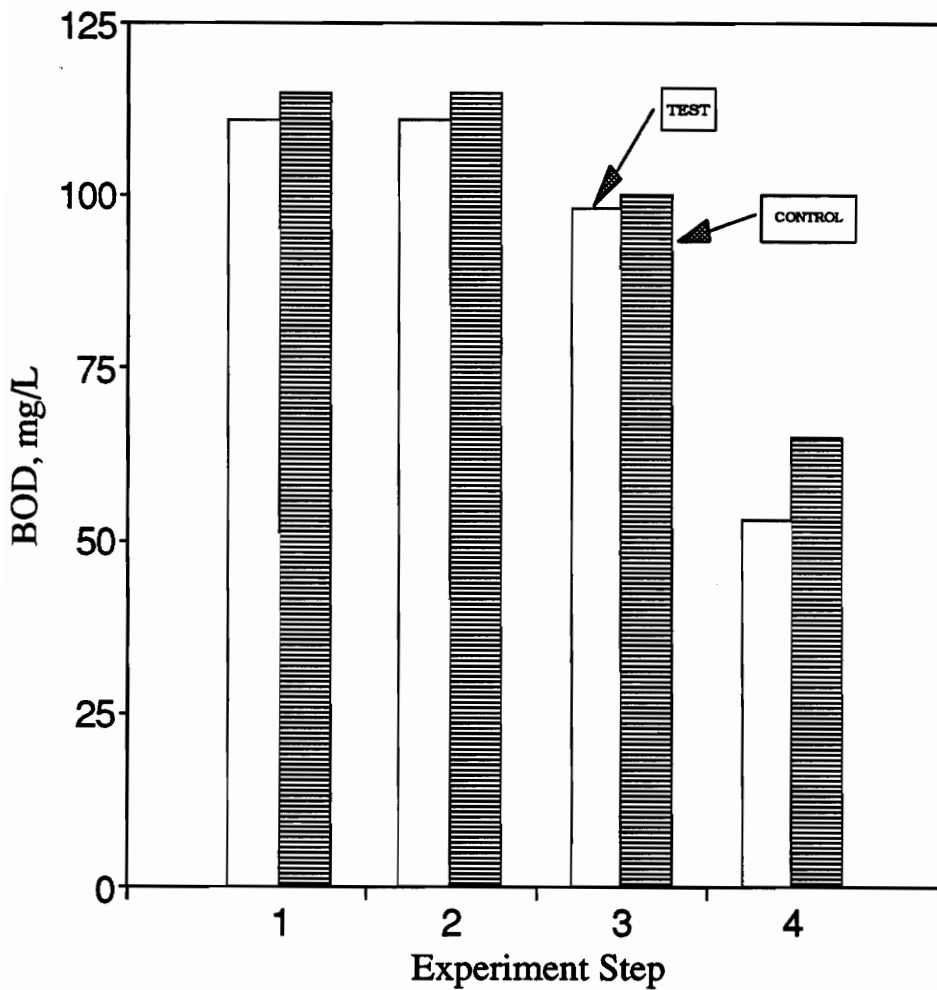
APPENDIX D-1

17 & TEXTILE DYE WASTEWATER PRETREATED



- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-1a. Relationship between test (17 % pretreated) and control reactor performance for COD removal.

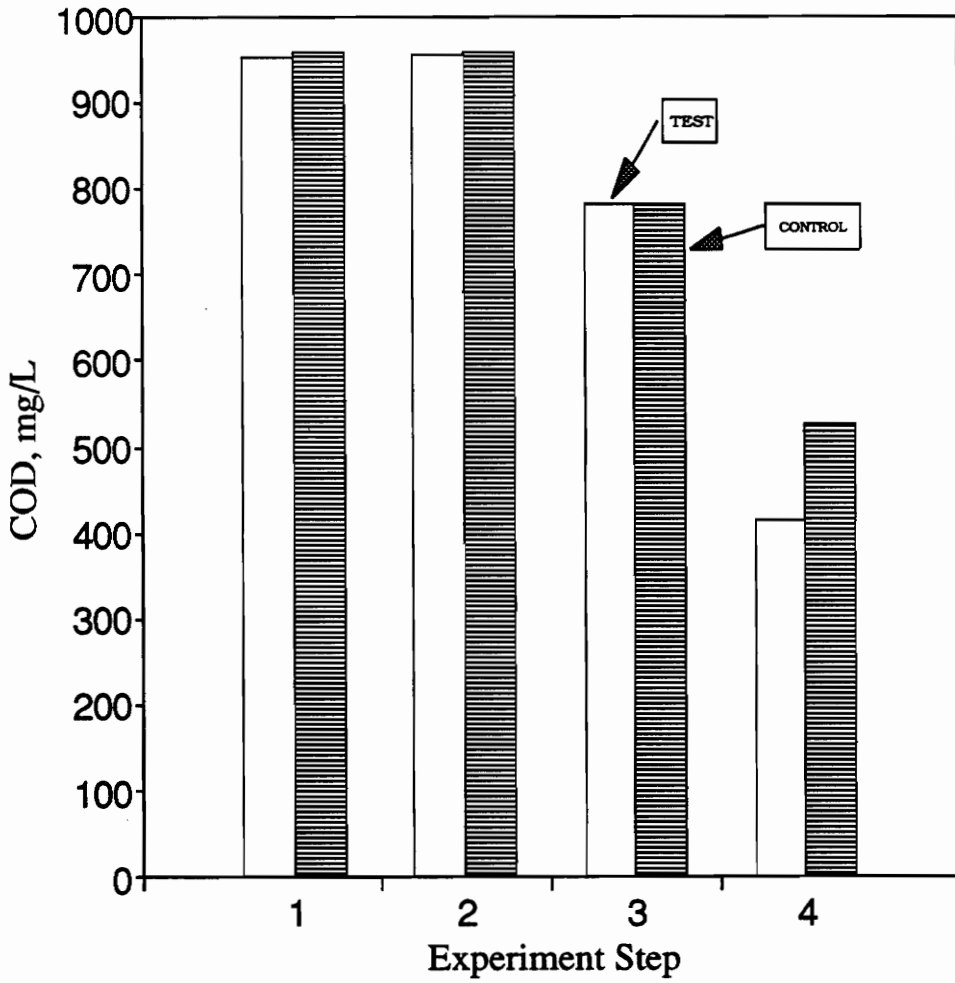


- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-1b. Relationship between test (17 % pretreated) and control reactor performance for BOD removal.

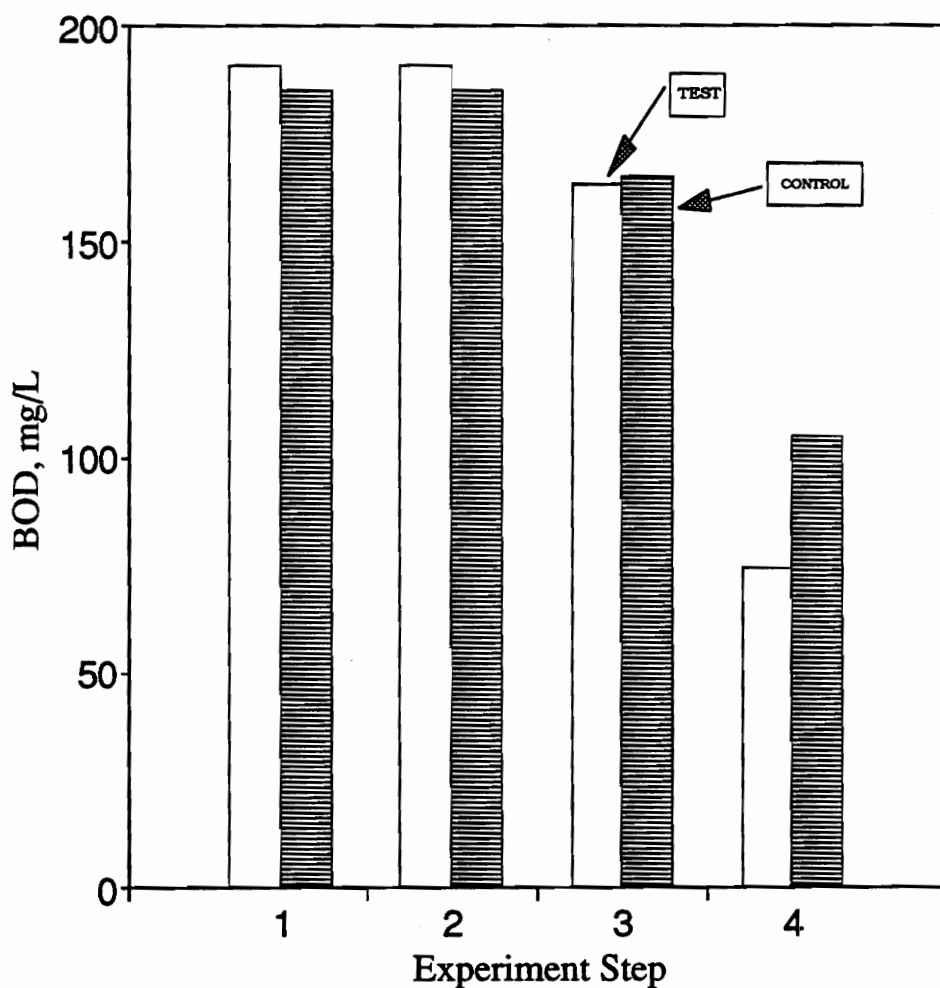
APPENDIX D-2

33 % TEXTILE DYE WASTEWATER PRETREATED



- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-2a. Relationship between test (33 % pretreated) and control reactor performance for COD removal.

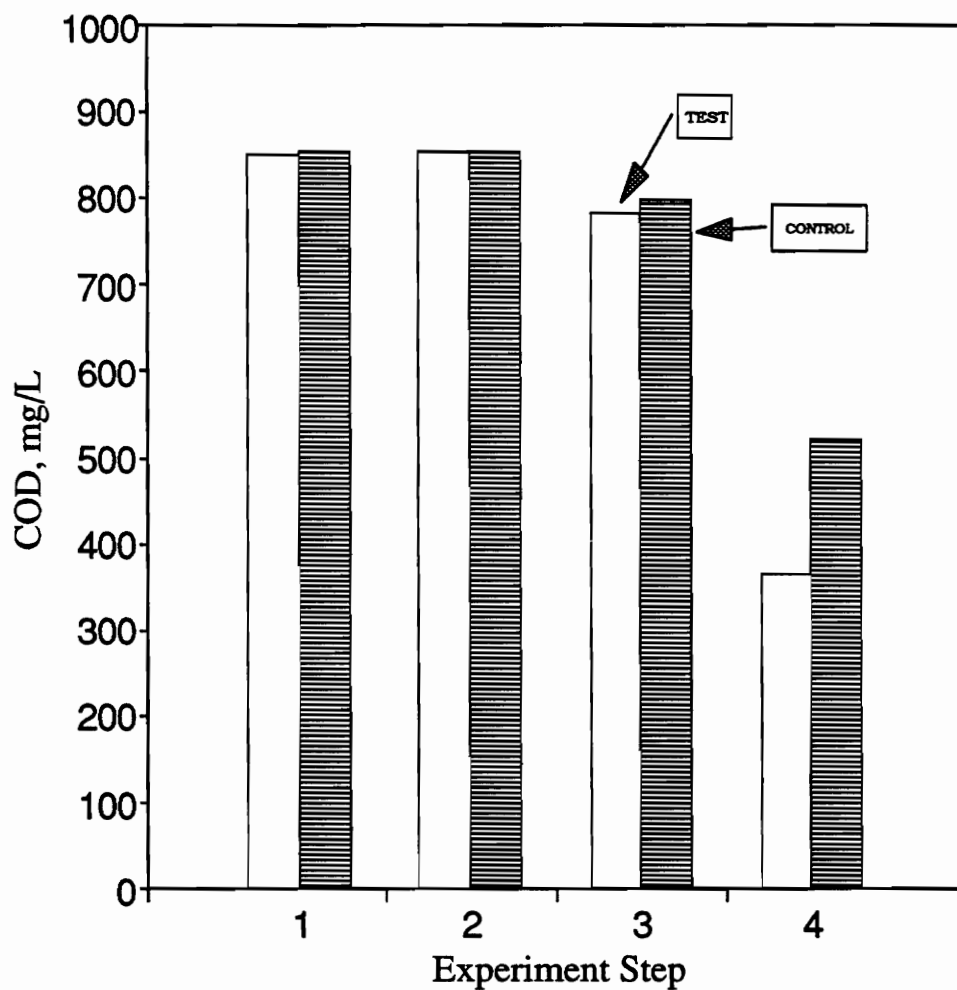


- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-2b. Relationship between test (33 % pretreated) and control reactor performance for BOD removal.

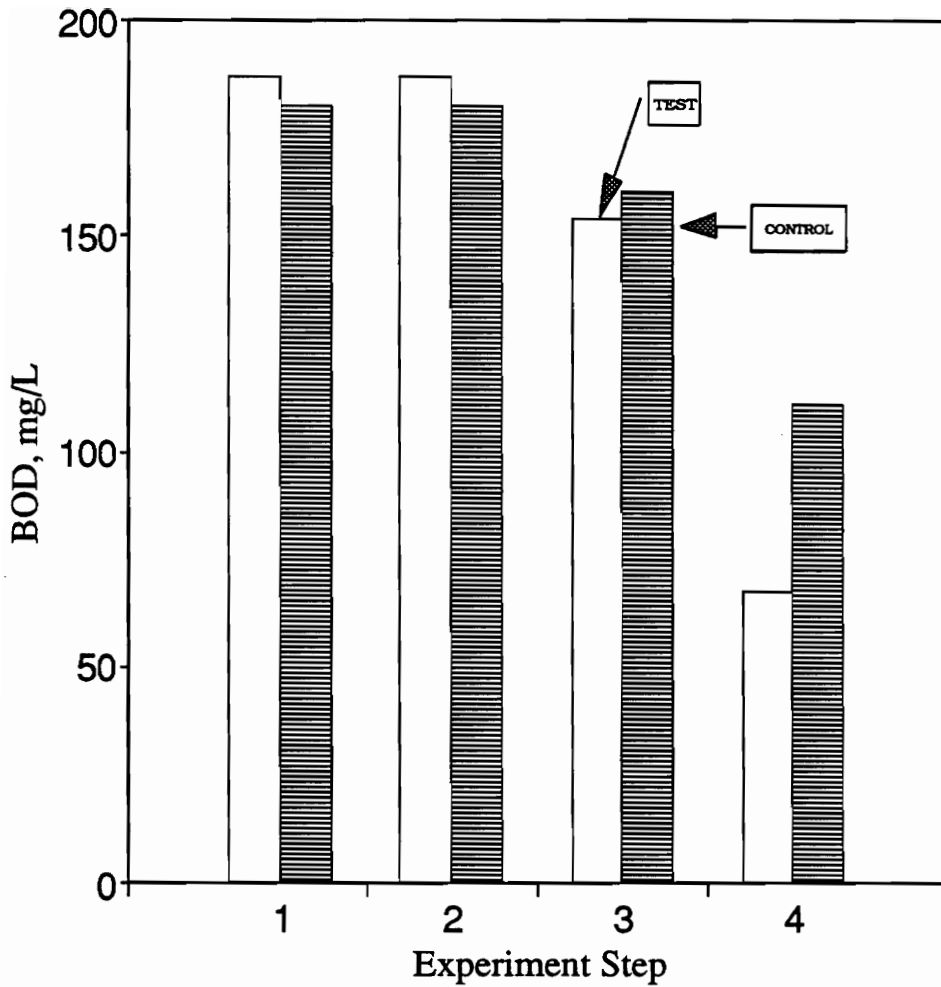
APPENDIX D-3

67 % TEXTILE DYE WASTEWATER PRETREATED



- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-3a. Relationship between test (67 % pretreated) and control reactor performance for COD removal.

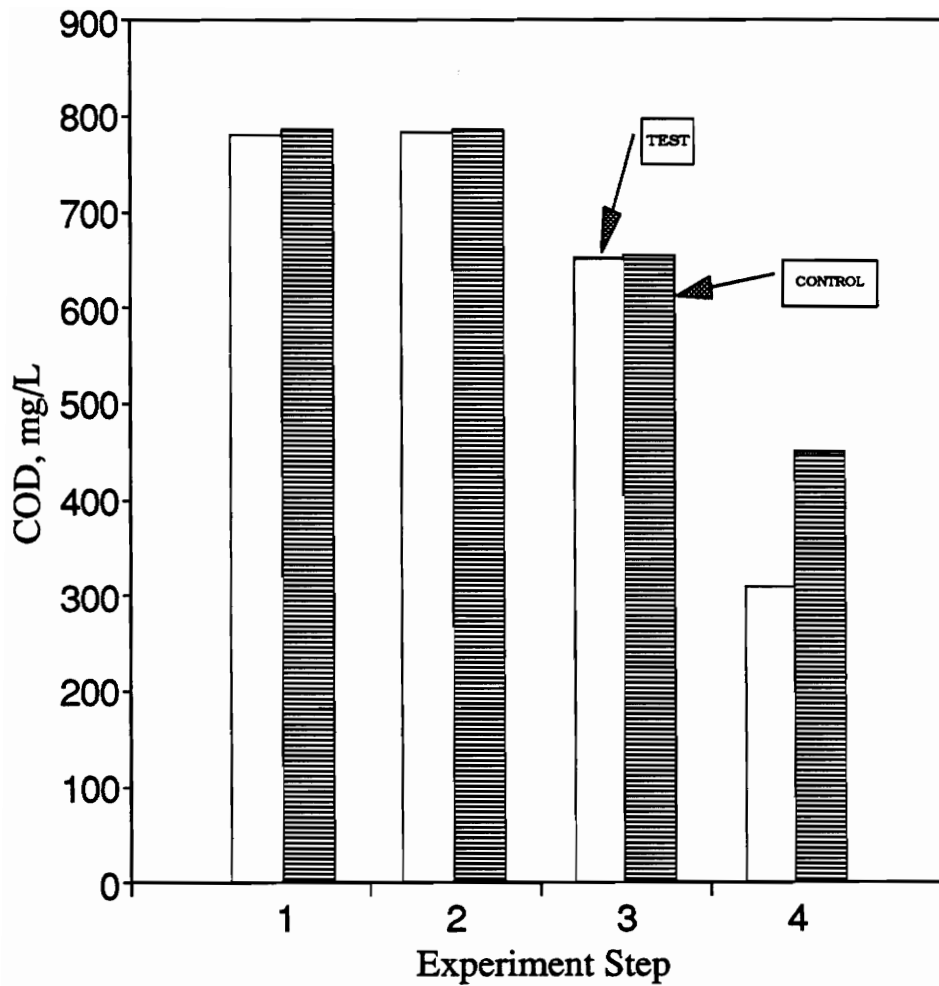


- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-3b. Relationship between test (67 % pretreated) and control reactor performance for BOD removal.

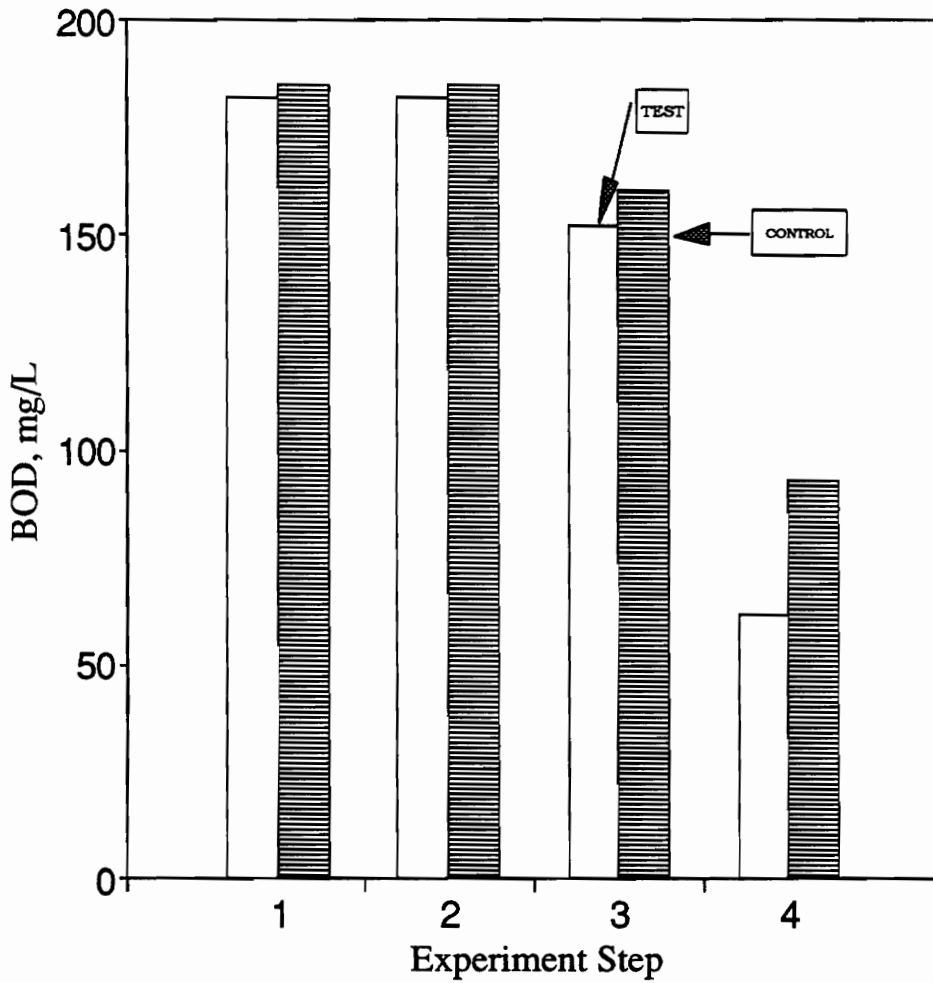
APPENDIX D-4

100 % TEXTILE DYE WASTEWATER PRETREATED



- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-4a. Relationship between test (100 % pretreated) and control reactor performance for COD removal.



- 1 = Initial, untreated textile dye wastewater.
- 2 = After reduction.
- 3 = After oxidation and municipal wastewater addition.
- 4 = After batch biological treatment.

Figure D-4b. Relationship between test (100 % pretreated) and control reactor performance for BOD removal.

APPENDIX E

ADMI COLOR VS REDUCING AGENT CONCENTRATION

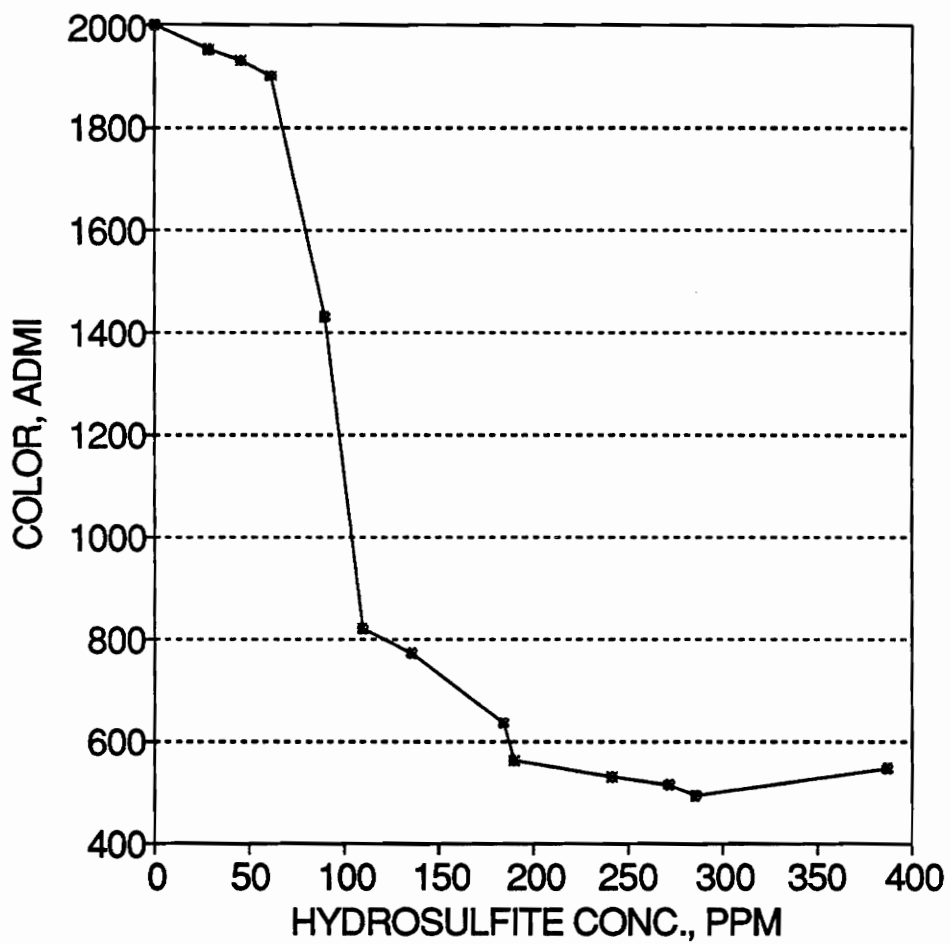


Figure E-1. Color vs hydrosulfite concentration.

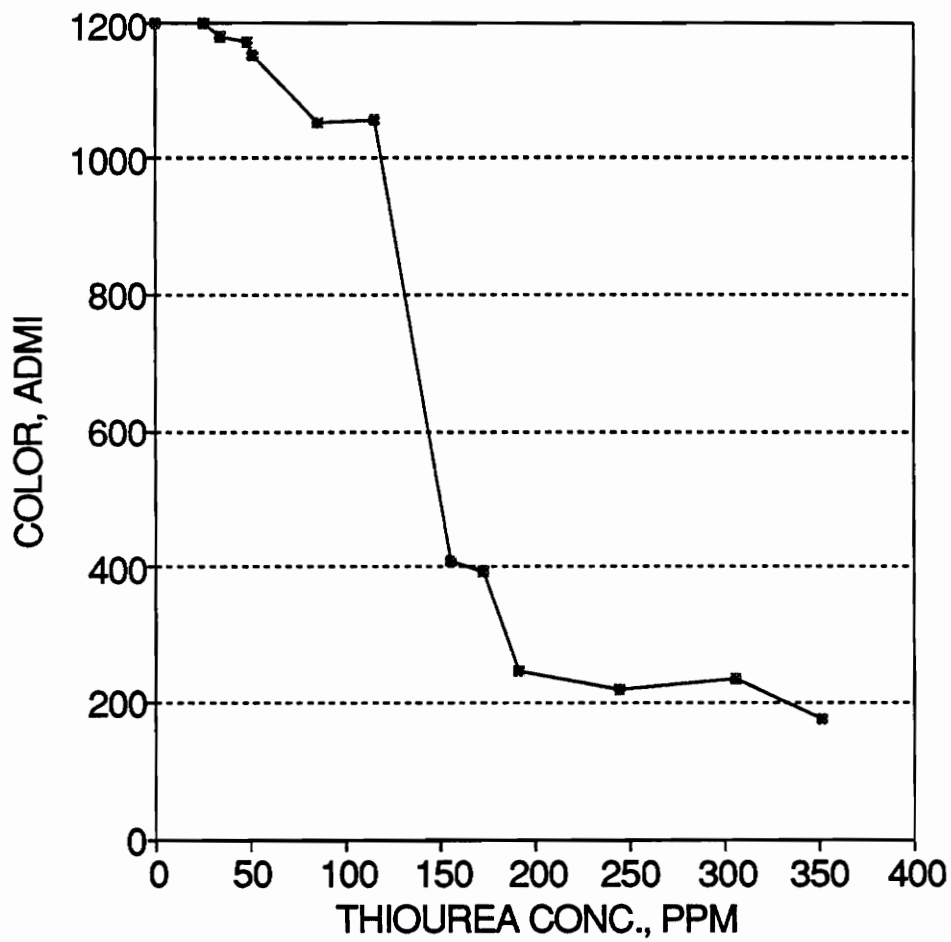


Figure E-2. Color vs thiourea dioxide concentration.

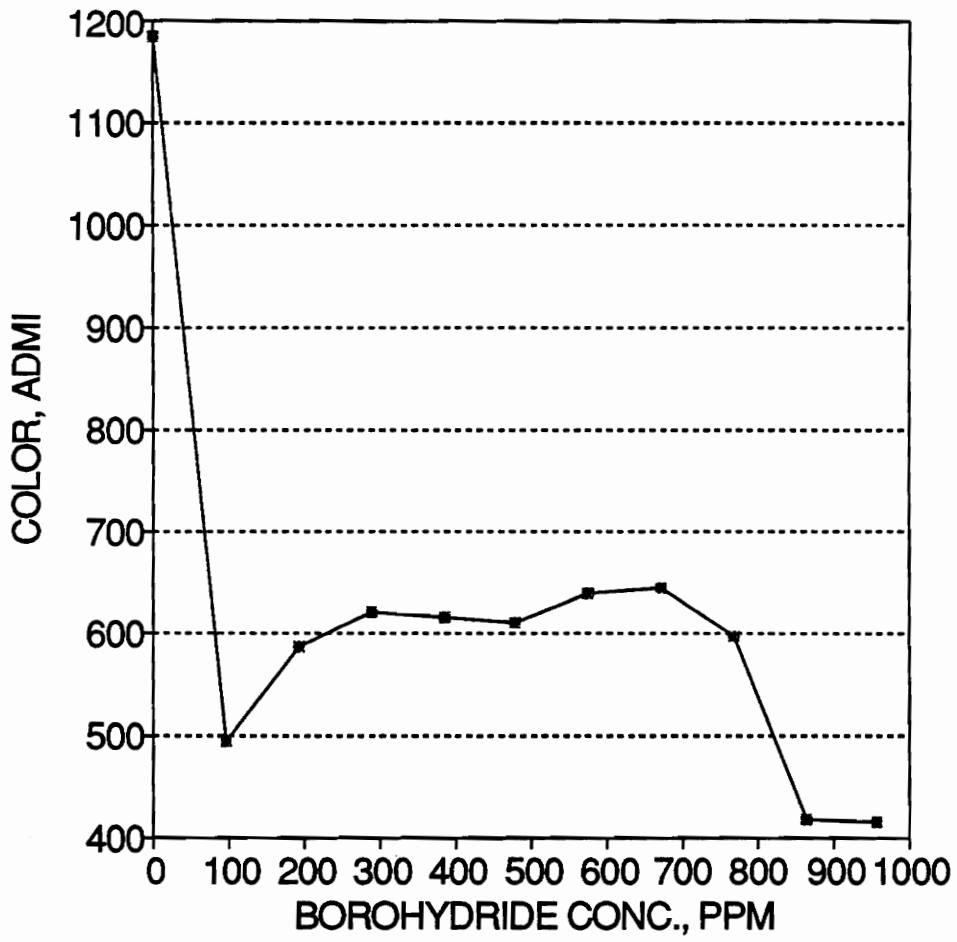


Figure E-3. Color vs borohydride concentration.

VITA

Michael W McCurdy was born in Baker, Oregon on June 4, 1965. After his family moved around the Pacific Northwest (Oregon, Washington, and Idaho), his family settled in the small community of Challis, Idaho where he attended high school. He attended the University of Idaho, Moscow, where he received a Bachelor of Science degree in Civil Engineering and a Bachelor of Science degree in Geological Engineering in May, 1989. During the summers of his college career, Michael has gained engineering experience in the mining industry, federal and state governments, and in consulting. Upon receiving his Master of Science in Environmental Engineering from Virginia Polytechnic Institute and State University, Michael will pursue a Doctor of Philosophy degree in Civil Engineering at Virginia Polytechnic Institute and State University.

Michael W McCurdy