Mitigation strategies for the removal of rinsate organics and lithium-based dyes from textile effluents

Kathryn W. Huddle
Louisiana State University and Agricultural and Mechanical College

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MITIGATION STRATEGIES FOR THE REMOVAL OF RINSATE ORGANICS AND LITHIUM-BASED DYES FROM TEXTILE EFFlUENTS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In partial fulfillment of the
Requirements for the degree of
Master of Science

in

The Department of Environmental Studies

By
Kathryn W. Huddle
B.S., Texas A&M University at Galveston, 2000
December 2002
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<td>Advanced BioSystems</td>
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<tr>
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ABSTRACT

Governmental agencies have set regulatory values on the concentration of dye-related color that can be released in textile mill effluents. A proprietary biotic and abiotic technology treatment train was built at a candidate facility in northwestern Georgia to reduce the organic content and dye-related color content in the textile mill’s effluent. Laboratory experimentation began with bench scale 4 L immobilized microbe (IMBR) bioreactor tests to biologically treat primary wastewater streams, namely skein dye and space dye, from this candidate facility. The biological treatment reduced the organic content levels, expressed as chemical oxygen demand (COD), from 3185±30 to 290±20 mg/L (COD reduction rate: 43.21±0.1 mg/L/h) in the skein dyeing effluent and from 5430±30 to 550±120 mg/L (COD reduction rate: 72.8 ± 1.3 mg/L/h) in the space dyeing effluent; however, the biological process did not remove all of the color from the effluent sample. An ozonation unit was added to the biological treatment process to aid in color reduction. The ozonation successfully reduced the residual color in both primary effluent streams. The skein dyeing effluent was reduced from 4.9 to 0.3 mg/L of residual color (color removal rate: 0.069 mg/L/h). The space dyeing effluent was reduced from 16.0 to 1.5 mg/L of residual color (color reduction rate: 0.21 mg/L/h). Both organic content and color removal exhibited >89% reductions. However, to produce water devoid of color from the effluent samples, activated carbon was added and filtered out to further clarify the ozone treated water. The resultant water was of recyclable quality. These laboratory processes were then adapted to create a commercial scale technology treatment train at the candidate facility. The commercial unit, operating at 110 gpm (gallons per minute) with a system hydraulic retention time of 41.6 hours, had reduction levels of >78% for both organic content reduction and color removal. These levels were acceptable treatment levels with the resultant effluent successfully
recycled into the dye house processes. Thus, recyclable process water was produced from the effluent waters of the candidate textile mill facility.
INTRODUCTION

The southeastern portion of United States is home to a large percentage of the textile mills in the U.S. The textile industry covers a variety of manufacturing purposes ranging from the making of fabrics and yarns to the dyeing of those products and finally the production of marketable items, such as carpets, fabrics, and apparel. Depending on which type of textile mill one is examining, different chemicals, such as dispersants, fixers, and conditioners, are added to baths used to dye or seal fabrics and yarn. As the years have progressed, the entire industry, including interests abroad, has faced a common dilemma, treatment of effluents containing these chemicals and excess dye products.

Municipal wastewater treatment facilities are one means of treating the effluents. Some of these treatment facilities use activated sludge containing microbes to treat the water so that it can be discharged. However, the effluent waters sent to these treatment facilities must conform to local, state, and/or national regulations on water quality. Chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), pH, and oxygen content are the main parameters of the effluents that are controlled by regulations. In recent years, one more parameter of effluent water has gained attention, color. The treatment facilities have not been successful in removing all of the color found in effluents. As a corrective action, these states have advocated the removal of color to those textile mills responsible for producing the colorful effluents.

One division of the textile industry that deals with a large amount of color is the carpet manufacturing industry. The northwestern portion of Georgia manufactures most of the carpet used in the United States with Dalton, GA, referred to as the “Carpet Capitol of the Country”. Adairsville, a smaller city located just south of Dalton, is home to Premier Yarn Dyers, which
is a textile dye house responsible for dyeing yarn to be woven into carpet. The yarn is sent to Premier un-dyed on hollow cardboard spools. The yarn is dyed in one of two ways, skein dyeing and space dyeing.

For skein dyeing, plant workers use machinery to remove the yarn from the spools to form skeins of yarn. The skeins are then hung on dyeing racks and lowered into large vats of dye solutions. These vats contain lithium-based dyes, chemicals to enhance dye adhesion, and dispersants to equalize dye concentrations, i.e. color uniformity, throughout the batch. The skeins are allowed to soak in the vats until the uptake of dye is completed based upon a preset dyeing program. The skeins are rinsed, removed, and dried. Once dry, the same machinery that removed the yarn from the spools runs in reverse to re-spool the yarn onto the cardboard spools thus creating a semi-continuous pathway.

In contrast, space dyeing uses the yarn directly off of the hollow cardboard spool. The space dyeing machines unwind the yarn as a taught straight line and thread through compartments that release controlled sprays of concentrated dye solutions. The excess dye is drained away. After the dye spraying, the yarn is exposed to a sealant solution to ensure adhesion of the dye to the yarn. The yarn is then allowed to dry and is wound around a new cardboard spool creating a continuous path from spool to spool.

In recent years, Georgia officials have found Premier Yarn Dyers (PYD) to be in a state of non-compliance with regulatory values for COD and color. The large amount of municipal water the plant requires (approximately 150,000 gallons/day or gpd) is also a concern of both the city and the state. Both of these problems have been further compounded by the drought on the eastern seaboard and the water requirements of the nearby metropolitan area of Atlanta, Georgia. PYD was obligated to investigate to novel ways of treating their
effluent wastewater. The process they decided to use was an industry first, the complete recycling of effluent water.

**Approach**

In order to recycle textile effluent water, the water required remediation of organics associated with yarn preparation prior to dye operations and removal of the lithium-based dyes in a polishing step. The initial treatment train installed in June, 2001 by Advanced Biosystems (ABS) under a sublicensing agreement with Louisiana State University (LSU) used an immobilized microbe bioreactor (IMBR) seeding system developed in earlier work by Portier et al (1). The system consists of two 12,000-gallon IMBR reactors with associated nutrient amendment tanks and a 350,000 gallon primary biological contact reactor tank wherein large volumes of effluent are seeded with excess biomass bleed from the IMBRs. The IMBRs' acclimated immobilized biomass also reduced BOD and COD content.

Although the IMBR system contributed to color reduction, the biological system did not completely remove it; residual color can interfere with new dye processes. The remnants of dye colors required a separate non-biological polishing system to further reduce color. To meet the water clarity requirement, an ozonation system coupled to an activated carbon bed filter was installed as this polishing unit. The different units of the combined “treatment train” worked in concert to remove different attributes as the water was pumped through the system.

This treatment train is unique because in the past biotreatment and ozonation have been used separately, but the combination of the two is a relatively new process for textile effluents. This study encompasses the laboratory research of the each stage in this treatment train and tracks field data from system operations at the facility in Adairsville, GA.
Laboratory research utilized a bench scale version of the operational commercial unit and related analytical methods for defining the remaining color issues.
LITERATURE REVIEW

IMBR Technology

The immobilized microbe bioreactor (IMBR) system has been used in industry to treat variety of effluents and contaminated wastewaters. Immobilization refers to using large surface area for biocatalyst (the microbe or enzyme) attachment. The attachment occurs by confining biocatalyst within a porous matrix or by fixing it to a solid surface. Friday et al. (1) stated “There are a number of notable advantages to this approach as follows:

- Higher culture densities can be attained with cell immobilization versus suspended cell systems.
- Flow rates can be in excess of the washout dilution rate, since washout cannot occur when the biocatalyst is immobilized.
- The carrier may have sorptive capacities which increase the surface concentration of the substrate.
- Intrinsic catalytic activity may increase or decrease, possibly due to physiological changes in the biocatalyst.
- Immobilization may have a stabilizing effect on enzyme activity.
- The composition of the carrier support material may be used to affect both product yield and selectivity.”

Scientists have further developed this process into a number of methods that relate to the immobilization process. These processes are categorized as (i) entrapment within a support, (ii) adsorption to a support, and (iii) covalent binding to a support. (1)

Portier et al. (2) initiated the development of the IMBR system with field pilot tests using simpler treatment units. The system used consisted of two biological towers run parallel to each other, a feed tank, and a feed pump. The first tower utilized 2-in. diameter Norton™
pall rings and was designated the conventional biotower (CBT). The tower functioned as a continuously stirred system using a draft tube and an aeration system of 0.5 standard cubic feet per minute (scfm). The second tower utilized 5.4 cu. Ft. of carrier (Celite™ R-630) provided by Manville Corporation and was designated Manville packed bead reactor (MPBR). This tower functioned as a plug flow reactor using fine bubble diffusion with aeration of 0.3scfm. Initially, a carbon column served as pretreatment before the biotowers but after initial start-up it was bypassed to feed directly to the towers. (2)

The biotowers have been refined in recent years and are now termed immobilized microbe bioreactor (IMBR). These reactors utilize porous biocatalyst material, such as Manville media, which is similar to small ceramic or porcelain beads. Generally, this system, which can be adapted to treat contaminated ground waters as well as plant effluents, includes an equalization (EQ) tank, two or more IMBRs containing biocatalyst media, a nutrient tank, and a sand filter. Each component serves a specific purpose. The EQ tank accomplishes two goals: 1) it serves as a settling tank for fine solids already in the water and 2) it serves as the influent source for the IMBRs. The influent is supplied at a continuous flow into the bottom of the IMBRs. It flows upward through the biocatalyst media until it exits at a point near the top of the bioreactor. If the IMBRs are working in parallel, each unit is self-contained and water exiting the reactors goes to a holding tank. If they are working in series, the water passes from one IMBR to the next allowing for successively longer treatment times. The resulting treated effluent is passed through the sand filter as a polishing step to remove bulk solids, consisting of sloughed-off biomass and bed material. After passing through the sand filter, the water goes to a storage tank for discharge back into the groundwater system or a local POTW. (3)
Complete IMBR systems have been running at the three sites, which contain groundwater contaminated with wood preserving materials, for more than five years with greater than 90% efficiency. In the past year, one site has closed their bioremediation system because they have achieved their remediation goals ahead of schedule. The other two sites are still being treated and monitored by the Aquatic Toxicology Laboratory.

**Ozone and Its Properties**

Ozone has been a part of the Earth’s atmosphere for one billion years but the molecule was not discovered until 1839 by German scientist Christian Friedrich Schonbein. The name for ozone originated from the Greek word ozein, which means “to smell”, due to the unique odor ozone emits. As part of the Earth’s atmosphere, ozone protects the Earth from the harmful ultra-violet light rays of the sun. Ironically, it is the sun’s UV rays that created and still create ozone. The UV light rays destroy the bonds of molecular oxygen (O₂) and create free radical oxygen molecules (O·). The solitary oxygen molecules then combine with molecular oxygen to form the tri-atomic oxygen molecule of ozone (O₃). This process and the destruction of ozone are photolytic reactions and are illustrated in Figure 1A and Figure 1B, respectively (4). As ozone accumulated, a protective shield in the atmosphere was created around 600 million years ago. UV light rays, however, are not the only source of ozone production. A strong electrical discharge passed through gaseous oxygen can also produce ozone. (5)

The UV shield version of ozone is known as protective ozone or “good ozone” but there is also destructive ozone or “bad ozone” (5). Destructive ozone exists because the atoms of ozone form a relatively unstable structure that UV light rays break creating a benign oxygen molecule and a highly reactive free radical atom (5). Free radicals are harmful
because they can oxidize materials and cause aging via protein, lipid, and DNA damage (5). Behind F₂, F₂O, and free radical oxygen atoms, ozone is ranked the fourth most powerful oxidizing agent (6). Ozone can be harmful to bacteria and humans but has proven to be a successful treatment agent for effluent wastewater.

(A)

**Ozone Formation**

![Diagram of Ozone Formation](image)

(B)

**Ozone Destruction**

![Diagram of Ozone Destruction](image)

* M is a third body, for example N₂, O₂

Figure 1. (A) Photolytic production of ozone. (B) Photolytic destruction of ozone. (Adapted from Spiro and Stigliani {4})
Ozone Use in Biological Treatment of Effluents

Ozone was introduced as an alternative to chlorination for disinfection of municipal water. It exhibits several advantages over chlorine “such as:

1. Safety problems of chlorine storage, handling, and transportation are eliminated. Ozone is produced on-site.
2. Ozone destroys both bacteria and viruses, while chlorine is not effective against viruses.
3. Shorter treatment times (1-10 min for ozone vs. 30-45 min for chlorine).
4. Lesser pH and temperature effects with ozone.
5. High dissolved oxygen concentration from ozonation improves receiving stream quality.
6. No toxicity to aquatic life has been found in studies of ozone disinfection.
7. No build-up of bioaccumulatable residuals has been observed in ozone-treated effluents.
8. There is no increase in total dissolved solids in ozone-treated water.
9. Wastewater quality improvements such as turbidity reduction and effluent decolorization accompany ozone treatment.”

Ozone can also be used in processes other than disinfection. Ozone is used in sludge treatment, odor control, tertiary treatment processes, and combined treatment with activated carbon, filtration, ultrasonics, and other chemicals. (7)

A new and expanding use for ozone is decolorization of effluents and wastewater. Chlorine has been used in the past but it has been shown to create potentially carcinogenic compounds. Ozone serves as a less harmful method of decolorization. Mock and Hamouda (8) experimented using different techniques to decolorize wastewater and other effluents. They had three criteria that the technology had to meet: “1) did not increase the chemical loading of the waste stream, 2) has shown to reduce color and 3) is a technology that has been applied in
industry and could be tested on site or by vendors.” The technologies tested were membrane filtration, carbon adsorption, ion exchange, ultraviolet light and hydrogen peroxide, and ozone. Of the five technologies, carbon adsorption and ozone were the only viable technologies with ozone being the more cost efficient. Ozone treatment proved more effective with greater dilutions as opposed to more concentrated effluents. (8)

As ozone was used more frequently for wastewater treatment, scientists began to compare it to other oxidizing agents. Aplin and Waite (9) compared ozone with standard Fenton’s reagent (Fe$^{+2}$/H$_2$O$_2$) and a modified photo-Fenton’s process (UV/Fe oxalate/H$_2$O$_2$) as oxidizing agents for textile effluents containing Reactive Red 235 dye. They observed that ozone and Fenton’s reagent decompose into two different forms of free radicals, O· and HO·, respectively. They found that both free radical species were able to quickly degrade the Reactive Red 235 dye. (9)

Aplin and Waite (9) also found that ozone and its free radical species, O·, were both oxidizing agents. They found that ozone oxidized more acidic solutions while the O· free radical was more efficient in alkaline solutions. The acidity or alkalinity also had an effect with respect to dye concentration. The rate of degradation by ozone in acidic solutions was much more sensitive to initial dye concentrations than the rate of degradation by the O· free radical in alkaline solutions. (9)

Degradation of dye by ozone did not produce any colored products, but both Fenton’s reagent and modified Fenton’s reagent produced a brown tint was produced in the water. In their final analysis, Aplin and Waite (9) concluded that ozone was most effective at low dye concentration and/or high initial pH but was not affected by NaCl. Both versions of Fenton’s reagent were inhibited by NaCl but each required different concentration and pH levels. (9)
MATERIALS AND METHODS

Treatment Processes

Field Setup

A commercial scale biological treatment facility was installed at Premier Yarn Dyers (PYD) and became operational in June, 2001. The schematic in Figure 2 illustrates the facility’s setup.

Figure 2. Commercial system schematic.

The first stage of the system is a Vibro-Energy® round separator called a SWECO filter, which clears large debris from the effluent water of the textile mill. The SWECO contains a large circular mesh screen that vibrators allowing water to flow through and vibrates solids off the periphery into collection receptacle. The SWECO then drains into a collection of three sump pumps that send the screened water of the mill into a large four
hundred thousand (400K) gallon equalization (EQ) tank, where the effluent water collects before going through the biological treatment plant. The EQ tank acts as the water source for both IMBRs (immobilized microbe bioreactors) and the contact (reactor) tank. Additionally, it can drain to the city sewer.

The IMBRs act as microbial seeding units for the three hundred and fifty thousand (350K) gallon contact tank. Each IMBR contains inoculated biocarrier having *Pseudomonas aeruginosa* (LSU 1251B), *Pseudomonas purifaciens* (LSU 1333A), and *Actinobacillus purifaciens* (LSU 1054A), which biodegrade macromolecules in the effluent such as starches. The effluent from the EQ tank is pumped to each IMBR, which act in parallel at a rate of 8-10 gpm. Given a total void volume of approximately 7500 gallons in each 12,000 gallon reactor packed with biocarrier, the hydraulic retention time of the IMBRs is approximately 12.5-15.5 hours. Treated effluent from both bioreactors flows to a one thousand (1K) gallon surge tank. The surge tank splits its feed between the EQ tank (20%) and the reactor tank (80%). The effluent to the EQ tank feeds microbes to that tank thus allowing a portion of the effluent to be recycled through the entire biological treatment system.

The other 80% of the screened plant effluent is sent to the reactor tank at a rate of 90-100gpm. The reactor tank contains two different types of media for microbial attachment: 1) perforated tanks of Grace media sitting on a grating five feet above the floor of the tank and 2) extruded media made of a plastic and wood mix floating in the water column. Thus inoculated effluent from the IMBRs is constantly added to the reactor tank and this along with the above mentioned media within the tank maintains a constant microbial population within the reactor tank that treats the effluent. From the reactor tank, treated effluent either drains to
the sump pumps or to a smaller ten thousand (10K) gallon tank. The 10K tank serves as a surge tank allowing consistent flow to the ozonation unit.

The effluent from the 10K tank is pumped by a 20HP pump into two Mazzi eductors at up to 220gpm at 50psi. Each eductor is capable of pulling up to 500 SCFH (standard cubic feet per hour) of oxygen/ozone gas into the effluent. The oxygen/ozone gas is supplied from the ozone generator that receives oxygen at up to 2,500 SCFH from a ~600,000 SCF oxygen tank. The ozone generator produces ozone at 12% by weight in oxygen.

The oxygen/ozone rich effluent flows into the ozone contact tank from the top and exits the bottom. This tank serves to allow contact time for the ozone in a low-pressure atmosphere. The ozone contact tank holds ~1,000 gallons total and releases the ozonated effluent into a foam fractionator tank. This tank allows for the separation of the effluent and any foam created during ozonation. Attached to the top of this tank is a vacuum header to draw off residual ozone to prevent exposure to workers. In combination with the vacuum header, an ozone monitor was installed that will shut down the septum if ozone concentrations reach 0.3 mg/L, which is the OSHA one-hour threshold limit value (TLV).

As a final polishing step, the ozonated water is sent through an activated carbon bed. The activated carbon bed is useful for two reasons. First, it is very porous and has an extremely high surface area to unit ratio. Second, the surface of the activated carbon attracts and holds the impurities in the effluent water through adsorption (10). The type of activated carbon bed used in this study is macro-porous coal with pores >500A. Currently, the effluent enters the top of the activated carbon bed and exits the bottom. In the near future, a unit that feeds from the bottom and exits near the top will be installed in order to accommodate flushing of the activated carbon bed if needed.
Laboratory Setup

A bench scale simulation of the field system was used for laboratory experimentation. The system was divided into three segments instead of a continuous system as in Georgia. The sample water was sent through a biological treatment system, then an ozonation system, and finally activated carbon was added for polishing.

The biological treatment system (Figure 3) recycled the sample water held in a five-gallon storage receptacle. The receptacle was constantly aerated as was the 2 gallon void volume biocarrier packed bioreactor. A small suction pump was used to pump water from the holding receptacle into the bottom of the bioreactor. The sample water percolated through a bed of inoculated ceramic media having *Pseudomonas aeruginosa* (LSU 1251B), *Pseudomonas purifaciens* (LSU 1333A), and *Actinobacillus purifaciens* (LSU 1054A) immobilized on the beads. These are the same species of organisms used at PYD. The sample water continued to fill the reactor column until it each an outflow spout. Tubing from this outflow spout returned the treated water to the storage receptacle where the system was allowed to recycle. Samples were pulled at different time intervals to be analyzed or sent through the ozonation system (Figure 4).

The heart of the ozonation system was a gas washing bottle (Figure 4) that allowed ozone to enter from the base, bubble through the water, and exit through a spout at the top on the washing bottle. The ozone sent through the gas-washing bottle was generated using an ozone generator from Clearwater Tech Inc. The ozone generator was supplied compressed O$_2$ at 4.5 L/ minute. The compressed O$_2$ entered at the base of the ozone generator and was exposed to UV light. As demonstrated in Figure 1, UV light breaks the O$_2$ bonds allowing single oxygen molecules to combine within whole O$_2$ molecules. This reaction
within the ozone generator produces O₃ at 0.5 g/h at 30 SCFH of ambient air. The resulting O₃ molecules then exit the generator through tubing connected to the gas-washing bottle. As the ozone passed through the sample water, the water was oxidized. This oxidation process converted the O₃ back to O₂. The entire ozonation system relied on a suction pump to pull the O₂ and O₃ through the system.

Activated carbon was added to the bio- and ozone treatment as a final polishing step. The carbon was added to known volumes of pretreated water at different concentrations until the desired water clarity was reached. The final required amount of activated carbon was recorded as were the time periods needed during biological treatment and ozonation.

Figure 3. Laboratory bioreactor schematic.
Figure 4. Laboratory ozonation schematic.

Sample Collection

Field Samples

Samples were collected from Premier Yarn, a textile mill in Georgia. The sampling period spanned from June of 2001 until August of 2002. There was not a fixed time interval between samplings. Several isolated sections of the textile mill dye operation and the treatment plant were sampled. Inside the plant, samples of dye water were taken from the skein and space dye vats. The samples for the treatment plant came from the SWECO filter, the EQ tank, the Reactor tank, the 10K tank, and both seed reactors. Once the ozonation system had been installed, samples were also taken from the water entering and leaving the ozone generator, as well as, leaving the activated carbon bed. The samples were then sent to
the Aquatic Toxicology Laboratory and stored in a refrigerator for analysis or further biological treatment and ozonation testing.

**Laboratory Samples**

To examine the effects of the treatment train on pure dye water, solutions were prepared with samples of powdered dye used by Premier Yarn. The dyes examined were those dyes that had the greatest contributions to the color of the effluent dye waters of the plant. These included Bordeaux 3R, Red LMF, Red YCN, and Red B-2B. Dilutions were prepared by mixing ethanol with the correct proportion of each dye to create samples that were from 1-1000 mg/L. A mixed dye sample was also prepared that contained all of the dyes at a concentration of 1000 mg/L. These samples were used for absorbency tests, while a separate set of dilutions were prepared for biological treatment tests. The samples prepared for biological treatment contained dye, starch, and a nutrient mixture (this mixture included ammonium phosphate, potassium phosphate dibasic, yeast/nitrogen base, yeast extract, ammonium nitrate, and sodium acetate).

**Water Quality Analysis**

**Color Assessment**

A SHIMADZU UV-2101PC a UV-VIS scanning spectrophotometer was used to measure the absorbency of the water samples from the textile mill. The cuvettes for the spectrophotometer were clear plastic and held one milliliter of sample. The spectrophotometer compared each sample to a blank containing de-ionized water. A baseline line absorbency trend was created using the mixed pure dye solution that ranged from 1-50mg/L. Each field sample was read and the peak absorbency taken. The sample’s absorbency reading was
compared to that of the baseline chart and assigned an approximate concentration value in mg/L units.

**Biomass Determination**

Biomass concentration was monitored to establish the productivity of the bacteria in the bioreactors. DIFCO heterotrophic HYcheck hygiene slides were used to determine biomass concentration throughout the treatment process. The HYcheck slides are double-sided plastic sticks containing a nutrient agar surface on each side. Individual HYcheck slides were immersed into the samples of water and left exposed for approximately 30 to 45 seconds. The slides were placed in their containers and sealed tightly. They were allowed to incubate at 37°C for at least 48hrs. Biomass concentration was determined by comparing the growth on the slides after incubation to that on a chart provided by DIFCO.

**Chemical Oxygen Demand**

Chemical Oxygen Demand (COD) is the amount of a specified oxidant that reacts with the sample under controlled conditions. The oxidant measured is the dichromate ion (Cr₂O₇²⁻) that is reduced to the chromic ion (Cr³⁺). The dichromate ion strongly absorbs 400nm but nearly zero at 600nm. The chromic ion has its strongest absorbency at 600nm thus allowing measurement of the reduction from the dichromate to the chromic ion. Pre-prepared solutions of the COD solution were obtained from HACH Company. To examine the COD’s of the effluent waters at Premier, a HACH COD reactor and DR/2000 (a direct reading spectrophotometer) were used. HACH method 8000 for colorimetric determination of COD’s was run on the water samples.

The COD reactor was preheated to 150°C. The sample vials were prepared as the reactor was heating. The COD digestion reagent vials used came in two concentrations. The
first set read 0-1500mg/L and the second set read 0-15000mg/L. To prepare the 0-1500mg/L vials 2 ml of each sample was added to its own vial. The 0-15000mg/L vials only required 0.2ml because each vial contained a built in dilution factor of ten. The vials containing the samples were sealed tightly and shaken. They were then put into the heated COD reactor and allowed to digest for two hours.

At the end of two hours, the vials were cooled and read in the spectrophotometer. The spectrophotometer-stored programs were used to read the vials. Program 435 was used to read high range COD’s at a wavelength of 620nm. These programs take the amount of absorption and insert it into an internal calculation to determine mg/L of COD. The spectrophotometer was first zeroed with a blank that contained de-ionized water with the digestion solution. Each sample’s exterior was wiped clean and read with results recorded in mg/L COD H.

**True Color**

HACH method 8025 for true and apparent color tests was run on the textile effluent samples. True color refers to filtered water in which the turbidity has been removed where apparent color refers to the untreated water. A filtering apparatus consisting of a Metricel® 0.45-micron membrane filter (#63069), filter holder, filter flask, and a suction pump was assembled to test the true color not apparent color of the samples. A volume of forty milliliters of each sample was filtered to obtain a particulate free sample. A similar volume of de-ionized water was also filtered and used as a blank for analysis. The filtered samples were then put into vials that were compatible with the vial receptacle of the DR/2000 which was used to analyze the samples. Program 120 for Color (PtCo) was used to read the samples at a wavelength of 455nm. The exterior of the sample vials was wiped clean and then inserted into the spectrophotometer. The blank was inserted first in order to zero the spectrophotometer.
Each sample was read and the results were recorded in platinum-cobalt units (UNITS PtCo COLOR).

**Nutrient Concentrations**

The biological treatment portion of the experiment was monitored for nutrient concentrations. Nutrients, such as ammonia and phosphate, are essential to the productivity of the microbial community within the bioreactors. CHEMets test kits were used to examine the nutrient concentrations.

The Ammonia CHEMets read concentrations of ammonia from 0-1 & 1-10 mg/L. Those samples that were above 10mg/L were diluted with de-ionized water until a suitable solution was achieved. The sample cup supplied by the kit was filled with 25ml of pure sample (or sample solution) and two drops of A-1500 stabilizer solution. The solution was stirred briefly. A CHEMet ampoule was placed in the solution and the tip snapped off, allowing a capillary action to draw the solution into the ampoule. The ampoule was inverted several times to allow mixture between the solution in the ampoule and the sample solution. The ampoule was set aside for one minute to allow the color to develop. This color was compared to color standards supplied in the CHEMet kit and the resulting concentrations were recorded in mg/L units.

The protocol for the phosphate test was similar to that of the ammonia with a few differences. The Phosphate CHEMets kit used the A-8500 stabilizer solution instead of the A-1500 and the ampoules were allowed two minutes for color development.

**Total Suspended Solids**

The total suspended solids (TSS) concentration was determined by filtration of the water samples. Using the same apparatus as in the true color test, 25ml of each sample was
filtered through Metricel® 0.45-micron filters. Each filter was weighed to obtain the initial weight. Multiple filters were needed in order to filter the complete 25ml of the samples. The filters containing the particulates were put into a 50°C oven overnight to allow them to dry. At the end of 24hrs, the filters were weighed again to obtain the dry weight of the filters. The initial weight was subtracted from the dry weight to determine the TSS. The TSS was recorded in mg/L units.
RESULTS

Phase 1: Initial Effluent Treatment Tests

The initial effluent water samples that Premier Yarn Dyers (PYD) sent to be analyzed were from the internal processes of the dye house. Samples from the skein dyeing process and the space dyeing process were analyzed in the laboratory to determine the biological treatment and color removal requirements needed to produce recyclable water. Samples were collected at defined intervals (see Table 1) from the reservoir containing untreated effluent. Water was continuously treated through a 4.0L IMBR at a flow retention time of 14 hours and allowed to discharge into the feed reservoir. Table 1 presents data from these initial tests with skein dye effluent. Initial readings were taken of the effluent reservoir to determine the dye concentration and the chemical oxygen demand (COD) of the PYD effluent. Biological treatment alone reduced the COD from 3185±30 mg/L to 360±10 mg/L after 67 hours of treatment in reservoir treated waters (COD reduction rate: 42.16±3 mg/L/h). There was also a reduction in visible dye concentration from 4.9 mg/L to 0.8 mg/L (color removal rate: 0.062 mg/L/h). However, subsequent ozonation of treated PYD effluent resulted in further reduction of both COD and dye concentration to 290±20 mg/L and 0.3 mg/L, respectively. These values each had a statistically significant >90% reduction from their initial values (p ≤ 0.01).

The Space dye effluent also followed the same general kinetic rate of reduction with initial values for COD somewhat elevated and anticipated to be more difficult to reduce than the skein dye effluent. The COD values were reduced from 5430±30 mg/L to 550±120 mg/L after 69 hours of total treatment (COD reduction rate: 72.8 ± 1.3 mg/L/h) while the dye
concentration values reduced from 16.0 mg/L to 1.5 mg/L, (color reduction rate: 0.21 mg/L/h) (see Table 2). The biological treatment and ozonation did reduce the concentrations for both COD and dye concentration by > 89 % (p ≤ 0.01).

Table 1. Analysis of skien dye effluent.

<table>
<thead>
<tr>
<th>BIO TREATED TIME (hrs.)</th>
<th>O3 TREATED TIME (hrs.)</th>
<th>ORGANIC CONTENT COD (mg/L)</th>
<th>ABSORBENCY (515 nm)</th>
<th>RESIDUAL COLOR**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>3185±30</td>
<td>0.272</td>
<td>4.9</td>
</tr>
<tr>
<td>Initial*</td>
<td>1</td>
<td>1945±55</td>
<td>0.272</td>
<td>4.9</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>3340±6</td>
<td>0.202</td>
<td>3.5</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>1165±25</td>
<td>0.112</td>
<td>2.1</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>655±45</td>
<td>0.039</td>
<td>0.8</td>
</tr>
<tr>
<td>67</td>
<td>-</td>
<td>360±10</td>
<td>0.035</td>
<td>0.8</td>
</tr>
<tr>
<td>67*</td>
<td>0.5</td>
<td>290±20</td>
<td>0.016</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* Indicates samples that were biologically treated and ozonated
** indicates mg/L for absorbency readings based on the mixed dye standard

Table 2. Analysis of space dye effluent.

<table>
<thead>
<tr>
<th>BIO TREATED TIME (hrs.)</th>
<th>O3 TREATED TIME (hrs.)</th>
<th>ORGANIC CONTENT</th>
<th>ABSORBENCY (515 nm)</th>
<th>RESIDUAL COLOR**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>5430±30</td>
<td>0.695</td>
<td>16.0</td>
</tr>
<tr>
<td>0*</td>
<td>3</td>
<td>5705±105</td>
<td>0.453</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>2925±105</td>
<td>0.525</td>
<td>11.2</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>920±40</td>
<td>0.371</td>
<td>6.8</td>
</tr>
<tr>
<td>24</td>
<td>-</td>
<td>845±185</td>
<td>0.327</td>
<td>5.8</td>
</tr>
<tr>
<td>24*</td>
<td>1</td>
<td>1220±100</td>
<td>0.149</td>
<td>2.7</td>
</tr>
<tr>
<td>46</td>
<td>-</td>
<td>535±15</td>
<td>0.363</td>
<td>6.6</td>
</tr>
<tr>
<td>69</td>
<td>-</td>
<td>585±15</td>
<td>0.319</td>
<td>5.7</td>
</tr>
<tr>
<td>69*</td>
<td>0.75</td>
<td>550±120</td>
<td>0.072</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* Indicates samples that were biological treated and ozonated
** indicates mg/L for absorbency readings based on the mixed dye standard
Color Assessment/ Rates of Removal Using Standard Dye Solutions

The dyes standard solutions prepared from the Bordeaux 3R, Red LMF, Red YCN, and Red B-2B dye created vivid color at 50 mg/L with visible color change at 1 mg/L (515 nm UV absorbance). This illustrated the potency of the dye used at Premier Yarn Dyers (PYD). As samples were received, a mixed dye standard using the above individual dyes at the stated concentration was used to determine the color in field effluent samples. The standard curve for mixed dye concentrations ranged from 0.1 mg/L to 50 mg/L at the optimal wavelength of 515 nm (see Figure 5).

![Figure 5. Absorbency of mixed dye standard (read at 515nm).](image)

\[ y = 0.0467x - 0.0056 \]

Table 3 shows reductions in color at plant treatment locations in PYD facility. Reductions in color concentration were noted from the SWECO (abiotic filtering) to IMBR #2 (biological treatment); the R1 reactor (biological treatment) had the largest variation in color.
A faster rate of color reduction was noted for the commercial IMBR system (Color reduction rate: ~ 0.94 mg/L/h). Color removal was acceptable for discharge to the municipal sewer in Adairsville; however, significant color remained in the bioplant effluent discharge making it unacceptable for re-use in dye formulation. The data suggested the need for using a commercial ozonator to further polish plant treated effluent.

### Table 3. Absorbency and color concentration values for biological treatment system samples.

<table>
<thead>
<tr>
<th>DATE</th>
<th>SWECO</th>
<th>EQ TANK</th>
<th>REACTOR TANK</th>
<th>SEED REACTOR #1</th>
<th>SEED REACTOR #2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abs.</td>
<td>mg/L*</td>
<td>Abs. mg/L*</td>
<td>Abs. mg/L*</td>
<td>Abs. mg/L*</td>
</tr>
<tr>
<td>7/24/2001</td>
<td>-</td>
<td>-</td>
<td>0.573 12.5</td>
<td>0.497 10.2</td>
<td>0.577 12.5</td>
</tr>
<tr>
<td>8/3/2001</td>
<td>-</td>
<td>-</td>
<td>0.568 12.3</td>
<td>0.479 9.6</td>
<td>0.226 4.0</td>
</tr>
<tr>
<td>8/8/2001</td>
<td>-</td>
<td>-</td>
<td>0.406 7.6</td>
<td>0.501 10.4</td>
<td>0.384 7.2</td>
</tr>
<tr>
<td>9/6/2001</td>
<td>0.360</td>
<td>6.6</td>
<td>-</td>
<td>0.204 4.2</td>
<td>0.268 4.7</td>
</tr>
</tbody>
</table>

* indicates mg/L for absorbency readings based on the mixed dye standard at 515 nm

### Phase Two: Modified Technology Treatment Train Tests

Phase 2 studies covers field and related laboratory tests in which a combined abiotic and biotic treatment train was used at the PYD facility. Data is presented for biological, ozone and final carbon polish, the three essential components of this technology treatment train.

#### Biomass Determination

The bioreactors were fed nutrients including urea and phosphate compounds to maintain the microbial growth on the bio-carrier. The reactors sustained viable colony growth when the proper nutrients and the control setting were not disturbed. The HYcheck dipsticks (DIFCO #290531) measured bacterial count per milliliter. The IMBR system had a bacterial count ranging from $10^2$ - $10^5$/ml bacteria.
Table 4. Biomass Concentrations (bacterial colony forming units /ml).

<table>
<thead>
<tr>
<th>DATE</th>
<th>EQ TANK</th>
<th>REACTOR TANK</th>
<th>SEED REACTOR #1</th>
<th>SEED REACTOR #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/24/2001</td>
<td>$10^5$</td>
<td>$10^4$</td>
<td>$10^4$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>8/3/2001</td>
<td>$10^3$</td>
<td>$10^4$</td>
<td>$10^3$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>8/8/2001</td>
<td>$10^4$</td>
<td>$10^3$</td>
<td>$10^4$</td>
<td>$10^3$</td>
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<td>-</td>
<td>-</td>
<td>$10^2$</td>
<td>$10^2$</td>
</tr>
<tr>
<td>10/30/2001</td>
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<td>-</td>
<td>$10^3$</td>
<td>$10^2$</td>
</tr>
<tr>
<td>1/22/2002</td>
<td>$10^4$</td>
<td>$10^4$</td>
<td>$10^5$</td>
<td>$10^6$</td>
</tr>
<tr>
<td>5/31/2002</td>
<td>$10^2$</td>
<td>$10^2$</td>
<td>$10^2$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>6/4/2002</td>
<td>$10^2$</td>
<td>$10^2$</td>
<td>$10^4$</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>

Reduction in Organic Content

With the biomass concentration maintained at a viable level, the effluent waters were biologically treated throughout the entire treatment train. The initial effluent water entering the EQ tank, the first step in the treatment train, had a COD range from 740±50 to 2690±10 mg/L (Table 5). The two IMBR units reduced the COD range to between 545±55 and 1940±0 mg/L. The variability in both of the ranges depends on nutrient feed and rate of effluent intake. The ideal effluent flow is between 80-90 gpm (gallons per minute). The variability in the range is visibly seen in Figure 6. The colors used in the Figure were chosen to illustrate that there was color change as the effluent past through the IMR system and the COD was reduced.

This reduction in the residual organic content by the IMBR units enabled the secondary segment of the treatment train to have full effect. Preliminary Ozonation tests were conducted at the field site to examine the reaction between the ozone and larger quantities of water than can be tested in the laboratory. The two flow rates examined were 0.97 g/gallon and 0.26 g/gallon and the results were recorded in Table 6. The 0.97g/gallon flow rate
exhibited a slightly lower residual organic content when first analyzed upon arrival in the laboratory. However after further ozonation and the addition of activated carbon, there was not a significant difference between the COD values of both flow rates.

With the preliminary tests concluded, the permanent ozonation system was installed and the effluents of the system were analyzed. The ozonation system released effluent with COD in range of 1055±7 to 1243±13 mg/L (Table 5 and Figure 7). These values still proved to be higher than desired for recycled water. To remedy the situation, an activated carbon bed filter was set inline after the ozonation system. The resultant effluents were analyzed and exhibited a COD reduction to a range between 553±7 and 700±28 mg/L. There was a value outside of the trend at 60±3 mg/L but a value this low has not been seen since. However, the main effect elicited by ozone is the reduction of color in the effluent seen in Figure 8 through Figure 10.

Table 5. Reduction of organic content of biological treatment system (expressed as COD*).

<table>
<thead>
<tr>
<th>DATE</th>
<th>EQ TANK</th>
<th>SEED REACTOR #1</th>
<th>SEED REACTOR #2</th>
<th>TO OZONE</th>
<th>FROM OZONE</th>
<th>FROM CARBON BED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>7/24/2001</td>
<td>2585±35</td>
<td>1110±20</td>
<td>860±100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8/3/2001</td>
<td>2350±10</td>
<td>645±15</td>
<td>795±15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8/8/2001</td>
<td>1670±40</td>
<td>760±0</td>
<td>545±55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/22/2002</td>
<td>2690±10</td>
<td>1940±0</td>
<td>1835±35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/25/2002</td>
<td>2115±5</td>
<td>1655±25</td>
<td>1480±100</td>
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<td>-</td>
<td>-</td>
</tr>
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<td>6/4/2002</td>
<td>2210±60</td>
<td>1320±20</td>
<td>1240±10</td>
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<td>-</td>
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</tr>
<tr>
<td>6/24/2002</td>
<td>1350±10</td>
<td>1220±30</td>
<td>875±15</td>
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<td>-</td>
</tr>
<tr>
<td>6/27/2002</td>
<td>2110±10</td>
<td>1215±5</td>
<td>1115±15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7/9/2002</td>
<td>1539±169</td>
<td>891±7</td>
<td>788±8</td>
<td>-</td>
<td>-</td>
<td>60±3</td>
</tr>
<tr>
<td>7/16/2002(11am)</td>
<td>1867±11</td>
<td>1062±14</td>
<td>1032±4</td>
<td>1175±9</td>
<td>1073±5</td>
<td>-</td>
</tr>
<tr>
<td>7/16/2002(5pm)</td>
<td>1779±17</td>
<td>1008±2</td>
<td>951±1</td>
<td>1241±8</td>
<td>1109±1</td>
<td>-</td>
</tr>
<tr>
<td>7/17/2002</td>
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<td>1083±13</td>
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<tr>
<td>7/18/2002</td>
<td>2050±22</td>
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<td>883±15</td>
<td>1210±8</td>
<td>1243±13</td>
<td>553±7</td>
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</table>

* APHA Method 5220 D (1998)
Table 6. Reduction of organic content of preliminary ozone treatment samples. (expressed as COD*)

<table>
<thead>
<tr>
<th>TYPE</th>
<th>O₃ TREATED (0.97G/gal)</th>
<th>O₃ TREATED (0.26G/gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>Premier Ozone Treatment</td>
<td>575±80</td>
<td>605±75</td>
</tr>
<tr>
<td>Additional Ozone Treatment</td>
<td>355±5</td>
<td>380±0</td>
</tr>
<tr>
<td>Activated Carbon Treatment</td>
<td>300±10</td>
<td>315±5</td>
</tr>
<tr>
<td>Ozone &amp; Carbon Treatment</td>
<td>160±10</td>
<td>145±5</td>
</tr>
</tbody>
</table>

* APHA Method 5220 D (1998)

Figure 6. Reduction of organic content in biological treatment system.
Figure 7. Reduction of organic content in ozonation system.

Figure 8. SWECO (No Treatment, Filtered [0.45µm Metricel® #63069], Filtered + Ozonation, [0.5g/h O$_3$ with 4.5 L/min O$_2$ feed]).
Figure 9. Reactor Tank (No Treatment, Filtered [0.45µm Metricel® #63069], Filtered + Ozonation, [0.5g/h O₃ with 4.5 L/min O₂ feed]).

Figure 10. Seed Reactor #1 (No Treatment, Filtered [0.45µm Metricel® #63069], Filtered + Ozonation, [0.5g/h O₃ with 4.5 L/min O₂ feed]).
Nutrient Concentrations

As mentioned, nutrient concentrations are important for both biomass growth and COD reduction. The microbes, present in the IMBR units, require the proper nutrient mixture in order to maintain ideal growth patterns. If the growth patterns are not maintained, the COD reduction is impaired. Table 7 displays the ammonia concentrations of the entire treatment system. Proper ammonia concentrations are at a one to ten ratio with the COD values of a sample. When compared to the COD values in Table 5, the ammonia concentrations were at a one to ten ratio with COD on May 31. The difference accounts for the large COD values present in both of the IMBRs. With the nutrient mix off scale, the system did not give the expected results.

Table 7. Ammonia concentrations* of the biological treatment system.

<table>
<thead>
<tr>
<th>DATE</th>
<th>EQ TANK</th>
<th>REACTOR TANK</th>
<th>10K TANK</th>
<th>SEED REACTOR #1</th>
<th>SEED REACTOR #2</th>
<th>TO OZONE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/22/2002</td>
<td>-</td>
<td>75</td>
<td>70</td>
<td>50</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>5/31/2002</td>
<td>70</td>
<td>80</td>
<td>-</td>
<td>70</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>6/4/2002</td>
<td>50</td>
<td>40</td>
<td>-</td>
<td>50</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>6/24/2002</td>
<td>90</td>
<td>90</td>
<td>-</td>
<td>70</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>6/27/2002</td>
<td>70</td>
<td>80</td>
<td>-</td>
<td>100</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td>7/18/2002</td>
<td>45</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>35</td>
<td>30</td>
</tr>
</tbody>
</table>

* APHA Method 4500-NH₃-C (1992)

True Color

True color was examined to obtain the concentration values of dye in the water. The true color tests required the water be filtered to remove particulate matter to achieve a pure sample. The results proved useful when the biological treatment samples were compared to the preliminary ozone samples. The tests displayed a basic 80% reduction in true color
between the SWECO sample from October 2001 (Table 8) and the 0.97 g/gallon ozone treated water (Table 9).

Table 8. True color analysis* of biological treatment system.

<table>
<thead>
<tr>
<th>DATE</th>
<th>SWECO</th>
<th>EQ TANK</th>
<th>REACTOR TANK</th>
<th>SEED REACTOR #1</th>
<th>SEED REACTOR #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/6/2001</td>
<td>PtCo Unit</td>
<td>PtCo Unit</td>
<td>PtCo Unit</td>
<td>PtCo Unit</td>
<td>PtCo Unit</td>
</tr>
<tr>
<td>10/30/2001</td>
<td>480</td>
<td>-</td>
<td>590</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>10/30/2001</td>
<td>970</td>
<td>660</td>
<td>-</td>
<td>930</td>
<td>830</td>
</tr>
</tbody>
</table>

* APHA Method 2120 B (1998)

Table 9. True color analysis* of preliminary ozone treatment samples.

<table>
<thead>
<tr>
<th>O3 TREATED (0.97G/GAL)</th>
<th>O3 TREATED (0.26G/GAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCo Unit</td>
<td>PtCo Unit</td>
</tr>
<tr>
<td>True Color</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>700</td>
</tr>
</tbody>
</table>

* APHA Method 2120 B (1998)

Total Suspended Solids

The results discussed have reported the efficiency of the treatment train but there has been a particular problem that requires a solution. The further along in the system the effluent reached the higher the occurrence of particulate matter. After examination of total suspended solids (TSS), this was proven. The EQ tank contained 185 mg/L TSS and while seed reactor #2 at the end of the IMBR system contained 310 mg/L TSS (Table 10). The largest species of particulate matter found in the system was yarn fibers (Figures 11 and 12). To correct this problem, Y-valves were installed to filter out yarn fibers and other particulate matter to inhibit transference between each tank.

Table 10. Total suspended solids in the pre-ozonation treatment.

<table>
<thead>
<tr>
<th>EQ Tank</th>
<th>Reactor Tank</th>
<th>Seed Reactor #1</th>
<th>Seed Reactor #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>185 ± 23</td>
<td>132 ± 32</td>
<td>158 ± 6</td>
</tr>
<tr>
<td></td>
<td>310 ± 38</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* APHA Method 2540 D (1998)
Figure 11. Fibers present in post-ozonation effluent (10x magnification)

Figure 12. Fibers Present in post-ozonation effluent (40x magnification)
CONCLUSIONS AND GENERAL DISCUSSION

Premier Yarn Dyers (PYD) in Adairsville, GA, felt the impact of the regulations on color when the State of Georgia began to fine the company for having effluent above regulatory levels of color and COD (chemical oxygen demand). Laboratory tests were conducted using a bench scale model of a bioreactor and ozonation system to reduce the color and COD levels. The initial samples examined were from two internal processes of PYD, i.e. space dyeing and skein dyeing. All samples received from both processes were biologically treated and ozonated. At the end of treatment, all laboratory samples exhibited >89% reduction in COD levels and dye concentration levels. The skein dye effluent had COD reductions from 3,185±30 mg/L to 360±10 mg/L (COD reduction rate: 42.16±3 mg/L/h) and color reduction from 4.9 mg/L to 0.8 mg/L (color removal rate: 0.062 mg/L/h). The space dye effluent was also reduced from 5,430±30 mg/L to 550±120 mg/L (COD reduction rate: 72.8 ± 1.3 mg/L/h) with subsequent color reduction from 16.0 mg/L to 1.5 mg/L (color reduction rate: 0.21 mg/L/h). These results led to the implementation of the full scale “technology treatment train” at PYD.

The “treatment train” was successful in reducing the COD throughout the commercial treatment system installed at PYD. The IMBR system reduced residual organic content levels from 2,690±10 mg/L in the EQ tank to 545±55 mg/L in the IMBRs. The ozonation and carbon polishing system continued to reduce the residual organic content levels to 553±7 mg/L (with the lowest recorded COD value being 60±3 mg/L). Color reduction was the goal of the ozonation and carbon polishing system and was also accomplished. The true color of the effluents was reduced from 970 to 210 PtCo units of color, i.e. approximately a 78% reduction.
Table 11 presents kinetic rates of reduction throughout the project year. Low kinetic rates noted in January were attributed to processing cold standing water from the EQ tank while the facility was down for maintenance. The low kinetic rate noted in June was a dilution event due to returning treated water from the R1 unit back to the EQ tank on a trial basis. As expected, higher kinetic rates of removal were noted for IMBR reactors. The R1 reactor having less biocarrier and a larger retention time for volume flow resulted in lower but acceptable kinetic rates of removal. Ozonation while contributing to color removal provided negligible reductions in COD rate of removal. Post carbon polishing removed non-degradable residuals and provided for acceptable treated effluent. The resultant effluent was successfully recycled into the dye house processes. Thus, recyclable process water was produced from the effluent waters of Premier Yarn Dyers.

Table 11. Kinetic rates of removal from biological and combined biological/ozonation/carbon systems.

<table>
<thead>
<tr>
<th>Date</th>
<th>Seed Reactor #1</th>
<th>Seed Reactor #2</th>
<th>R1 System</th>
<th>Post Ozone</th>
<th>Post Carbon Bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/24/2001</td>
<td>167.61±1.7</td>
<td>196.02±7.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8/3/2001</td>
<td>193.75±0.6</td>
<td>176.7±0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8/8/2001</td>
<td>103.41±4.5</td>
<td>127.84±1.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/22/2002</td>
<td>85.23±1.1</td>
<td>97.16±2.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/25/2002</td>
<td>52.27±2.3</td>
<td>72.16±10.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6/4/2002</td>
<td>101.14±4.5</td>
<td>110.23±5.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6/24/2002</td>
<td>14.77±2.3</td>
<td>53.98±0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6/27/2002</td>
<td>101.70±0.6</td>
<td>113.07±0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7/9/2002</td>
<td>73.64±18.4</td>
<td>85.34±18.3</td>
<td>-</td>
<td>-</td>
<td>35.21±3.9</td>
</tr>
<tr>
<td>7/16/2002 (11:05)</td>
<td>91.48±0.3</td>
<td>94.87±0.8</td>
<td>16.63±0.1</td>
<td>18.90±0.1</td>
<td>-</td>
</tr>
<tr>
<td>7/16/2002 (5:30)</td>
<td>87.60±1.7</td>
<td>94.09±1.8</td>
<td>12.93±0.2</td>
<td>15.95±0.4</td>
<td>-</td>
</tr>
<tr>
<td>7/17/2002</td>
<td>113.64±0.9</td>
<td>121.25±1.5</td>
<td>20.70±0.2</td>
<td>24.48±0.3</td>
<td>32.93±0.2</td>
</tr>
<tr>
<td>7/18/2002</td>
<td>121.36±1.8</td>
<td>132.61±0.8</td>
<td>20.19±0.3</td>
<td>19.21±0.2</td>
<td>35.64±0.4</td>
</tr>
</tbody>
</table>
RECOMMENDATIONS

The biotic and abiotic treatment of the effluents of PYD proved successful; however these test results do not encompass research on the chemical processes undertaken in the ozonation of the effluents. With chemical research, the exact abiotic process by which ozone oxidizes the dye compounds must be more clearly understood so as to further develop a more efficient treatment process. Currently, adjustment of the ozonation system is by visual control. The ozone unit manufacturer is addressing a technical solution to this problem.

A problem involving the biotic process has already been discovered in the treatment of textile dye effluent. The dispersant that textile mills use, i.e., sulfonated naphthalene formaldehyde condensates (SNFC), in their dye vats has caused the discoloration of effluent waters. (11). Studies have shown that SNFCs undergo photo-chemically enhanced reactions forming yellow-brown organic products in the water (11). The SNFCs can extend the biological treatment retention time and cause the process to be more expensive (11). As a solution to this problem, other dispersants that are not photosensitive should be examined as replacements for SNFCs. Finally, an optimal microbial isolate may be identified to further biodegrade SNFCs to non color forming intermediates.
BIBLIOGRAPHY


APPENDIX: GEORGIA WATER QUALITY REGULATIONS

RULES AND REGULATIONS FOR WATER QUALITY CONTROL

CHAPTER 391-3-6

REVISED – June 2002

GEORGIA DEPARTMENT OF NATURAL RESOURCES
ENVIRONMENTAL PROTECTION DIVISION
2 MARTIN LUTHER KING JR DRIVE, SE
FLOYD TOWERS EAST
ATLANTA, GEORGIA 30334

(Referenced from http://www.state.ga.us/dnr/environ/rules_files/exist_files/391-3-6.pdf)
VITA

Kathryn Wallace Huddle was born Kathryn Wallace Martin in Oak Ridge, Tennessee, on August 15, 1978. She is the daughter of James and Beverly Martin of Sulphur, Louisiana, and has two older brothers, Phillip and David. She graduated May of 1996 from Saint Louis Catholic High School in Lake Charles, Louisiana, with an honors diploma. In December of 2000, she received her bachelor of science in marine biology from Texas A&M University at Galveston in Galveston, Texas. In the spring of 2001, she married John Huddle of Lake Charles, Louisiana. In the summer of 2001, she accepted a graduate assistantship from the Department of Environmental Studies at Louisiana State University, Baton Rouge, Louisiana and began her study of environmental toxicology. Mrs. Huddle is currently a candidate for a master of science in environmental sciences to be awarded on December 20, 2002.