PHYSICOCHEMICAL AND BIOLOGICAL TREATABILITY STUDY OF TEXTILE DYE WASTEWATER

by

Christine Ann Gorgone

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APPROVED:

Greg D. Boardman
Gregory D. Boardman, Chairman

Andrea M. Dietrich
Andrea M. Dietrich

Nancy G Love
Nancy G. Love

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(ABSTRACT)

The textile industry discharges a highly colored wastewater characterized by high organic levels. Industrial wastewater with these characteristics can be harmful to receiving streams and municipal plants, and must be treated prior to discharge. In this project, a yarn dyeing facility was studied that uses biological treatment followed by chemical coagulation to treat their highly colored wastewater prior to discharging to the local river. Occasionally, color, organic, and metal concentrations exceed the effluent discharge limits set by the state. In this research project, many physical, chemical, and biological treatment processes were attempted on the facility's wastewater to determine the most economical and efficient way to treat the wastewater.

Initially, the wastewater was segregated into eight waste streams and characterized. These waste streams included three dye waste streams (acid dye, premetallized dye, and cat-acid dye), three rinse water waste streams (acid rinse water, premetallized rinse water, and cat-acid rinse water), a boiler water waste stream and a combination of dye, rinse, and boiler wastes called the combined waste stream.

Chemical coagulation, oxidation, and adsorption were attempted on several of these waste streams with limited success. Ferric chloride and the polymer Color Katch

50 were the most effective chemicals used on dye waste streams, producing color removals greater than 90%.

Aerobic biological treatment was attempted on several waste streams in continuous flow and batch tests. Batch tests indicated that the combined waste stream did not require the addition of supplemental nutrients for biological treatment and that at least a five day hydraulic residence time (HRT) was needed for maximum color and organic removals. Two day HRT, continuous-flow reactors receiving combined wastewater were very unstable and failed to biologically treat the waste. Increasing the residence time to seven days improved biological treatment. Soluble COD removal from the combined wastewater was about 93% and color removal was about 80% in the seven day reactor. A seven day HRT, continuous-flow reactor receiving a combination of rinse waters and boiler water was also successful. Eighty-four percent of the soluble COD and up to 70% of the color was removed from this waste combination. Color Katch 50 was used to remove residual color from the effluent of the seven day HRT reactors. On average, color in the combined effluent was reduced from 1,826 ADMI units to 163 ADMI units, and color in the rinse and boiler water effluent was reduced from 581 ADMI units to 356 ADMI units.

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TABLE OF CONTENTS

LIST OF FIGURES

Figure **Page**

Figure **Page**

LIST OF TABLES

1.0 INTRODUCTION

Effluent discharge limits for industries are becoming more strict to preserve waterways and make them safer for aquatic and human life. Treating to these limits is getting harder, especially for the textile industry which typically has a highly colored wastewater, characterized by high organic levels. Discharging highly colored wastewater to surface waters is not only visually displeasing, but it inhibits the transmission of light to aquatic plants.

Color in textile wastewater comes from wasted dyes and finishes. Finishes include a wide range of chemicals that can make fabrics flame-resistant, mothproof, stain resistant, mildew-resistant, and wrinkle resistant. Treatments for removing color vary from plant to plant and can include one or more of the following: chemical coagulation, adsorption, membrane filtration, flotation, or biological treatment.

The facility (hereafter referred to as "the Plant") studied in this project dyes yarn and uses biological treatment followed by chemical coagulation to treat their highly colored wastewater. Color, organics, and a few metals occasionally exceed the effluent limits set by the state to discharge to the local river. Various treatments were attempted on this wastewater to improve effluent quality.

Figure 1 is a schematic diagram of the yarn dyeing process utilized by the Plant. After the yarn is dyed, it enters a steam box to set the dye. Then, the yarn is rinsed in a wash box and rung through a set of rollers before a final rinse and drying step. There are six dye lines of this type, and one smaller dye line used for samples. The main source of wastewater is rinse water from the two rinsing steps. This amounts to about 55,000 gallons per day (gpd). The remainder of the wastewater is from wasted dye (10,000 gpd) and condensate from the boilers (15,000 gpd). The amount of dye wasted is decreasing

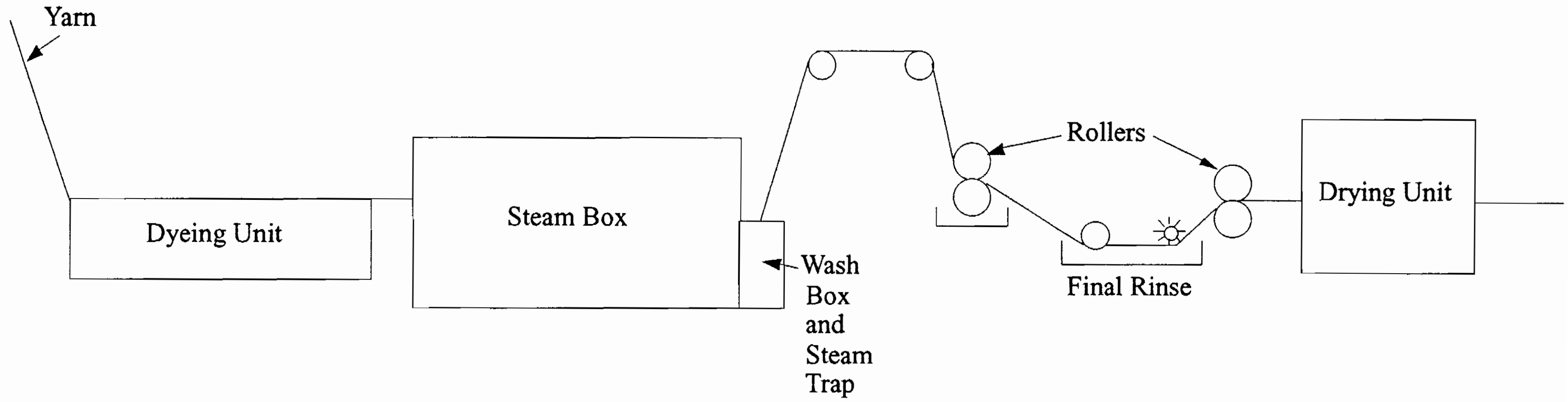


Figure 1 - Yarn Dyeing Process.

because a greater effort is being made to recycle dye. Currently, the total wastewater flow from the Plant is about 80,000 gpd.

The Plant's wastewater enters an aerated stabilization pond where some biological treatment occurs. After leaving the pond, polymers are added to remove the color. The wastewater is then filtered and sent to the receiving stream. About 85% of the dyes used by the Plant are acid dyes. The remainder of dyes used are premetallized (about 10%) and cationic (about 5%). When cationic dyes are used, they are mixed with acid dyes and are referred to as cat-acid dye by Plant personnel. The Plant's treatment system is not effective on cat-acid dyes. When these dyes are in use, the color of the treated wastewater increases. Treatment is also inhibited in the winter time when biological treatment effectiveness is low.

An alternative is for the Plant to discharge to the publicly owned treatment works (POTW). However, color and ultraviolet (UV) light transmittance limits for discharge to the sewer are strict because a UV light disinfection system is used at the POTW. The POTW is also concerned about the toxicity of industrial wastes to their activated sludge system and has also set limits on five day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and various metals. Table 1 provides the sewer limits set by the POTW.

The objectives of this study were to (1) determine the most economical and efficient way to treat the textile wastewater, and (2) determine whether the effluent should be discharged to the sewer or directly to the receiving stream.

Table 1 - Sewer Discharge Limits

Pollutant	Limit
ammonia	35 mg/L
arsenic	0.05 mg/L
benzene	0 mg/L
beryllium	0 mg/L
BOD_5	350 mg/L
barium	5 mg/L
boron	1 mg/L
cadmium	0.02 mg/L
chromium	5 mg/L
COD	1500 mg/L
copper	55 ppb
cyanide	0 mg/L
lead	8.3 ppb
mercury	0.24 ppb
nickel	1 mg/L
oil and grease	100 mg/L
selenium	0.02 mg/L
silver	0.02 ppb
total phenols	0.001 mg/L
total suspended solids	300 mg/L
color	150 ADMI
UV light transmission	40% (253.7 nm)

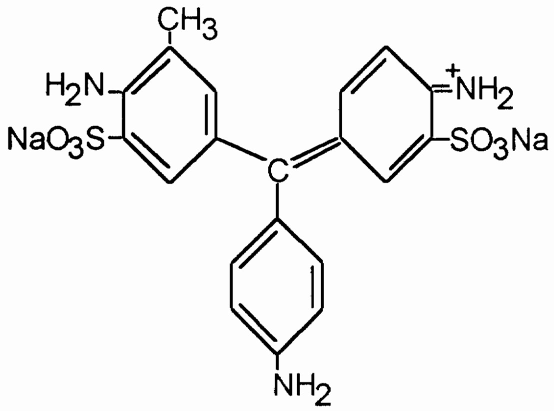
2.0 LITERATURE REVIEW

Researchers would like to find one ultimate treatment system capable of removing significant amounts of organics and color from textile wastewater. However, when these systems are found, high capital or operating costs make them unaffordable to textile industries (Demmin, 1988). Many physicochemical treatments are effective in removing color, but achieve small organic removals. On the other hand, biological treatment can remove organics, but has difficulty decolorizing many stable dyestuffs. Of course, the variability of the waste from plant to plant forces treatment of each wastewater to be a "tailored solution requiring a combination of methods" (Weeter and Hodgson, 1977). This literature review presents a brief discussion of the dyes used by the Plant; then, presents the results of some of the physical, chemical, and biological treatability studies conducted by other researchers on dyes and various textile wastes.

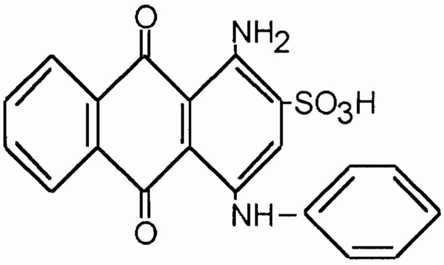
2.1 Dyes

Dyes can be classified in many different ways. Two of the most common ways are based on the structure of the dyes and the application of the dyes. In the textile industry, basic, acid, mordant, sulfur, azoic, vat, disperse, reactive, and direct dyes are some of the common classes based on application. Vat and disperse dyes are insoluble in water, while the remaining classes are readily soluble. There are numerous classes based on structure; some discussed in this review are azo, anthraquinone, triphenylmethane, acridine, methine, cyanine, and azine.

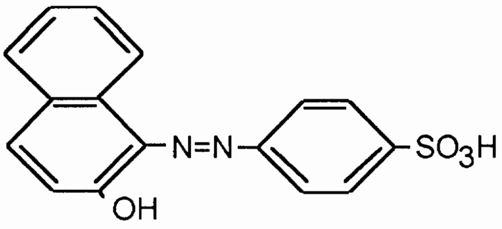
The Plant uses a variety of acid and basic dyes. Acid dyes are salts of sulfonic or carboxylic acids (Waters, 1979). Most acid dyes have either azo, anthraquinone, or triphenylmethane structures. Figure 2 gives examples of acid dyes in each structure.



Acid Violet 19 (triphenylmethane)



Acid Blue 25 (anthraquinone)



Acid Orange 7 (azo)

Figure 2 - Acid Dye Structures (Waring and Hallas, 1990; Seshadri *et al.*, 1994)

These dyes are used to dye wool, silk, nylon, and modified acrylic fibers. They are applied from an acidic dye bath with added sulfuric, formic, or acetic acid. In cases when a slightly alkaline bath is needed, ammonium sulfate is added. Acid dyes produce bright hues with a wide range of fastness properties. They attach to the fiber through a salt formation between the anionic dye and the cationic fiber.

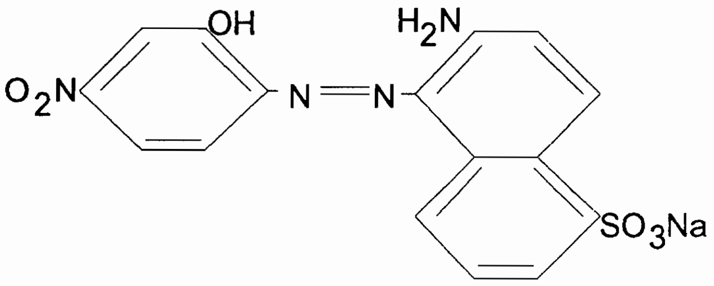
Another type of dye used by the Plant are premetallized acid dyes. These dyes are complexes of the acid azo dyes with either copper, chromium, or cobalt. Most premetallized dyes used by the Plant are chromium complexed dyes. They exhibit similar characteristics and properties to the acid dyes with premetallized dyes providing better light fastness properties over nonmetallized dyes. Figure 3 gives some examples of premetallized dyes.

Basic dyes are also called cationic dyes because their chromophores (the part of the dye structure that provides the color) are positively charged. Acridine, azo, methine, cyanine, azine, and triphenylmethane are some of the structures common to basic dyes. The hues of these dyes are extremely brilliant, with some exhibiting fluorescent hues. Their fastness is poor on wool, silk, cotton, acetate and nylon, but basic dye's color fastness on acrylic fibers is good. Acrylic has anionic sites to which the cationic dyes can bond. These dyes are often applied from an acidic dye bath with the addition of acetic acid. Figure 4 gives examples of a cationic dyes in the acridine, azo, and triphenylmethane structures.

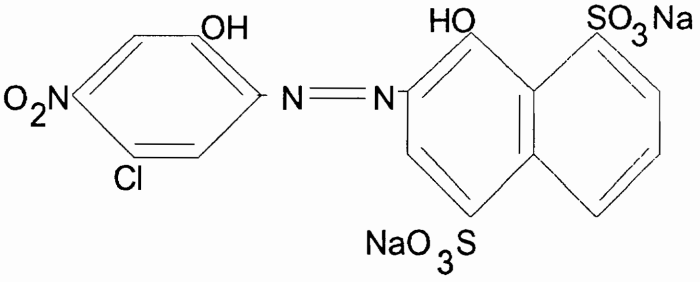
2.2 Physical and Chemical Treatments

2.2.1 Coagulation

Chemical coagulation has proven to be effective in removing color from many dye types. Kuo (1992) believes coagulation works best on insoluble dyes. Since dye

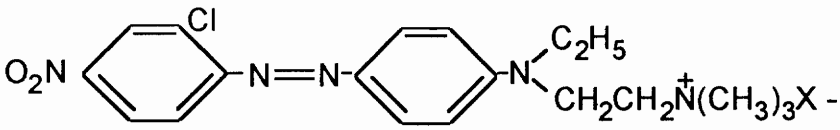


Acid Green 12
(will complex with chromium)

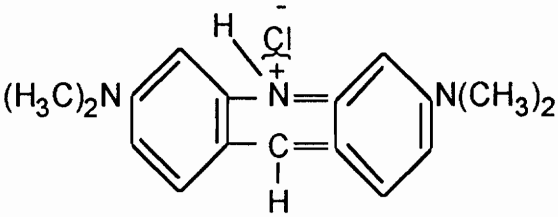


Acid Blue 169
(will complex with chromium)

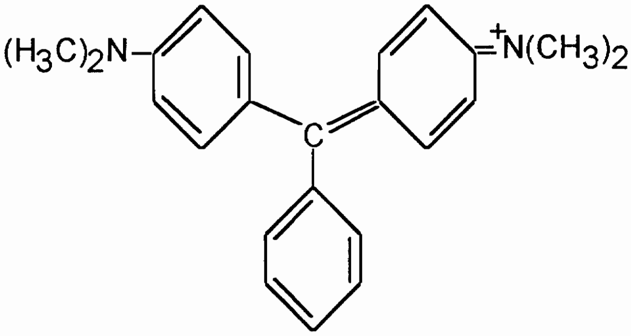
Figure 3 - Premetallized Dye Structures (Color Index, 1971).



Basic Red 18 (azo)



Basic Orange 14 (acridine)



Basic Green 4 (triphenylmethane)

Figure 4 - Cationic Dye Structure (Zollinger, 1991; Color Index, 1971).

waste is highly variable from plant to plant, the results obtained from coagulation studies are also highly variable. Common chemical coagulants include lime, aluminum sulfate (alum), ferrous and ferric sulfate, ferric chloride, and polyelectrolytes. References from 1979 and 1984 indicate that lime is the most popular coagulant in use (McKay, 1979; Park and Shore, 1984). Alum and ferric salts are also popular, but inorganic coagulants produce large volumes of sludge that need to be dewatered and disposed (Davis, 1991).

Asplaugh's (1973) research at Cone Mills revealed alum to be "the most successful chemical found to date" in removing color from Cone Mills wastewater. Alum also produced the best results with Waters' (1979) research on dye waste from industries in Severn-Trent , Washington. Horning (1977) conducted a treatability study on twenty different dyeing processes for the American Dye Manufacturers Institute (ADMI). A pilot-scale system was run and the exhausted dye bath, scour, and rinse waters were collected for each process. In his study, aluminum sulfate reduced the color to 100 ADMI units or lower for all dyeing process wastewaters from initial color values of 300 to 2,000 ADMI units. Typical doses ranged from 8-80 mg/L as Al^{3+}. Shelly *et al.* (1976) also successfully removed color from a textile dyeing and finishing waste with alum. A 600 mg/L alum dose removed 62.8% of the color and 44% of the COD. Yang and Pescod (1977) tried removing color from a dye wastewater from a fiber company in Thailand using alum and lime. Their results with alum were also positive. A 1,000 mg/L alum dose at pH = 9 gave COD removals from 24% to 50% and increased the transmittance through the wastewater above 80% across the entire visible spectrum. Kennedy *et al.* (1992) did not have as much success with alum for color removal from their dye waste from Lexingtion Fabrics Inc., in Lexington, Alabama. High doses of alum would only remove color when the pH was increased above 11 during the slow mix stage of their jar tests. Keinath and Pollock (1980) conducted jar tests on a 1/100 dilution of a composite of three dyes (Acid Yellow 151, Basic Yellow 28, and Acid Blue 25) and measured total organic carbon (TOC) removals. Aluminum sulfate removed less than 15% of the TOC with a 200 mg/L alum dose, higher doses did not improve TOC removal.

Coagulation using iron showed a little more variability. Abo-Elela *et al.* (1988) studied BOD_5 and COD removals from dyeing and finishing wastewater from an Egyptian textile mill using ferrous sulfate. Doses between 200 and 450 mg/L ferrous sulfate removed on average 81% of the COD and 85% of the BOD_5. Horning (1977) found that ferric salts removed color from some of his dye waste streams, but at times the color was enhanced. Color enhancement was probably due to the presence of colloidal ferric hydroxide. Waters (1979) found iron salts removed some of the color from his dye wastes, but sometimes the color changed hue which could cause an increase in the ADMI color value. Shirazi *et al.* (1977) found that color removal from a synthetic textile dyeing wastewater with ferric chloride ($FeCl_3$) is pH dependent. A 50 mg/L dose of $FeCl_3$ could remove 60% of the color (measured as optical density) but only at pHs below 5.5 and above 9.5. Kennedy *et al.* (1992) reported poor color removals (45% to 85%) with 1,000 mg/L $FeCl_3$ on Lexington Industry wastewater. Keinath and Pollock's (1980) jar tests on dyes with $FeCl_3$ resulted in a 24% TOC removal with a 250 mg/L $FeCl_3$ dose.

Work has also been done using ferrous ions for color removal. Kuo (1992) used ferrous ions with hydrogen peroxide (commonly called Fenton's reagent) to decolorize five simulated dye waste streams. Average color removals were above 97% for all five waste streams. Further tests on actual dye wastewater resulted in similar color removals. Demmin (1988) discussed the electrochemical treatment of synthetic and actual carpet mill waste and its success in removing BOD_5, COD, color, and heavy metals. This method utilizes iron electrodes to produce ferrous hydroxide which removes pollutants from the wastewater as it precipitates.

According to McKay (1979) and Park and Shore (1984), lime is one of the most popular coagulants used in the textile industry. Thus, it has been utilized in many treatability studies and has produced varying results. Alspaugh (1973) had no success using lime as a coagulant on the Cone Mills wastewater. Horning (1977) found that lime was effective only in wastewater with enough carbonate alkalinity to precipitate calcium carbonate. A high dose of 4,500 mg/L lime allowed Shelley *et al.* (1976) to obtain 62% COD and 81.5% color removal from their textile waste. Yang and Pescod (1977) achieved 30% COD removal from their dye waste with 2,200 mg/L lime, but decided not to pursue color removal studies because alum provided better COD removal at smaller doses. Keinath and Pollock (1980) obtained small organic removals (25% as TOC) when lime was added to a pH of about 11.5. Although organic removals were high (maximum COD and BOD_5 removals of 82% and 92% respectively), lime coagulation for Abo-Elela *et al.* (1988) resulted in a wastewater with a high pH (greater than 12) which is greater than is allowed for the Egyptian regulatory standards for discharging wastewater into surface waters.

Many researchers found a combination of lime and magnesium carbonate was more effective than either alone for color removal. Magnesium carbonate will form solid magnesium hydroxide ($Mg(OH)_2$) which precipitates and removes pollutants through sweep floc. A pH above 10.7 is optimum for sweep floc to occur. Lime is the chemical often added to maintain this optimum pH. Judkins and Hornsby (1978) studied how $MgCO_3$, lime (as $Ca(OH)_2$), and both chemicals together removed color from four dyes (two vat, one sulfur, and one disperse). The combination of $MgCO_3$ and $Ca(OH)_2$ worked best for all four dyes. A lime dose of 330 mg/L was able to maintain a pH above 10.7.

Ninety-eight percent of the color was removed from one vat dye with 40 mg/L $MgCO_3$ and 330 mg/L lime. Ninety-one percent of the color was removed from the other vat dye with 50 mg/L $MgCO_3$ and 330 mg/L lime. One hundred percent color removal for the sulfur dye and 54% color removal for the disperse dye was achieved with 50 mg/L $MgCO_3$ and 330 mg/L lime. Panswad and Wongchaisuwan (1986) followed up on Judkins and Hornsby's research by doing similar studies using magnesium carbonate-hydrated basic ($3MgCO_3{\bullet}Mg(OH)_2{\bullet}3H_2O$) and lime ($Ca(OH)_2$) on reactive red dye. Lime alone resulted in no color removals with dosages up to 4,000 mg/L lime, but lime and magnesium carbonate added together resulted in color removals up to 100%. Kennedy *et al.* (1992) conducted jar tests with lime and magnesium chloride on dye wastewater and found color removals up to 98% when the pH was above 11.

Some polymers and polyelectrolytes have been found to be effective in removing color from textile wastewater. Davis (1991) conducted pilot-scale tests at a dyeing and finishing plant that use disperse, acid, cationic, and direct dyes. Davis coagulated the wastewater with organic polymers, then removed the flocs with dissolved air flotation (DAF). This journal article did not specify the types of polymers used. Although this process did not remove any color, it did remove 67% of the BOD_5. Following the DAF, the wastewater was sent through a sand filter to remove solids not removed by the DAF unit. This process removed an additional 3% of the BOD_5 and 19% of the color. Kennedy *et al.* (1992) was able to remove over 88% of the color from dye wastewater. Kennedy first added a highly cationic polymer (2,000 mg/L polymer) that produced a pin floc. Then a medium cationic was added at 480 mg/L to enhance the pin floc for better settling. Kace and Linford (1975) studied three cationic polyelectrolytes (PEI 400, PEI 1000, and PEI 1090) and found that all three could achieve greater than 90% color removal from disperse dyes at a pH of 7. Kace and Linford found that polymer doses could be reduced if the pH was reduced. Further studies with inorganic coagulants and polyelectrolytes together determined that when alum and polymer were added to the dye, color removal improved slightly (95%) and the sludge formed was easier to filter than sludge formed by alum alone. Gardiner and Borne (1978) also found that larger, faster-settling flocs form if a little polymer or polyelectrolyte is added to a textile waste that has been treated with an inorganic coagulant.

Students at Virginia Tech have tried a variety of polymers on textile waste as pretreatments to biological treatment. Weber (1994) and Opdycke (1995) studied pretreatment methods for the dye, print, and bleach and finish wastewaters of a textile plant. Weber (1994) found that doses of the cationic polymer Al220 between 400 and 600 mg/L removed from 71% to 90% of the color and around 25% of dissolved organic carbon (DOC) from a mixture of the dye and print wastewaters. Al220 removed up to 84% of the color from the bleach and finish wastewater, but organic removal (as soluble COD) were generally less than 20% (Opdycke, 1995).

2.2.2 Adsorption

Since the prime mechanism for many dyes adhering to fabrics is adsorption, it's natural to try using adsorbents to remove color from wastewater. The most popular adsorbent used is activated carbon. Activated carbon is effective in adsorbing soluble dyes, but not effective in removing suspended solids or insoluble dyes. Davis (1991) used an activated carbon filter to treat the textile wastewater leaving the sand filter. Results from the sand filter treatments are discussed earlier in the "Coagulation" section of this review. The activated carbon filter removed an additional 25% of the BOD_5 and 78% of the color. Horning (1977) tried powdered activated carbon (PAC) on dye wastewaters and found doses between 500 to 1,500 mg/L PAC could remove color down to 100

ADMI units or lower from 700 to 12,000 ADMI units. However, these high doses are very costly. Since PAC and granular activated carbon (GAC) filters are expensive, activated carbon tends to be used as a polishing step. Shelley *et al.* (1976) successfully used activated carbon after chemical coagulation to remove 55% to 66% of the TOC from the wastewater. Not all studies with activated carbon have been successful. Despite contact times up to twenty minutes, Waters (1979) had little success removing color or COD from his dye wastes using an activated carbon filter. COD removals varied from 0% to 65% for the wastewater samples tested and color removals were not reported because they were so low.

2.2.3 Oxidation

Oxidation has been found to be effective in removing color from most dye waste (except disperse dyes), but is not effective in removing COD (Kuo, 1992). According to Park and Shore (1984), chlorine is a popular oxidant to use. Ghosh *et al.*(1978) reduced the color in the effluent of their biological reactor from 350 American Public Health Association (APHA) units to 80 APHA units with 150 mg/L chlorine. Their reactor contained textile dying and finishing wastewater from Guilford Industries in Guilford, Maine. Chlorine doses less than 100 mg/L left no significant chlorine residual. Rhee *et al.* (1980) and Goronszy and Tomas (1992) are others who found success in using chlorine on their wastewater. Rhee *et al.* (1980) studied the hypochlorination system of a carpet dying wastewater. This system was used as a pretreatment prior to discharge to the sewer and could remove all visible color from the wastewater. Goronszy and Tomas (1992) used chlorine to remove the residual color in the effluent from their biological reactor which received textile bleaching, dying, and rinsing wastewaters.

Brower and Reed (1986), however, tried chorine as NaOCl and hydrogen peroxide on dye wastes with no success. A 1,050 mg/L dose of NaOCl resulted in a 0% color reduction, and a 765 mg/L dose of H_2O_2 resulted in a 10% color reduction. Weber (1994) and Opdycke (1995) also had little success with hydrogen peroxide on their waste streams. No visual color change was obtained using up to 100 mg/L H_2O_2 on the dye and print waste stream (Weber, 1994). Thirty-five percent of the color was removed from the bleach and finish waste stream (Opdycke, 1995). McCurdy (1991) tried H_2O_2 on Navy 106 wastewater which resulted in low color and COD removals. Color was reduced from 2,650 ADMI units to 2,040 ADMI units and COD was reduced from 785 mg/L to 653 mg/L COD.

2.3 Biological Treatment

Aerobic biological treatment has been successful in removing BOD, but not quite as successful in removing COD or color from textile waste (Germirili *et al.*, 1990; Alspaugh, 1973). Most dye structures contain aromatic rings which increases a compounds resistance to biodegradation (Gardiner and Borne, 1978). However, because of its efficiency with respect to BOD removal, evidence of biosorption of some dyes, and its cost effectiveness, many varieties of biological treatment have been explored to try to obtain optimum color and organic removals.

2.3.1 Aerobic Treatment

In biological systems, dyes have been found to be eliminated through either adsorption to biomass (commonly called biosorption) or biodegradation. Many biological studies have been conducted to determine the most prominent method of dye elimination in biological treatment. Pagga and Brown (1986) studied the biodegradability of 87 dye stuffs. The dyes chosen were readily water-soluble which would presumably make the dyes "less likely to be adsorbed to a significant extent onto activated sludge" (Pagga and Brown, 1986). If color removal was significant within the first few hours of the experiment, it was presumed to be due to the adsorption of the dye onto the sludge and not due to biodegradation. Pagga and Brown (1986) found that adsorption was the prime mechanism of dye removal. However, they did not eliminate the possibility of biodegradation of the dyes. Small biotransformations may occur that assist in the removal of the dyes.

Shaul *et al.* (1988) conducted a study for the EPA on the fate of azo dyes in an activated sludge system. Of the eighteen dyes studied, eleven passed through the activated sludge system untreated, four were adsorbed onto the sludge, and three appeared to be biodegraded. In order to determine whether the dyes were adsorbed or biodegraded, a mass balance was calculated for the reactor. If the sum of the mass of dye in the effluent and the mass of dye in the wasted sludge was between 80% to 120% of the mass of dye entering the reactor, then biodegradation was not considered to be a significant factor in dye removal. The dyes that passed through were highly water soluble which is believed to play a role in whether the dye is adsorbed or biodegraded. Horning (1977) attempted aerobic biodegradation studies on 1/10 dilutions of twenty dye wastewaters. His results showed little color removal, high BOD_5 removals but lower TOC removals indicating the presence of some material in the wastewater that was not readily biodegradable. Most of the dye wastewaters had less than 30% color removal with five of the wastewaters obtaining 60% to 85% color removals. As for BOD_5 and TOC removals, BOD_5 reductions were generally greater than 97% and TOC reductions were from 55% to 95% for all wastewaters tested.

Since adsorption to biomass seemed to be the primary mechanism for color removal in biological systems, some researchers began studying biosorption more closely. Dohanyos *et al.* (1978) studied the adsorption of twenty different textile dyes onto activated sludge. The presence of hydroxy, azo, and nitro groups in the dye structure increased the removability of the dye where sulfo groups decreased it. The sorption process was modeled by both the Freundlich and Langmuir isotherm. Dohanyos *et al.* (1978) found that the Freundlich isotherm provided a better fit. Hu (1992) concentrated his work on the sorption of reactive dyes on an *Aeromonas* culture and found that sorption followed the Freundlich model.

Ganesh *et al.* (1994) studied the fate of Reactive Black 5 dye in activated sludge. Two different dye concentrations were added to two batch reactors with approximately 3,500 mg/L of municipal activated sludge. Two sets of reactors were studied. One set contained Reactive Black 5 in its vinyl sulfone form (a hydrophobic form) and the other set contained Reactive Black 5 in its hydrolyzed form (a hydrophilic form). Color was removed from the vinyl sulfone dye reactors through sorption of these dyes onto the sludge. Color values reduced from 1,197 ADMI units to 320 ADMI units in one reactor and from 1,967 ADMI units to 770 ADMI units in the other. The biomass turned from the typical muddy, brown color to a blue color indicating dye removal was through biosorption. Soluble TOC increased in both of these reactors indicating little or no biodegradation of the dyes. The hydrolyzed dye reactors had no evidence of dye sorption or biodegradation. ADMI color values remained the same and soluble TOC increased through out the experiment. Ganesh (1994) states that "cell lysis and the release of non-biodegradable organics from the viable microbes in the reactors" was the reason for the increase in soluble TOC in both sets of reactors.

Shaul *et al.* (1988) reported that "some researchers have shown azo dyes to be slowly biodegraded under aerobic conditions". Therefore, a biological reactor with longer detention times may be more effective in treating dye waste. Shriver and Daugue (1978) tried treating Wansona Industries textile processing wastewater in four different reactors at four different hydraulic detention times (12, 24, 36, 48 hours). The longer detention times were needed to break down the large dye structures into smaller compounds that were easier to biodegrade. The 12 and 24 hour reactors had color removals of 22% and 33.6%, respectively, where the 36 and 48 hour reactors had color removals of 41.4% and 50%, respectively. One of the goals of Shriver and Daugue's (1978) study was to obtain 85% BOD_5 removal from these reactors. This goal was barely met in the 12 and 24 hour reactors (84% BOD removal), but easily met in the 36 and 48 hour reactors (87% and 92% BOD removals, respectively).

Research conducted by Weber (1994) and Opdycke (1995) also indicated that a longer detention time improves biological treatment. Weber (1994) had three day hydraulic residence time (HRT), lab-scale reactors with a combination of dye, print, and bleach and finish wastewaters from a textile industry. COD removals from these reactors were from 55% to 68% and color removals were from 42% to 53%. Opdycke (1995) set up reactors with the same wastewaters at an HRT of 7 days. Both COD and color removals were improved with COD removals from 89% to 92% and color removals from 51% to 70%. This textile industry also had a toxicity limit of 100% for the no observed effect concentration (NOEC). The effluent from the three day reactors did not meet these limits (NOEC of 50% to 75%), but the effluent from the seven day reactors did.

Some researches have conducted long term biodegradation studies to determine the extent of dye biodegradation. Porter and Snider (1976) conducted a 30 day biological oxygen demand (BOD) test on various textile dyes (three disperse, two reactive, two vat, and one direct). Samples were seeded and BOD and color density changes were measured over the thirty day period. For the reactive and direct dyes tested, there was no evidence of color loss. For the insoluble dyes tested (disperse and vat), the average color loss was 15%. Weeter and Hodgson (1977) conducted a 25 day test on six dyes (three direct and three acid). All samples were seeded and oxygen uptake was measured over the twenty five day period. The oxygen uptake was low, indicating that the dyes were not degradable and there was no significant color removal. The study was repeated with the addition of 2,300 to 2,600 mg/L of an acclimated mixed liquor. The mixed liquor was allowed to settle and apparent color and COD were measured on the supernatant. Both parameters increased with the addition of the mixed liquor.

2.3.2 Anaerobic-Aerobic Treatment

In anaerobic systems, it is possible to reduce azo dyes into aromatic amines. These aromatic amines do not readily degrade in an anaerobic environment, but there is evidence that they can be degraded aerobically (Seshadri, 1994). Recently, researchers have tried a two stage, anaerobic-aerobic biological system to completely degrade dye waste. Brown and Hamburger (1987) conducted anaerobic-aerobic degradation studies on fourteen azo dyes. They found that azo dyes were decolorized in the anaerobic system and believed the azo bond was cleaved into aromatic amines through the reduction of the dye (see Figure 5). Most of these amines were further degraded in the aerobic system, but some sulfonated aromatic amines did not degrade. All dyes and metabolites in this study were identified in the wastewater by chromatographic techniques.

More recently, Seshadri *et al.* (1994) studied anaerobic-aerobic treatment of azo dyes using an anaerobic fluidized bed reactor followed by activated sludge. They

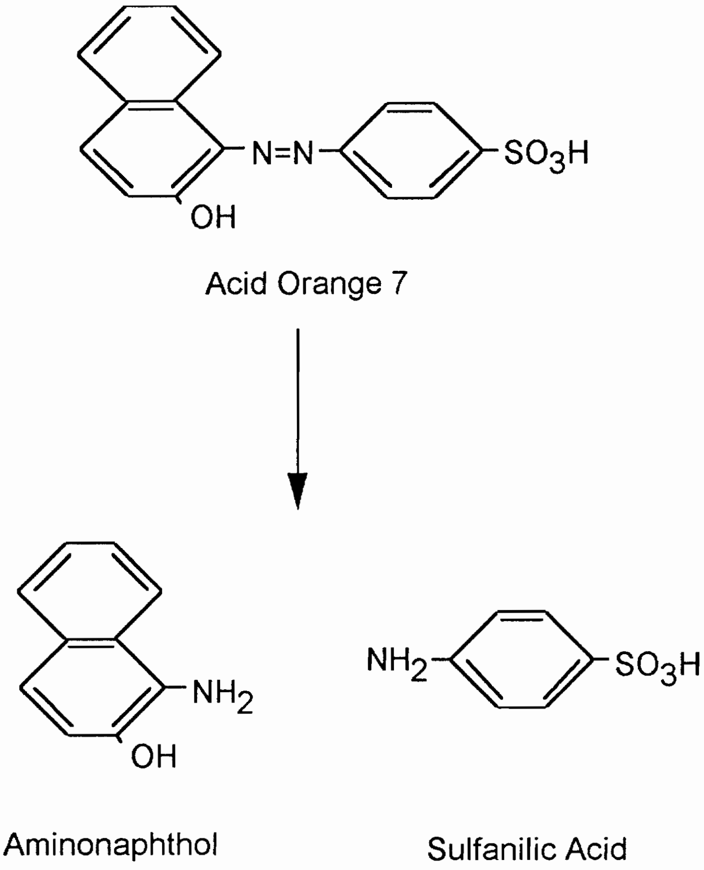


Figure 5 - Azo Bond Cleavage (Seshadri *et al.*, 1994).

measured the transformation of four dyes (Acid-Orange 7, Acid-Orange 8, Acid-Orange 10, and Acid-Red 14) in the anaerobic fluidized bed reactor. This transformation was the cleavage of the azo bond reducing the dye to aromatic amines. Transformations were measured by changes in dye concentration in the reactors. Dye concentrations were measured using a spectrophotometer. Ninety percent of Acid-Orange 7 was transformed at a 24 hour hydraulic residence time (HRT). Eighty two percent of Acid-Orange 10 was transformed at HRT's greater than 8 hours. Ninety-eight percent of Acid Orange 8 was transformed at a 12 hour HRT, and eighty-six percent of Acid Red 14 was transformed in 24 hours. On average, the anaerobic treatment reduced COD by 40% and the aerobic treatment reduced the COD from 160 mg/L COD to below 20 mg/L COD.

Loyd (1992) compared a combined anaerobic-aerobic treatment system with aerobic treatment on Navy 106 dye wash water and Martinsville POTW wastewater. Approximately 75% of the influent to the Martinsville POTW is wastewater from textile industries. The anaerobic-aerobic treatment of the Navy 106 wash water resulted in a total color removal of 88%. The wash water was mixed with the primary effluent of a municipal plant in a 3:1 ratio of wash water to primary effluent. This dilution accounted for 40% of the color reduction while the anaerobic pretreatment accounted for 50%. The aerobic treatment that followed contributed a two percent increase in the color of the wastewater. Aerobic treatment without the anaerobic pretreatment resulted in much lower color removals (29%). TOC removals from this wastewater was accomplished mainly through dilution and aerobic treatment. The anaerobic-aerobic system removed 82% of the TOC with only 3% of the TOC reduction from anaerobic treatment. The aerobic system removed 74% of the total TOC. For the Martinsville POTW wastewater, the anaerobic/aerobic treatment system reduced the color by 59% while the aerobic system increased the color by 13%. TOC removals from the POTW wastewater were mostly from the aerobic phase of the anaerobic-aerobic and aerobic treatment processes with overall TOC removals in the anaerobic-aerobic process at 73% and TOC removals in the aerobic process at 71%. Boe (1993) conducted a pilot-scale study on the anaerobic-aerobic treatment of the Martinsville POTW wastewater and obtained similar results to Loyd (1992). Anaerobic treatment removed 55% to 60% of the color and the subsequent aerobic treatment removed 10% of the color. TOC removals were between 70% and 75% and was essentially all removed in the aerobic treatment process.

Weber (1994) tried to anaerobically pretreat dye, print, and bleach and finish waste streams with little success. The color in the dye waste decreased by 24% and the color in the print and the bleach and finish wastes increased from the anaerobic treatment.

2.3.3 Bacterial Degradation

Some researchers have tried isolating bacteria to decolorize dyestuffs. Idaka and Ogawa (1978) isolated *Aeromonas hydrophila* var. 24B from Japanese dye waste. Tests with azo disperse dyes indicated the bacteria could eliminate the color. Itoh *et al.* (1993) found *Bacillus subtilis* could degrade a few anthraquinone dyes. Pigment Violet 12, Disperse Red 15, Disperse Orange 11 and Disperse Violet 1 were the anthraquinone dyes tested. The greatest color reduction occurred with Pigment Violet 12 (73%) which contains 2 hydroxy groups within its structure. There was no color reduction in Disperse Violet 1 which contains two amino groups and no hydroxy groups within its structure. Disperse Red 15 contains one hydroxy and one amino group within its structure and *Bacillus subtilis* decolorized the dye 38%. Disperse Orange 11 was decolorized 24%. Its structure contains one methyl group and one amino group. The number of amino and hydroxy groups within the structure appears to have affected the decolorization of the dyes by this bacterium.

Kanekar and Sarnaik (1991) acclimated cattle dung to dye waste and identified the microorganisms *Pseudomonas alcaligenes* and *P. mendocina* on the acclimated dung. Further tests with this wastewater found these microorganisms reduced the color of the wastewater from an optical density of 0.915 to 0.36 at a wavelength of 580 nm. The COD of this waste was reduced 60% and the TOC was reduced 37% by these microorganisms.

Mou *et al.* (1991) tested color removal from acid, basic, direct, reactive, and disperse dyes using several species of white rot fungi. All visible color was removed from all dyes tested. Color removals for some of the dyes tested were up to 99%.

2.3.4 Textile and Municipal Waste Treatment

Treating textile wastewater in combination with municipal sewage is often favored (Grau, 1991). The combination can help reduce fluctuation in flow, alkalinity, and strength that are associated with textile waste. Also, the municipal wastewater can supply additional nutrients needed for biological treatment (Grau, 1991). Ghosh *et al.* (1978) found it more economical to treat a combined mill and sewer waste than just the mill waste. Sweeny's (1977) lab-scale biological test was performed with one part textile plant effluent and two parts city sewage. Color removals from this wastewater combination were from 500 APHA units to 150 APHA units. Abo-Elela *et al.* (1988) needed a 50:50 mixture of domestic and textile waste to compensate for phosphorus deficiencies in the textile waste. Their reactors accomplished high organic removals with average initial COD and BOD_5 levels of 974 mg/L and 396 mg/L, respectively and average residual COD and BOD_5 levels of 82 and 20 mg/L, respectively. Shirazi *et al.*

(1977) compared biological treatment of a sewage/textile waste mixture with biological treatment of a textile waste alone. The effluent of the mixture had higher optical density (OD) removals, but the COD removals were the same in both reactors. The reactor with the sewage/textile mix reached a maximum of 48% OD removals where the textile waste reactor only reached a maximum OD removal of 33%. COD removals for both reactors were from 45% to 50%.

2.4 Two Stage Treatments

Often two stage treatments are employed to remove both color and organics from textile waste. Physicochemical treatments are generally effective in removing color, but remove little organics; and biological treatments generally remove significant amounts of organics, but little color. Most two stage treatments use a chemical pretreatment prior to biological treatment. Weber (1994) and Opdycke (1995) pretreated the dye and print wastewater with polymer prior to biological treatment to remove the necessary color and organics to meet state limits. Shelly *et al.* (1976) pretreated textile waste with both alum and lime then followed each pretreatment with activated sludge. Results of the pretreatments are presented above under the "Coagulation" section of this literature review. The pretreatments removed more COD than expected by Shelly *et al.* (62% with lime and 44% with alum) thereby reducing the organic load on the biological reactors. Average organic removals in the biological reactors were 55% to 80%, but color removals were minimal. When the wastewater was pretreated with lime, the reactor removed less than one percent of the color from the wastewater. When alum was used for pretreatment, color removals from the reactor were less than 20%. Shirazi *et al.* (1977) compared COD and optical density removals from two reactors: one contained wastewater pretreated with $FeCl_3$ and one contained untreated wastewater. On average, the reactor with untreated wastewater had greater removals (63% COD and 51% OD) than the reactor with pretreated wastewater (49% COD and 23% OD). However, the effluent residuals in the reactor with untreated waste were still higher than the reactor with pretreated waste. Yang and Pescod (1977) conducted unsuccessful batch biological studies on untreated dye wastewater. When this wastewater was pretreated with alum, the batch reactor removed 73% of the COD.

Other two stage treatments involve biologically treating the wastewater first, then using a physicochemical treatment to remove residual color. Ghosh *et al.* (1978) and Goronszy and Tomas (1992) used chlorination after biological treatment to remove excess color from their wastewaters. Their success is detailed in the "Oxidation" section of this review.

2.5 Summary

Research with textile dye wastewater showed that physicochemical treatments such as chemical coagulation, activated carbon, and chlorination often removed significant amounts of color, but minimal amounts of organic matter. Research also showed that aerobic biological systems removed small amounts of color, but a significant amount of organics. This literature review indicated that color removal for many dye wastes in aerobic systems is primarily due to adsorption onto activated sludge with little evidence of biodegradation. However, anaerobic biological systems were successful in degrading azo dye waste, but left aromatic amines that require aerobic treatment for further degradation. Most textile plants require a combination of physicochemical and biological treatments to remove enough color and organics to meet discharge limits. Due to the variability of the industry's processes, these treatments must be determined on a case-by-case basis.

3.0 METHODS AND MATERIALS

In this treatability study, several physical, chemical, and biological treatments were considered to treat the Plant's wastewater. This section explains how this study was conducted and the analytical procedures used in the process.

3.1 Characterization

The Plant's wastewater was segregated into eight waste streams which were characterized for BOD_5, COD, TOC, total suspended solids (TSS), total ammonia (NH_3-N), total Kjeldahl nitrogen (TKN), total phosphorus, color (ADMI units), UV light transmittance, oil and grease, benzene, total phenols, total cyanide, and twelve metals (arsenic, beryllium, barium, boron, cadmium, chromium, copper, lead, mercury, nickel, selenium, and silver). The eight waste streams included three types of dyes (acid, premetallized, and cat-acid dyes), their respective rinse waters (acid rinse water, premetallized rinse water, and cat-acid rinse water), boiler water, and a combined waste stream which included a mixture of the dye, rinse water, and boiler water waste streams that enter the Plant's current wastewater treatment system. All dye samples were taken from the dye tanks that supply the dyeing unit, and all rinse water samples were taken from the wash box (See Figure 1 in the "Introduction"). The combined and boiler water waste samples were taken from manholes outside the Plant. A minimum of three sets of samples were tested for all the above parameters to ensure proper characterization.
If a parameter was not detected in one or more of the sample sets, averages were calculated using the detection limit of the instrument.

3.2 Treatment

After characterization, many different physical, chemical, and biological treatments were attempted. The final treatment selected should either meet the state requirements to discharge into the local river or meet the town requirements for discharging into the sewer. Treatment effectiveness was initially measured by color and organic (either COD or TOC) removals from the waste stream. The influent and effluent from the treatments that were promising underwent a complete final characterization.

3.2.1 Chemical Coagulation

Chemical coagulation was attempted on several different waste streams. Initial coagulation studies were performed on the dyehouse and combined waste streams. The six dye lines at this plant discharge their dye waste to a single channel. The dyehouse waste stream came from this channel. Jar tests were conducted using inorganic coagulants such as lime ($Ca(OH)_2$), aluminum sulfate ($Al_2(SO_4)_3 \bullet 18H_2O$), ferric chloride ($FeCl_3$), and magnesium carbonate ($MgCO_3$), and organic polymers such as Al220, A130, Selfloc 1438, Selfloc 1740, Color Katch 50, and Calgon WT 2392. A130 is an anionic polymer and the remaining polymers are cationic. Table 2 indicates the doses of chemicals used for the dyehouse and combined waste streams. Also included in this table are the pH of the samples tested and information on whether alkalinity or clay was added.

Jar tests were conducted using a Phipps and Bird (Richmond, VA) six paddle jar test apparatus. Each jar contained 500 mL of sample. First, the pH was adjusted (if necessary), then the chemical was added to five of the jars at five different doses and the sixth jar was the control (no chemical addition). The samples were mixed at 100 rpm for 1 minute, then mixed between 40 and 50 rpm for 15 minutes. Samples were allowed to settle for 10-15 minutes and TOC and color were measured on the supernatant. TOC and

Table 2 - Chemical Coagulation Jar Tests - Dyehouse and Combined Waste Streams[1]

	Coagulation Conditions: pH, Chemical Dosage	
Coagulant	**Dyehouse Waste Stream**	**Combined Waste Stream**
Al220	pH = 3.9, 100-350 mg/L	pH = 4.2, 100-300 mg/L
	pH = 6.5, 5-90 mg/L	
	pH = 7, 100-350 mg/L	
A130	pH = 3.9, 5-40 mg/L	
Selfloc 1438	pH = 3.3, 50-500 mg/L	pH = 4.8, 50-300 mg/L
		$NaHCO_3$, pH = 6.9, 50-250 mg/L
Selfloc 1740		pH = 4.2, 50-250 mg/L
		pH = 7, 50-250 mg/L
Color Katch 50	pH = 7, 300-500 mg/L	pH = 4.2, 50-250mg/L
		pH = 4.5, 400-1,400 mg/L
WT2392		$NaHCO_3$, pH = 6.9, 100-480 mg/L
		$NaHCO_3$,pH = 6.9, A Clay, 1,300 mg/L
Lime	pH = 3.3, $NaHCO_3$, 600-4,500 mg/L	pH = 4.5, 200-1,200 mg/L
		pH = 4.5, 400 mg/L $MgCO_3$, 200-1200 mg/L
Alum	pH = 3.4, 500-1,000 mg/L	pH = 4.5, 100-600 mg/L

Table 2 - Chemical Coagulation Jar Tests - Dyehouse and Combined Waste Streams(Cont.)[1]

Alum (cont.)	$NaHCO_3$, pH = 6.6, 500-1,600 mg/L	$NaHCO_3$, pH = 7, 100-600 mg/L
$FeCl_3$	pH = 3.4, 200-1,200 mg/L	pH = 4.5, 100-500 mg/L
	$NaHCO_3$, pH = 6, 200-600 mg/L	$NaHCO_3$, pH = 7, 100-600 mg/L
$MgCO_3$	pH = 3.1, 200 - 1,000 mg/L	pH = 7, 200-1,000 mg/L
		800 mg/L Lime, 400-800 mg/L

1. In most jar test, pH was adjusted with sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). Jar tests in which pH was adjusted with sodium bicarbonate ($NaHCO_3$) are noted in table. Sodium bicarbonate was added until the pH stated in the table was reached.

Table 3 - Polymer Jar Tests - Dye Waste Streams (1.)

	Coagulation Conditions: pH, Coagulant Dose			
Polymer	**Acid Dye**	**Premetallized Dye**	**Cat-Acid Dye**	**Dye Mix**
Color Katch 50	pH=2.8, AClay,1000-5000 mg/L	pH=2.4, 1000-5000mg/L	pH=3.9, 1000-5000mg/L	pH=2.9, 3000-4000mg/L
	pH=2.8, 3000mg/L		pH=7, 4000mg/L	
WT2392	pH=2.8, AClay, 500-5000 mg/L			pH=2.8, 80-240mg/L
				NaHCO3, pH=6.5, 680mg/L
				pH=2.8, Kaolin, 80-400mg/L
				NaHCO3, pH=6.6, Kaolin, 320mg/L

1. In most jar tests, pH was adjusted with sodium hydroxide (NaOH) and sulfuric acid (H2SO4). Jar tests in which pH was adjusted with sodium bicarbonate (NaHCO3) are noted in table. Sodium bicarbonate was added until the desired pH was reached.

2. AClay and Kaolin are types of clays used as coagulant aids in these jar tests.

color were only performed on samples with visible color change. Samples where ferric chloride and a lime/magnesium carbonate combination were used as coagulants were filtered through either a 1.2 or 1.5 µm glass fiber filter before TOC analysis. The floc formed in these jar tests settled poorly, and filtering ensured total floc removal.

Chemical jar tests were also performed on the individual dye streams (acid, premetallized, and cat-acid) and a combination of these three streams referred to as the dye mix. The dye mix included 67% acid dye, 16.5% premetallized dye, and 16.5% cat-acid dye. This ratio was determined based on a worst case scenario. The Plant has six dye lines. A worst case scenario would have four of those lines running acid dye, one running premetallized dye, and one running cat-acid dye. The percentages of each dye in the dye mix waste stream were based on a 4:1:1 mixture of acid, premet, and cat-acid dye, respectively. The cationic polymers Color Katch 50 and Calgon WT2392 were used on all four waste streams. The anionic polymer A130 was tried on the cat-acid dye since cationic dyes are positively charged. Table 3 indicates the polymer doses to these waste streams and if clay was added or pH adjusted. TOC and color were measured on samples filtered through a 1.2 µm glass fiber filter.

3.2.2 Adsorption

Powdered activated carbon (PAC) was added to the dyehouse and combined waste streams in jar tests to determine if carbon adsorption was a suitable treatment. The samples were mixed at 100 rpm for one minute then mixed between 40 and 50 rpm for thirty minutes.

3.2.3 Oxidation

Chemical oxidation was attempted on the combined waste stream using hydrogen peroxide (H_2O_2) and chlorine (NaOCl). Oxidation tests were performed as jar tests similar to the chemical coagulation jar tests. If there was visible color removal, the COD and color of the sample were measured. Table 4 indicates the doses of PAC and oxidants used and if the pH was adjusted or alkalinity added.

3.2.4 Biological Treatment

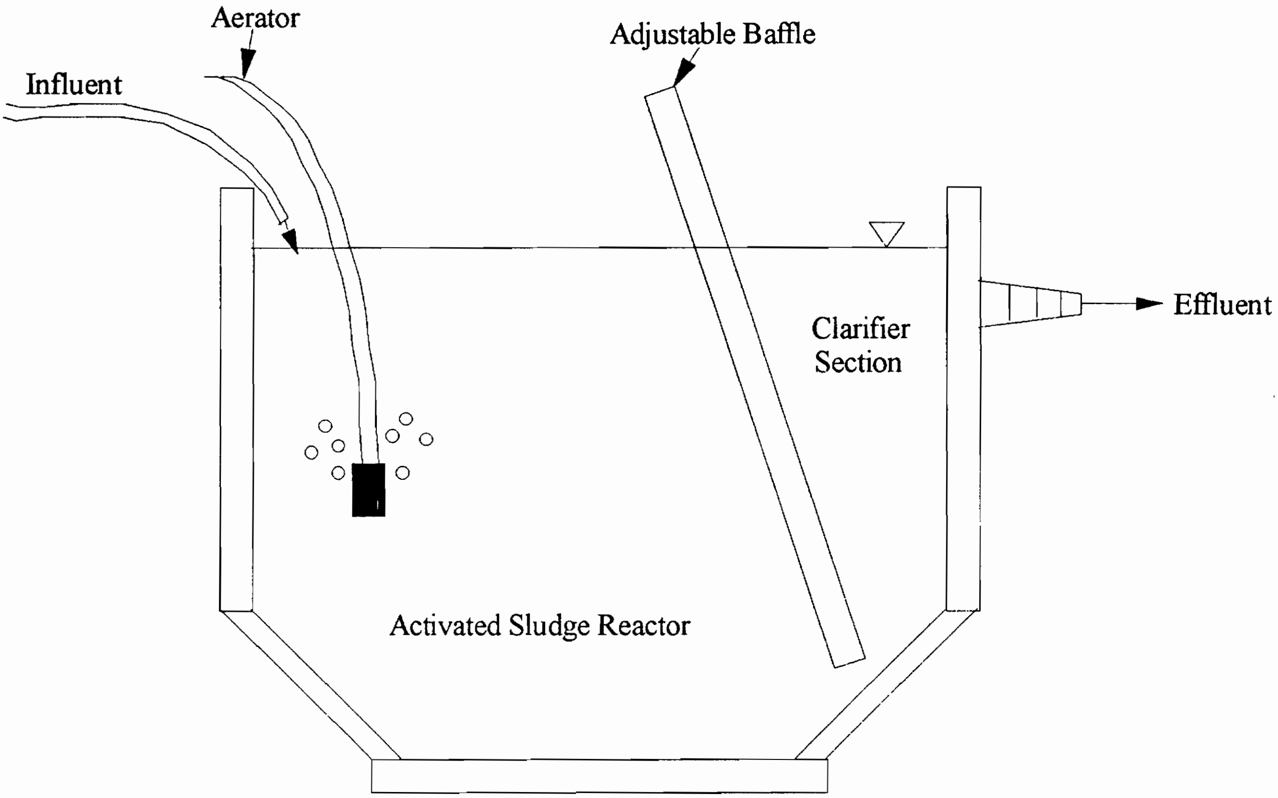
3.2.4.1 Continuous Flow Reactors

Four continuous flow reactors were set up with a two day hydraulic residence time (HRT) and seeded with return sludge from the POTW to provide a final mixed liquor concentration of about 4,000 mg/L. Figure 6 provides a schematic diagram of the reactor used. Each reactor had a total volume of approximately 10 L and was split into two compartments by a baffle. One compartment was the activated sludge reactor, constituting about 85% of the total volume, and the other compartment was the clarifier. The reactor section was aerated and mixed with lab air which was distributed through two or three small diffusers. Enough air was introduced to keep the reactor completely mixed. The reactor's baffle was adjusted to allow for the recycle of settled sludge into the activated sludge section. In order to maintain a two day HRT, a Masterflex peristaltic pump was used to pump influent into the reactors at a rate of 3.4 mL/min.

These lab reactors were operated with the same HRT and mixed liquor suspended solids (MLSS) concentration as the oxidation ditch at the POTW. These reactors were used to determine if any of the waste streams tested could be discharged directly to the sewer without pretreatment by the textile plant. If the lab reactors could treat 100% of these waste streams, then the POTW would be able to treat the waste streams diluted by

Table 4 - Activated Carbon and Oxidation Jar Tests

	Jar Test Conditions: pH, Chemical Dosage	
Chemical	**Dyehouse Waste Stream**	**Combined Waste Stream**
PAC	pH = 3.1, 100-600 mg/L	pH = 4.2, 100-600 mg/L
	pH = 6.5, 140-860 mg/L	$NaHCO_3$, pH = 6.9, 100-600 mg/L
H_2O_2		pH = 3.7, 50-250 mg/L
		pH = 7, 250 mg/L
Chlorine		pH = 3.7, 50-250 mg/L
		pH = 7, 50-250 mg/L



Reactor Volume - 10 L

Figure 6 - Continuous Flow Reactor for Biological Treatment Studies

the rest of the municipal waste. If a reactor was not operating to satisfaction, it was taken off-line and a new reactor was started. Described here are the continuous flow reactors set up during this study. Mixed liquor suspended solids (MLSS) and effluent TSS were monitored for all reactors. This information was used to calculate the volume of sludge wasted from the reactors to maintain a given sludge age. The following formula was used to calculate volume wasted:

$$\Theta_c = \frac{XV}{XV_w + QX_e}$$

where Θc is the sludge age [day], X is the MLSS concentration [mg/L], X_e is the effluent TSS [mg/L], V is the volume of the reactor [L], Q is the flow rate into the reactor [L/day], and V_W is the volume [L] wasted per day. Unless otherwise stated, the reactors were operated at a 30 day sludge age. Performance of these reactors will be presented in the results section along with the reasons for the elimination of any reactor.

Initially, two continuous flow reactors were set up, each with a two day HRT and 4,000 mg/L MLSS. One reactor received dyehouse wastewater and the other received combined wastewater. Within two weeks, the dyehouse reactor was taken off-line and a second combined wastewater reactor was started with the same HRT and MLSS concentration. These reactors were operated at different sludge ages (one at 15 days and one at 30 days) with the goal of gathering enough data to calculate kinetic coefficients of the biodegradation of the combined waste stream. TOC and color were measured on the influent and effluent of these reactors every other day to monitor performance. MLSS and effluent TSS were measured once a week.

A third continuous flow reactor with a two day HRT containing acid rinse water was started. It was also seeded with return sludge from the POTW to provide a final MLSS concentration of 4,000 mg/L. Color and soluble COD were measured on the influent and effluent of this reactor every three to four days. Total influent and effluent

COD and mixed liquor volatile suspended solids were measured once a week. MLSS and effluent TSS were also measured every three to four days and these values were used to calculate the volume of biomass wasted from the reactor each day. Eventually, the influent was diluted 1/10 with tap water and color, total and soluble COD, and solids measurements were continued as above. This dilution represented the dilution of acid rinse waste that would occur with municipal waste, if discharged to the sewer.

After about two months, the two combined wastewater reactors were eliminated due to ineffective treatment, and two seven day HRT reactors were started. One contained combined wastewater and the other contained a rinse water mixture and boiler water. The rinse water mixture contained 80% acid rinse, 10% premetallized rinse, and 10% cat-acid rinse water. The rinse water mixture was combined with boiler water in proportion to the plant flows (see “Introduction”). These reactors were also seeded with return sludge from the POTW and operated with a 30 day sludge age. Color and soluble COD were measured on the influent and effluent of these reactors every three to four days. Total influent and effluent COD and MLVSS were measured once a week. Sludge was wasted from these reactors every day based on MLSS and effluent TSS concentrations measured every three to four days. These lab reactors represented possible reactors the Plant might use as a pretreatment before discharging to the sewer. Influent flows were regulated with a two head Masterflex peristaltic pump operating at 1 mL/min.

3.2.4.2 Batch Reactors

Two sets of batch biological reactors were set up during this study. Each reactor was aerated by lab air through a small diffuser. Color and organic analyses were performed on the supernatant of these reactors after the air was shut off and the biomass was allowed to settle.

The first batch study began when the two day HRT, combined wastewater, continuous flow reactors were in operation. This batch test was set up in 300 mL BOD bottles to see if nutrients were needed to biodegrade the combined waste. Four bottles were set up with return sludge from the POTW and combined wastewater. In one jar, 10 mg/L of phosphorus was added in the form of orthophosphate (H_2PO_4). In another, 50 mg/L of nitrogen was added as ammonium chloride. The third had both phosphorus and nitrogen added (10 mg/L and 50 mg/L, respectively), and no nutrients were added to the fourth jar. Nutrients were added in a 100:5:1 ratio of BOD_5, nitrogen, and phosphorus, respectively. The BOD_5 of the combined waste used during this experiment was assumed to be the value determined during characterization (around 1,000 mg/L BOD_5). At start up and on the fifth and tenth day of operation, aeration was discontinued, the sludge was allowed to settle, and a sample of the supernatant was tested for color and TOC.

The second batch test was set up to see how long it would take to reach maximum color and organic removals for the combined waste stream and a rinse water mix. This rinse water mix was a combination of the three rinse water waste streams in a 4:1:1 ratio of acid, premetallized, and cat-acid rinse waters. This combination is similar to the three dye waste stream combination used for the dye mix chemical coagulation jar tests. Two reactors were operated for 10 days with TOC, dissolved organic carbon (DOC), and color measured at start up and on the third, fifth, seventh, and tenth days. One reactor contained the combined wastewater and the other contained the rinse water mix. Both reactors were seeded with return sludge from the POTW. Mixed liquor suspended solid concentrations were also measured at start up and on the fifth and tenth day.

3.2.4.3 Respirometer Tests

Two respirometer tests were set up with premetallized rinse water and cat-acid rinse water using a HACH model 2173A apparatus to determine if either of the waste streams were inhibitory to biological treatment. This instrument can monitor the biological oxygen demand (BOD) of a sample over time. There were five samples set up for each seven day test, two premetallized rinse water dilutions, two cat-acid rinse water dilutions, and a blank. Each one pint (about 500 mL) sample bottle was seeded with a small amount (approximately 2 mL) of return sludge from the POTW, then filled with 158 mL of diluted sample or distilled water for the blank. The bottles were sealed, and BOD was measured as a change in air pressure within the sealed BOD bottle. In the first test, premetallized rinse water was diluted 1/5 and 1/10, and cat-acid rinse water was diluted 1/10 and 1/20. In the second test, premetallized rinse water was diluted 1/2 and 1/4, and cat-acid rinse water was diluted 1/4 and 1/8.

3.2.5 Two Stage Treatment

Two stage treatments to remove enough color and organics to meet discharge limits were attempted using the two seven day HRT, continuous flow reactors. Jar tests were conducted on the effluent of these reactors using the polymers Color Katch 50 and WT 2392. Jar tests were performed as described in Section 3.2.1. No pH adjustment or other chemical addition was performed on the samples before coagulation. The coagulated samples were allowed to settle and color was measured on the supernatant. TSS and soluble COD were measured on samples with greater than fifty percent color removal. TSS was measured on a well-mixed jar, and soluble COD was measured on the filtered supernatant. Doses from 50-200 mg/L polymer were added to the combined reactor effluent, and doses from 20-100 mg/L polymer were added to the rinse and boiler water reactor effluent.

3.2.6 Final Characterization

A characterization of the influent, effluent, and coagulated effluent of the seven day HRT reactors was performed before the reactors were shut down. A characterization was also performed on the influent and effluent of the continuous flow reactor for the 1/10 dilution of acid rinse water. The coagulant doses used on the effluent of the seven day HRT reactors for characterization were determined from the jar tests described in the "Two Stage Treatment" section above. These doses were the minimum doses that resulted in final color values less than 150 ADMI units. The full characterization included BOD_5, TOC, TSS, total ammonia, TKN, color, UV light transmission, total cyanide, oil and grease, total phenols, benzene, and twelve metals (barium, cadmium, chromium, copper, lead, nickel, silver, arsenic, beryllium, boron, mercury, selenium). TSS levels in the coagulated effluent were measured on a well-mixed sample immediately following coagulation. All other parameters were measured after the coagulated effluent was filtered through a 1.2 μm filter. BOD_5 and TOC levels on the effluent (prior to coagulation) were measured on unfiltered and filtered (through a 1.2 μm filter) samples. Three sets of samples taken from each of the seven day reactors were characterized. One set of samples taken from the two day HRT, acid rinse reactor was characterized. If a parameter was not detected in one or more of the sample sets, averages were calculated using the detection limit of the instrument.

3.3 Analytical Procedures

Described here are the analytical procedures used throughout this study. Most test methods are from *Standard Methods for the Examination of Water and Wastewater* (later referred to as *Standard Methods*, 1992).

3.3.1 Five Day Biological Oxygen Demand (BOD_5)

Biological oxygen demand was performed as described in *Standard Method* (1992), method 5210B (5-Day BOD). No seeding or filtering was required. Dissolved oxygen (D.O.) was measured with a YSI Model 54 Oxygen Meter (Yellow Springs, OH). Dilutions ranged from 0.001 for the dye wastes to 0.2 for the effluent of the biological reactors.

3.3.2 Chemical Oxygen Demand (COD)

COD was performed using the closed reflux titrimetric method (5220C) in *Standard Methods* (1992). The total COD of the samples were measured unless otherwise stated. Samples in which soluble COD was measured were first filtered through a 0.45 μm membrane filter.

3.3.3 Total and Dissolved Organic Carbon (TOC and DOC)

TOC and DOC were measured on the DC-80 Dohrmann Carbon Analyzer (Santa Clara, CA) in conjunction with a combustion furnace. The combustion-infrared method (5310B) in *Standard Methods* (1992) was followed. Samples in which DOC was measured were first filtered through a 0.45 μm membrane filter.

3.3.4 Solids

Three types of solids tests were performed: total suspended solids (TSS), mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS). *Standard Methods* (1992) defines suspended solids as the solids retained on a filter with a 2 μm pore size or smaller. All solids tests conducted in this study were filtered through a 1.5 μm glass fiber filter. TSS was measured on the effluent of the reactors, the supernatant of some jar tests, and on individual waste streams for characterization. For the continuous flow reactors, MLSS and MLVSS samples were taken by removing the baffle and mixing the contents of the reactor before sampling. In the batch reactor, MLSS and MLVSS samples were taken on a well-mixed reactor. TSS and MLSS were performed using *Standard Methods* (1992), method 2540D, where samples are dried at 103 °C. MLVSS was performed using *Standard Methods* (1992), method 2540E, where samples are ignited at 500 °C.

3.3.5 Total Ammonia and Total Kjeldahl Nitrogen (TKN)

In order to measure total ammonia (NH_3-N), samples were first distilled according to *Standard Methods* (1992), method 4500- NH_3 B. For TKN, samples were first digested and distilled according to *Standard Methods* (1992), method 4500-N_{org} B (Macro-Kjeldahl Method). One hundred mL sample volumes were used in these distillations. Ammonia and TKN levels were then determined using *Standard Methods* (1992), method 4500- NH_3 E (titrimetric method), with 0.02 N H_2SO_4 used as the titrant.

3.3.6 Total Phosphorus

Total phosphorus was measured according the ascorbic acid method (4500-P E) in *Standard Methods* (1992). Before this analysis, samples were digested following method

4500-P B (Sample Preparation-Persulfate Digestion Method). This method was altered slightly by using a digestion block set between 120 °C and 130°C instead of the autoclave for digestion.

3.3.7 Color

A Beckman DU 640 spectrophotometer (Fullerton, CA) was used to measure transmittance through samples at wavelengths of 438 nm, 540 nm, and 590 nm. Color was calculated according to *Standard Methods* (1992), method 2120 E (ADMI Tristimulus Filter Method). A calibration curve was developed using platinum-cobalt standards with known ADMI values. The ADMI color of samples was determined through comparison with this standard curve. All color measurements taken during this study were true color measurements, therefore, samples were filtered through a 1.2 µm filter before analysis. Since the pH can effect the color of a sample, the pH of most samples was adjusted to 7.6±0.2 before analysis. For the final characterization (see "Section 3.2.6"), pH was not adjusted prior to measuring color. The pH of these samples was around 8. The color of these samples remained the same for a pH range from about four to about ten; therefore, pH adjustment was not necessary.

3.3.8 UV Light Transmittance

The POTW uses a UV light disinfection system. To ensure this system can effectively disinfect the wastewater entering the POTW, the town has set a limit of 40% or greater on the UV light transmittance of any wastewater discharged to the sewer. Transmittance was measured at a wavelength of 253.7 nm on a sample filtered through a 1.2 µm filter. A Beckman DU 640 spectrophotometer (Fullerton, CA) with a 1 cm pathlength was used for this measurement.

3.3.9 Metals

Barium, cadmium, chromium, copper, lead, nickel and silver were measured using a Perkin-Elmer Zeeman 5100 Atomic Absorption Spectrophotometer. Total metals concentrations were measured in each sample, and digestions were performed according to method 3030G (Nitric Acid/Sulfuric Acid Digestion) in *Standard Methods* (1992).

3.3.10 pH and Dissolved Oxygen

The pH of all samples was measured using a Fisher Accumet pH meter. The meter was calibrated using pH 7 and pH 4 buffers prior to each use. Dissolved oxygen (D.O.) was monitored in all reactors using a YSI Model 54 Oxygen Meter (Yellow Springs, OH).

3.3.11 Other Analyses

Total cyanide, oil and grease, total phenols, benzene, and five total metals (arsenic, beryllium, boron, mercury, and selenium) were measured by Olver Laboratories in Blacksburg, VA.

4.0 RESULTS AND DISCUSSION

4.1 Characterization

Tables 5 and 6 characterize the pollutants in the eight waste streams of the Plant. The most significant pollutants detected were the organics (BOD_5, COD, TOC) and color. The three types of dye waste streams (acid, premetallized, and cat-acid) were highly organic and colored with high variability of both of these parameters from one sample to the next. The average BOD_5 of the dye wastes ranged from 2,859 mg/L to 6,296 mg/L BOD_5. Average COD ranged from 8,436 mg/L to 16,931 mg/L COD, and average TOC ranged from 2,813 mg/L to 5,610 mg/L TOC. The average color for the three dye wastes ranged from 60,351 ADMI to 74,715 ADMI units.

The three rinse waters (acid rinse water, premetallized rinse water, and cat-acid rinse water) and combined waste streams contained significantly less organic matter and color than the dye wastewaters, but still contained high levels and were highly variable. The rinse waters had average BOD_5 levels from 1,534 mg/L to 3,196 mg/L BOD_5, average COD levels from 3,176 mg/L to 8,304 mg/L COD, and average TOC levels from 820 mg/L to 2,620 mg/L TOC. The average color of the rinse waters ranged from 463 ADMI to 4,202 ADMI units. The combined waste stream had average BOD_5, COD, and TOC levels of 1,161 mg/L, 2,977 mg/L, and 886 mg/L, respectively. The average color of the combined waste stream was 2,027 ADMI units. The boiler water waste stream had low levels of all pollutants tested.

Levels of the nutrients, nitrogen and phosphorus, were important to know since biological treatment was considered. Phosphorus testing provided highly variable results, but indicated that phosphorus was present in all waste streams (from 0.63 mg/L to 13.4 mg/L phosphorus). Nitrogen was also present in all waste streams, mostly as

Table 5 - Concentration of Organic Matter, Nutrients, and Color in the Various Waste Streams

	Wastestream							
Pollutant	**Acid Dye**	**Premetallized Dye**	**Cat-Acid Dye**	**Acid Rinse Water**	**Premet. Rinse Water**	**Cat-Acid Rinse Water**	**Boiler Water**	**Combined Wastewater**
pH	2-3	2-3	4-5	4-5	4-5	4-6	8-10	3-5
BOD (mg/L) avg	4,974	6,296	2,859	3,196	1,534	2,321	13	1,161
max	5,817	8,733	3,725	3,825	1,762	2,796	13	1,495
min	3,640	5,042	2,353	2,688	1,305	2,000	0.0	890
COD (mg/L) avg	8,436	11,426	16,931	5,262	3,176	8,304	42	2,977
max	11,040	13,500	18,952	7,200	3,600	10,320	54	4,320
min	7,020	9,116	13,416	4,050	2,752	6,956	31	2,160
TOC (mg/L) avg	2,813	3,936	5,610	1,477	820	2,620	5.7	886
max	3,998	4,358	6,095	1,853	831	3,261	5.7	1,308
min	2,001	3,320	4,994	1,145	809	2,119	0.0	644
TSS (mg/L) avg	49	205	72	43	42.5	204	14.6	48.4
max	168	494	112	95	76	568	29	75.5
min	6	8	49	16	9	19	3.6	27.8
Total Ammonia (mg/L)	6.30	ND	5.60	0.56	ND	5.6	2.24	0.98
max								
min								
TKN (mg/L) avg	103	119	131	97	50.4	120	1.96	60
max	174	162	137	120	56.0	140	1.96	64.4
min	33.6	67.2	123	84.0	44.8	106	0.0	53.2
Total Phosphorus(mg/L)	0.63	13.4	4.25	3.09	6.71	2.06	2.98	9.04
max	0.91	17.6	4.5	3.98	9.3	2.8	3.50	14.0
min	0.35	9.1	4.2	2.00	4.12	1.2	2.43	4.37
Color (ADMI) avg	60,351	74,715	60,677	1,146	463	4,202	79	2,027
max	167,957	142,670	70,070	1,450	757	5,035	122	3,979
min	10,375	27,163	52,503	872	168	2,585	53	479
UV Light Trans. (%) avg	0.24	0.22	0.17	0.13	10.6	1.0	70.0	1.69
max	0.49	0.44	0.25	0.17	20.2	1.8	70.2	2.17
min	0.054	0.043	0.11	0.07	1.07	0.48	69.5	0.99

Table 5 - Concentration of Organic Matter, Nutrients, and Color in the Various Waste Streams (cont.)

	Wastestream							
Pollutant	**Acid Dye**	**Premetallized Dye**	**Cat-Acid Dye**	**Acid Rinse Water**	**Premet. Rinse Water**	**Cat-Acid Rinse Water**	**Boiler Water**	**Combined Wastewater**
Total Cyanide (mg/L)avg	ND (0.005)	ND (0.005)	0.013	ND (0.005)	0.037	ND (0.005)	ND (0.005)	ND (0.005)
max			0.022		0.052			
min			ND (0.005)		0.023			
Oil and Grease (mg/L)	272	312	16.5	38	13.5	9.5	9	23
max	540	499	23	80	17	14	12	43
min	87	125	ND (10)	9	ND (10)	ND (5)	ND (6)	ND (5)
Total Phenols (mg/L) avg	ND (0.18)	ND (0.18)	ND (0.15)	0.006	ND (0.005)	ND (0.008)	ND (0.005)	ND (0.012)
max	ND (0.25)	ND (0.25)	ND (0.25)	0.006		ND (0.01)		ND (0.02)
min	ND (0.05)	ND (0.10)	ND (0.05)	ND (0.005)		ND (0.005)		ND (0.005)
Benzene (mg/L) avg	ND (0.012)	ND (0.25)	ND (0.25)	ND (0.005)	ND (0.25)	ND (0.25)	ND (0.005)	0.024
max	ND (0.025)	ND (0.5)	ND (0.5)		ND (0.5)	ND (0.5)		0.063
min	ND (0.005)	ND (0.005)	ND (0.005)		ND (0.005)	ND (0.005)		ND (0.005)

Note: 1. ND - not detected

2. Samples of most waste streams were taken between 10/11/95 and 11/8/95. Cat-acid dye and cat-acid rinse samples were taken between 1/17/95 and 2/22/95.

3. Instrument detection limits are presented in parentheses for the samples in which pollutants were not detected.

Table 6 - Concentration (in ug/L) of Total Metals in the Various Waste Streams

		Wastestream							
Metal		Acid Dye	Premetallized Dye	Cat-Acid Dye	Acid Rinse Water	Premet. Rinse Water	Cat-Acid Rinse Water	Boiler Water	Combined Wastewater
barium	avg	57.5	94.5	28.3	31.5	22	22.3	22	45
	max	96	160	38.0	40	26	28.0	34	52
	min	38	48	21.0	24	18	19.0	8.0	30
cadmium	avg	5.7	6.65	1.23	4.5	4.3	0.97	6.0	5.5
	max	8.2	11.4	2.30	6.4	4.6	1.30	10.4	10.4
	min	1.8	3.4	0.70	2.0	4.0	0.60	3.8	2.8
chromium	avg	86	37,135	7.87	28.7	167	6.2	35.8	305
	max	118	48,000	9.6	48.0	188	7.9	74	620
	min	34	18,240	6.4	10.6	146	4.4	13	96
copper	avg	160	103	99	65	41	8.7	60	70
	max	312	146	207	88	48	11.0	98	90
	min	50	62	28	52	34	7.0	24	58
lead	avg	145	173	5.67	121	103	3.33	102	135
	max	190	266	9.00	146	112	5.00	136	208
	min	64	102	3.00	98	94	2.00	80	74
nickel	avg	48	52	8.33	25	30	8.0	52	30
	max	74	68	9.00	30	34	13.0	102	32
	min	24	24	7.00	18	26	5.0	26	28
silver	avg	2.1	3.7	0.8	2.65	2.2	0.87	2.7	1.7
	max	3.8	5.8	0.9	5.0	2.2	1.30	4.2	3.0
	min	1.2	2.0	0.7	1.2	2.2	0.60	1.6	0.8
arsenic	avg	ND (1)	ND (1)	ND (1)	4	ND (1)	ND (1)	4.7	9.3
	max				10			13	24
	min				ND (1)			ND (1)	ND (1)
beryllium	avg	0.2	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	0.23	ND (0.2)
	max	0.2						0.3	
	min	ND (0.2)						ND (0.2)	

Table 6 - Concentration (in ug/L) of Total Metals in the Various Waste Streams (cont.)

		Wastestream							
Metal		Acid Dye	Premetallized Dye	Cat-Acid Dye	Acid Rinse Water	Premet. Rinse Water	Cat-Acid Rinse Water	Boiler Water	Combined Wastewater
boron	avg	167	ND (200)	ND (150)	ND (100)	ND (200)	ND (100)	ND (200)	ND (200)
	max	ND (200)		ND (200)					
	min	100		ND (100)					
mercury	avg	0.63	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	0.8	ND (0.2)
	max	1.1						2	
	min	0.2						ND (0.2)	
selenium	avg	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)	10.3
	max								15
	min								ND (2)

Note: 1. ND - not detected

2. Samples of most waste streams were taken between 10/11/95 and 11/8/95. Cat-acid dye and cat-acid rinse samples were taken between 1/17/95 and 2/22/95.

3. Instrument detection limits are presented in parentheses for the samples in which pollutants were not detected.

TKN. TKN was significant in all waste streams (from 50 mg/L to 131 mg/L TKN) except the boiler water waste stream (1.96 mg/L TKN). Total ammonia was only detected in one set of the three sets of samples tested and levels were very low (from 0.56 mg/L to 6.3 mg/L NH_3-N).

Oil and grease appeared in the acid dye (272 mg/L oil and grease) and premetallized dye (312 mg/L oil and grease) waste streams at levels above the discharge limits (100 mg/L oil and grease). The concentration of oil and grease in the other waste streams averaged below 45 mg/L.

The three metals of concern in these waste streams are lead, copper, and silver. These three metals exceeded the POTW discharge limits in most, if not all, of the waste streams. The limit for lead is 8.3 ppb (µg/L). Lead levels averaged from 102 µg/L to 173 µg/L lead in all waste streams except the cat-acid dye and cat-acid rinse water waste streams in which lead levels were below the town limit (5.67 µg/L and 3.33 µg/L lead, respectively). Copper exceeded the town limit of 55 µg/L in all waste streams except the premetallized rinse and cat-acid rinse waters. Copper levels in the other waste streams averaged from 60 µg/L to 160 µg/L copper. The limit for silver is 0.02 µg/L. The silver levels in all waste streams averaged from 0.8 µg/L to 3.7 µg/L silver. Chromium levels in the premetallized dye waste stream were high (37,135 µg/L chromium) because these dyes are complexed with chromium.

4.2 Physical and Chemical Treatments

The chemicals that were successful in removing color from one or more waste streams were aluminum sulfate (alum), ferric chloride, lime and magnesium carbonate, Color Katch 50, and chlorine. Lime and magnesium carbonate were only effective when used together. Graphs in Appendix B show how color and TOC varied with chemical dose.

Alum removed color from the dyehouse waste stream. A dose of 1,000 mg/L (as $Al_2(SO_4)_3 \bullet 18H_2O$) resulted in a 66% decrease in color from about 12,500 ADMI color units to about 4,300 ADMI units. A dose of 1,500 mg/L alum removed 76% of the color (final color was 2,926 ADMI units). TOC removals were 26% (from 588 to 438 mg/L TOC) for 1,000 mg/L alum and 53% (final TOC was 274 mg/L) for 1,500 mg/L alum. Alum was only successful on samples that were pH adjusted to around neutral (pH = 6.6).

Ferric chloride was capable of removing color from the dyehouse and combined waste streams. Coagulation with ferric chloride was attempted on three different dyehouse wastewater samples, collected on three different days. Jar test analyses of the first sample (taken on December 19, 1994) indicated that there was 97% color removal (from 14,163 to 460 ADMI units) and 73% TOC removal (from 910 to 250 mg/L TOC) when 800 mg/L $FeCl_3$ was added. No TOC or color removal was noted in the second jar test (sample taken December 22, 1994), and there was no floc formation. The third jar test (sample taken January 2, 1995) resulted in 76% color removal (from 46,932 to 11,347 ADMI units) and 55% TOC removal (from 2,559 to 1,149 mg/L TOC). The initial color and TOC of the third sample was more than three times the initial color and TOC of the first sample. The differences in results from the ferric chloride jar tests are attributed to the different strengths and characteristics in the samples tested. The pH of these samples before the test was between 3 and 4. Figures 7 and 8 are graphs of the TOC and color removals versus $FeCl_3$ dose. The plot for the January 2, 1995 sample indicated an increase in both color and TOC with 1,000 mg/L $FeCl_3$. The jar with this

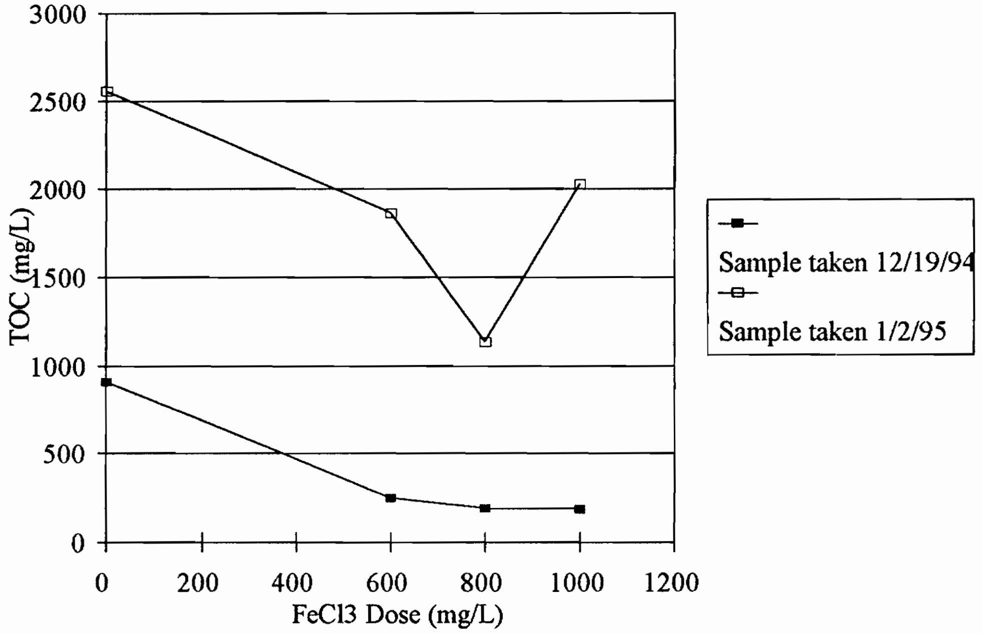


Figure 7 - TOC Removal with Ferric Chloride Coagulation of the Dyehouse Wastewater

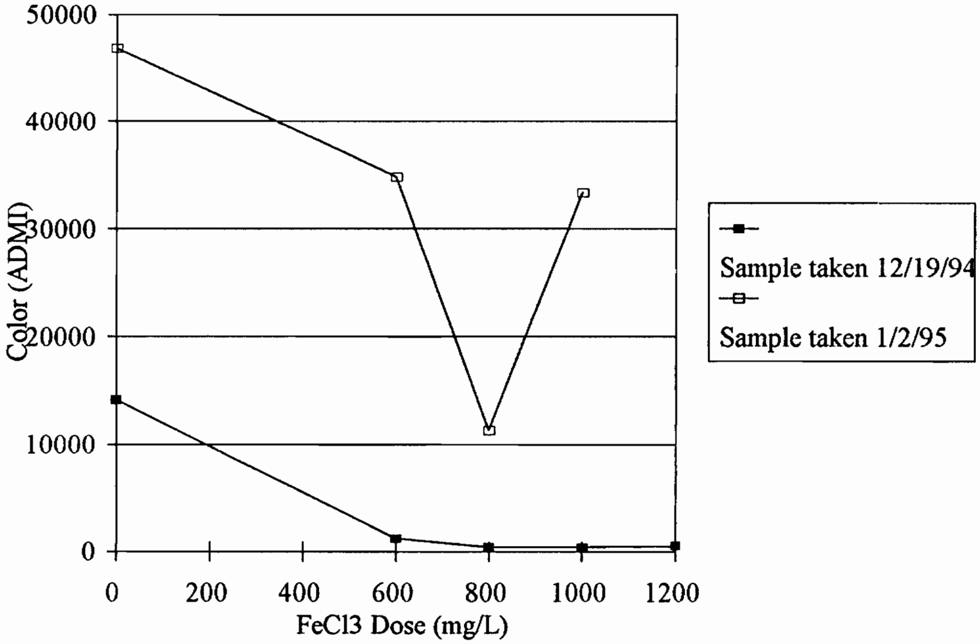


Figure 8 - Color Removal with Ferric Chloride Coagulation of the Dyehouse Wastewater

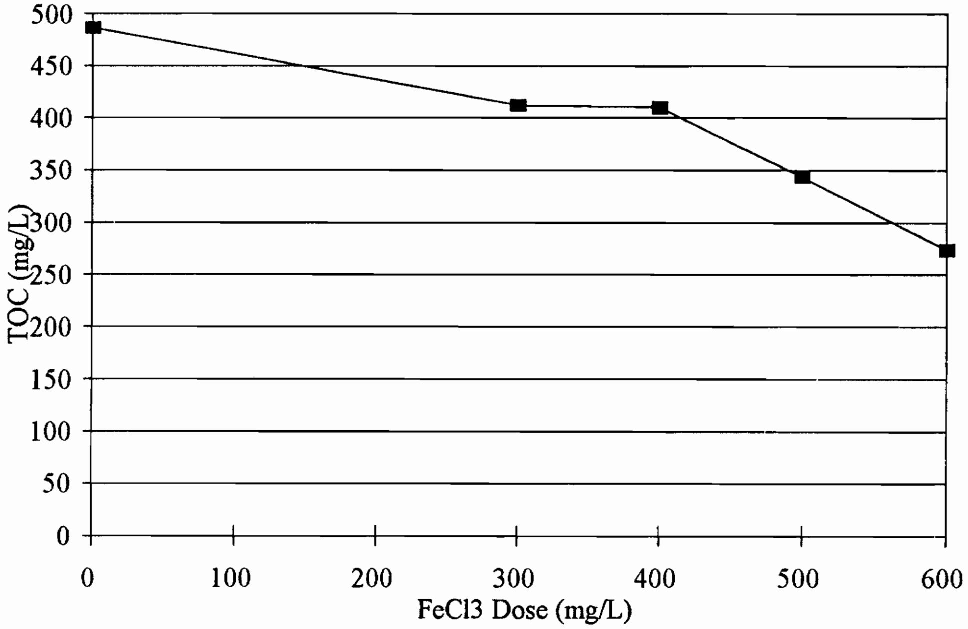


Figure 9 - TOC Removal with Ferric Chloride Coagulation of the Combined Wastewater

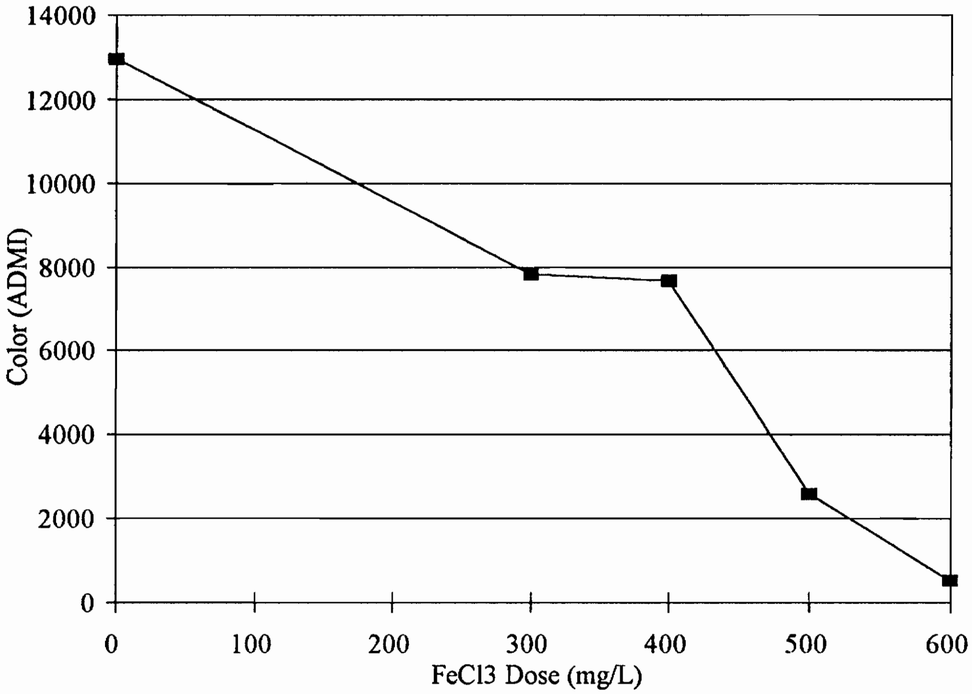


Figure 10 - Color Removal with Ferric Chloride Coagulation of the Combined Wastewater

dose was pH adjusted to 7 following the jar test. This caused some of the flocs to dissolve into the wastewater, which increased the color and TOC.

For the combined waste stream, a 600 mg/L dose of $FeCl_3$ resulted in a 96% color removal (from 12,976 to 531 ADMI units) and a 44% TOC removal (from 487 to 274 mg/L TOC). However, color removals only occurred only when the pH was adjusted to 7 with sodium bicarbonate prior to testing. Figures 9 and 10 show how TOC and color removals in the combined wastewater varied with $FeCl_3$ dose.

Lime and magnesium carbonate removed color from the combined wastewater. A dose of 800 mg/L lime and 400 mg/L magnesium carbonate resulted in a maximum color removal of 87% (from 12,976 to 1,615 ADMI units) and a maximum TOC removal of 16% (from 487 to 407 mg/L TOC).

Chlorine appeared to remove all visible color from the combined wastewater with as little as 100 mg/L chlorine. ADMI color measurements indicated 42% color removal with 50 mg/L chlorine (from 1,613 to 931 ADMI units) and 55% color removal with 200 mg/L chlorine (final color was 726 ADMI units). Although visually it appeared that all the color was removed, the wastewater remained cloudy. The cloudiness could not be filtered out with a 1.2 μm filter, and it reduced the light transmittance of the sample, resulting in a higher color value. Chemical oxygen demand (COD) was used to measure the organic content of the sample. Maximum COD removal was 27.5% at a dose of 200 mg/L chlorine (from 2,880 to 2,088 mg/L COD). No pH adjustment was necessary to remove color with chlorine. The pH of the wastewater was 3.7 prior to testing. Chlorination was also attempted on the combined waste stream with the pH adjusted to 7. Similar color removals resulted with 57% being removed at a 250 mg/L chlorine dose. COD removals were insignificant.

At high doses, the polymer, Color Katch 50, removed significant amounts of color from the acid and premetallized dye streams. For the acid dye, two jar tests were performed: one with clay and one without. Color removals were the same in both tests. A 3,000 mg/L dose of polymer with 400 mg/L AClay removed 99.5% of the color (from 64,322 to 326 ADMI units). A 3,000 mg/L dose of polymer with no clay addition resulted in 99.4% color removal (final color was 397 ADMI units). TOC removals were also not affected by the presence of clay. About 57% of the TOC was removed in both cases (from 2,699 to around 1,130 mg/L TOC). Since clay did not seem to affect color or TOC removal, premetallized dye jar tests were conducted without it. A 2,000 mg/L dose of Color Katch 50 reduced the color from 37,308 ADMI units to 280 ADMI units (99%). The final color with 3,000 mg/L polymer was 324 ADMI units. TOC removals from premetallized dye were a little less than from the acid dye. TOC was reduced from 2,506 mg/L to 1,593 mg/L TOC (36.4%) with 2,000 mg/L polymer and to 1,554 mg/L TOC (38%) with 3,000 mg/L polymer. This polymer was also used on cat-acid dyes with no success.

The desired results from these jar tests was to identify one chemical that could remove enough color and other pollutants to discharge these wastes directly to the sewer. Although excellent color removals resulted (up to 99%), none of the chemicals tested could remove color down to the 150 ADMI color units standard. The two most promising chemicals were ferric chloride and Color Katch 50. They both achieved greater than 95% color removal on the dye waste streams tested. It is possible when these dye streams are mixed with the rinse waters and boiler water streams, the resulting wastewater could be treated by the POTW.

There are problems in using Color Katch 50. One problem is the high dose needed (3,000 mg/L polymer) to remove the color. Not only are these doses excessive, but sludge disposal becomes an issue. Another problem is that this polymer did not work on all dye waste streams. A separate treatment for the cat-acid dye needs to be found.

Based on the physicochemical treatment results presented in the literature review, the low organic removals obtained in this study were expected. In general, organic removals were less than 60%. There was one exception in which ferric chloride removed 73% of the TOC from the dyehouse waste stream. Chlorine and the lime/magnesium carbonate mixture removed the least amount of organics, ranging from no removal to 27.5% removal.

4.3 Biological Treatment

4.3.1 Continuous Flow Reactors

The first two reactors of this study were used to treat dyehouse wastewater and combined wastewater. Within two weeks, the activated sludge concentration in the dyehouse reactor decreased to 710 mg/L MLSS. This reactor was taken off-line and jar tests were begun on the dyehouse waste to determine if a physicochemical pretreatment was possible. These results are presented in Section 4.2. The activated sludge in the combined wastewater reactor fluctuated from 1,100 to 3,540 mg/L MLSS, and the effluent solids concentration fluctuated from 44 mg/L to over 7,000 mg/L TSS (See Appendix C for data). Slugs of biomass would occasionally leave the reactor in the effluent. The second combined waste reactor experienced similar solids fluctuations. Dissolved oxygen (D.O.) in these reactors should be greater than 2 mg/L D.O., but were generally around 0.7 mg/L D.O. The air diffuser was replaced with several fine bubble diffusers and the D.O. began fluctuating between 0.7 and 6 mg/L D.O. Biomass was not manually wasted from these reactors, because it was being wasted in the effluent.

Because the actual volume of sludge lost in the effluent is unknown, the sludge age of these reactors is also unknown.

TOC and color were monitored on these reactors. Figures 11 and 12 show how these parameters fluctuated in the influent and effluent over time. The reactors were labeled Reactor C and Reactor D in order to distinguish between the two. The operating conditions of the two reactors were identical. Reactor C averaged around 35% TOC removal, and Reactor D averaged around 22% TOC removal. There was no evidence of color removal from these reactors. Since the effectiveness of these reactors was poor, one of these reactors was eliminated and the other was modified to a seven day HRT.

The acid dye rinse water reactor accomplished a maximum color removal of 48% and a maximum soluble COD removal of 59%. Although this reactor seemed to treat the rinse water effectively, dissolved oxygen levels could not be maintained above 1 mg/L D.O. This reactor simulated the biological treatment system at the municipal plant. If this lab-scale reactor could handle 100% acid rinse water, the Plant might be able to discharge the acid rinse water directly to the town's sewer system. Since the municipal wastewater will be diluting this waste stream approximately 1 to 10, the lab-scale reactors influent was diluted 1/10 with tap water to see if appropriate D.O. levels could be maintained and if treatment was possible. With the dilution, D.O. was between 5 and 7 mg/L. Maximum soluble COD removal was from 307 mg/L to 7.7 mg/L COD (97%) and maximum color removal was 64%, with final color values consistently under 40 ADMI color units. Figures 13 and 14 show how soluble COD and color fluctuated over time in the reactor treating diluted acid rinse water.

The final two reactors had HRTs of seven days. The Plant's current treatment system consists of a storage lagoon that experiences some biological activity followed by mixing tanks where coagulation/flocculation occurs with polymers. When biological

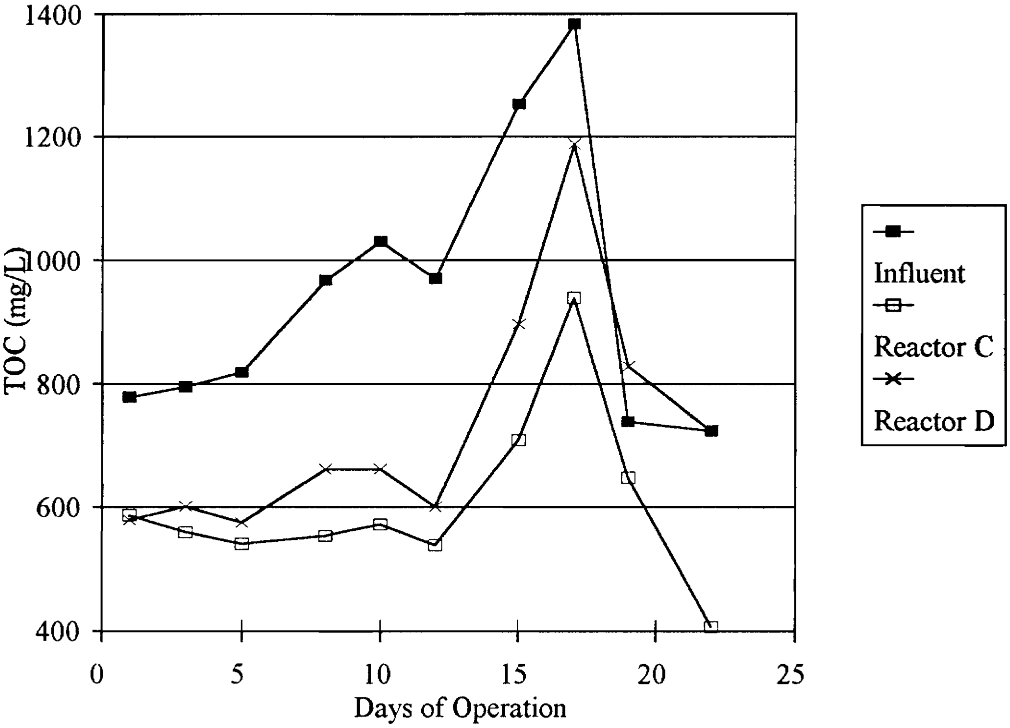


Figure 11 - TOC Removal from the 2 Day HRT Combined Wastewater Continuous Flow Reactors.

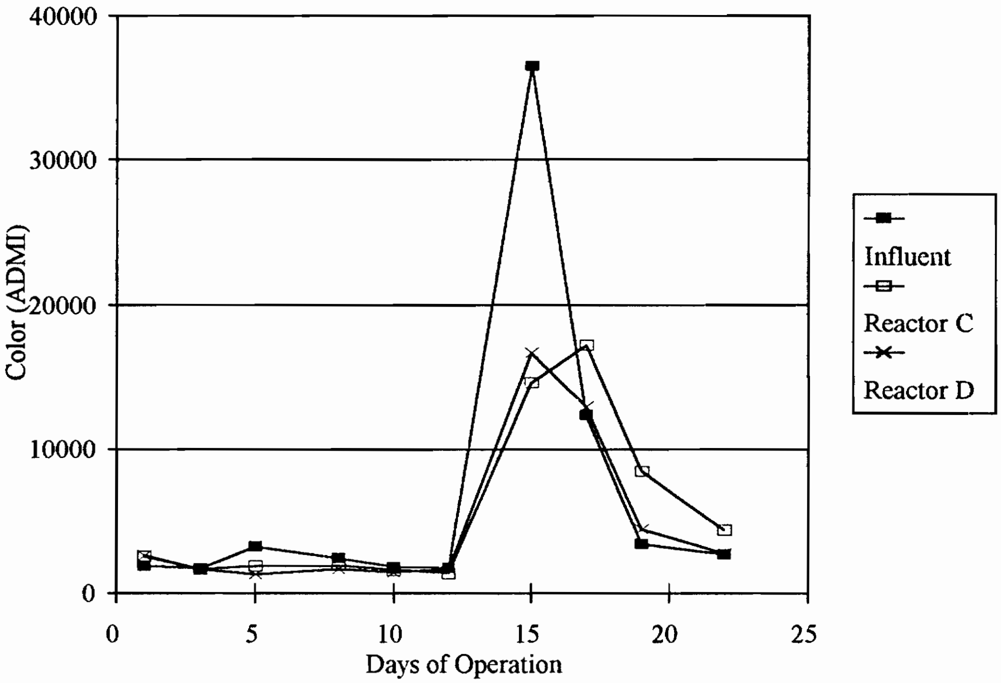


Figure 12 - Color Removal from the 2 Day Combined Wastewater Continuous Flow Reactors.

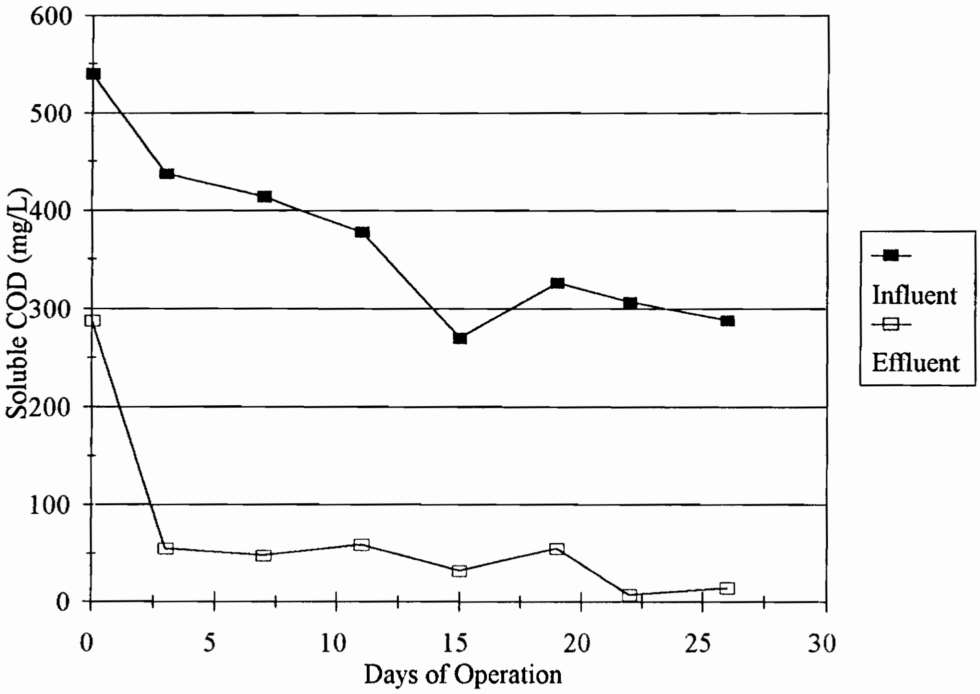


Figure 13 - Soluble COD Removal from the 1/10 Diluted Acid Rinse Water Continuous Flow Reactor.

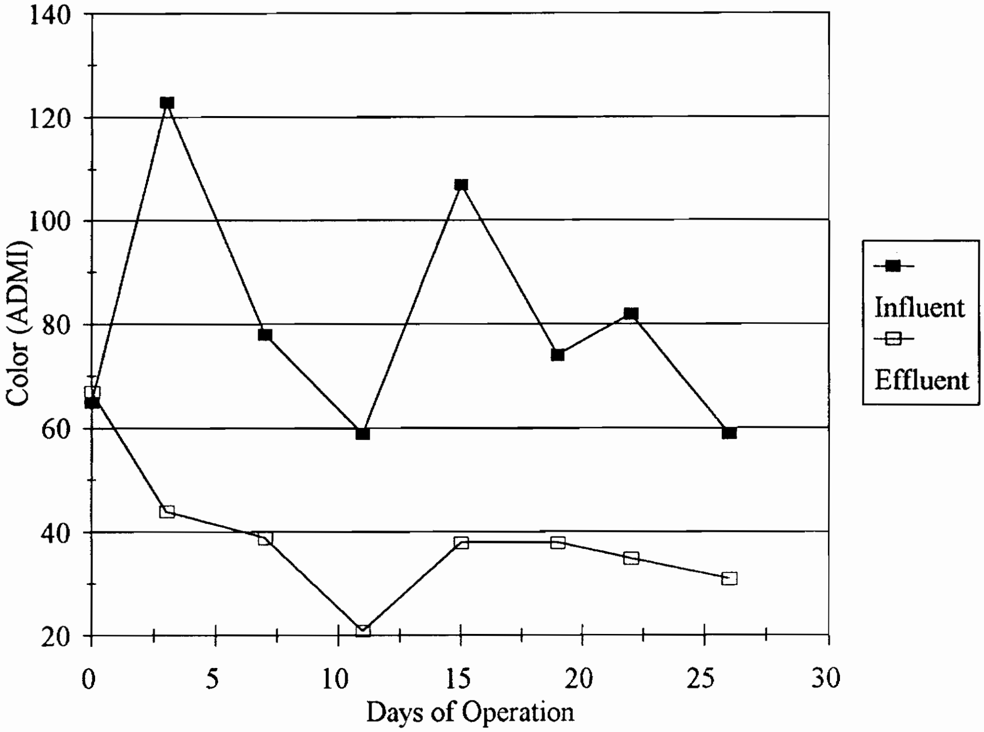


Figure 14 - Color Removal from the 1/10 Diluted Acid Rinse Water Continuous Flow Reactor.

treatment is evident in the lagoon, the Plant's treatment system is rather effective. These lab-scale reactors were used to find a better biological treatment system for the Plant. One reactor received the combined waste stream and the other received a combination of rinse waters and boiler water. If a separate pretreatment was found for the dyes, the rinse/boiler water lab reactor indicated if the rinse and boiler waters were amenable to biological treatment.

The combined wastewater reactor obtained between 77% and 93% soluble COD removal with final CODs around 260 mg/L COD, well below the 1,500 mg/L COD standard set by the POTW. Color removals were between 40% and 80% with effluent color ranging between 800 and 2,000 ADMI color units depending on the strength of the influent. The rinse/boiler reactor achieved an average of 84% soluble COD removal with final soluble CODs between 400 and 500 mg/L COD. Color removals were from 45% to 70% with final color values around 150 to 300 ADMI units. Figures 15 through 18 show how soluble COD and color vary in the influent and effluent throughout the operation of these reactors.

The 7 day HRT reactors were very effective in removing COD from the wastewater and also had some success in color removal. The longer detention time allowed for some equalization of the highly variable waste. It also decreased the organic loading on the reactors allowing the oxygen levels to stabilize. D.O. levels in these reactors were easily maintained between 4 and 6 mg/L D.O.

Earlier attempts to biologically treat the combined wastewater with a two day HRT failed, but the seven day HRT reactor was successful in biologically treating the waste. Other researchers have reported that extending the HRT of their biological reactors improved biological treatment. Shriver and Daugue (1978) had four reactors of textile waste with HRT's of 12, 24, 36, and 48 hours. The reactors with the higher HRTs

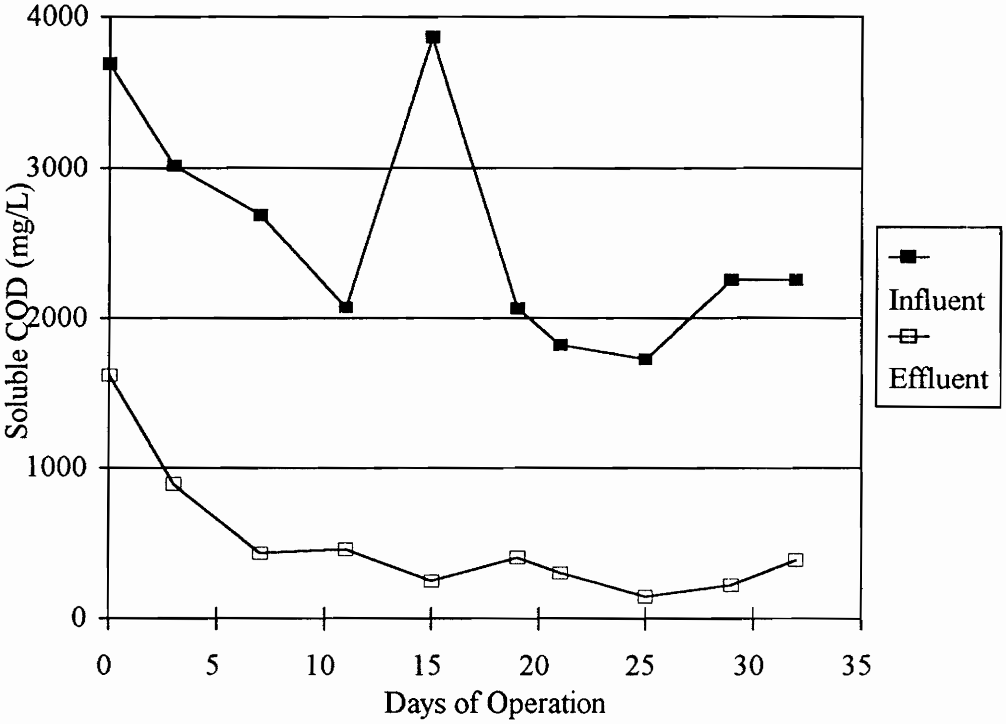


Figure 15 - Soluble COD Removal from the 7 Day HRT Combined Wastewater Continuous Flow Reactor.

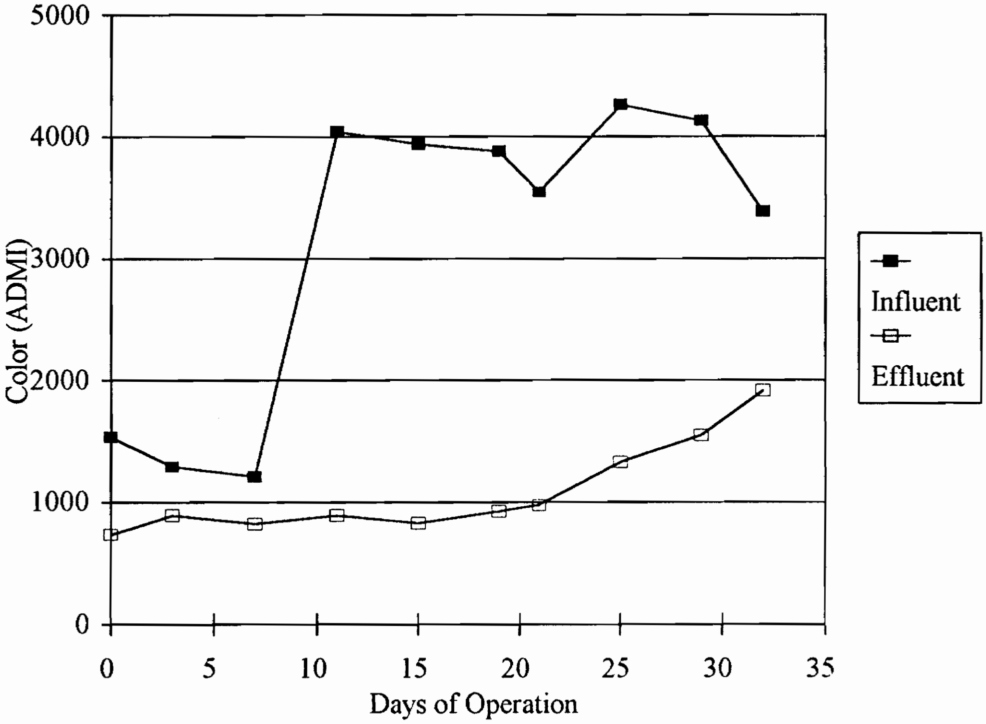


Figure 16 - Color Removal from the 7 Day HRT Combined Wastewater Continuous Flow Reactor.

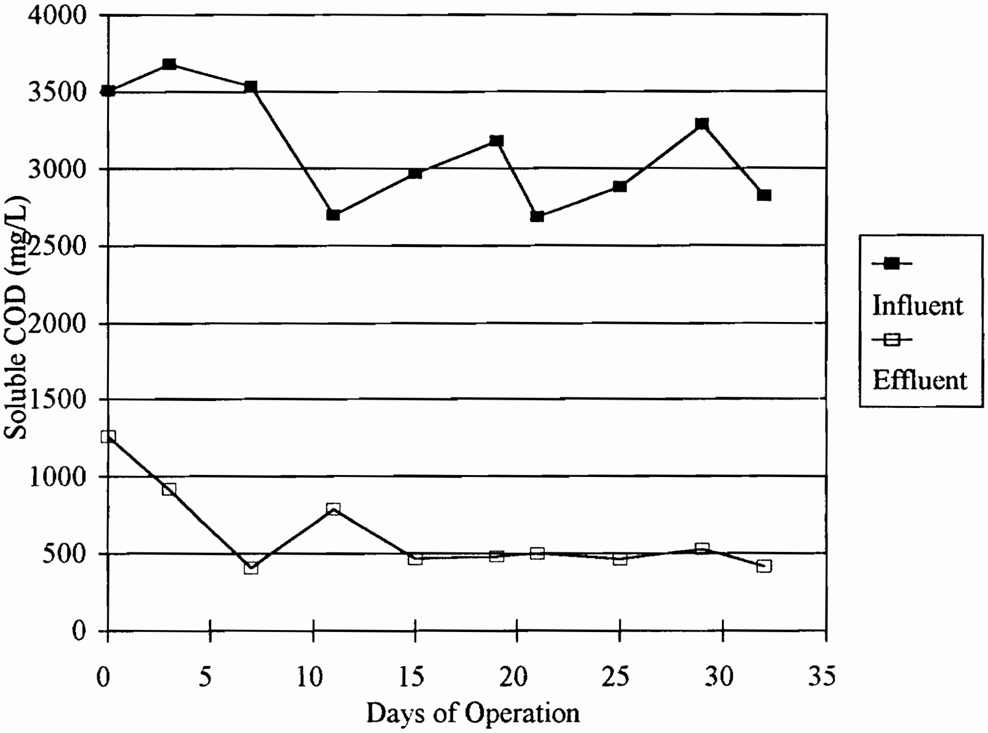


Figure 17 - Soluble COD Removal from the 7 Day HRT Rinse/Boiler Water Continuous Flow Reactor.

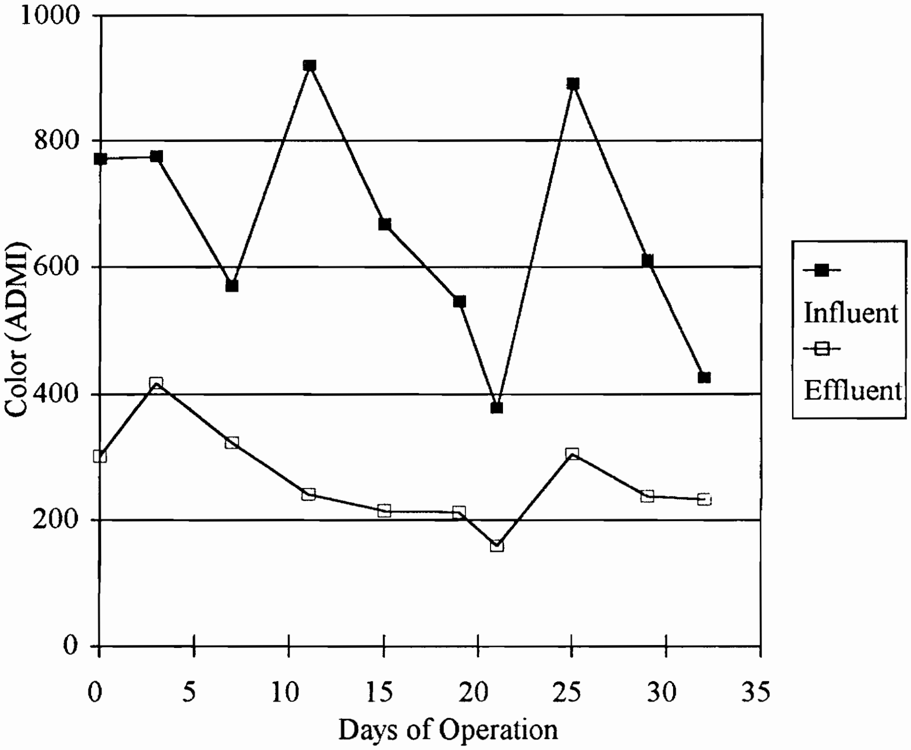


Figure 18 - Color Removal from the 7 Day HRT Rinse/Boiler Water Continuous Flow Reactor.

accomplished higher color and BOD_5 removals. Weber (1994) and Opdycke (1995) conducted biological treatability studies on the same textile waste in reactors with different HRTs. Weber's (1994) three day reactors achieved lower color and soluble COD removals than Opdycke's (1995) seven day reactors. Also, the effluents of the seven day reactors passed toxicity tests, whereas effluents of the three day reactors did not. Specifics about these studies can be found in Chapter 2.0.

Color removals from the combined and rinse/boiler water reactors were accomplished through different mechanisms. Color in the rinse/boiler water reactor was mainly due to finishes that rinsed off the yarn. These colors seem to have biodegraded within the reactor. Color in the combined wastewater reactor was caused mainly by dyes. The hue of the combined wastewater ranged in appearance from dark green to black, depending on the sample. Color removal from this reactor appeared to be due to adsorption of dyes onto the activated sludge. Sludge in the rinse/boiler water reactor was a muddy brown color. The combined wastewater reactor contained black sludge. Ganesh *et al.* (1994) noticed the sludge in their batch reactors turn from brown to dark blue, and attributed this color change to the adsorption of azo dyes to the sludge.

Jar tests were conducted on the effluents of these reactors using the polymers, Color Katch 50 and WT 2392. Both polymers reduced the color and soluble COD of both effluents. On the rinse/boiler water reactor effluent, 40 mg/L of the Color Katch 50 reduced the color 57% from 139 ADMI units to 60 ADMI units. An 80 mg/L polymer dose reduced color 70% (final color was 42 ADMI units). The polymer reduced the COD of the effluent, as well. The 40 mg/L polymer dose reduced the soluble COD 16%, from 480 mg/L to 403 mg/L COD, and an 80 mg/L polymer dose reduced the soluble COD 44% (final COD was 269 mg/L). The WT 2392 polymer was not as affective at removing color or COD from the rinse/boiler water reactor effluent. A 40 mg/L polymer dose only removed 18% of the color (from 146 to 120 ADMI units), and 80 mg/L polymer dose removed 57% of the color (final color was 63 ADMI units). Soluble COD removal using 80 mg/L of the WT 2392 was only 20% (final COD was 384 mg/L).

Color removal using Color Katch 50 on the combined wastewater effluent was 93% with a 200 mg/L polymer dose (from 1,635 to 116 ADMI color units). This polymer dose resulted in a small soluble COD removal of 33% (from 338 to 226 mg/L COD). As with the rinse/boiler water effluent, the WT 2392 polymer was a little less effective for color removal. A 200 mg/L polymer dose resulted in 89% color removal. However, the WT 2392 polymer appeared to be more effective for soluble COD removal. A 200 mg/L polymer dose removed 78 % of the soluble COD from the effluent.

Low doses of polymers could be used on the effluent of these reactors to remove additional color and COD. Jar tests indicated that these polymers were ineffective on the waste streams prior to biological treatment. Biological treatment either reduces the strength of the wastewater enough for the polymers to work or transforms the dyes and finishes within the wastewater to a more amenable form for coagulation.

4.3.2 Batch Reactors

Because the two day HRT, combined wastewater, continuous flow reactors were not performing as desired, a small batch test was set up to see if additional nutrients were needed for the biological treatment of the combined waste stream. Figures 19 and 20 provide the TOC and color removals over a ten day period. The combined wastewater did not need additional nutrients. All four batch reactors achieved a maximum color removal of 50% after five days. As for TOC removal, the reactor in which no nutrients were added obtained the highest removals at 74%. The lowest removals (48%) occurred in the reactor in which both nitrogen and phosphorus were added. These experiments

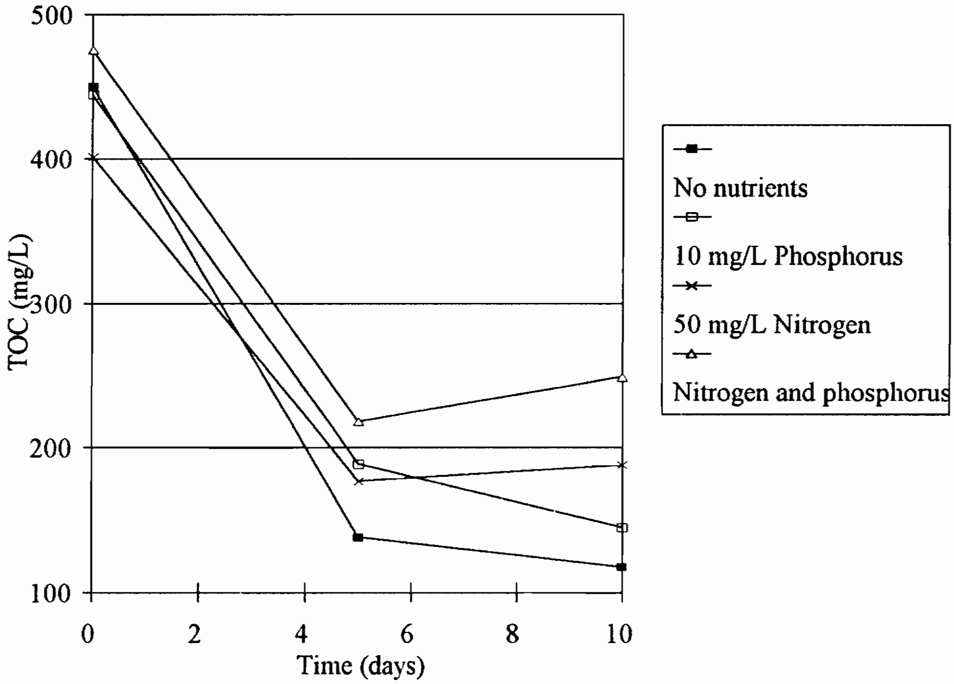


Figure 19 - TOC Removals from Combined Wastewater Batch Reactors with and without Nutrient Addition.

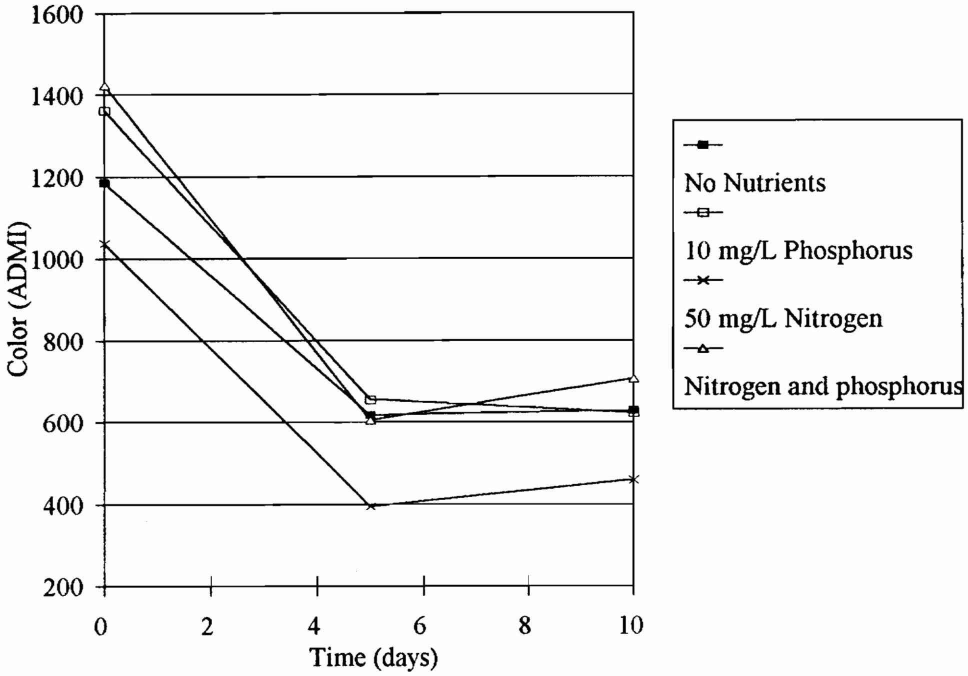


Figure 20 - Color Removals from Combined Wastewater Batch Reactors with and without Nutrient Addition.

also indicated that maximum color and TOC removals from the combined wastewater occurred in five days or less.

A second batch study was done to confirm the extent of the biodegradability of the combined wastewater and to determine the biodegradability of a mixture of rinse waters. Figures 21 and 22 provide TOC, DOC, and color reductions over a ten day period for the combined wastewater batch reactor; and, Figures 23 and 24 show TOC, DOC, and color reductions for the rinse water mix batch reactor. After five days, the combined reactor had 43% color removal, 51% TOC removal, and 22% DOC removal. As for the rinse reactor, color removal after five days was 35% and TOC removal after three days was 12.5%. DOC continuously increased over the ten day period for the rinse water mix reactor. No data was collected from the rinse reactor for the tenth day due to the evaporation of the remaining wastewater. This test confirmed that maximum color and organic removals occurred in 5 days for the combined waste stream.

Since there was little evidence of biodegradation of the rinse waters during this test, it revealed that there was some type of inhibition by one or more of the rinse waters in the rinse water mix batch reactor. At this point during the research, the acid rinse, continuous flow reactor was operating and biological treatment was evident. Therefore, the biological inhibition seen in this batch study was presumed to be due to either the premetallized or cat-acid rinse waters, or possibly both rinse waters.

The increase in the DOC of the rinse water mix batch reactor indicated possible cell lysis. After five days, the TOC and DOC in the combined wastewater reactor began to increase, also indicating possible cell lysis. Ganesh *et al.* (1994) reported cell lysis was the reason for the increase in soluble TOC in his batch reactors. If biodegradation was occurring in these reactors, the extent of degradation was smaller than the release of DOC.

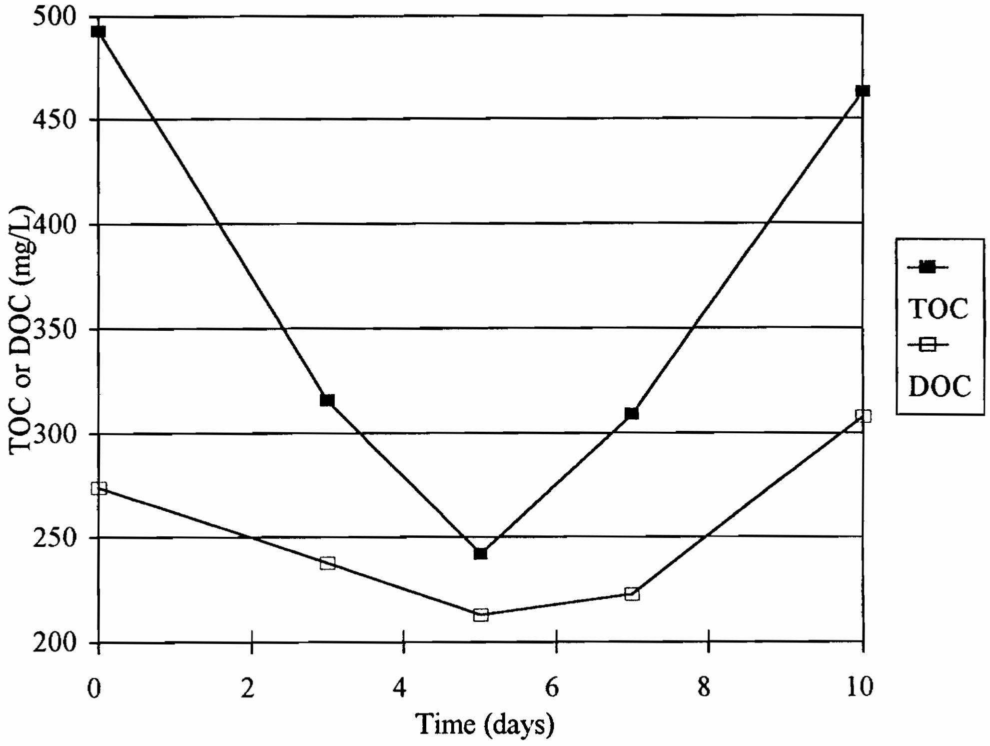


Figure 21 - TOC and DOC Levels in the Combined Wastewater Batch Reactor.

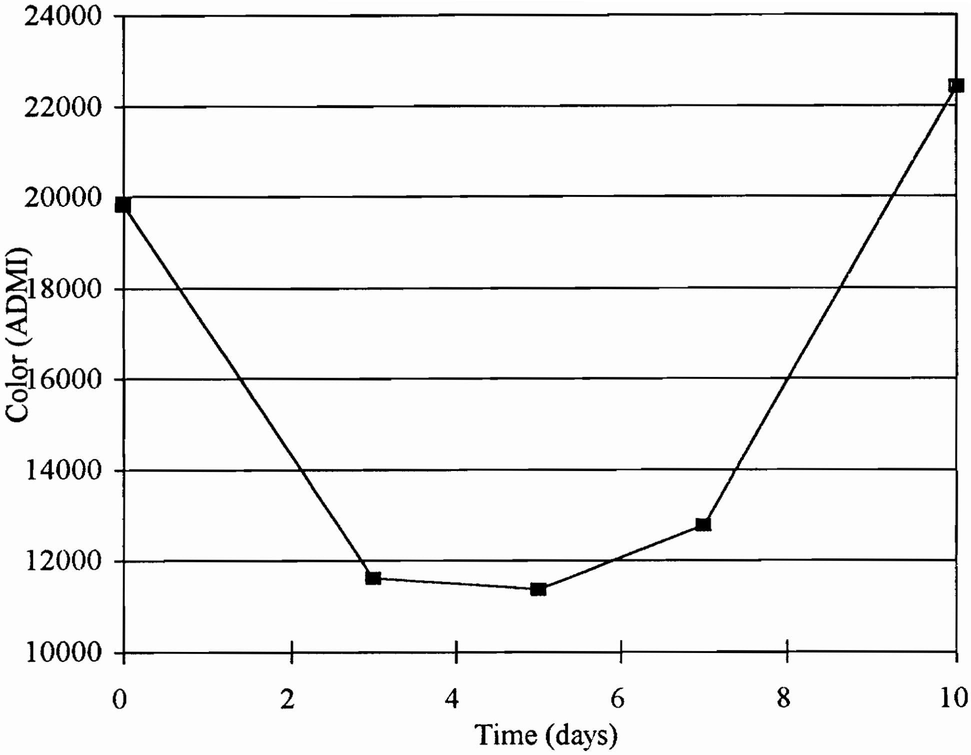


Figure 22 - Color Levels in the Combined Wastewater Batch Reactor.

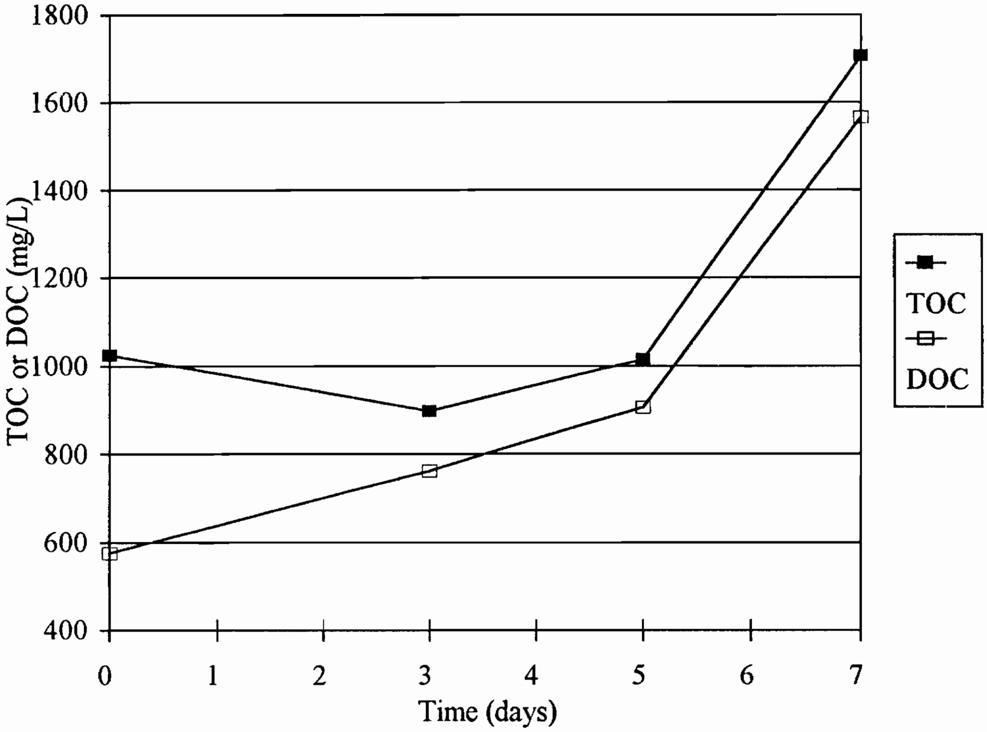


Figure 23 - TOC and DOC Levels in the Rinse Water Mix Batch Reactor.

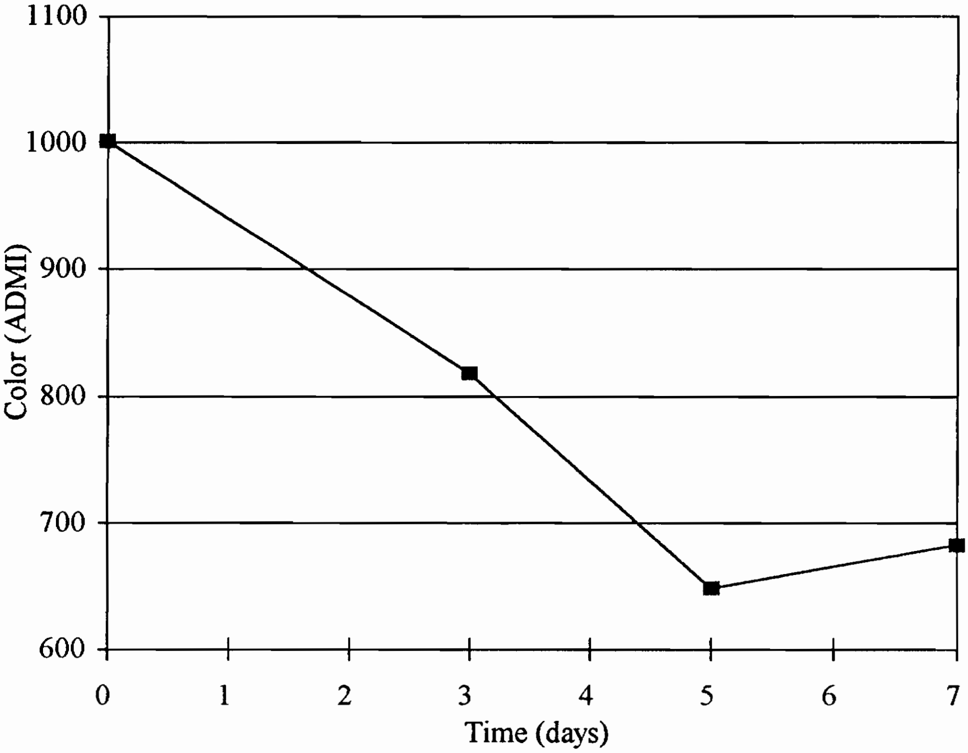


Figure 24 - Color Levels in the Rinse Water Mix Batch Reactor.

4.3.3 Respirometer Tests

Respirometer tests were performed on the premetallized and cat-acid rinse waters to determine the extent of their inhibition to biological treatment. Two separate tests were performed on two different sets of dilutions. The following figures show how BOD varied over the seven day test period for these two waste streams. Figures 25 and 26 were derived from the first test and Figures 27 and 28 from the second test. In these tests, biological inhibition is evident when a more concentrated sample consumes less oxygen than a less concentrated sample of the same wastewater. A lower oxygen consumption would result in a BOD plot with a smaller slope.

In the first test, the two plots for the two dilutions of premetallized rinse water had similar slopes; therefore, the two premetallized rinse water dilutions consumed the same amount of oxygen and inhibition was not evident. The plots of the two cat-acid rinse water dilutions also had similar slopes indicating no inhibition. In the second test, the slopes of the BOD plots of the two premetallized rinse water dilutions were the same until about 125 hours passed. Then, the BOD plot of the 1/2 diluted premetallized rinse water started to level off, where the BOD plot of the 1/4 diluted premetallized rinse water continued to increase. The differences in the slopes of these two plots at this point indicated inhibition by the premetallized rinse water. There was no evidence of inhibition in the cat-acid rinse water since the less diluted sample seemed to consume more oxygen than the more diluted sample.

The second test showed evidence of inhibition by the premetallized rinse water. This rinse water is difficult to biologically treat in high concentrations; however, if the premetallized rinse water is mixed at a lower concentration with other wastewaters that are amenable to biological treatment, effective biological treatment is possible. Rinse waters were mixed in different proportions in the rinse/boiler continuous flow reactor

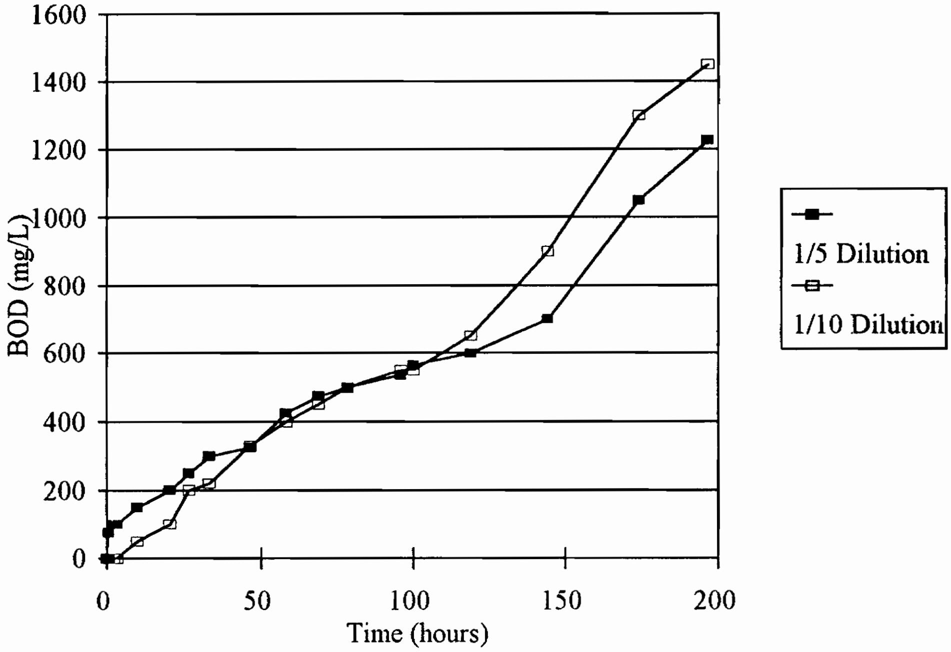


Figure 25 - BOD Over Time for Premetallized Rinse Water in Respirometer Test 1.

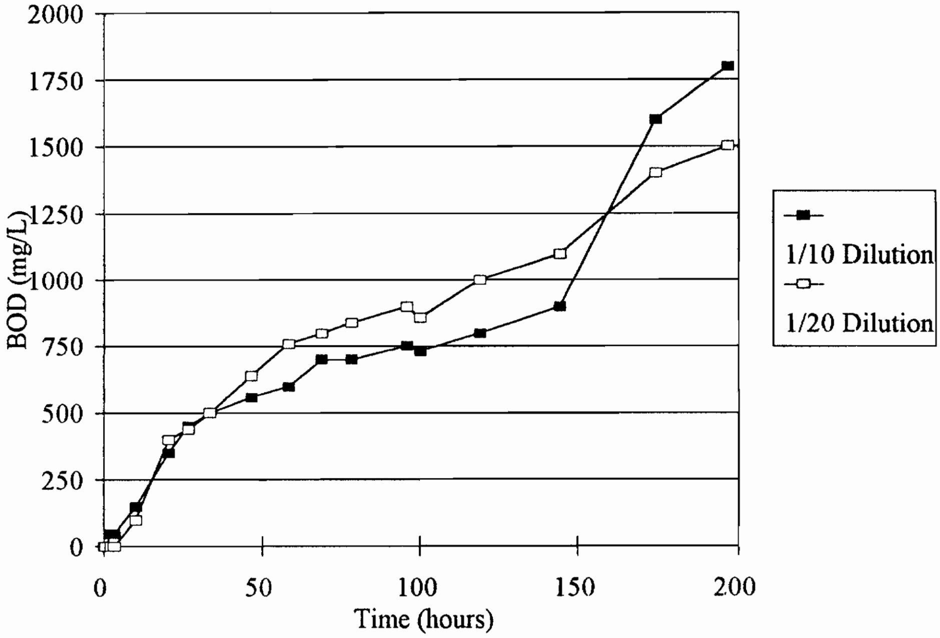


Figure 26 - BOD Over Time for Cat-Acid Rinse Water in Respirometer Test 1.

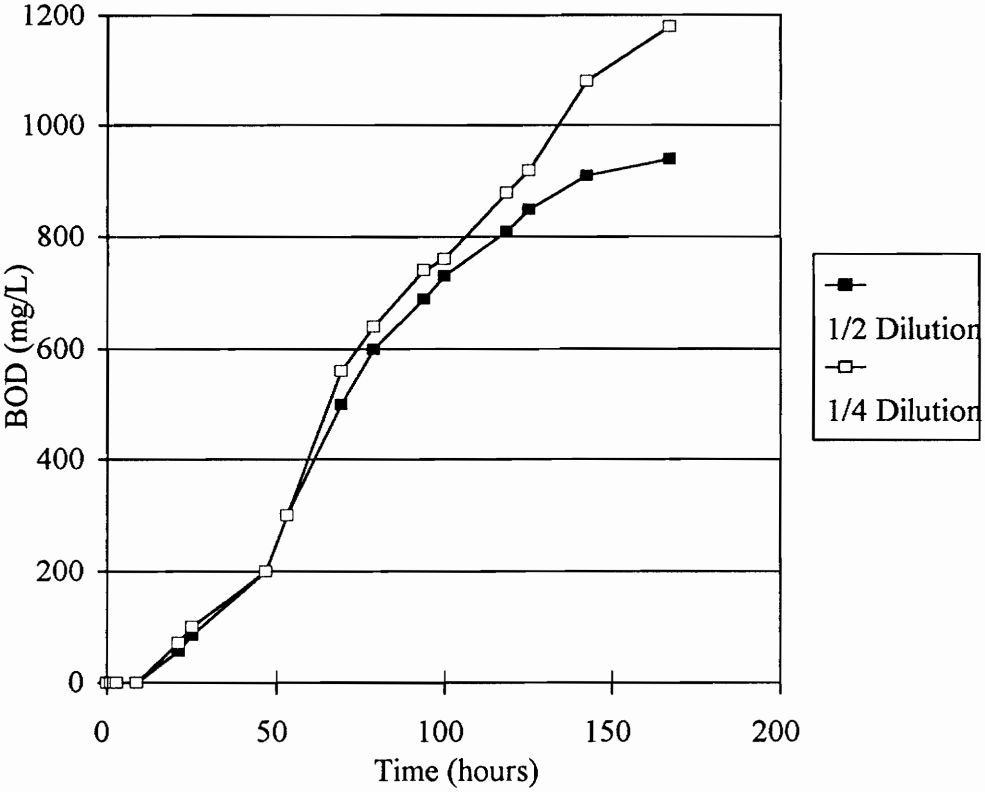


Figure 27 - BOD Over Time for Premetallized Rinse Water in Respirometer Test 2.

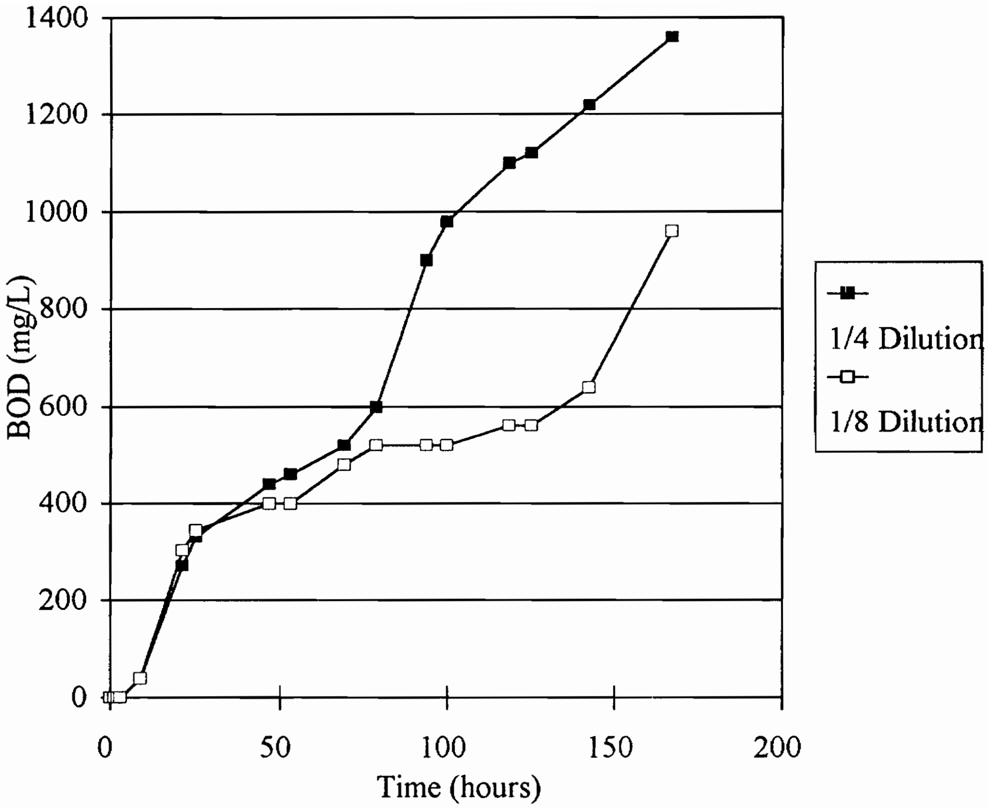


Figure 28 - BOD Over Time for Cat-Acid Rinse Water in Respirometer Test 2.

than in the rinse water mix batch reactor. In the continuous flow reactor, 80% of the rinse water mixture was acid rinse water, 10% was premetallized rinse water, and 10% was cat-acid rinse water. The batch reactor contained 67% acid rinse water, 16.5% premetallized rinse water, and 16.5% cat-acid rinse water. Although biological inhibition was evident in the batch reactor, it was not evident in the continuous flow reactor, probably due to the lower concentration of premetallized rinse water in this reactor.

4.4 Final Characterization

Three continuous flow reactors performed well enough in removing color and COD that the following parameters in and out of the reactors were measured: BOD_5, TOC, TSS, color, UV light transmittance, ammonia, TKN, total cyanide, oil and grease, total phenols, benzene, and twelve metals. These reactors were the two day HRT, acid rinse water reactor (with the 1/10 dilution), the seven day HRT, combined wastewater reactor, and the seven day HRT, rinse/boiler water reactor. Table 7 displays the data obtained for all three reactors.

The purpose of the two day acid rinse water reactor was to see if the POTW could biologically treat the acid rinse water if it was discharged directly to the sewer. This reactor contained a 1/10 dilution of acid rinse water to tap water. The final characterization showed that BOD_5, TOC, color, ammonia, TKN, and total phenols could be removed from this 1/10 dilution by biological treatment. The effluent of this reactor met all town limits for discharge to the sewer except the limit for silver.

The effluent of the seven day combined reactor met all discharge limits set by the town except for the limits set for total phenols, color, UV light transmittance, and the metals, copper, mercury, and silver. The effluent of the seven day rinse/boiler water

Table 7 - Final Characterization of Three Biological Treatment Systems

	2 Day Acid Rinse		7 Day Combined				7 Day Rinse/Boiler			
Pollutant	**Influent**	**Effluent**	**Influent**	**Effluent**	**Filtered Effluent**	**Coagulated Effluent**	**Influent**	**Effluent**	**Filtered Effluent**	**Coagulated Effluent**
BOD (mg/L)	82.5	6.2	1078	92	33	17	2080	>100	>100	58
TOC (mg/L)	92.2	20.9	827	180	150	114	1383	335	300	261
TSS (mg/L)	NT	NT	71	55	NT	355	109	61	NT	144
Color (ADMI)	50	17	2041	1826	NT	163	947	581	NT	356
UV light trans. (%)	62	82	0.13	0.17	NT	0.35	0.44	7.00	NT	8.94
Ammonia (mg/L)	1.7	0.56	0.47	1.12	NT	3.65	0.28	1.12	NT	1.69
TKN (mg/L)	12.3	2.8	49	23	NT	36	88	18	NT	16
Total Cyanide (mg/L)	ND	ND	0.0075	ND	NT	0.006	ND	ND	NT	ND
Oil and Grease (mg/L)	ND	ND	5.5	ND	NT	ND	15.5	ND	NT	ND
Total Phenols (mg/L)	0.009	ND	0.0375	0.058	NT	0.0325	0.066	ND	NT	ND
Benzene (mg/L)	ND	ND	ND	ND	NT	ND	ND	ND	NT	ND
Total Barium (ug/L)	38	38	57	95	NT	123	42	59	NT	179
Total Cadmium (ug/L)	0.2	0.4	1.53	0.47	NT	0.33	0.40	0.73	NT	1.87
Total Chromium (ug/L)	5.8	7.8	139	73	NT	7.33	22	11	NT	6.80
Total Copper (ug/L)	22	36	57	58	NT	32	44	28	NT	21
Total Lead (ug/L)	2.0	8.0	13	6.67	NT	2.67	10.00	9.33	NT	8.00
Total Nickel (ug/L)	8.0	8.0	17	83	NT	27	19	14	NT	13
Total Silver (ug/L)	1.6	1.6	2.13	2.07	NT	1.67	1.07	3.53	NT	2.20
Total Arsenic (ug/L)	0.015	0.01	2.50	6	NT	12.5	12	3.00	NT	6.50
Total Beryllium (ug/L)	ND	ND	2.10	ND	NT	ND	ND	ND	NT	ND
Total Boron (ug/L)	ND	0.14	145	225	NT	285	160	170	NT	145
Total Mercury (ug/L)	ND	ND	2.10	0.25	NT	0.30	0.50	0.35	NT	0.20
Total Selenium (ug/L)	ND	ND	ND	ND	NT	ND	5.50	ND	NT	ND

Note: 1. ND - Not Detected, NT - Not Tested

2. The combined wastewater reactor's coagulated effluent was coagulated with 200 mg/L Color Katch 50.

3. The rinse/boiler water reactor's coagulated effluent was coagulated with 40 mg/L Color Katch 50.

4. Instrument detection limits for the waste streams in which pollutants were not detected are provided in Appendix F.

reactor met all discharge limits except color, UV light transmittance, and the metals, lead, mercury, and silver. These effluents were then coagulated with Color Katch 50 to see if additional pollutant removals were possible. Forty mg/L of the polymer was used on the effluent of the rinse/boiler water reactor, and 200 mg/L polymer was used on the effluent of the combined wastewater reactor. Based on the jar tests conducted (See section 4.3.1), these doses were the minimum doses needed to obtain color values below the discharge limits. Coagulation removed enough copper from the combined wastewater effluent and enough lead and mercury from the rinse/boiler water effluent to meet the sewer discharge limits for these parameters. However, total cyanide appeared in the coagulated effluent of the combined wastewater. Any presence of cyanide exceeds the town sewer discharge limits.

The final characterization indicated that although coagulation removed additional color, color values were still above town sewer limits and UV light transmittance was not significantly improved. Color removals from the combined wastewater through biological treatment and coagulation were relatively consistent throughout the final characterization (See Appendix F). Total color removals ranged from 87% to 95% for the three sets of samples tested. One sample set tested achieved final color values of 120 ADMI units which is just under the 150 ADMI limit, where the other two sample sets achieved final color values just above the limit (185 ADMI). The UV light transmittance through the final coagulated effluent was less than one percent. However, the Plant's wastewater will be diluted approximately 1/10 with the municipal wastewater once discharged to the sewer. The coagulated effluent was diluted 1/10 with distilled water and UV light transmittance was measured to see if the diluted sample could meet the standard. The UV light transmittance through this diluted sample was 53%.

Color removals from the rinse/boiler water mix during biological treatment and coagulation were highly variable (See Appendix F). Total color removals ranged from 33% to 93% for the three sets of samples tested. The coagulated effluent of the initial sample set had final color values of 46 ADMI units, but the coagulated effluent of the final sample set had final color values of 777 ADMI units. This variability is attributed to inconsistent treatment by both the biological and physicochemical treatments. The coagulated effluent from the final set tested was diluted 1/10 with distilled water to see how much the UV light transmittance would be improved. The UV light transmittance of the diluted sample was 50%. Without the dilution, the UV light transmittance of this sample was less than one percent.

TOC removals (>75%) were lower than the BOD_5 removals (>90%) in both 7 day HRT reactors and the 2 day HRT, diluted acid rinse water reactor. According to Horning (1977), this indicates the presence of not readily biodegradable material in the wastewater. Coagulation removed additional BOD_5 and TOC from the effluents of the seven day reactors. Forty-eight percent of the BOD_5 and 24% of the TOC was removed from the combined wastewater effluent. Thirteen percent of the TOC was removed from the rinse/boiler water effluent. BOD_5 removals from the rinse/boiler water effluent can not be reported since actual BOD_5 levels in the effluent were not determined. BOD_5 and TOC levels in the coagulated effluent were compared to levels measured in the filtered effluent. Since the coagulated effluent was filtered after coagulation, comparing BOD_5 and TOC levels in the filtered effluent with BOD_5 and TOC values in the coagulated effluent determined BOD_5 and TOC removals due to coagulation only and not due to coagulation and filtration.

Biological treatment removed all detectable oil and grease from both the combined wastewater and the rinse/boiler water mix. Total phenols were not removed in the 7 day HRT, combined wastewater reactor. Coagulating the effluent of this reactor had no effect on total phenols and appeared to introduce total cyanide to the wastewater. The town discharge limits for these two parameters are 0.001 mg/L for total phenols and 0 mg/L for total cyanide; therefore, the final effluent of this treatment system does not meet the town limits. As for the 7 day HRT, rinse/boiler water reactor, cyanide was not present in the rinse/boiler water waste stream and biological treatment removed all detectable phenols from the wastewater.

Metal removals varied for each metal and each reactor. The four metals that appear to be a problem based on the final characterization are copper, lead, mercury, and silver. Copper was not removed biologically from the combined waste stream, and the effluent exceeded the 55 ppb (µg/L) limit. As for the rinse/boiler water, 36% of the copper was removed biologically and the effluent of this reactor met the town limit. Additional copper was removed from both the combined and rinse/boiler water waste streams through coagulating the effluent of the two 7 day HRT reactors. Coagulation removed an additional 45% of the copper from the combined waste stream bringing copper levels in the coagulated effluent below the town limits.

Lead removals were evident from both seven day reactors and from subsequent coagulation. Seventy-nine percent of the lead was removed from the combined wastewater through biological and physicochemical treatment, and 20% of the lead was removed from the rinse/boiler water through biological and physicochemical treatment. The town discharge limit for lead is 8.3 ppb (µg/L). Both the effluent and the final coagulated effluent of the combined wastewater reactor met this limit. The effluent of the rinse/boiler water reactor prior to coagulation was just above this limit at 9.33 µg/L lead, but the coagulated effluent was just below this limit at 8 µg/L lead. Although the final coagulated effluent of the rinse/boiler water reactor met the lead discharge limits, this metal remains a concern. Of the three sample sets tested, one sample set indicated no lead removals in the rinse/boiler water by biological or physicochemical treatments, and the final coagulated effluent exceeded the lead discharge limit at 12 μg/L lead.

Eighty-eight percent of the mercury in the combined wastewater appeared to be removed biologically, and 30% of the mercury was removed biologically from the rinse/boiler water. Coagulating the rinse/boiler water reactor effluent removed an additional 43% of the mercury, and coagulating the combined wastewater reactor effluent removed no additional mercury from the wastewater. The town discharge limit for mercury is 0.24 ppb (μg/L). This limit is met by the rinse/boiler water reactor's coagulated effluent, but not by the combined wastewater reactor's coagulated effluent.

Silver was not removed in either treatment system and exceeded the 0.02 ppb (μg/L) standard set by the town.

Table 8 summarizes the results of the final characterization.

Table 8 - Final Effluent Pollutant Levels and Sewer Discharge Limits

Pollutant	Limit	2 Day Acid Rinse Reactor Effluent	7 Day Combined Wastewater Reactor Coagulated Effluent		7 Day Rinse/Boiler Water Reactor Coagulated Effluent	
			Avg.	Range	Avg.	Range
BOD (mg/L)	350	6.2	17	17-17	58	35-81
TSS (mg/L)	300	NT	355	332-373	144	100-182
Color (ADMI)	150	17	163	120-185	356	46-777
UV light trans. (%)	40	82	0.35	0.17-0.45	8.9	0.15-20
Ammonia (mg/L)	35	0.56	3.65	3.1-4.5	1.7	1.1-2.2
Total Cyanide (mg/L)	0	ND	0.006	ND-0.007	ND	ND
Oil and Grease (mg/L)	100	ND	ND	ND	ND	ND
Total Phenols (mg/L)	0.001	ND	0.0325	0.011-0.054	ND	ND
Benzene (mg/L)	0	ND	ND	ND	ND	ND
Total Barium (ug/L)	5000	38	123	76-184	179	166-192
Total Cadmium (ug/L)	20	0.4	0.33	0.2-0.4	1.9	0.4-4
Total Chromium (ug/L	5000	7.8	7.3	6.4-8.0	6.8	5.8-7.8
Total Copper (ug/L)	55	36	32	4.0-70	21	12-36
Total Lead (ug/L)	8.3	8.0	2.7	2.0-4.0	8	4.0-12
Total Nickel (ug/L)	1000	8.0	27	20-32	13	10-18
Total Silver (ug/L)	0.02	1.6	1.7	0.8-2.6	2.2	2.0-2.6
Total Arsenic (ug/L)	50	0.01	12.5	10-15	6.5	5.0-8.0
Total Beryllium (ug/L)	0	ND	ND	ND	ND	ND
Total Boron (ug/L)	1000	0.14	285	ND-370	145	ND-90
Total Mercury (ug/L)	0.24	ND	0.3	ND-0.4	0.2	ND-0.2
Total Selenium (ug/L)	20	ND	ND	ND	ND	ND

Note: Coagulated effluent solids were measured on a well mixed sample prior to filtration.

5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary and Conclusions

The goal of this study was to find an economical and efficient method to treat the Plant's wastewater. Initially, the Plant's wastewater was segregated into eight waste streams and characterized for levels of organic matter, color, nutrients, and metals. Then, a series of physical, chemical, and biological treatments were tried on individual waste streams and combinations of these waste streams.

The conclusions derived from this study are given below.

1) Two chemicals used on certain dye waste streams were promising. Ferric chloride removed from 76% to 97% of the color from the dyehouse waste stream and removed 96% of the color from the combined waste stream. High doses (3000 mg/L) of Color Katch 50 removed 99% of the color from the acid and premetallized dye waste streams.

2) The success of the 2 day HRT, diluted acid rinse water reactor indicated that the POTW may be able to biologically treat the acid rinse water without any pretreatment.

3) A seven day HRT biological treatment system is effective in removing organic matter and color from the combined waste stream and a combination of rinse waters and boiler water waste streams. Maximum soluble COD removals from the combined waste stream were 93%, and maximum color removals from the combined waste stream were

80%. As for the rinse/boiler water combination, soluble COD removals averaged 84%, and maximum color removals were 70%.

4) Based on the final characterization, the effluent of the 7 day HRT, combined wastewater reactor met all town sewer discharge limits except the limits for color, UV light transmittance, total phenols, and the metals, copper, mercury, and silver. The effluent of the 7 day HRT, rinse/boiler water reactor met all town sewer discharge limits except the limits for color, UV light transmittance, and the metals, lead, mercury, and silver.

Coagulating these effluents improved most of these parameters, but most still did not meet the town sewer discharge limits. Although color and UV light transmittance were improved, average color values in the coagulated effluent were still above the town limits. Color in the coagulated effluent of the combined wastewater was 163 ADMI units, and color in the coagulated effluent of the rinse/boiler water reactor was 356 ADMI units. UV light transmittance was less than 1% through the coagulated effluent of the combined wastewater and less than 9% of the coagulated effluent of the rinse/boiler water.

Coagulation removed enough copper in the combined effluent and enough lead and mercury in the rinse/boiler water effluent to meet the discharge limits set by the town.

Total cyanide appeared in the coagulated effluent of the combined wastewater reactor. This is a concern since the sewer discharge limits for cyanide are 0 mg/L.

5) UV light transmittance through the final coagulated effluent of both the combined waste water and rinse/boiler water reactors was improved when diluted 1/10 with distilled water. The dilution brought the UV light transmittance above the 40% limit.

5.2 Recommendations

Included here are recommendations for further treatability studies and for possible treatments to be adopted by the Plant.

1) A continuous flow, aerobic biological treatment system operated at a 7 day HRT and 30 day sludge age followed by chemical coagulation with Color Katch 50 is recommended for pretreatment of the Plant's combined waste stream.

2) Biological tests should be conducted on a combination of the Plant's pretreated waste and the municipal waste entering the POTW to ensure the POTW can treat the Plant's pretreated waste.

3) Further studies should be conducted on pretreating the dye waste streams. The polymer, Color Katch 50, was effective at very high doses on the acid and premetallized dyes, but nothing was identified which could treat the cat-acid dyes. If a suitable treatment can be found for the three dye waste streams, then biological treatment of the rinse/boiler water mix followed by chemical coagulation may be a viable treatment alternative for the Plant.

4) Time limitations restricted the number of jar tests which could be conducted on the effluent of the biological reactors. Further studies should be conducted using other chemicals to ensure that the most effective treatment will be used.

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APPENDIX A

Abbreviations

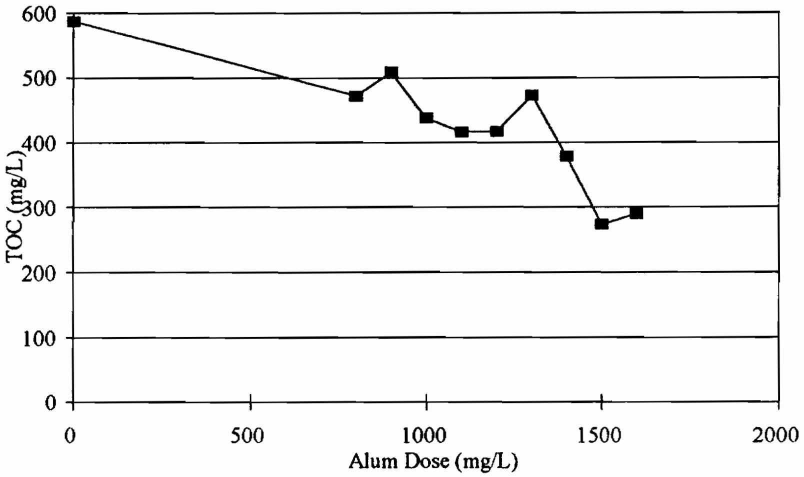
LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers Institute
BOD_5	5 day biological oxygen demand
BOD	biological oxygen demand
COD	chemical oxygen demand
DAF	dissolved air flotation
D.O.	dissolved oxygen
DOC	dissolved organic carbon
HRT	hydraulic residence time
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
NH_3-N	ammonia nitrogen
NOEC	no observed effect concentration
OD	optical density
POTW	publically owned treatment works
ppb	parts per billion, µg/L
Θ_c	sludge age, sludge retention time
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TSS	total suspended solids

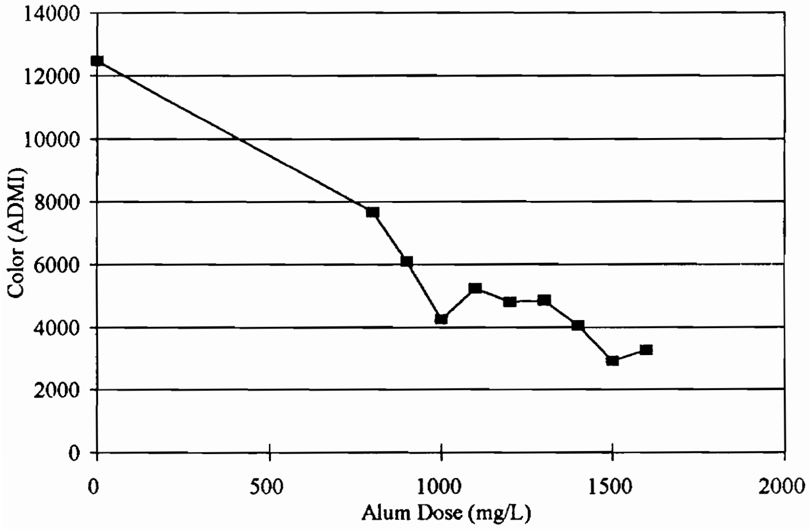
APPENDIX B

Jar Test Graphs

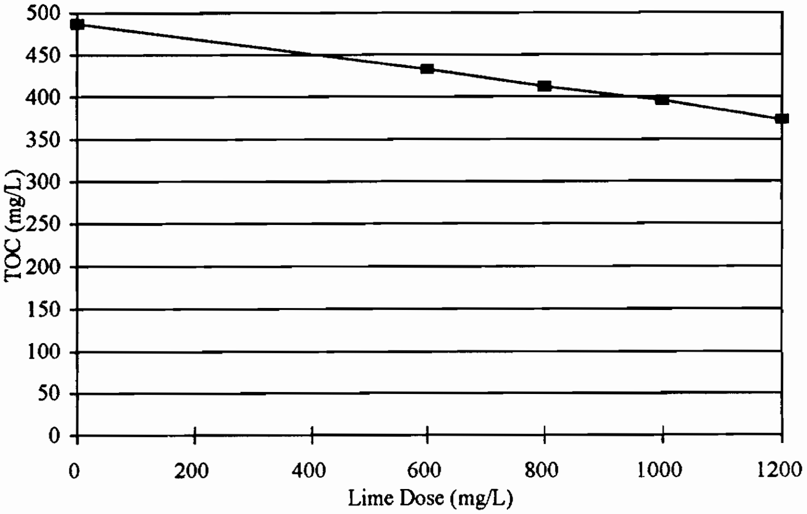
TOC Removal with Alum Coagulation
of the Dyehouse Wastewater



Color Removal with Alum Coagulation
of the Dyehouse Wastewater



TOC Removal from the Combined Waste
with Lime and 400 mg/L MgCO3



Color Removal from Combined Waste
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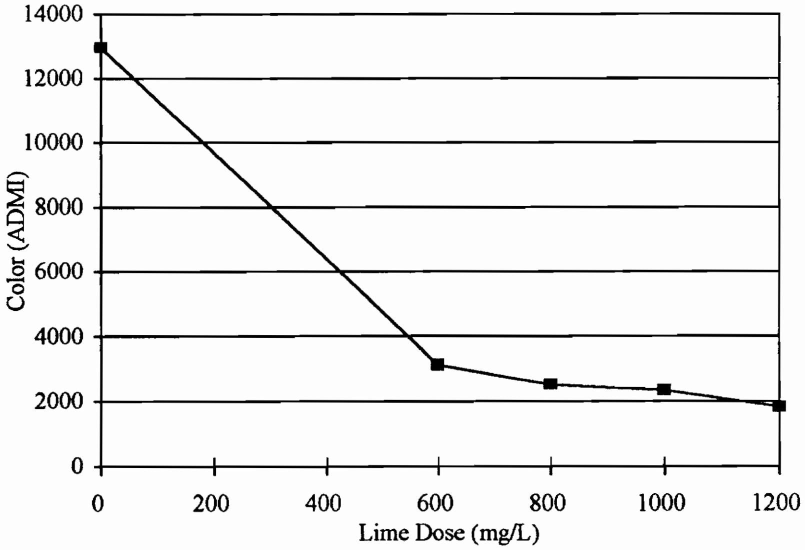
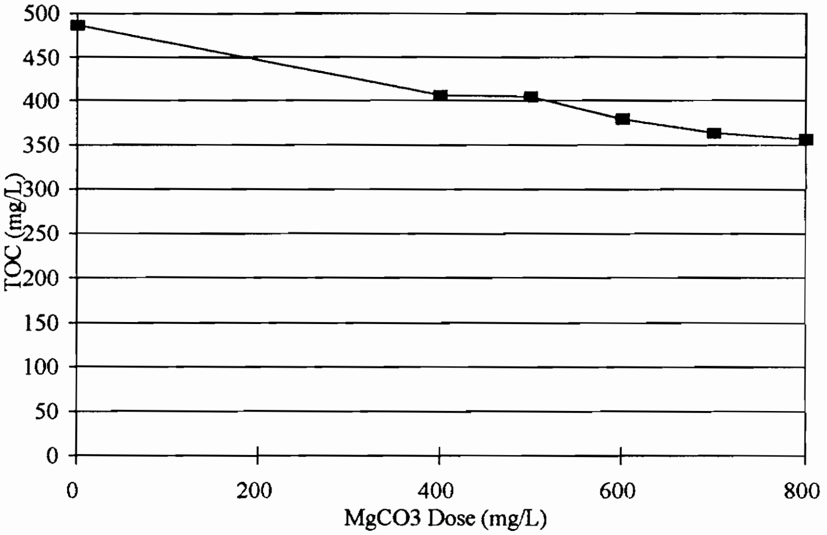
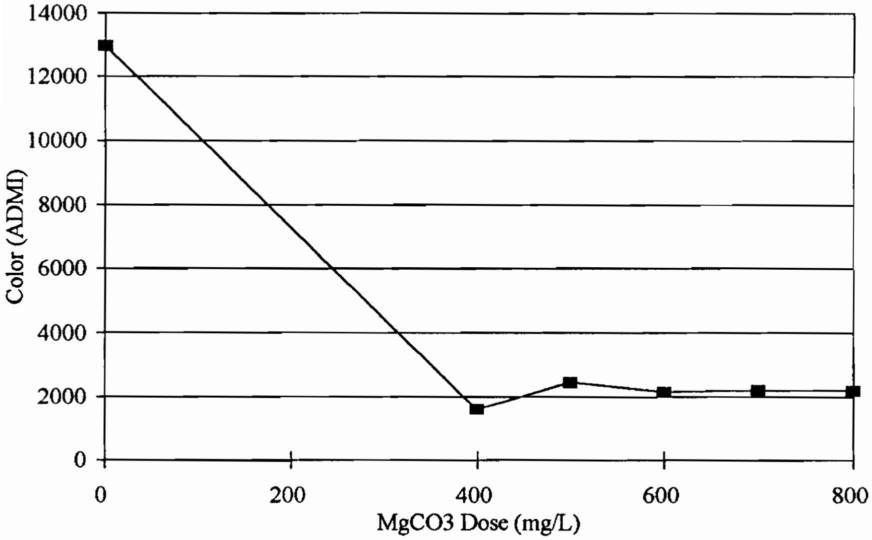


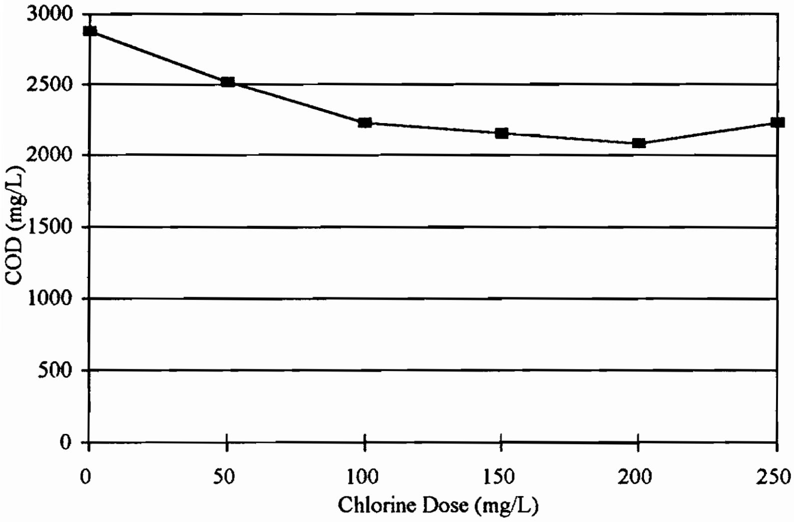
TOC Removal from Combined Waste
with MgCO3 and 800 mg/L Lime



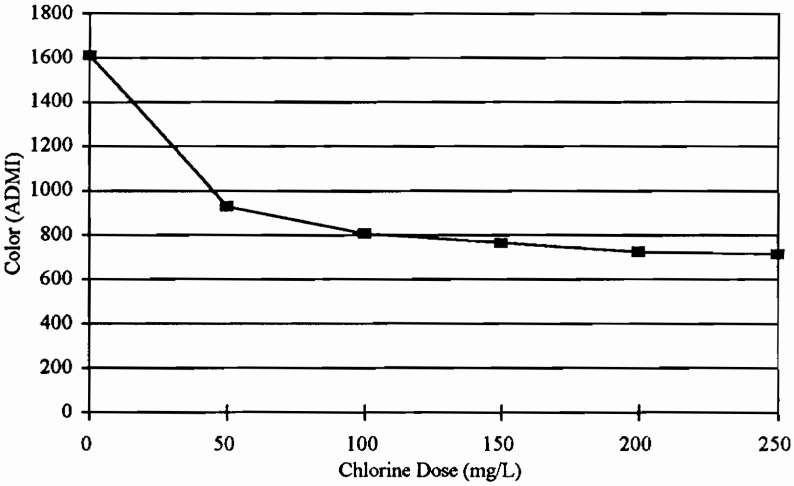
Color Removal from Combined Waste
with MgCO3 and 800 mg/L Lime



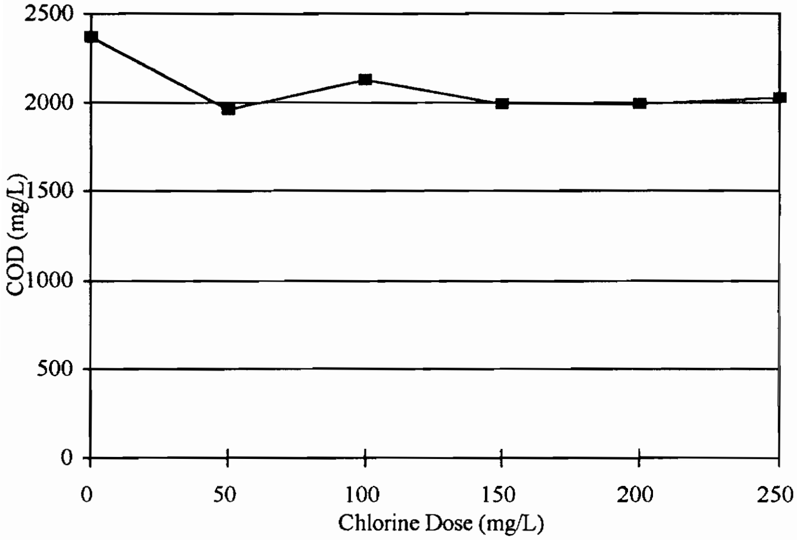
COD Removed by Chlorination
of the Combined Wastewater



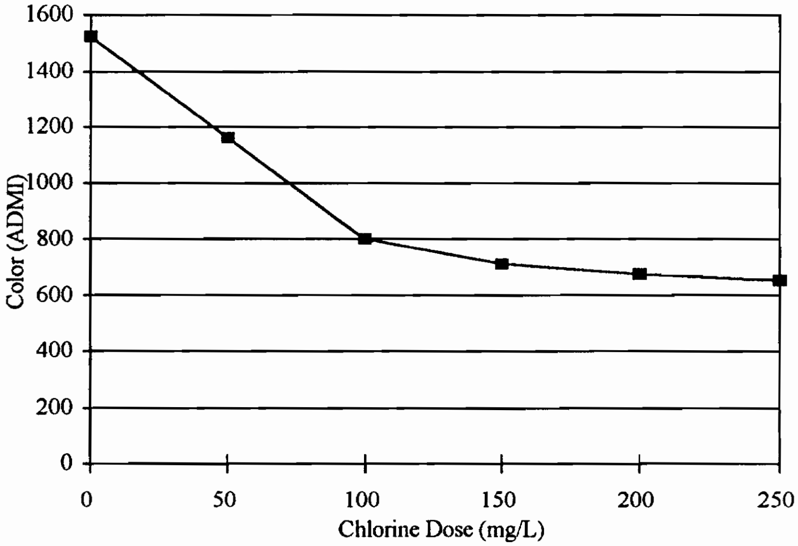
Color Removed by Chlorination
of the Combined Wastewater



COD Removed by Chlorination
of the Combined Wastewater (pH=7)



Color Removed by Chlorination
of the Combined Wastewater (pH=7)



APPENDIX C

Continuous Flow Reactor Data

Two Day Combined Wastewater Continuous Flow Reactors

Reactor C

Date	**D.O.**	**MLSS**	**MLVSS**	**%Volatile**	**Effluent Solids**	**Influent Color**	**Effluent Color**	**Influent TOC**	**Effluent TOC**
12/06/94		1530			125				
12/09/94		3695			263				
12/13/94		3540			619				
12/15/94		2475			354				
12/20/94		1095			44				
12/28/94		3145			72				
01/03/95		2780			287				
01/10/95		3030			7700				
01/18/95	5.3	1425	1080	75.79	98	1896	2585	779	587
01/20/95	0.8	3495	2965	84.84	107	1738	1666	796	560
01/22/95	0.5	2700	2270	84.07	179	3227	1902	819	540
01/25/95		1320	1140	86.36	111	2447	1964	969	553
01/27/95	0.6	1900	1613.5	84.92	159	1838	1631	1031	572
01/29/95	4	2300	1930	83.91	125	1801	1387	971	538
02/01/95	0.5	3130	2715	86.74	123	36579	14641	1254	710
02/03/95	0.5	3580	3000	83.80	198	12359	17190	1385	940
02/05/95	3	2990	2452	82.01	137	3415	8486	740	649
02/08/95	3	2902	2475	85.29	150	2713	4370	725	407

Two Day Combined Wastewater Continuous Flow Reactors

Reactor D

Date	D.O.	MLSS	MLVSS	%Volatile	Effluent Solids	Influent Color	Effluent Color	Influent TOC	Effluent TOC
12/20/94		1325			2681				
12/28/94		1080			58				
01/03/95		1535			277				
01/10/95		2960			88				
01/18/95	4.5	1445	940	65.05	114	1896	2640	779	579
01/20/95	1.5	1890	1610	85.19	86	1738	1685	796	602
01/22/95	3.5	2120	1794	84.62	110	3227	1335	819	575
01/25/95		1900	1575	82.89	130	2447	1687	969	663
01/27/95	0.5	1885.5	1560	82.74	113	1838	1450	1031	664
01/29/95	3	2510	2000	79.68	125	1801	1682	971	601
02/01/95	0.4	2130	1830	85.92	177	36579	16651	1254	897
02/03/95	0.5	1723	1381	80.15	157	12359	12957	1385	1188
02/05/95	0.5	1324	1004	75.83	187	3415	4450	740	830
02/08/95	4.2	1343	1198	89.20	110	2713	2809	725	725

Acid Rinse Water Continuous Flow Reactor (Data begining 3/19/95 is for the 1/10 diluted acid rinse water reactor)

Date	Days of Operation	MLSS	MLVSS	Effluent Solids	Influent Color	Effluent Color	Influent Total COD	Effluent Total COD
02/24/95		3820		88	843	434	4136	2397
02/28/95		6530		105	817	479		
03/03/95		7015	5955	150	860	615	4092	1672
03/07/95		6958		569	855	525		
03/10/95		6610		918	840	839		
03/19/95	0	4800		41	65	67	648	360
03/22/95	3	3675	3270	15	123	44		
03/26/95	7	3308		0	78	39	423	66.2
03/30/95	11	3258	2795	12	59	21		
04/03/95	15	2950		2.3	107	38	369	
04/07/95	19	2570	1950	15	74	38		
04/10/95	22	2260		3	82	35	346	31
04/14/95	26	1950	1590	9	59	31		

Date	Days of Operation	Influent Soluble COD	Effluent Soluble COD
02/24/95		4089	2068
02/28/95		4606	2820
03/03/95		3036	1320
03/07/95		4738	1932
03/10/95		4876	3864
03/19/95	0	540	288
03/22/95	3	437	55
03/26/95	7	414	47.8
03/30/95	11	378	59.5
04/03/95	15	270	32.4
04/07/95	19	327	55
04/10/95	22	307	7.7
04/14/95	26	288	15

Seven Day Combined Wastewater Continuous Flow Reactor

Date	Days of Operation	MLSS	MLVSS	Effluent Solids	Influent Color	Effluent Color	Influent Total COD	Effluent Total COD
03/19/95	0	2975		56	1537	740	4140	1800
03/22/95	3	2702	2293	50	1294	897		
03/26/95	7	2070		64	1210	826	2944	662
03/30/95	11	1860	1410	97	4041	894		
04/03/95	15	1529		89	3934	836	1890	540
04/07/95	19	1530	1260	35	3879	928		
04/10/95	21	1430		41	3543	979	2112	461
04/14/95	25	1770	1450	58	4264	1334		
04/18/95	29	2050		40	4128	1552	2444	263
04/21/95	32	1376	1218	51	3382	1914		

Date	Days or Operation	Influent Soluble COD	Effluent Soluble COD
03/19/95	0	3690	1620
03/22/95	3	3017	902
03/26/95	7	2686	442
03/30/95	11	2070	468
04/03/95	15	3870	252
04/07/95	19	2064	413
04/10/95	21	1824	307
04/14/95	25	1728	150
04/18/95	29	2256	226
04/21/95	32	2256	395

Seven Day Rinse and Boiler Water Continuous Flow Reactors

Date	Days of Operation	MLSS	MLVSS	Effluent Solids	Influent Color	Effluent Colo	Influent Total COD	Effluent Total COD
03/19/95	0	3277		27	771	301	4410	1080
03/22/95	3	3775	2900	27	775	418		
03/26/95	7	2125		19	570	323	3827	515
03/30/95	11	2870	2130	11	920	241		
04/03/95	15	2660		14	667	215	3150	432
04/07/95	19	2400	1950	15	546	213		
04/10/95	21	2010		34	377	160	2880	461
04/14/95	25	2730	2190	28	890	305		
04/18/95	29	3810		27	611	238	2162	489
04/21/95	32	3550	2970	45	426	233		

Date	Days of Operation	Influent Solubl COD	Effluent Soluble COD
03/19/95	0	3510	1260
03/22/95	3	3680	920
03/26/95	7	3533	405
03/30/95	11	2700	792
04/03/95	15	2970	468
04/07/95	19	3182	482
04/10/95	21	2688	499
04/14/95	25	2880	461
04/18/95	29	3290	526
04/21/95	32	2820	414

APPENDIX D

Effluent Jar Tests

Jar Tests on the Seven Day Combined Wastewater Reactor Effluent

Polymer	**Dose (mg/L)**	**Color (ADMI)**	**Soluble COD (mg/L)**	**TSS (mg/L)**
None	0	1635	338	30
Color Katch 50	50	893		
	100	212	263	253
	150	149	244	265
	200	116	226	296
WT 2392	50	1307		
	100	1013		
	150	307	188	209
	200	186	75.2	238

Jar Tests on the Seven Day Rinse/Boiler Water Reactor Effluent

Polymer	**Dose (mg/L)**	**Color (ADMI)**	**Soluble COD (mg/L)**	**TSS (mg/L)**
None	0	140	480	10.5
Color Katch 50	20	105		
	40	60	403	54.5
	60	52	134	93
	80	42	269	111
	100	41	269	109
WT 2392	20	140		
	40	120		
	60	73	154	79
	80	63	384	73

APPENDIX E

Batch and Respirometer Test Data

Batch Biological Test 1 - Nutrient Addition

Color Removals

Time (days)	No nutrients	Phosphorus	Nitrogen	Nitrogen and Phosphorus
0	1186	1363	1038	1425
5	618	656	396	606
10	629	623	459	707

TOC Removals

Time (days)	No nutrients	Phosphorus	Nitrogen	Nitrogen and Phosphorus
0	451	445	402	476
5	138	189	177	218
10	118	145	188	249

Batch Biological Test 2 - Biodegradability Test

Combined Wastewater

Time (days)	Color	TOC	DOC	MLSS
0	19827	493	274	2215
3	11614	316	238	
5	11362	242	213	3220
7	12765	309	223	
10	22428	463	308	7590

Rinse Wastewater

Time (days)	Color	TOC	DOC	MLSS
0	1001	1026	577	2880
3	818	898	763	
5	649	1016	907	2305
7	683	1704	1566	

Respirometer Test 1 Data

	BOD levels				
Time (hrs)	**1/5 Premet**	**1/10 Premet**	**1/10 CatA**	**1/20 CatA**	**Blank**
0.00	0	0	0	0	0
0.67	75	0	0	0	0
2.25	100	0	50	0	0
3.25	100	0	50	0	0
9.92	150	50	150	100	0
20.33	200	100	350	400	0
26.58	250	200	450	440	0
33.25	300	220	500	500	0
46.58	325	330	560	640	0
58.25	425	400	600	760	0
68.92	475	450	700	800	0
78.34	500	500	700	840	0
95.92	535	550	750	900	5
100.09	565	550	730	860	7
119.00	600	650	800	1000	10
144.42	700	900	900	1100	10
174.42	1050	1300	1600	1400	10
196.67	1225	1450	1800	1500	15

Respirometer Test 2 Data

	BOD Levels				
Time (hrs)	**1/2 Premet**	**1/4 Premet**	**1/4 CatA**	**1/8 CatA**	**Blank**
0.00	0	0	0	0	0
1.33	0	0	0	0	5
2.25	0	0	0	0	5
2.92	0	0	0	0	5
9.00	0	0	40	40	10
21.33	56	72	272	304	12
25.25	86	100	332	344	12
47.00	200	200	440	400	20
53.33	300	300	460	400	20
69.25	500	560	520	480	20
78.67	600	640	600	520	20
93.67	690	740	900	520	25
100.00	730	760	980	520	25
118.50	810	880	1100	560	30
125.17	850	920	1120	560	30
142.50	910	1080	1220	640	30
167.33	940	1180	1360	960	35

APPENDIX F

Final Characterization Data

Final Characterization
Sample Set 1

	2 Day Acid Rinse		7 Day Combined			7 Day Rinse/Boiler		
Pollutant	**Influent**	**Effluent**	**Influent**	**Effluent**	**Coagulated Effluent**	**Influent**	**Effluent**	**Coagulated Effluent**
BOD (mg/L)	82.5	6.2	1021	<20	<20	946	<85	<85
TOC (mg/L)	92.2	20.9	808	166	100	976	189	164
TSS (mg/L)			83	51	373	131	45	100
Color (ADMI)	50	17	2599	1904	120	667	174	46
UV light transmittance	62.15	81.8	0	0	0.43	1.32	19.56	20.48
Ammonia (mg/L)	1.7	0.56	0.56	1.4	4.5	0.56	0.56	1.7
TKN (mg/L)	12.3	2.8	50.4	20.2	35.3	64.4	10.6	14
Total Cyanide (mg/L)	ND (0.005)	ND (0.005)	0.008	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)
Oil and Grease (mg/L)	ND (5)	ND (5)	6	ND (5)	ND (5)	19	ND (5)	ND (5)
Total Phenols (mg/L)	0.009	ND (0.005)	0.019	0.11	0.011	0.09	ND (0.005)	ND (0.005)
Benzene (mg/L)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)
Total Barium (ug/L)	38	38	76	86	184	46	50	178
Total Cadmium (ug/L)	0.2	0.4	1.4	0.4	0.4	0.6	0.2	0.4
Total Chromium (ug/L)	5.8	7.8	120.0	43.0	7.6	28.6	9.2	6.8
Total Copper (ug/L)	22.0	36.0	80.0	64.0	22.0	32.0	20.0	16.0
Total Lead (ug/L)	2.0	8.0	16.0	8.0	2.0	12.0	6.0	4.0
Total Nickel (ug/L)	8.0	8.0	26.0	90.0	20.0	16.0	14.0	10.0
Total Silver (ug/L)	1.6	1.6	1.6	2.0	1.6	0.4	2.4	2.0
Total Arsenic (ug/L)	15	10	4	ND (1)	15	21	ND (1)	8
Total Beryllium (ug/L)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)
Total Boron (ug/L)	ND (90)	140	90	250	370	120	140	90
Total Mercury (ug/L)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	0.2	ND (0.2)	ND (0.2)
Total Selenium (ug/L)	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)	ND (2)

Note: 1. ND - Not Detected, NT - Not Tested
2. Instrument detection limits are presented in parentheses for the samples in which pollutants were not detected.

Final Characterization
Sample Set 2

	7 Day Combined			7 Day Rinse/Boiler		
Pollutant	Influent	Effluent	Coagulated Effluent	Influent	Effluent	Coagulated Effluent
BOD (mg/L)	1140	>50	17	2385	>50	35
TOC (mg/L)	769	175	105	1597	369	240
TSS (mg/L)	47.2	42.7	332	79.3	73.8	182
Color (ADMI)	2140	1955	185	1012	575	244
UV light transmittance	0.39	0.51	0.45	0	1.23	6.18
Ammonia (mg/L)	0.56	0	3.36	0.28	0.28	1.12
TKN (mg/L)	42	20.7	31.9	98	17.4	11.8
Total Cyanide (mg/L)	0.007	ND (0.005)	0.007	ND (0.005)	ND (0.005)	ND (0.005)
Oil and Grease (mg/L)	5	ND (5)	ND (5)	12	ND (5)	ND (5)
Total Phenols (mg/L)	0.056	0.006	0.054	0.042	ND (0.005)	ND (0.005)
Benzene (mg/L)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)	ND (0.005)
Total Barium (ug/L)	42	66	110	40	64	192
Total Cadmium (ug/L)	2.0	0.6	0.4	0.4	1.0	1.2
Total Chromium (ug/L)	171.8	92.0	6.4	20.6	9.2	5.8
Total Copper (ug/L)	48.0	46.0	4.0	42.0	26.0	12.0
Total Lead (ug/L)	10.0	6.0	4.0	8.0	8.0	8.0
Total Nickel (ug/L)	14.0	90.0	32.0	28.0	16.0	12.0
Total Silver (ug/L)	2.4	1.8	2.6	2.0	4.6	2.0
Total Arsenic (ug/L)	ND (1)	11	10	3	5	5
Total Beryllium (ug/L)	4	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)
Total Boron (ug/L)	ND (200)	ND (200)	ND (200)	ND (200)	ND (200)	ND (200)
Total Mercury (ug/L)	4	0.3	0.4	0.8	0.5	0.2
Total Selcnium (ug/L)	ND (2)	ND (2)	ND (2)	9	ND (2)	ND (2)

Note: 1. ND - Not Detected, NT - Not Tested

2. Instrument detection limits are presented in parentheses for the samples in which pollutants were not detected.

Final Characterization
Sample Set 3

	7 Day Combined				7 Day Rinse/Boiler			
Pollutant	**Influent**	**Effluent**	**Filtered Effluent**	**Coagulated Effluent**	**Influent**	**Effluent**	**Filtered Effluent**	**Coagulated Effluent**
BOD (mg/L)	1074	91.5	33.2	17	2910	>100	>100	81
TOC (mg/L)	903	198	150	137	1576	448	300	380
TSS (mg/L)	84	71	NT	361	117	63	NT	149
Color (ADMI)	1384	1619	NT	185	1161	993	NT	777
UV light transmittance	0	0	NT	0.17	0	0.2	NT	0.15
Ammonia (mg/L)	0.28	1.96	NT	3.08	0	2.52	NT	2.24
TKN (mg/L)	53.2	26.9	NT	41.44	100.8	25.76	NT	22.96
Total Cyanide (mg/L)	NT	NT	NT	NT	NT	NT	NT	NT
Oil and Grease (mg/L)	NT	NT	NT	NT	NT	NT	NT	NT
Total Phenols (mg/L)	NT	NT	NT	NT	NT	NT	NT	NT
Benzene (mg/L)	NT	NT	NT	NT	NT	NT	NT	NT
Total Barium (ug/L)	52	132	NT	76	40	64	NT	166
Total Cadmium (ug/L)	1.2	0.4	NT	0.2	0.2	1	NT	4
Total Chromium (ug/L)	126.0	84.2	NT	8	16.8	14.4	NT	7.8
Total Copper (ug/L)	42.0	64.0	NT	70	58	38	NT	36
Total Lead (ug/L)	12.0	6.0	NT	2	10	14	NT	12
Total Nickel (ug/L)	12.0	68.0	NT	30	14	12	NT	18
Total Silver (ug/L)	2.4	2.4	NT	0.8	0.8	3.6	NT	2.6
Total Arsenic (ug/L)	NT	NT	NT	NT	NT	NT	NT	NT
Total Beryllium (ug/L)	NT	NT	NT	NT	NT	NT	NT	NT
Total Boron (ug/L)	NT	NT	NT	NT	NT	NT	NT	NT
Total Mercury (ug/L)	NT	NT	NT	NT	NT	NT	NT	NT
Total Selenium (ug/L)	NT	NT	NT	NT	NT	NT	NT	NT

Note: ND - Not Detected, NT - Not Tested

VITA

Christine Ann Gorgone was born in Waltham, Massachusetts on June 17, 1970 and was raised in New Jersey. In the summer of 1993, Christine received a B.S. in mechanical engineering from Drexel University. Later that summer, she began studying for her M.S. in environmental engineering at Virginia Polytechnic Institute and State University. She received her degree the summer of 1995 and accepted a job with the Maryland Department of the Environment.

Christine A Gorgone