PHYSICOCHEMICAL AND BIOLOGICAL TREATMENT OF A TEXTILE DYEING AND FINISHING WASTEWATER

by

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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Environmental Engineering

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February, 1995

Blacksburg, Virginia

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(ABSTRACT)

Wastewaters from textile dyeing and finishing industries are often high in color, organic matter, metals and toxicity. Treatment is usually required before discharge into a sewer or body of water. Pretreatment often consists of chemical coagulation to remove color and solid matter. Aerobic biological treatment is incorporated to remove degradable organic matter and additional color and solid matter.

The wastewater studied in this research project consisted of thermosol dye, print, and bleach and finish waste streams. The goal of this research project was to continue work on this wastewater that was initiated by Weber (1994). Pretreatment experiments were performed on the bleach and finish stream in an attempt to reduce organic content. Also, bench scale, aerobic biological reactors were operated at hydraulic residence times (HRT) of 4 and 7 days, to determine if higher reductions in color, organic matter or solids would be seen compared to Weber's results from the 3 day HRT operation. Toxicity tests were performed on reactor effluents to determine if toxicity remained after treatment was performed.

The bleach and finish did not respond favorably to the majority of pretreatments. An 84% color reduction was produced with adjustment of the pH to 4.5 and chemical coagulation with 400 mg/L of a blend of inorganic aluminum and a polyamine (AL220; Polymer Systems, Inc.). A 65% reduction in COD resulted from coagulation using 100 mg/L of Nalco polymer 9764, a polyamine.

The bench scale reactors were operated at sludge ages of 15, 20 and 30 days and hydraulic residence times of 4 and 7 days. The 4 day HRT COD removal results were similar to Weber's (1994) results, while the 7 day HRT operation resulted in COD removals of 89 to 92%. Analysis of the steady state data produced kinetic coefficient values K_s, k, Y and k_d for the 7 day operation of 2.6 mg/L, 0.16 day^{-1}, 0.74, and 0.05 day^{-1}.

Toxicity tests performed on effluent from the 7 day HRT operations were passed. Short term chronic tests, using *Pimephales promelus*, resulted in No Observed Effect Concentrations of 100%. Acute tests, using *Ceriodaphnia dubia*, yielded LC50 values of greater than or equal to 100%.

ACKNOWLEDGMENTS

I would like to thank Dr. Greg Boardman for the support and direction he provided over the course of this research project. Appreciation is also extended to Dr. John Novak and Dr. Cliff Randall for providing additional support and for agreeing to act as my committee members.

Special thanks to the Plant and Tetra Tech for continuing this research project and providing the necessary funding. I would especially like to thank Earlie and Kevin for answering questions and for delivering the waste to Virginia Tech for the final year of research. I also want to thank all the others at the Plant who did not hesitate to help in any way they could.

Thanks to Julie Petruska, Marilyn Grender and Betty Wingate. They all provided unconditional support in the lab and brightened many dark days.

Finally, I would like to thank my family for the support and encouragement they provided. I would particularly like to thank my mother, Esther Gandee, for the many trips she made to Virginia to provide in person encouragement and care.

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CHAPTER I. INTRODUCTION

Years ago, industries were not strictly regulated regarding the treatment and disposal of wastes that were generated. Recently, regulations for all industries, including the textile industry have become much more strict. Industries are being forced to look more closely at the pollutant composition of the wastes that are produced and to utilize treatment methods capable of removing the pollutants prior to discharge to water bodies or publicly owned treatment works.

Due to the aqueous volume of dyeing and printing processes and the variety of dyes in use, the textile industry generates a large amount of liquid waste with high color content. Colored water is not only aesthetically displeasing to humans, it can also signal the possible presence of other pollutants. Colored effluent that is discharged to a receiving stream that is incapable of diluting the color can block the transmission of sunlight to aquatic organisms that require sunlight for metabolism, thus leading to a breakdown in the aquatic ecosystem.

Another contaminant of textile waste, due to fabric preparation processes, is chemical oxygen demand. The fabric preparation processes produce waste streams with large amounts of natural fibers, synthetic compounds, surfactants and resins. Many of the constituents present in the waste stream require

treatment to meet discharge limits imposed through regulations.

Effluent toxicity is also a concern for the textile industry. Metals, dyes, surfactants, various auxiliary compounds and finishing agents contribute to the toxicity of waste streams. These agents should be removed or degraded to an acceptable level prior to discharge.

A study of effluent from a bleaching and finishing plant (hereafter referred to as "the Plant") was continued from the point at which Michelle Weber concluded her research. The resulting thesis, entitled *Pretreatment and Biodegradation of Wastewater from a Dyeing and Finishing Industry*, contains additional information that may be of interest to the reader. The Plant continues to work with 100% cotton, and 50/50 and 70/30 polyester cotton blends. Textile industry processes include preparation, which covers scouring, sizing/desizing and bleaching, and thermosol dyeing, printing and finishing.

The Plant provides on-site treatment for the waste that is produced. Pretreatment of the thermosol dyeing and printing effluent is provided by chemical coagulation and dissolved air flotation (DAF). Much of the color and some metals and organic material are removed in pretreatment. Secondary treatment, which provides the majority of organic reduction and further reduction of color, occurs in an aerated lagoon, followed by a clarifier that provides for removal of biomass and precipitated chemicals. The bleach and finish effluent moves directly to the aerated lagoon. Sludge from the DAF and clarifier is

digested aerobically, then put through a belt filter press and subsequently dried in a sludge dryer before transport to a landfill. Clarifier supernatant flows through a chlorine contact system for disinfection, then a dechlorination system prior to discharge into a small stream. The addition of the sludge dryer is the only major change that has occurred since the completion of Weber's work. Figure 1, drawn by H.R. Diz, another Environmental Engineering graduate student, shows the Plant's treatment layout.

Flow equalization is not provided, either before pretreatment or secondary treatment. As mentioned earlier, the bleach and finish waste stream is currently untreated prior to introduction into the aerated lagoon. This waste stream carries a high organic concentration, hence a high COD. Pretreatment to reduce the COD could lessen the impact on the aerated lagoon. Also, Plant personnel have limited knowledge concerning biomass concentrations and fluctuations in the aerated lagoon. Treatment optimization cannot be obtained without control of the lagoon. In the past, the Plant has failed effluent toxicity tests. Metals or some other agent used in one of the processes are thought to be the cause for failure.

On the basis of the above information, the goals of this study included:

(1) investigation of pretreatment processes for the bleach and finish waste stream, primarily to remove COD, secondarily color;

(2) operation of bench scale aerobic reactors, at HRT levels of 4 and 7 days, to treat the Plant's waste stream combination and determine biological kinetic coefficients.

(3) measurement of chromium concentration in reactor influent and effluent waste streams to determine if discharge limits were met; and,

(4) acute and chronic toxicity assessment of bench scale effluents using *Pimephales promelus* and *Ceriodaphnia dubia*.

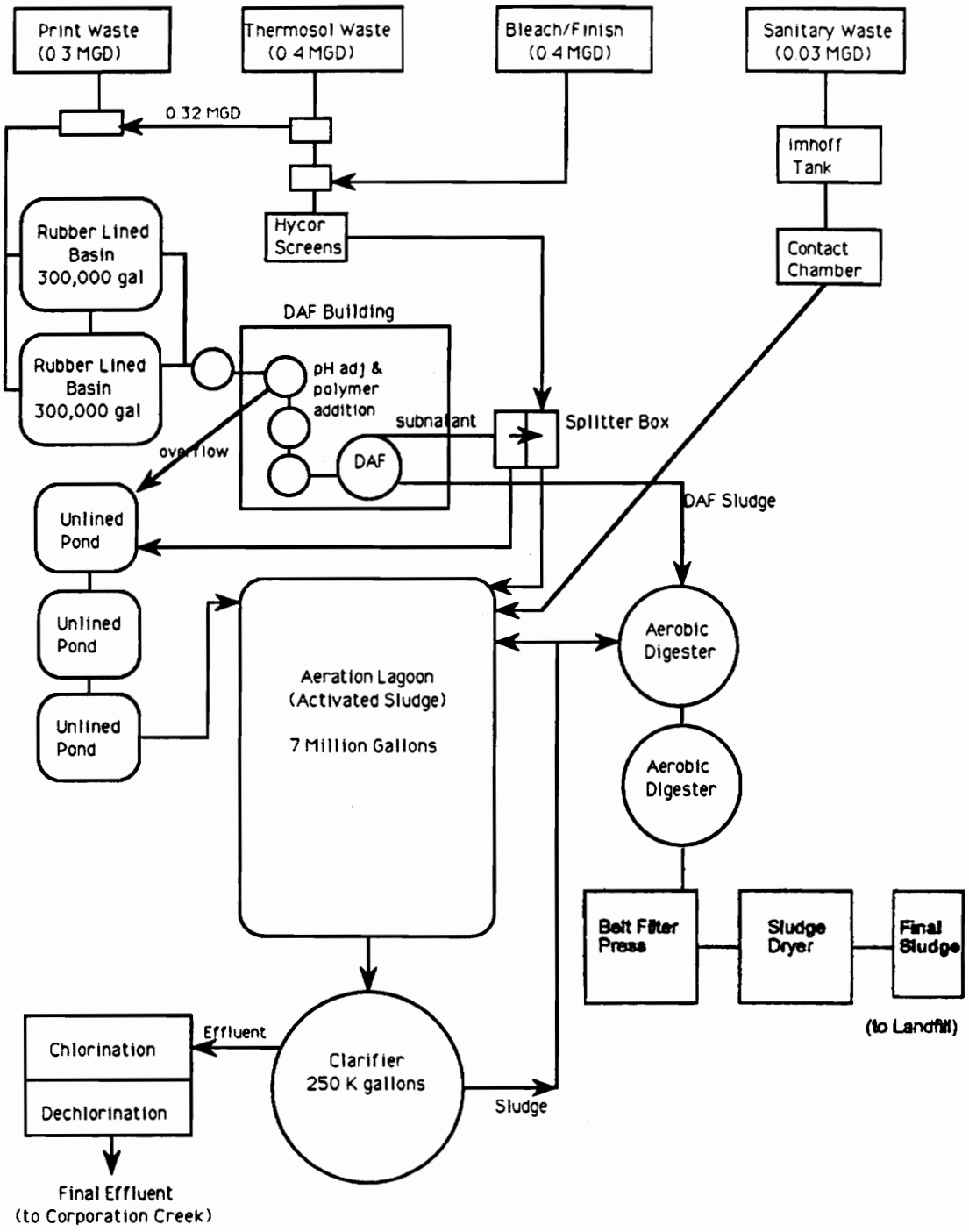


Figure 1. Flow diagram of the Plant's wastewater treatment facility

CHAPTER II. LITERATURE REVIEW

Dyes and pigments are used to provide colored products in several industries, with almost 0.5 billion pounds per year (lb/yr) of commercial color production occurring in the U.S. The textile industry is a heavy user of dyes and colorants. It has been estimated that "the total dye consumption of the textile industry is 1 billion lb/yr". (Porter, 1973)

Production of textiles is accomplished using both wet and dry processes. The EPA (1978) has categorized the wet processes, which produce the majority of aqueous waste, as:

(1) Scouring
(2) Bleaching
(3) Dyeing or Printing
(4) Special Finishing

It is easy to see how volumes of liquid waste can accrue from the manufacture of textiles when one considers that 10% of cotton fabric weight consists of natural impurities which are removed during processes such as scouring (Junkins, 1983). In many dyeing processes, only 85-90% of the dye is retained by the fabric, the remaining 10-15% of the dye in solution is discharged with the liquid effluent (Barker and Barbour, 1994).

Often, textile effluents do not have a large BOD content but starches,

surfactants and synthetic sizing agents such as polyvinyl alcohol (PVA), which is removed in the scouring process and used in the sizing and dyeing operations, can contribute as much as an additional 10,000 mg/L COD to the overall mill effluent (Lin and Lin, 1993).

Current technology has provided textile manufacturers with an abundance of sizes, dyes, auxiliary chemicals, and finishing formulas that were not available before. Sometimes biodegradability information is not known. Many mills are having to cope with tightened regulations concerning discharge limits for polluting effluent constituents such as biological oxygen demand (BOD), COD, total suspended and dissolved solids (TSS and TDS), fats, grease, and metals as regulatory agencies are becoming more vigorous about the problem of effluent pollution (Davis, 1991). Although color is not currently regulated, many state and federal environmental agencies are contemplating the establishment of limits (Tincher, 1993). Constituent toxicity is also an area of growing concern. A number of studies have been conducted in areas such as dye, surfactant, metal and chlorinated organic toxicities (Carlson and Kosian, 1987; Horning, 1974; Huber, 1984; Little and Lamb, 1973).

The fact that mills use batch style production and can change chemicals, dyes, and types of fabrics being produced from a day to day, even hour to hour basis, makes the waste that is produced highly variable and difficult to treat. Treatment system design is almost "a matter of custom tailoring" due to all the

possible production variable combinations (Leary, 1980). Regardless of the variability involved, waste treatment usually consists of some form of primary, secondary, and often tertiary treatment. Equalization is a recommended first step due to the changing characteristics of the waste, especially prior to biologic treatment to reduce shock to the microorganisms. For the removal of color and organics, many mills use a combination of chemical coagulation and biological treatment (Junkins, 1983). There are many coagulants, polymer formulas, and biological treatment schemes available to choose from when designing a system. Often, jar testing with the various chemicals coagulants and operation of bench scale biologic systems will aid in determining the best form of treatment for a particular waste stream.

An outline of textile manufacturing processes which are conducted at the Plant will be discussed in the following literature review. Waste treatment processes will also be presented, as will toxicity issues which effect the textile industry.

2.1 TEXTILE MANUFACTURING PROCESSES

Manufacturing processes themselves have not changed much recently. Natural fiber growth and synthetic fiber manufacture, combing, spinning, preparation, coloring and finishing still comprise the work done by the industry. The processes described below occur at the Plant to produce natural, and

natural and synthetic blends of woven fabric.

2.1.1 Bleaching

The bleaching process, along with processes like sizing, desizing, and scouring, is considered to be a preparatory step in the textile manufacturing industry. Fabric known as "grey" material enters the plant and is first scoured to remove excess fibers and other nonessential matter. Bleaching is performed by "soaking the cloth in a standing bath containing an oxidizing agent in solution, or in a continuous bleaching process". Cotton bleaching involves the use of hypochlorite or hydrogen peroxide. Those two agents as well as peracetic acid or sodium chlorite are used on synthetic fabrics (EPA, 1978).

More recently, mills have begun to use hydrogen peroxide more exclusively due to the fact that it reacts to form water and oxygen, two much less harmful products than are formed by some of the other bleaching agents. In some cases, the production of oxygen can increase the dissolved oxygen content of the effluent. (Porter, 1970)

The bleaching process in a cotton mill regularly consumes almost 50% of the water required for all of the manufacturing processes (Park and Shore, 1984). Bleach effluent alone can be acidic and toxic, but in general does not add to the overall organic load of the mill effluent (EPA, 1978). However, bleach effluent combined with desizing and scouring effluents can contribute up to 87%

of the COD load from a cotton textile mill (Park and Shore, 1984).

2.1.2 Dyeing and Printing

Once the fabric has been through the preparatory stages, it is ready to be dyed and or printed. Fabric appearance is changed through the use of dye. "The purpose of a dye is to penetrate the fabric or yarn thoroughly and reflect certain wavelengths of light to give the fabric or yarn a characteristic appearance" (Childers, 1993). Demands for better and brighter fabrics and colors have driven the development of new fabrics and dyes (Porter, 1970).

Continuous or exhaust methods can be used to dye (ATI, 1990). Some of these methods include stock, top, piece, and cross or union dyeing (Childers, 1993). Some of the commonly used dyes can include reactive, disperse, direct, basic, vat or sulfur. Sulfur dyes have a poor affinity for cotton making it necessary to maintain a high concentration of dye in the bath. Due to the inability of the dye to penetrate and remain on the fabric, much is lost in the effluent (Nemerow, 1952). Sulfur dyes can also contribute to the toxicity of the effluent due to the presence of chromium in the compounds used in the necessary oxidation step (Hickman, 1993). Direct dyes are resistant to light degradation and have varying adsorptive tendencies onto organic matter. Sometimes, physical or chemical treatment is required for removal (Porter, 1973). Basic dyes are water soluble and can be readily adsorbed to organic

matter (Porter, 1973). Special carriers are sometimes required to "achieve satisfactory penetration of the dye into the fiber" when synthetic materials are undergoing the dyeing process.

Many auxiliary chemicals are used in the dyeing process and are discharged with the effluent once the process is completed. Many of the auxiliaries are not biodegradable and may cause a problem in activated sludge systems (Porter, 1970).

"For printing, the fundamentals of dyestuffs, fabrics, fastness properties, and many other factors are similar to dyeing. However, the aim of printing is the localized application of color." Printing can be accomplished through the use of pigments or dyes (ATI, 1990). It is necessary to follow the printing operation with a chemical wash to fix the color, followed by another wash and rinse as the final step to remove any remaining chemical (EPA, 1978).

According to the EPA (1978), effluents from the dyeing and printing of cotton and synthetics can represent 15 to 35% and 5 to 80% of the total plant BOD and solids loads, respectively. Furthermore, dyeing and printing processes in cotton textile production contribute between 10 and 20% of the total effluent pollution load while consuming 15% of the water that is used (Park and Shore 1984). The major concern is often the high color content that the dye and print solutions contribute to the effluent.

2.1.3 Finishing

Finishes are often added before or after the dyeing process to give a certain quality to the material. According to Porter (1970), "a treatment of a fabric that modifies its physical or chemical properties may be classified as finishing". Among the many possible finishes are waterproofing, fireproofing, and brightening (EPA, 1978).

Finishes do not usually contribute heavily to the volume of effluent or to the pollution level. Park and Shore (1984) and EPA (1978) estimate approximately 15% of the total pollution load can be traced back to finishing compounds. Finishing at the Plant is considered a dry process which can utilize PVA, resins, acrylic emulsion binders, softeners and silicone. These constituents enter the waste stream only when it is necessary to dump the finishing mix (Barker and Barbour, 1994).

2.2 WASTE TREATMENT

Many treatment options exist for textile and other process waste effluents. The variability of textile waste, due to the numerous types of dyes in use and the batch style processes used by many mills, makes workable treatment design difficult. Each effluent is unique and many times a procedure designed for one type of effluent stream will not achieve the same levels of constituent removal, whether it be color, COD, or total suspended solids, in another effluent stream.

2.2.1 Pretreatment Options

There was not much information available in the literature that discussed pretreatment of bleaching and finishing wastes. The bulk of the literature focused on pretreatment of effluents from dyeing processes. Pretreatments which are commonly used include chemical oxidation, ion exchange, reverse osmosis, carbon adsorption, filtration, chemical coagulation, sedimentation, and equalization. The majority of the following section will describe studies that focus on equalization, chemical coagulation and oxidation, but other methods will be touched upon.

Equalization is often utilized as a form of pretreatment, although descriptions are often included with discussions concerning primary treatments like screening and neutralization. According to Rodriguez and Quimicas (1991), "equalization of fluid effluent is understood to be the operation of installing a basin which lessens flow rate and concentration variations in liquid effluents". They go on to say that it is often the biological systems that suffer the most from highly variable influents because of their "sensitivity and specificity to the medium in which they find themselves". Foess *et al.* (1977) stated that equalization "benefits biological treatment by producing increased uniformity in the concentration and flux of organics and nutrients in the wastewater, as well as more stable retention periods and biomass concentrations in the aeration basin" and that equalization "improves the settleability of wastewater and provides

some BOD reduction and odor removal (if aeration is used for mixing in the aeration basin)".

Yu and Lo (1992) undertook a pilot-plant study in an attempt to save a full-scale treatment plant. The wastewater treatment plant was receiving industrial influent flows from various types of surrounding industrial plants. This influent fluctuated widely with COD values ranging from 100-1660 mg/L, high metal concentrations (e.g. Cu to 19 mg/L and Zn to 37 mg/L), pH levels varying from 1.4-12.0, and grease concentrations of up to 470 mg/L. They studied equalization periods of 8, 12 and 24 hours and chemical precipitation with sodium hydroxide or calcium hydroxide as a means of reducing the wide variations in influent flow parameters before introduction of the flow to the aeration basin. They concluded that the combination of equalization to dampen pH and COD variations and chemical precipitation to remove metals and grease produced a much safer influent to the aeration basin.

Foess *et al.* (1977) studied two flow equalization systems in southeastern Michigan. One system featured in-line equalization and the other featured side-line equalization where only greater than average flow was introduced into the equalization tank. Foess *et al.* (1977) concluded that influent flow variations were dampened and made more uniform by both equalization systems, but that secondary effluent analysis indicated that variables other than flow equalization were important in determining the quality of effluent flow from the aeration basin.

They listed those variables to include "mixed liquor settleability, organic loading intensity, and wind and density currents". According to Foess *et al.* (1977), the municipal pollution control field has not widely accepted and applied flow equalization regardless of the advantages which are thought to exist. Operating problems and questions concerning cost effectiveness were to blame. He cited that the 24-hour composite BOD removal was not significantly effected by equalization in a pilot study conducted by Boon and Burgess (1972).

The effectiveness of $FeSO_4$, alum, and $FeCl_3$ with polyelectrolytes for the removal of COD from knit and woven fabric mills wastewaters was studied by Germirli *et al.* (1990). $FeSO_4$ was able to remove 83 and 92% of the COD at a dose of 100 mg/L, while 400 mg/L of alum could only remove 33% of the COD. Nearly as poor results were cited for $FeCl_3$, with 200 mg/L removing 50% of the COD. A dose of 800 mg/L was required before reductions of 93% were obtained.

Tunay *et al.* (1990) performed treatability studies on reactive and direct dye process effluents using alum, ferric and ferrous salts, and anionic polymers. It was concluded that ferric chloride provided optimum results for the direct dye samples at a 400 mg/L dose, plus 5 mg/L of a polymer, administered at pH 9. Reported COD removals were in the 30 to 40% range. Only 250 mg/L of ferric chloride with the same polymer dose and pH level was required to remove 50% of the COD from a weak reactive dye sample. Alum provided poor results in

each case.

Alum and cationic polymers were examined by Stahr *et al.* (1981) for effective effluent color removal. When a cationic polymer was used alone, 200 mg/L was required to bring about effective color removal. Only 10 mg/L of the polymer was required when used in combination with 300 mg/L of alum. Alum alone was also unable to reduce color effectively. The researchers noted that initial color of sample and type of dye used influenced the amount of removal that was possible. In particular, the highly water soluble acid dyes which were studied did not respond well to chemical coagulation.

Horning (1977) studied the effects of precipitation by lime, alum, and ferric iron salts, adsorption by powdered activated carbon (PAC), and oxidation by ozone on a wide variety of dyes used in the textile industry. He found that dosages of 8 to 80 mg/L alum or 1500 mg/L PAC could generally reduce color to less than 100 ADMI units. PAC provided more color removal than alum when reactive or basic dyes were studied, but PAC was not useful with vat or disperse dyes. He noted that if the dyes contained enough carbonate alkalinity to cause formation of calcium carbonate, then lime was the most effective coagulant. An ozone dose of 1 mg/L was effective for color removal in reactive and basic dyes, but ineffective for use on disperse dyes. Results concerning direct dyes were highly variable. Ozone was not effective in producing significant reductions in total organic carbon (TOC) levels.

According to Hatton and Simpson (1986), disperse vat and sulfur dyes are not readily adsorbed by carbon at any pH, but that good coagulation results from aluminum sulfate addition.

A pilot test conducted by Davis (1991) at a dyeing and finishing mill, which processed mostly woven synthetics and blended fabrics, attempted to determine if levels of BOD, COD, TSS, fats, oils, grease and color, could be removed through pretreatment prior to discharge to the local sewage treatment plant. The system included chemical coagulation with organic polymers followed by dissolved air flotation (DAF). Following that treatment, the effluent was put through a sand filter and an activated carbon filter. The results included a 70 to 95% reduction in BOD, COD, fats, oils, greases, and suspended solids from the chemical coagulation and the DAF alone. Color was not effectively removed here, but was in the activated carbon filter. Chemical coagulation and DAF did remove enough constituents prior to entrance into the carbon filter to prolong the life of the carbon and require regeneration less often.

Gardiner *et al.* (1978) indicated that chlorine is the cheapest oxidant available, but that ozone and hydrogen peroxide can also be used. They further state that these chemicals are often used in textile bleaching processes and that the chemicals may be effective in treatment of the effluent. A warning about the non-biodegradability of chlorinated organics was included to illustrate that chlorine is most likely not the best choice for color removal when

biodegradability is of concern.

According to Woldman (1974), oxidation with 35 mg/L of chlorine for 30 minutes was sufficient to remove color from some dye and print effluents, but that others required 500 mg/L of alum or 400 mg/L of ferric chloride each, plus 1 mg/L of an anionic polymer to remove color. An additional benefit from the metal coagulant polymer combination was removal of BOD and COD.

Brower and Reed (1986) noted that chlorine and hydrogen peroxide doses of 100 and 300 mg/L are often sufficient to remove color from some dye wastes. With that in mind, they performed a study using oxidation with sodium hypochlorite and hydrogen peroxide to remove color from two dye wastes. The results showed variable effectiveness.

Groff's (1991) discussion of textile wastes included several references to various methods of pretreatment utilized by other researchers, including the following. Mamontova (1990) studied the effects of in-bulk coagulation with $Fe_2(SO4)_3$ followed by contact coagulation in a filtering bed for a textile waste which contained anionic and nonionic surfactants, dyes, chromium, iron, wool keratin decomposition products, dispersents, and inorganic dissolved substances. A neutralization-clarification study by Berezin (1989) resulted in color removal of 99%, dye removal of 98%, and suspended solids removal of 80%. Polyvinyl alcohol (PVA) could be recovered at a level of 90-96% by ultrafiltration membranes (Pudysheva *et al.*, 1989). Another study (Wang, 1989)

reported that polyvinyl acetate and COD could be removed at greater than 90% and 85-90%, respectively. Wang's (1989) study focused on various elements such as temperature, pH, flow, processing pressure and effects of membrane pore diameter to reach conclusions on removal efficiency.

2.2.2 Treatment Options

Historically, the textile industry has relied on biological treatment of process effluent. Biological treatment has repeatedly proven to be more able to provide reduction of organic matter than chemical coagulation. Biological treatment can be aerobic or anaerobic, performed with suspended media or fixed. Adsorption with carbon is used more often now than in the past for removal of organic matter. Problems do exist with regeneration and some form of pretreatment is usually recommended to prolong the adsorptive life of the carbon.

Horning (1977) studied biologic treatment and found that BOD was readily removed while total organic carbon (TOC) was more resistant to degradation by the microbes. He suggested that there was most likely some portion of the waste material that was not readily biodegradable. Also noted was the fact that color removal was difficult and was not achieved to any extent.

A case history presented by Kertell and Hill (1982) concerned the treatment of waste from the dyeing and finishing of synthetic knit fabrics.

Aeration basins that contained solids concentrations ranging from 640 to 860 mg/L, with 90% being volatile, were operated to treat the process effluents. The basins operated very smoothly and consistently produced effluent with BOD_5 averages of close to 22 mg/L, and COD, TSS, and color averages of 150 mg/L, 15 mg/L, and 40 platinum-cobalt (Pt-Co) units, respectively.

Another study (Abo-Elela *et al.*, 1988) detailed the operation of continuous flow biological reactors that treated effluent after coagulation with a lime-ferrous sulfate combination. Reactor influent COD and BOD ranged between 99 and 143 and 19 and 23 mg/L, respectively. Removal efficiency was not encouraging with effluent COD and BOD values averaging 82 and 20 mg/L, respectively.

Germirli *et al.* (1990) reported on the effects of biologic treatment alone on removal of COD and BOD. The effluents that were studied were from woven and knit fabric finishing mills. Reported COD removals ranged from 74 to 80%, while BOD removals ranged from 61 to 99%. The authors noted that it was most difficult to remove BOD from direct dyeing process effluents.

A system which included screening, preaeration, flotation, and chemical treatment with ferrous sulfate, hydrated lime and a polyelectrolyte in a coagulation, flocculation and settling step, prior to an extended aeration activated sludge process was described by Nicolaou and Hadjivassilis (1992). In this case, the primary and chemical treatment combination was able to

remove 50 and 70% of BOD and COD, while biological treatment was able to increase the overall removals to 90 and 80%, respectively.

Groff (1991) cited a study by Tong *et al.* (1989) concerning a system which included chemical coagulation, fixed film biological oxidation, pressurized air flotation, and filtration. Tong described increased COD and color removal when the surface area of the fixed film media was increased. Also cited was a discussion by Seekamp (1990) which detailed the treatment of natural and synthetic sizing compounds with a two stage anaerobic loop reactor. The reported COD reduction, from the original concentration of 27,400 to 5,480 mg/L, was 80%.

Some research has been conducted to compare biological treatment to adsorption by carbon. Hagar and Reilly (1970) replaced a biological system with a carbon adsorption system to determine the levels of BOD and suspended solids (SS) removal that would result. In every case, they found that removals of both parameters by the carbon system were identical to, or greater than removals by the biological system.

Shelley *et al.* (1976) conducted a study which included individual pretreatment schemes for a textile dyeing and finishing waste; one using alum and the other, excess lime. The effluents from each pretreatment scheme were then treated with batch activated sludge treatment or adsorption using granular activated carbon. The objective was to compare removal efficiencies of the

pretreatment chemicals and of the biologic and adsorptive systems. The researchers found that lime outperformed alum as a pretreating agent, providing as much as 62% removal of COD. Both the biologic and carbon treatment systems performed fairly evenly in this study, providing a satisfactory level of treatment. The biologic system did not remove much additional color from the system and a non-removable TOC fraction remained after treatment by carbon.

Treatability studies are often performed with biologic systems in order to determine the kinetic coefficients of the system. An understanding of the kinetic coefficients of a system will help to ensure "proper waste stabilization" (Metcalf & Eddy, 1991). The coefficients are used to design the full size system. A treatability study was performed by Ghosh *et al.* (1978) using two different waste combinations. The first was an effluent from a mill that performed dyeing and finishing of synthetics and wool. The second was a combination of the same dye mill effluent and a municipal effluent. Continuous flow, complete mix, activated sludge, bench scale reactors with mixed liquor concentrations of 3,000 mg/L were used. Sludge ages ranged from 9 to 50 days, while the hydraulic retention times ranged from 8 to 20 hours. The following kinetic coefficients illustrated in Table 1 were obtained from the study.

A treatability study of textile waste was performed by Weber (1994). This study involved chemical coagulation pretreatment to remove color and organics from a combined dye and print waste stream. Following pretreatment with a

Table 1. Kinetic coefficients from a textile effluent treatability study (Ghosh *et al.*, 1978)

Kinetic Coefficients	Mill	Mill plus Municipal
K_s	not reported	40
k	0.19	0.24
Y	0.52	0.53
k_d	0.013	0.024

K_s - half velocity coefficient, mg/L
k - maximum rate of substrate utilization per unit mass of organisms, $days^{-1}$
Y - maximum yield coefficient,
k_d - endogenous decay coefficient, $days^{-1}$

blend of inorganic aluminum and a polyamine, and an organic polymer, the dye and print stream was combined with a bleach and finish waste stream for activated sludge treatment. A hydraulic residence time of 3 days and sludge ages of 8, 15, 20 and 30 days were utilized. Average mixed liquor concentrations, at steady state, for the four sludge ages were reported to be 1076, 1805, 2345 and 3353 mg/L. COD and color removals ranged from 55 to 68% and 42 to 53%, respectively. Weber did not report values for K_s and k, but did report values of 0.619 and 0.032 day^{-1} for Y and k_d, respectively.

2.3 TOXICITY

Egypt, India and Mesopotamia displayed a well developed dyeing industry by 3000 B.C. (Little and Lamb, 1973), yet information concerning the toxic effects of dyes and other textile industry process streams has only come to light recently despite the length of time that the industry has been in operation. The American Dye Manufacturer's Institute Inc. (ADMI), was one of the first groups to begin research into the area of textile effluent toxicity. Many studies have been performed by ADMI regarding the effects of dyes on the environment and aquatic organisms like fish and algae.

2.3.1 Test Procedures and Species

The Environmental Protection Agency (EPA) has published a set of

recommended effluent toxicity test conditions for both chronic and acute analysis of effluent waste streams (EPA, 1989, 1993). Acute toxicity is typically determined with a single dose and observation over a short time period, often 48 hours. Chronic toxicity is measured over a longer time period and entails repeated dosing with renewed samples. Chronic toxicity is concerned with observing survival, growth and reproduction in the test species (Smith, 1994). One of three test types may used when conducting an acute toxicity evaluation: static non-renewal, static-renewal, or flow through. Only static renewal is accepted for the chronic analysis. According to Little and Lamb (1973), the static procedure permits flexibility, but has come under attack because it does not represent true conditions. Regardless of the problems surrounding the analysis, the static procedure will continue to be utilized due to its simple nature.

Ceriodaphnia dubia and *Pimephales promelus* (fathead minnows) are two species commonly used in toxicity analyses. *Ceriodaphnia dubia* typically reproduce three times in seven days allowing for a close look at reproductive effects during a seven day chronic test. *Daphnia pulex* reproduce more slowly, usually requiring 28 days. Therefore that species is often used for chronic tests of longer than 28 days. Fathead minnows are easy to culture and maintain in the lab. They also typically exhibit a good seven day response. (Smith, 1994)

Ceriodaphnia dubia, as invertebrates, are generally more sensitive to both the chronic and acute tests regardless of toxic agent under testing than are

vertebrates (fathead minnows) (Smith, 1994). Carlson and Kosian (1987), in citing McKim (1977) stated that fathead minnows are reported to be the most sensitive to toxicity during the embryo to early juvenile stage of life when compared to later stages of life. Ammonia is one compound which is generally more toxic to vertebrates than to invertebrates.

2.3.2 Selective Causative Agents Within the Textile Industry and Levels of Toxicity

A variety of agents exist within the textile industry which can cause limited to extreme toxicity to various organisms. These agents can include heavy metals, chlorinated organic compounds, surfactants, dyes, oils, finishes, PVA, and ammonia. Temperature has been noted to effect the relative level of toxicity of various agents according to Warren (1971) and Cairns *et al.* (1971), as cited by Little and Lamb (1973).

According to the EPA, as hardness and pH decrease, the acute toxicity of hexavalent chromium increases (EPA, 1985). They also suggest that "the acute toxicity of chromium (VI) is salinity dependent".

Little and Lamb (1973) evaluated the effects of numerous dyes to the fathead minnow, and concluded that "overall, the cationic dyes are most likely to be toxic". Cationic dyes are used in the industry today, usually in conjunction with a certain type of dyeing process (Barker, 1994).

Horning *et al.* (1972) attempted to place the metal content of dyes into the

"proper perspective". Vat dyes were investigated and shown to have higher concentrations of copper and chromium than acid dyes. Basic dyes contained the highest concentrations of zinc. The introduction of heavy metals from non-dye sources was discussed as was the fact that some dyeing operations include oxidative steps which utilize dichromates and top chroming. It was noted that flame retardant finishes can contain compounds of aluminum and antimony, while heavy metal compounds are often used as catalysts in the application of wash-wear, durable press and water repellent finishes.

Horning (1974) again evaluated the effects of selected dyes to the environment. He reached the same conclusions that he and the others had reached previously concerning acid, basic and direct dyes. Acid dyes, when compared to basic and direct dyes, were shown to have the highest concentrations of chromium, copper and lead. Basic dyes were again found to contain the highest concentration of zinc. Concentrations of arsenic, cadmium, cobalt, and mercury in 900 unmetalized acid, basic, and direct dyes were less than 1 part per million (ppm). Sixteen out of thirty dyes tested by Horning, on fathead minnows in a static bioassay, had 96-hr TL50 concentrations greater than 180 mg/L, while the remaining dyes had concentrations of between 0.047 and 165 mg/L. Horning concluded that "dyes are not likely to present serious difficulties with the environment". He did stress however, that fathead minnows displayed enough sensitivity to the various dyes that direct discharges

containing high concentrations of untreated dye waste should be avoided.

Surfactants pose another toxicological risk inherent in textile wastewater. Huber (1984) looked at the ecological behavior of cationic surfactants from fabric softeners in the aquatic environment. He cited work by Beveridge and Pickering (1983) that showed that cationic surfactants will sorb to negative binding sites on clay and activated sludge before metals will. It was not known whether this competitive binding disturbed the activated sludge. He stated that various cationic surfactants used in fabric softeners have been shown to produce 48 to 96-hr LC50 values of 0.6 to 2.6 mg/L. This range of values placed these surfactants into the high toxicity category of chemicals. As a result of these concentrations, Huber (1984) stated that cationic surfactants "are more toxic on average than the majority of anionic and neutral surfactants used in detergents for textiles". For *Daphnia magna*, the 48-hr LC50 values ranged from 0.16 to 1.06 mg/L. Another important fact that should be emphasized, which Huber related to surfactant study, was that cationic surfactants combine with anionic surfactants and produce neutral salts, thus leading to a decrease in toxicity. In order to avoid problems with toxicity, the Plant specifies nonionic surfactants, as much as possible, for use in all processes where surfactants are necessary.

A study conducted by Benson and Birge (1985) concerning heavy metal tolerance in fathead minnows, concluded that metal tolerance increased for

minnows that were exposed to sublethal concentrations of copper and cadmium, but not zinc. Tolerance was lost once the organisms were removed from the source of stress. The authors stated that "it is clear that natural populations of fathead minnows can develop elevated tolerances to certain metals".

In a study to determine the suitability of hexavalent chromium as a reference toxicant, Dorn *et al.* (1987) reported various species sensitivities in terms of LC50 or EC50 in mg/L of hexavalent chromium (Cr^{6+}). The most sensitive species was *Ceriodaphnia dubia* at 0.031, with *Daphnia pulex* next at 0.086. Fathead minnows were shown to be much less sensitive at 26.13 and *Lepomis macrochirus* (bluegill) were the least sensitive species at 182.91.

Jop *et al.* (1993) evaluated chromium and copper as reference toxicants. They reported the following mean, 48-hr LC50 concentrations for *Daphnia pulex* and 96-hr LC50 concentrations for fathead minnows, respectively: 0.188 mg Cr^{6+}/L and 0.003 mg Cu/L and 83 mg Cr^{6+}/L and 0.18 mg Cu/L.

Carlson and Kosian (1987) studied the toxicities of chlorinated benzene compounds to fathead minnows. They found the following ranges between the highest no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC): 1.0 to 2.3 mg/L for 1,3-dichlorobenzene (1,3-DCB), 0.57 to 1.0 mg/L for 1,4-DCB, and 0.24 to 0.41 mg/L for 1,2,3,4-tetrachlorobenzene (1,2,3,4-TCB). Solubility problems hindered the pentachlorobenzene and hexachlorobenzene results, but these compounds were determined to be non-

toxic at concentrations of 0.055 and 0.0048 mg/L, respectivley. These concentrations were the highest that could be maintained for the test procedure, due to the limited solubilities of the compounds. Deformities were caused by high doses of 1,3-DCB (3.9 mg/L), while premature birth was caused by elevated doses of 1,4-DCB (8.7 mg/L). A dose of 0.41 mg/L of 1,2,3,4-TCB was enough to disrupt fish survival and survival weights, although no effect on embryo development was reported to have occurred.

Carrier and Beitinger (1988) studied the reduction in thermal tolerance of *Notropis lutrensis* (red shiners) and fathead minnows exposed to cadmium. They stated that "other investigators have suggested that long term exposure to sublethal levels of toxicants may have effects similar to acute, near-lethal toxicant exposures". Carrier and Beitinger in citing Carrol *et al.*(1979) stated that cadmium toxicity, like chromium toxicity (EPA, 1985), is reduced in hard water. Carrol *et al.* also reported 96-hr LC50 values in the range of less than 0.0015 to 66.5 mg/L cadmium, depending on hardness, for a variety of fish species. They concluded that cadmium decreased temperature tolerance in fish, as do dieldrin, arsenic, nickel, nitrite, and selenium. The 96-hr LC50 for both shiners and fathead minnows in EPA hard water was less than 10 mg/L.

A study was performed by Carlson (1987) to determine the effects of lowered dissolved oxygen concentrations on the toxicity of 1,2,4-trichlorobenzene to fathead minnows. He found that a mean 1,2,4-TCB

concentration of 0.92 mg/L and dissolved oxygen concentration of 8.1 mg/L was sufficient to reduce mean survival and mean weight by 37.5% and 28.7% respectively, when compared to the 8.1 mg/L dissolved oxygen control. Mean survival rates and weights were dramatically affected at the same mean 1,2,4-TCB concentration of 0.92 mg/L and dissolved oxygen concentration of 4.5 mg/L. In this case, mean survival and mean weight were reduced 88.5 and 60.5%, respectively. These results led Carlson to state that "exposure under natural conditions at this 1,2,4-TCB concentration may have significant biological implications".

CHAPTER III. METHODS AND MATERIALS

This chapter contains descriptions of the methods and materials that were used in the research operations and analyses that were conducted from January of 1993 through November of 1994 on effluent waste streams from the dyeing, printing, and bleaching and finishing processes at the Plant. Waste stream pretreatments, continuous flow, stirred tank reactor (CFR) operations, and analytical methods are described.

3.1 WASTE STREAM PRETREATMENT

The primary pretreatment emphasis of this study was on the bleach and finish waste stream. A small pretreatment study was conducted on the thermosol dye and print streams with organic polymers that were not used in the previous research by Weber (1994). Weber's thesis covered pretreatment of the thermosol dye and print waste streams in detail. Weber did attempt some pretreatment of the bleach and finish stream, but the methods used were unsuccessful.

3.1.1 Pretreatment Methods

In the current study, several different experiments were attempted involving a single pretreatment method or a combination of pretreatment

methods. Filtration, pH adjustment, oxidation and chemical coagulation are the pretreatment methods which were utilized and are described in the sections below. All of the methods were used on the bleach and finish waste stream, but only chemical coagulation was used on the dye and print waste stream combination. The letters in parentheses, following the method name, serve as a method identification tool throughout the remainder of the text. More detailed descriptions of the individual experiments that were conducted follow the method descriptions.

3.1.1.1 Filtration (F)

Effluent filtration was performed to determine the particle size distribution of the effluent. An aliquot of effluent was filtered through the following range of filters much like a sieve analysis would be conducted on a sample of soil. Table 2 lists the range of filters that were used in the filtration experiments.

3.1.1.2 pH Adjustment (pH)

Sample pH values were adjusted using concentrated or 1 normal (N) sulfuric acid, depending on the amount of adjustment that was required. A bench-top, Fisher Accumet pH meter model 610A was used to measure pH during adjustment.

Table 2. Filters used in filtration experiments

Filter Type	Average Porosity, μm
Whatman No. 4	>20-25
Whatman No. 1	>11 μm
Whatman No. 2	>8 μm
Fisher Q5	>2 μm
Whatman 934AH	1.5 μm
Whatman GF/C	1.2 μm

3.1.1.3 Oxidation (O)

A Swan® (Smyrna, TN) hydrogen peroxide solution, 3% by weight, was used as an oxidant. Various concentrations of the oxidant solution were used in the pretreatment attempts. All oxidation experiments were performed using a Phipps and Bird (Richmond, VA), six paddle jar test apparatus. All samples were stirred at a rate of 50 rpm for 20 minutes and allowed to settle for 1 hour before samples aliquots were drawn. A decision was made not to use chlorine as an oxidant due to concerns surrounding the possible formation of chlorinated byproducts.

3.1.1.4 Chemical Coagulation (CC)

The Phipps and Bird (Richmond, VA), six paddle jar test apparatus was

used for all chemical coagulation studies. All samples were stirred at 100 rpm for 30 seconds then 50 rpm for 1.5 minutes. Samples were allowed to settle for 1 hour. Polymers AL220, A130, Nalco 7135 and Nalco 9764 were used at several concentrations in the coagulation experiments. AL220 is currently used at the Plant and is a highly positively charged blend of an inorganic aluminum compound and a polyamine polymer. A130, also used at the Plant, is a moderately anionic organic polymer. Nalco 7135 is an aqueous solution of a polyquaternary amine chloride, while Nalco 9764 is an aqueous solution of a cationic polyamine.

3.1.2 Pretreatment Experiments

Ten different experiments were performed on the bleach and finish waste stream with the methods described above. One experiment was conducted on the dye and print waste stream combination. The sections below will present a description of the experiments and list the analytical procedures performed for each. The letters in parentheses, following the experiment, number indicate which pretreatment methods were employed singly or in combination. Pretreatment method(s) that were applied and analytical procedures that were performed in each experiment are summarized in Table 3. Analytical procedures that were performed on samples include, total suspended solids (TSS), chemical oxygen demand (COD), color and dissolved organic carbon (DOC). All COD

measurements were of soluble COD, meaning samples were filtered through a 0.45 μm filter prior to analysis.

Table 3. Pretreatment methods and analytical procedures per experiment

Experiment	Pretreatment Method	Analytical Procedures*
1	F	filtered solids, color
2	pH	COD, color
3	pH, F	filtered solids
4	O	COD, TSS
5	pH, O	COD, TSS, color, DOC
6	pH, O, CC	COD, TSS, color, DOC
7	pH, CC	COD, TSS, color, DOC
8	pH, CC, O	COD, TSS, color, DOC
9	pH, CC	COD, color, DOC
10	CC	COD, TSS, color
11	pH, CC	COD, TSS, color

*All COD samples were soluble

3.1.2.1 Experiment $1_{(F)}$

This analysis was performed on the bleach and finish stream. One sample was tested. A 250 mL volume of bleach and finish at a pH of 7 was filtered through the range of filters listed in Table 2 . Filtered solids

concentrations were measured to determine the particle size distribution of the waste stream. Apparent color was also analyzed, meaning samples were not filtered through 1.2 μm filters prior to the color analysis. The pH was not adjusted to 7.6.

3.1.2.2 Experiment $2_{(pH)}$

The pH of the control sample was 6.0. The pH levels of eight other samples were adjusted in increments of 0.5 to range from 2 through 5.5. Sulfuric acid with a normality (N) of one was used to adjust the pH level. Samples for COD analysis were diluted 1 to 50 and 1 to 16.7 (0.1 and 0.3 mL in 5 mL). Two dilutions were used for the COD analysis due to the fact that the COD concentrations of the bleach and finish were initially unknown at the time. Apparent (unfiltered) color was determined for the nine samples. Also, the pH of the samples was not readjusted to 7.6 prior to the color analysis because only the effect of pH adjustment on the bleach and finish was desired.

3.1.2.3 Experiment $3_{(pH, F)}$

Two 500 mL samples were adjusted to pH levels of 3 and 5. Each sample volume was then filtered through the range of filters listed in Table 2. This experiment was performed to determine whether pH adjustment might affect the particle size distributions which resulted from Experiment 1. Filtered solids

concentrations were determined for each of the samples across the range of filters that was used.

3.1.2.4 Experiment $4_{(O)}$

Six 500 mL samples of bleach and finish, at an unadjusted pH of 6.5, were dosed with 0, 10, 30, 50, 75, and 100 mg/L of a 3% by weight hydrogen peroxide solution to determine if oxidation would remove organics, color, or both. Sample aliquots of 100 mL were removed from each sample for soluble COD and TSS analyses.

3.1.2.5 Experiment $5_{(pH, O)}$

Five 500 mL samples of bleach and finish were used to determine if oxidation preceded by pH adjustment would induce removal of organics, color, or both. The pH values of three samples were adjusted to 3, 4, and 5. The pH of the fourth sample was unadjusted at 6.8. These four samples were then dosed with 100 mg/L of a 3% hydrogen peroxide solution. A fifth sample with a pH of 6.8 acted as the control and received no hydrogen peroxide. Sample volumes of 150 mL were analyzed for soluble COD, TSS, color, and DOC.

3.1.2.6 Experiment $6_{(pH,O,CC)}$

Experiment 6 was a repeat of experiment 5 except for the addition of 785

mg/L of the inorganic aluminum compound and polyamine blend polymer, AL220, following oxidation, to determine how a polymer might affect removal of organic material and color. Weber (1994) reported that addition of AL220, alone, to the bleach and finish waste stream provided discouraging results. It was possible that the combination of oxidation and chemical coagulation would provide more encouraging results. Weber stated that "high doses (of AL220) were used because preliminary results indicated that such doses were necessary". The oxidant was stirred as described in section 3.1.1.3, then the polymer was added. The chemical coagulation mixing scheme was then performed, as described in section 3.1.1.4. Soluble COD, TSS, color, and DOC were measured.

3.1.2.7 Experiment $7_{(pH,CC)}$

Two 500 mL samples of bleach and finish were maintained at existing pH conditions of 6.8 and dosed with 400 and 785 mg/L of AL220. Two additional 500 mL samples were adjusted to pH 4.5 and dosed with the same two concentrations of AL220. This experiment, AL220 addition at a pH of 4.5, was conducted because it was unclear what pH values were incorporated into the discouraging AL220 experiments which were performed by Weber (1994) on the bleach and finish stream. It was possible that a significant reduction in pH may have provided better results than were reported. The control used in this

experiment was the same control that was used in Experiment 5. After settling, soluble COD, TSS, color and DOC were measured.

3.1.2.8 Experiment $8_{(pH,CC,O)}$

A new shipment of bleach and finish was used for this experiment. The pH was adjusted to values of 4.5, 5, 8; 9 and 10.5 in five 500 mL samples. The sixth sample pH was left unadjusted at 9.75 to serve as the control. A concentration of 785 mg/L of AL220 was added to the five pH adjusted samples. After mixing and settling, 100 mL samples were removed and 100 mg/L of hydrogen peroxide was added to the remaining 400 mL of bleach and finish. Samples were stirred again, settled and sampled. Soluble COD, TSS, color and DOC analyses were performed on all samples. In this experiment the method application order was changed, from the application order in Experiment 6, to chemical coagulation then oxidation to determine whether method order would affect removal of organics or color.

3.1.2.9 Experiment $9_{(pH, CC)}$

This experiment was conducted on a new shipment of bleach and finish with a pH of 6.6. All six 500 mL samples were adjusted to pH 4.5. Two polymers were used in this case; AL220 first, followed by the addition of A130 after the pH was readjusted to 7. The following polymer dose combinations, listed as the

concentration of AL220/A130 in mg/L respectively, were used: 250/10, 400/5, 400/10, 400/20, and 785/10. A control with pH adjusted to 4.5, but without polymer addition, was also tested. After mixing and settling, samples were analyzed for soluble COD, color and DOC.

3.1.2.10 Experiment $10_{(CC)}$

This experiment involved the use of Nalco polymers 7135 and 9764 to treat the bleach and finish effluent. The bleach and finish had an original pH of 7.5. Therefore, the pH values of the samples remained unadjusted due to neutral pH values typically being conducive to organic polymer reaction mechanisms. Polymer 7135 doses of 10, 25, 50 and 100 mg/L and polymer 9764 doses of 50 and 100 mg/L were applied to 500 mL samples of bleach and finish. Also tested was a sample adjusted to pH 2.5 with no polymer addition and a control with no pH adjustment or polymer addition. Mixing and settling were identical to the procedure described in Section 3.1.1.3, except slow mixing was conducted at 30 rpm instead of 50 rpm. Samples were analyzed for TSS, soluble COD and color

3.1.2.11 Experiment $11_{(pH, CC)}$

Dye and print samples were combined in a four parts to three parts mixture that totaled a volume of 500 mL. Original pH was 11.3; therefore,

reduction to a pH of 7 was required for polymer use. Polymers 7135 and 9764 were added in concentrations of 25, 50 and 100 mg/L to two sets of six, 500 mL samples. A control was used with pH adjusted to 7. Slow mixing was performed at 30 rpm as opposed to 50 rpm. Again, TSS, soluble COD and color were analyzed. This experiment was performed to determine whether higher removal of solids, COD or color might result from use of the Nalco polymers than was accomplished by the use of AL220 and A130, the standard pretreatment scheme recommended by Weber (1994). The standard pretreatment scheme was then applied to a 500 mL sample of the combined dye and print waste streams for comparison.

3.2 CONTINUOUS FLOW REACTOR OPERATION

Three bench scale CFRs had been operating to treat textile effluent from the Plant for approximately 4 months in December of 1993. At that time, a chemical pretreatment process was being applied to the thermosol dye and print streams of the Plant's effluent. A decision was made to continue with the same pretreatment scheme through the remaining period of research, targeted for late 1994. This section describes the chemical pretreatment scheme and the CFR setup and operation. Further information that describes the CFR setup and operation is provided by Weber (1994).

3.2.1 Chemical Pretreatment

Chemical pretreatment was performed on the thermosol dye and print waste streams in a batch process. The waste, which was brought to Virginia Tech approximately every two weeks from the Plant, represented effluent from the most recent processes performed at the Plant. The waste was collected and transported to Virginia Tech within 24 hours. Pretreatment apparatus and materials included a 30 gallon Nalgene tank, an American Model LR-41C variable speed stirrer, a Masterflex peristaltic pump and solid state pump control (Cole Parmer Instrument Co., Chicago, IL), a 35 gallon rubber tank, concentrated sulfuric acid, a dilute sodium hydroxide solution and two polymers, one highly cationic, the other moderately anionic.

The waste streams were combined in a 4 parts dye to 3 parts print mixture to maintain the same ratio used at the Plant. The Nalgene tank was used to contain 10 gallons of dye and 7.5 gallons of print for the coagulation, flocculation, and settling procedure. The pH of the mixture was adjusted to approximately 6, from the initial value which ranged from 10 to 12, with concentrated sulfuric acid. The highly cationic blend of an inorganic aluminum compound and a polyamine, AL220, was added at a concentration of 785 mg/L. A rapid mix period of 1.5 minutes at a stirrer speed setting of 3 was followed by a slower mixing period of 7 minutes at a stirrer speed setting of 2. The pH was then adjusted upward to 7 with the dilute sodium hydroxide solution prior to the

addition of 10 mg/L of a 0.5% solution of the moderately anionic, organic polymer, A130. The mixture was stirred for an additional period of 5 minutes at a stirrer speed setting of 2. The stirrer was turned off and the mixture was allowed to settle for 1 to 2 hours. This pretreatment scheme differs slightly from that described by Weber (1994). The changes consist of the increase in AL220 concentration from 600 to 785 mg/L, and the increase in A130 concentration from 5 to 10 mg/L. Weber stated that additional work, which was performed following the completion of Weber's thesis, suggested that the higher coagulant concentrations produced greater removal of organics and color.

Once settled, the supernatant was pumped out of the tank, at a pump speed of 10, into transfer carboys, then poured into the 35 gallon (gal) rubber tank. The settled sludge was disposed of. A volume of 3 parts (7.5 gallons) of bleach and finish was added to the 35 gal tank at this point, plus 1.3 liters (L) of sanitary waste from the Plant. The volume of sanitary waste was determined by assuming each of the 130 employees at the Plant produced 30 gal/day of waste. Sanitary waste from the Plant is added to the aerated lagoon following partial treatment in an Imhoff tank. The pH was checked and readjusted to between 7 and 8, if the level had changed due to addition of the bleach and finish waste. This mixture was then pumped into the CFRs at a specific rate, as discussed in the following paragraph.

3.2.2 Biological Treatment

Three 9.7 L reactors were used for the biological stage of treatment. A Masterflex peristaltic pump with three heads was used to pump influent from the 35 gal rubber tank into the reactors. In January of 1994, the flowrate of influent into the reactors was decreased to a rate of 1.7 mL/min (0.24 L/day) to provide a hydraulic residence time (HRT) of 4 days in each of the reactors. The reactors had been operating at a rate of 2.2 mL/min which provided a 3 day HRT. A baffle divided the interior of each reactor into two parts. The larger volume, approximately 85% of the whole volume, was aerated and occupied by the mixed liquor suspended solids that degraded the waste. The remaining 15% of the volume was used for clarification of the treated effluent. Outlet tubing carried the effluent to a sink for disposal or to beakers for analysis. Figure 2 illustrates the bench scale CFR setup and Figure 3 illustrates the reactor schematic. Dissolved oxygen in the activated sludge chamber was maintained at or above 5 mg/L.

Sludge ages ($\theta_c$or SRT) of 15, 20, and 30 days were maintained in the reactors over the course of the research. The same θ_cs were used during Weber's research (1994), along with an additional reactor operating at a θ_c of 8 days. Due to the poor results exhibited by the 8 day θ_c reactor, it was decided not to continue operation at that sludge age for the subsequent 4 and 7 day HRT operations. Mixed liquor was wasted daily from the reactors. The volume which

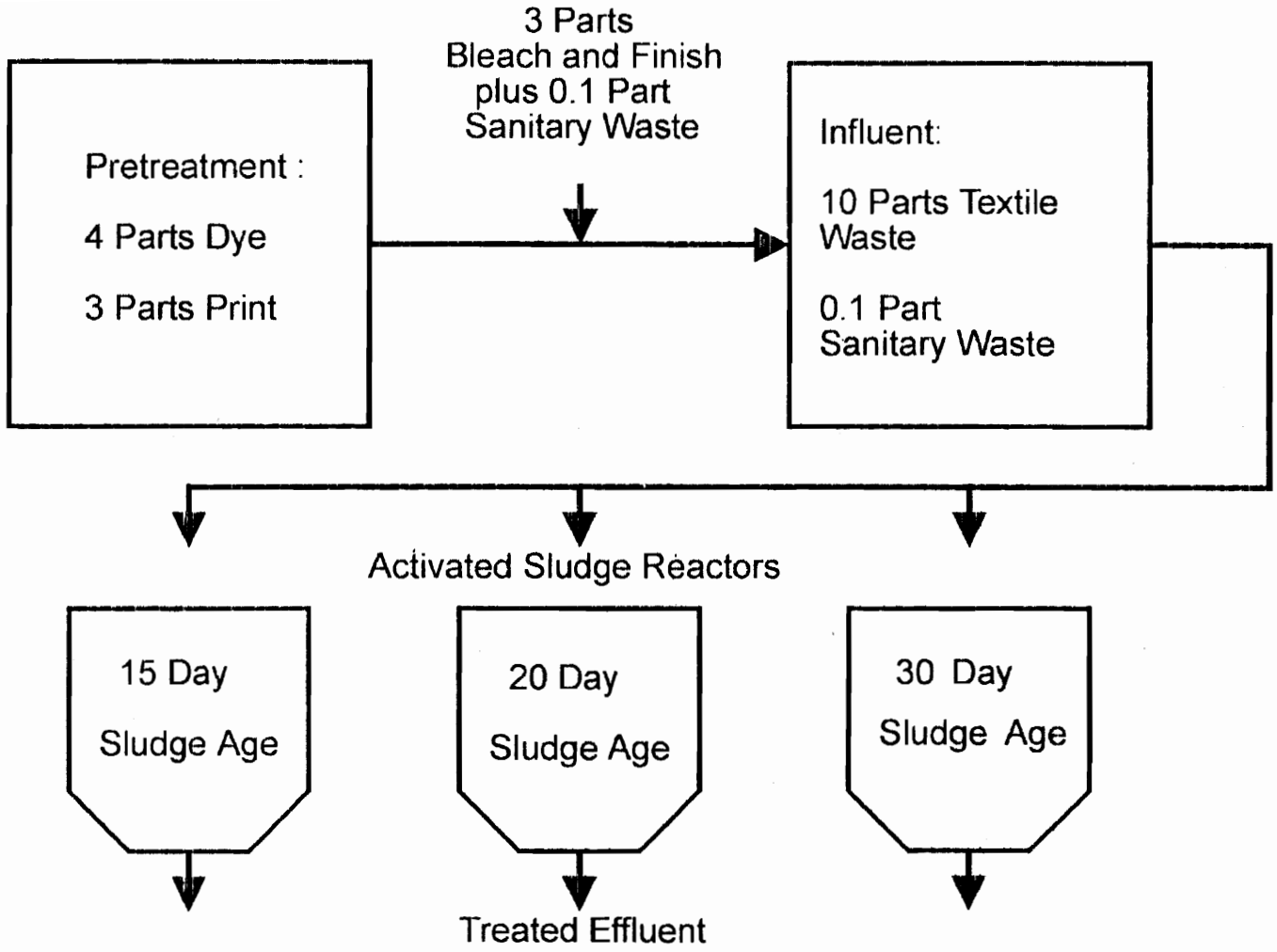


Figure 2. Flow diagram of bench scale CFR setup

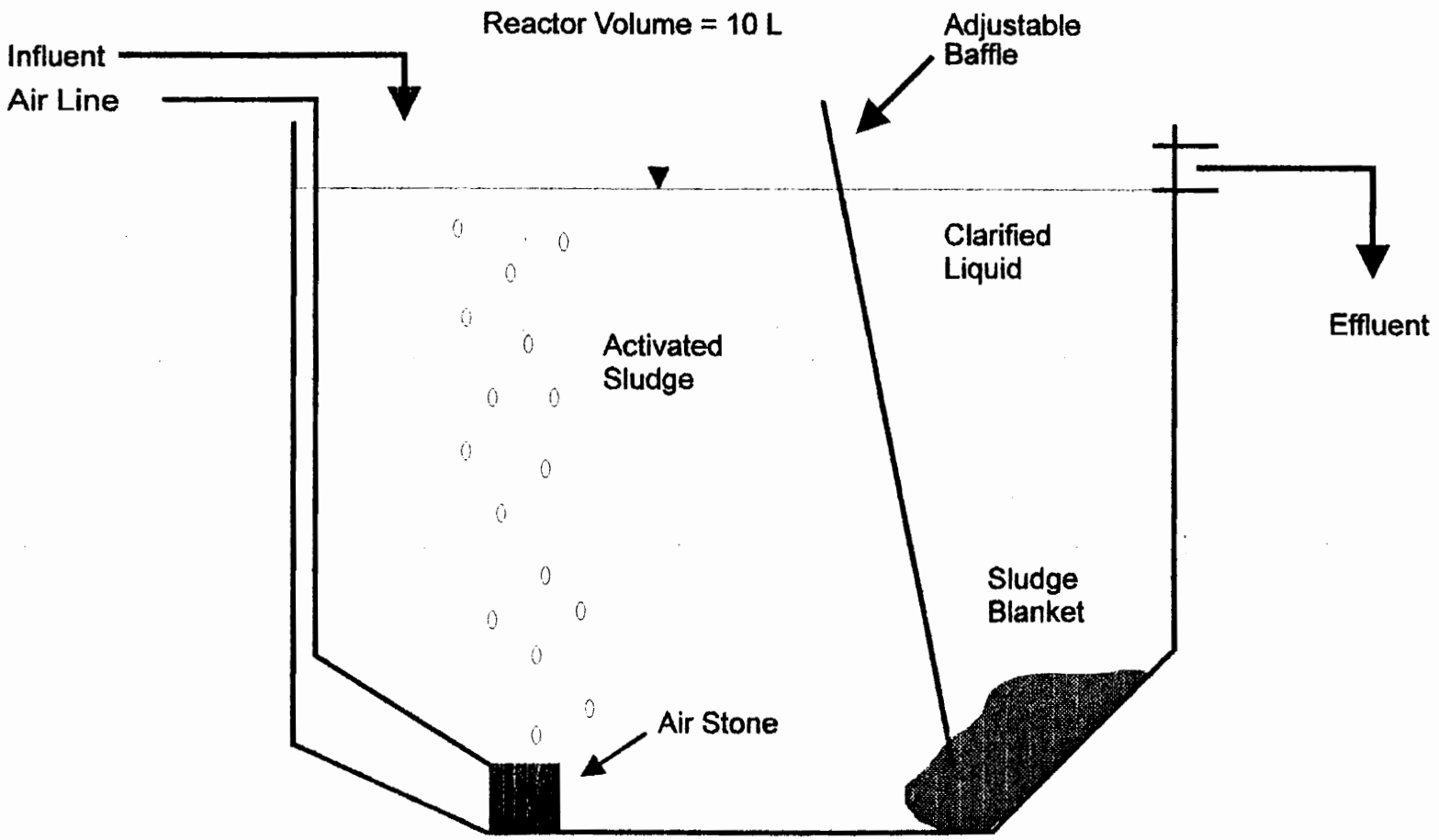


Figure 3. Reactor schematic

was wasted was replaced by influent waste from the 35 gal rubber tank. Wastage (Q_w) was calculated with the following equation.

$$Q_w = \frac{\frac{XV}{\theta_c} - X_e Q}{X}$$

where: θ_c = sludge age, days
X = mixed liquor suspended solids, MLSS, mg/L
V = volume of reactor, L
Q = influent flow rate, L/day
X_e = effluent total suspended solids, TSS, mg/L
Q_w = wastage rate, L/day

The reactors were operated for 6 months at the 4 day HRT. Weekly pretreatments continued as described in section 3.2.1. Analyses including mixed liquor suspended and volatile solids (MLSS and MLVSS), TSS, COD and color were performed 3 times per week to determine the arrival of steady state. Those analyses plus 5 day biological oxygen demand (BOD_5), cations, anions, total phosphorus (Total P), ammonia nitrogen (NH_3-N), and total Kjeldahl nitrogen (TKN) were conducted during steady state operation. MLVSS and COD were used to determine the 4 day HRT operation kinetic coefficients.

Once sufficient data was collected at the 4 day HRT, the pumping rate was decreased to 1.0 mL/min (1.4 L/day) to readjust the flow so that the reactors would operate at a 7 day HRT. The same analyses which were

performed during the 4 day HRT study plus DOC and 20 day biological oxygen demand (BOD_{20}) were conducted on the reactor effluents for the 7 day HRT study. Again, data were collected to determine steady state conditions and kinetic coefficients.

3.3 ANALYTICAL PROCEDURES

Analyses were performed on the waste streams as they progressed through the pretreatment phase and on the reactor's influent and effluents. These analyses allowed for the determination of waste characteristics and the organic matter, color and metal removal efficiencies of the pretreatment scheme and the reactors. The analyses were followed as set forth in *Standard Methods for the Examination of Water and Wastewater* (hereafter referred to *Standard Methods*, 1992). Table 4 provides a summary of storage conditions. Samples were stored only when necessary, most analyses were performed within a few hours after sample collection.

Limited analyses were performed on the individual waste streams from the pretreatment steps during this study. Analyses were limited due to the scope of Weber's research (1994). The wastewater samples used for this research were collected at the same locations as those used for Weber's work. Metals, anions and color analyses were performed on samples of the dye, print, pretreated dye and print, bleach and finish, and influent (pretreated dye and

Table 4. Sample storage conditions

Analyses	Storage Conditions
Solids	Plastic, 4°C, <2 days
Color	Plastic, 4°C, <2 days
TOC/DOC	Plastic, -17°C, <2 weeks
COD	Plastic, 4°C, <7 days, pH <2
BOD	Plastic, 4°C, <1 day
Total Phosphorus	Plastic, 4°C, <7 days, pH <2
Ortho Phosphorus	Glass, 4°C, <2 days
TKN/NH_3-N	Plastic, 4°C, <7 days, pH <2
Metals	Plastic, 20°C, 4 weeks, pH<2
Anions	Plastic, 20°C, <2 weeks

print, bleach and finish, and sanitary waste) waste streams. Samples were collected throughout the pretreatment procedure. Analyses performed on pretreatment samples, and all the additional analyses performed on influent and effluent samples are presented in the sections below.

3.3.1 Solids

TSS and MLSS were measured according to *Standard Methods* (1992)

method 2540 D (Total Suspended Solids Dried at 103-105°C). Whatman glass fiber filters with a pore size of 1.5 μm were used for all solids measurements. TSS samples were either taken from the reactor clarifiers or composited samples collected in beakers over time. MLSS samples were collected from the reactors by removing the baffle, stirring the contents, then removing a sample. MLVSS were measured according to *Standard Methods* (1992), method 2540 E (Fixed and Volatile Solids Ignited at 500°C). Filters that were used for MLVSS measurements were prepared in a muffle furnace at 500°C for 20 minutes before use.

3.3.2 Color

Samples were prepared for color analysis by filtering through a Whatman 1.2 μm glass fiber filter. Sample pH was then adjusted to 7.6. A Bausch and Lomb, Spectronic 20 spectrophotometer was used for all the measurements. Platinum-cobalt color standards were used to calibrate the spectrophotometer. Samples were placed in cuvets and percent transmittance was read at three different wavelengths; 438 nm, 540 nm, and 590 nm. *Standard Methods* (1992), method 2120 E (the ADMI Tristimulus Filter Method, Proposed), was used for color measurement. With this method, color values are determined independent of hue. A computer program, developed by former Virginia Tech graduate students, provided conversion of percent transmittance

values to ADMI units of color.

3.3.3 Total/Soluble Chemical Oxygen Demand

Standard Methods (1992), method 5220 C (Closed Reflux, Titrimetric Method), was used for COD analysis. Soluble COD samples were filtered through 0.45 μm filters. Total COD samples were unfiltered.

3.3.4 Total/Soluble Organic Carbon

Dissolved organic carbon (DOC) samples were filtered through a 0.45 μm membrane filter prior to analysis. Both total organic carbon (TOC) and DOC samples were purged of CO_2 prior to analysis by bubbling oxygen through the sample after it had been acidified to pH<2 with the addition of an 85% solution of phosphoric acid. TOC and DOC samples were analyzed on a DC-80, Dohrmann, Automated TOC Analyzer in conjunction with a Horiba, PIR2000, General Purpose Infrared Gas Analyzer. *Standard Methods* (1992) method 5310 C, Persulfate-Ultraviolet Oxidation Method, was followed. Due to high organic content, the bleach and finish DOC concentration was analyzed at the 2000 ppm setting, while all other sample DOC concentrations were analyzed at the 400 ppm setting. TOC was infrequently analyzed due to particulate matter in the samples clogging the equipment.

3.3.5 Biological Oxygen Demand

Soluble five and twenty day BOD tests (BOD_5, BOD_{20}) were performed on samples which had been filtered through 0.45 μm membrane filters. Total BOD samples were unfiltered. Dilution water was unseeded due to the seed provided by addition of sanitary waste during each pretreatment. *Standard Methods* (1992) methods 5210 B (5-Day BOD Test) was used for analysis of BOD_5. The only change from the methodology in section 5210 B for the BOD_{20} test was the additional 15 days of incubation. Dilution factors for the various BOD tests, which were calculated from the estimated final BOD values, ranged from 0.003 to 0.67.

3.3.6 Total Phosphorus

A combination of *Standard Methods* (1992) methods 4500-P E (Ascorbic Acid Method) and 4500-P B (Persulfate Digestion Method) were used to analyze samples for total phosphorus. A modification regarding sample digestion was followed. Samples were digested in a block heater set at 125°C, rather than autoclaving as the method directs. A Bausch & Lomb Spectronic 20 spectrophotometer was used for the colorimetric analysis. Due to the use of a spectrophotometer with a range of 400 to 700 nm, the samples and blanks were analyzed at a wavelength of 685 nm, also a phosphorus peak, rather than an 880 nm wavelength, as the method suggests.

3.3.7 Total Kjeldahl and Ammonia Nitrogen

Standard Methods (1992) method 4500-N_{org} B (Macro Kjeldahl Method) and method 4500-NH_3 E (Titrimetric Method) were followed to determine Total Kjeldahl Nitrogen (TKN). Titrations were performed with 0.02 N sulfuric acid. Sample sizes used were 25 mL of influent and 50 mL of effluent.

Method 4500-NH_3 E was also used to determine ammonia nitrogen (NH_3-N) after a distillation step was performed as outlined in section 4500-NH_3 B (Preliminary Distillation Step). Sample sizes used were 50 mL of influent and 100 mL of effluent.

3.3.8 Metals

Various cations, total chromium, and dissolved hexavalent chromium were determined as outlined below.

3.3.8.1 Dissolved Copper, Chromium, Silver and Zinc

Samples were filtered through a 0.45 μm filter and acidified to pH<2 with concentrated nitric acid prior to concentration determination. A Perkin-Elmer, Model 703, Atomic Absorption Spectrophotometer was used for determination of zinc concentrations. Zinc was present in the parts per million range (mg/L), therefore Model 703 (flame) was used. Copper, silver and chromium concentrations were determined using the Perkin-Elmer, Zeeman 5100 PC,

Spectrophotometer. Because those cations were present in the parts per billion range (μg/L), the Zeeman 5100 PC (furnace) was appropriate. *Standard Methods* (1992) methods 3111 B, Direct Air-Acetylene Flame Method, and 3113 B, Electrothermal Atomic Absorption Spectrometric Method, were used. Calibration was performed on each apparatus according to the instructions that were provided with the spectrophotometers.

3.3.8.2 Total Chromium

Unfiltered samples (75 mL) were analyzed for total chromium using *Standard Methods* (1992) method 3113 B, Electrothermal Atomic Absorption Spectrometric Method. Method 3113 B was preceded by a Nitric Acid-Sulfuric Acid Digestion as outlined in method 3030 G. The Perkin-Elmer, Zeeman 5100 PC, Spectrophotometer, described in section 3.3.8.1, was used for the analysis. The calibration was identical to that described in section 3.3.8.1.

3.3.8.3 Dissolved Hexavalent Chromium

Standard Methods (1992) method 3500-Cr D, Colorimetric Method, was used to determine dissolved hexavalent chromium. Sample volumes of 75 mL were filtered through 0.45 μm filters. A standard curve of 5 mg/L through 25 mg/L was used initially, instead of the curve range suggested by method 3500-Cr D (25-100 mg/L), because samples were expected to contain less than 25

mg/L dissolved hexavalent chromium. A standard additions analysis was also used due to interference by the sample color during transmittance readings. Samples were spiked with 5, 10, 15 and 25 μg/L of chromium solution and analyzed for absorbance along with unspiked samples in the same range. The absorbance of the standards was then subtracted to yield the absorbance due to the original chromium in the samples. Bausch and Lomb Spectronic and Beckman DU 640 spectrophotometers were used for the analysis at pathlengths of 1 centimeter (cm).

3.3.9 Anions

Samples were filtered through a 0.45 μm filter prior to analysis. A Dionex, 2010i, Ion Chromatograph was used to measure concentrations of chloride, nitrate, phosphate, and sulfate ions. EPA Method 300.0, Determination of Inorganic Ions by Ion Chromatography, Revision 2.1 (August, 1993) was used for the analysis. A sample size of 50 μL was used. The eluent solution used was 1.8 millimolar (mM) sodium carbonate plus 1.7 mM sodium bicarbonate.

3.3.10 Toxicity

Toxicity analyses were performed at Biological Monitoring Incorporated (BMI), located in Blacksburg, Virginia. Both short term chronic and acute tests

were conducted on effluents from the 15 and 30 day θ_c, 7 day HRT CFR operations. Testing procedures followed those outlined in *Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms*, EPA/600/4-89/001, and *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*, EPA/600/4-90/027F. Tables 5 (EPA, 1989) and 6 (EPA, 1993) summarize the chronic and acute test procedures that were followed.

Composite samples were collected over the course of a week from the 30 day θ_c reactor. Following that period of analysis, composite samples were collected over the course of a week from the 15 day θ_c reactor. Samples were collected on ice in a cooler and immediately taken to BMI for toxicity determination. Although samples were promptly taken to BMI, it was sometimes necessary to aerate the samples during the analyses because the concentration of dissolved oxygen would often decline to unacceptable levels (see line item 15 in Table 5).

Acute tests were performed with *Ceriodaphnia dubia* since the State has specified that daphnids be used in acute toxicity tests performed with the Plant's effluent. All organisms were less than 24 hours old. Four replicates of 5 organisms were used and a typical screen test was performed with 0 and 100% effluent. Organisms were not fed over the 48 hour test.

Short term (7 day) chronic tests were performed with *Pimephales*

Table 5. Summary of recommended effluent toxicity test conditions for the fathead minnow (*Pimephales promelus*) larval survival and growth test, (EPA, 1989)

1. Test type:	Static renewal
2. Temperature (°C):	25 ± 1°C
3. Light quality:	Ambient laboratory illumination
4. Light intensity:	10-20 μE/m^2/s (50-100 ft-c) (ambient laboratory levels)
5. Photoperiod:	16 h light, 8 h darkness
6. Test chamber size:	500 mL
7. Test chamber volume:	250 mL/replicate
8. Renewal of test concentrations:	Daily
9. Age of test organisms:	Newly hatched larvae less than 24 h old.
10. Number larvae per test chamber:	15 (minimum of 10)
11. Number replicate chambers per concentration:	4 (minimum of 3)
12. Number larvae per concentration:	60 (minimum of 30)
13. Feeding regime:	Feed 0.1 mL newly hatched (less than 24 h old) brine shrimp nauplii three times daily at 4 h intervals or, as a minimum, 0.15 mL twice daily, 6 h between feedings (at the beginning of the work day prior to renewal, and at the end of the work day following renewal). Sufficient larvae are added to provide an excess. Larvae are not fed during the final 12 h of the test.
14. Cleaning:	Siphon daily, immediately before test solution renewal.

Table 5. Summary of recommended effluent toxicity test conditions for the fathead minnow (*Pimephales promelus*) larval survival and growth test, (EPA, 1989), Continued

15. Aeration:	None, unless DO concentration falls below 40% saturation. Rate should not exceed 100 bubbles per minute.
16. Dilution water:	Moderately hard synthetic water is prepared using MILLIPORE MILLI-Q^{R} or equivalent deionized water and reagent grade chemicals, or 20% DMW.
17. Effluent concentration:	Minimum of 5 and a control
18. Dilution factor:[1]	Approximately 0.3 or 0.5
19. Test duration:	7 days
20. Endpoints:	Survival and growth (weight)
21. Test acceptability:	80% of greater survival in controls; average dry weight of surviving controls equals or exceeds 0.25 mg
22. Sampling requirement:	For on-site tests, samples are collected daily, and used within 24 h of the time they are removed from the sampling device.
23. Sample volume required:	2.5 L/day

[1] Surface water test samples are used as collected (undiluted)

Table 6. Summary of test conditions and test acceptability criteria for *Ceriodaphnia dubia* acute toxicity test with effluents and receiving waters, (EPA, 1993)

1. Test type:	Static non-renewal, static-renewal, or flow-through
2. Test duration:	24, 48, or 96 h
3. Temperature:[1]	20 ± 1°C; or 25 ± 1°C
4. Light quality:	Ambient laboratory illumination
5. Light intensity:	10-20 μE/m^2/s (50-100 ft-c) (ambient laboratory levels)
6. Photoperiod:	16 h light, 8 h darkness
7. Test chamber size:	30 mL (minimum)
8. Test solution volume:	15 mL (minimum)
9. Renewal of test solutions:	Minimum, after 48 h
10. Age of test organisms:	Less than 24 h old
11. Number of organisms per test chamber:	Minimum, 5 for effluent and receiving water tests
12. Number of replicate chambers per concentration:	Minimum, 4 for effluent and receiving water tests
13. Number of organisms per concentration:	Minimum, 20 for effluent and receiving water tests
14. Feeding regime:	Feed YCT and *Selenastrum* while holding prior to the test; newly-released young should have food available a minimum of 2 h prior to use in a test; add 0.1 mL each of YCT and *Selenastrum* 2 h prior to test solution renewal at 48 h
15. Test chamber cleaning:	Cleaning not required

[1]Acute and chronic toxicity tests performed simultaneously to obtain acute/chronic ratios must use the same temperature and water hardness.

Table 6. Summary of test conditions and test acceptability criteria for *Ceriodaphnia dubia* acute toxicity test with effluents and receiving waters, (EPA, 1993), Continued

16. Test chamber aeration:	None
17. Dilution water:	Moderately hard synthetic water is prepared using MILLIPORE MILLI-Q^{R} or equivalent deionized water and reagent grade chemicals, or 20% DMW, receiving water, ground water, or synthetic water, modified to reflect receiving water hardness.
18. Test chamber concentrations:	Effluents: Minimum of five effluent concentrations and a control Receiving Waters: 100% receiving water and a control
19. Dilution series:	Effluents: ≥ 0.5 dilution series Receiving Waters: None, or ≥ 0.5 dilution series
20. Endpoint:	Effluents: Mortality (LC50 or NOAEC) Receiving Waters: Mortality (Significant difference from control)
21. Sampling and sample holding requirements:	Effluents and Receiving Waters: Grab or composite samples are used within 36 h of completion of the sampling period
22. Sample volume required:	1 L
23. Test acceptability criterion:	90% or greater survival of controls

promelus (fathead minnows). Although *Ceriodaphnia dubia* are typically more sensitive in both acute and chronic tests, fathead minnows were chosen for the chronic test because they have proven in the past to be the more sensitive organism in chronic tests with the Plant's effluent. Due to the sensitivity that the minnows repeatedly displayed to the Plant's effluent, the State has specified that the Plant shall use fathead minnows in all chronic toxicity tests (Diamond, 1995). All minnows were less than 24 hours old at the start of testing. Effluent concentrations used were 0, 50, 75 and 100%. Two replicates per concentration and 10 organisms per replicate were used. The minnows were fed three times a day.

3.3.11 pH/Temperature/Dissolved Oxygen

The pH was measured using a bench top, Fisher Accumet pH meter or a portable Corning, Model 106, pH meter. The meters were calibrated with standard solutions of pH 4.0 and 7.0 prior to use. A thermometer graduated in degrees Celsius (C) was used to measure temperature. Dissolved oxygen concentrations were measured using a YSI, Model 54 Oxygen Meter (Yellow Springs, Ohio). These parameters were measured continuously throughout the course of the research.

CHAPTER IV. RESULTS AND DISCUSSION

The first section of this chapter discusses the outcome of the pretreatment experiments which were performed with the bleach and finish waste stream, and a combination of the thermosol dye and print waste streams. The second section discusses the results of the CFR operations at both 4 day and 7 day HRT.

4.1 WASTESTREAM PRETREATMENT EXPERIMENTS

Although each experiment was described and numbered separately in Chapter 3, Methods and Materials, many of the experiments are related, therefore, results of related experiments are grouped together for illustration and discussion in this chapter. The results of Experiments 1, 2 and 3 are discussed first, followed by Experiments 4 and 5, Experiments 6 and 8, and finally Experiments 7, 9, 10 and 11. Figures 4 through 15, which illustrate the results of each experiment or set of experiments, are included within the discussion. Data that was collected during the pretreatment studies are tabulated in Appendix A.

4.1.1 Experiments 1, 2 and 3 $_{(pH, F)}$

The filtration step in Experiment 1 was performed to determine a typical particle size distribution for the bleach and finish. Bleach and finish with an

unadjusted pH of 7 was filtered through the group of filters appearing on the x-axis in Figure 4. A solids concentration was not determined for an unfiltered sample. The highest concentrations of particles were found in the 1.5 and 1.2 μm range. Also, it appears that higher particle concentrations may have existed at particle sizes less than 1.2 μm. Figure 4 also illustrates that more color was removed with each successive sample filtration. Color levels decreased from 2032 to 918 ADMI units. Filtration through a 1.2 m filter is necessary for determination of color in true ADMI units. Since color measurements were conducted on samples filtered through the individual filter porosities shown on the x-axis and the pH was not readjusted to 7.6, the reported color levels were not reported in true ADMI units.

Figure 5 illustrates the results of Experiment 2 which determined the effect of pH adjustment on soluble COD and color of the bleach and finish. The color measurements were made on unfiltered samples because only determination of an apparent trend was desired. Both COD and color were unaffected between pH 6 and 4. An overall decreasing trend is apparent for both parameters at pH values below 4. The overall COD and color reductions were 12% and 62%, respectively. The increase in COD from pH 2.5 to 2 may be an error in measurement, but another possible explanation may be due to the nature of the bleach and finish. Biological flocs often display good coagulation at pH levels of 2.5, but lower pH levels can disperse the flocs and disrupt

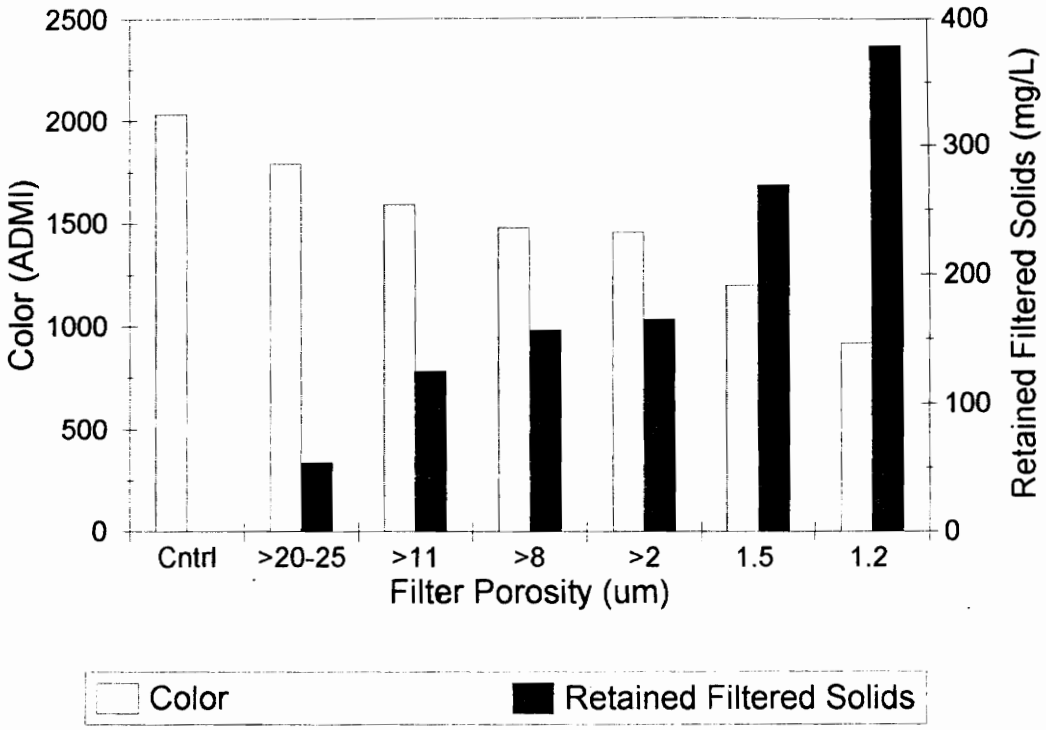


Figure 4. Color and filtered solids of bleach and finish following filtration through range of filters, Experiment 1 (color determined for samples not filtered through 1.2 μm filter not reported in true ADMI units)

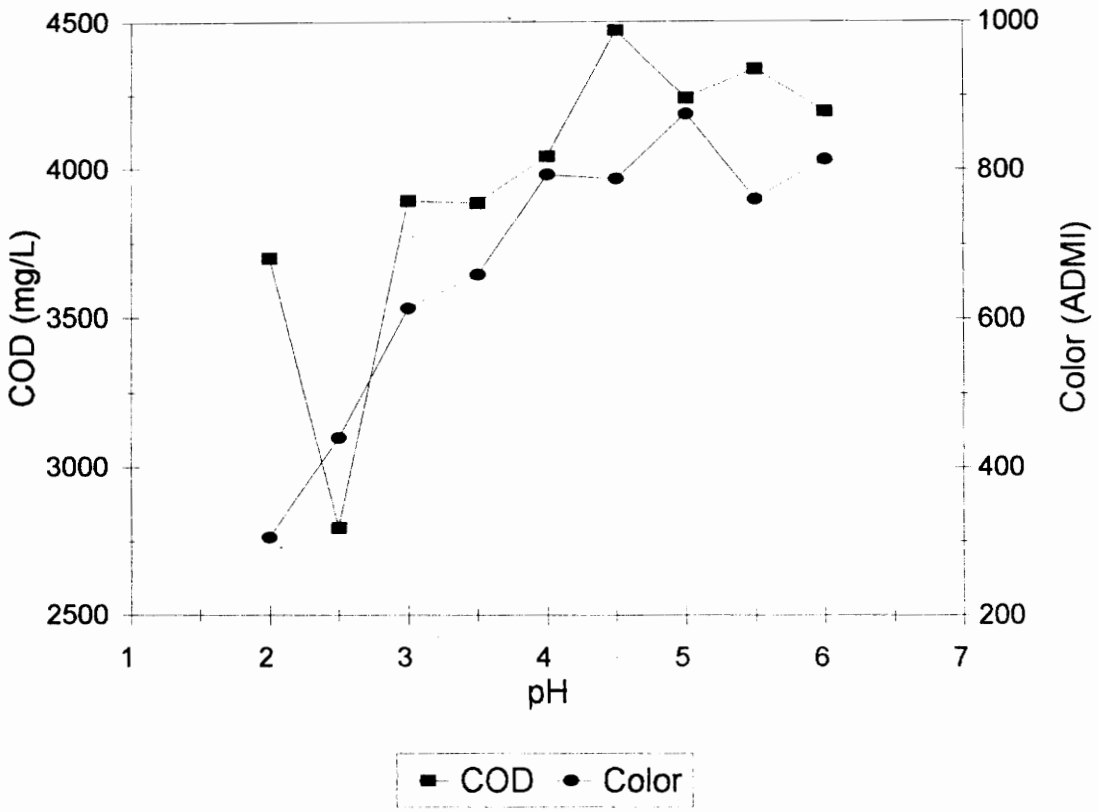


Figure 5. Effect of pH adjustment on soluble COD and unfiltered color of bleach and finish, Experiment 2 (color not reported in true ADMI units as samples were unfiltered)

settling. The reduction of pH from 2.5 to 2 may have caused a settling disruption, therefore increasing the measured COD concentration. Color is readily removed at pH levels of less than 3.5, but this level is usually not feasible as it can require expensive materials to withstand the highly acidic level. It should be noted, as described in section 3.1.2.2, the samples were unfiltered and were not adjusted to pH 7.6 prior to color analysis.

The pH of the bleach and finish was adjusted to values of 3 and 5, in Experiment 3, to determine if pH adjustment would affect the particle size distribution. The results, on Figure 6, show that although a decrease in pH level increased the concentration of particles at a given filter porosity, the highest concentration of particles remained near 1 μm. The adjustment of pH appeared to increase particle concentrations but not to affect the distribution of particles in the bleach and finish. The appearance of the bleach and finish was unaffected by filtration and only showed a slight decrease in overall opaqueness as the pH level was adjusted below 4.

4.1.2 Experiments 4 and 5 $_{(O)}$

In Experiment 4, 0 through 100 mg/L doses of a 3% hydrogen peroxide solution were applied to samples of bleach and finish for an oxidation analysis. No adjustment of pH was performed. At the time of the analysis, the pH was 6.1. After the oxidation was completed, no visual differences were evident except the

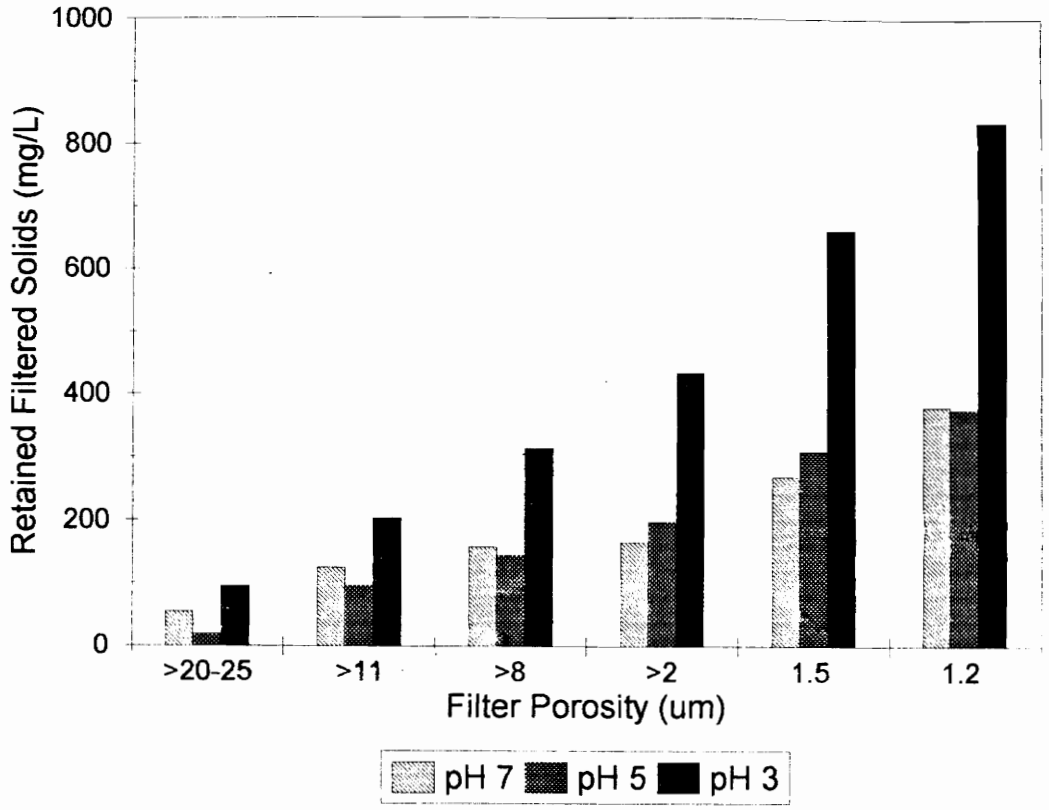


Figure 6. Effect of pH adjustment on filtered solids of bleach and finish, Experiment 3

formation of a floc at the bottom of the jars. Soluble COD and TSS analyses were conducted on the 0, 50 and 100 mg/L samples to determine any changes which may have occurred. Figure 7 shows TSS concentrations increased from 144 to 163 mg/L as concentrations of hydrogen peroxide increased. COD values varied from 5000 to 5900 mg/L with no apparent trend. A color analysis was not performed due to the lack of results in the TSS and COD analyses. Results were comparable to those found by Weber (1994).

An attempt was made in Experiment 5 to determine if pH adjustment prior to addition of 100 mg/L of hydrogen peroxide would produce any changes in soluble COD, DOC, color or TSS. After settling occurred, all of the samples remained cloudy with stringy precipitate attached to the sides of jars and accumulated at the bottom of the jars. The amount of precipitate increased as the pH values decreased. Figure 8 illustrates that COD and DOC were unaffected by the combination of pH adjustment and oxidation. A maximum TSS concentration occurred in the pH 6.8 control and decreased with the addition of hydrogen peroxide at pH 6.8, then increased slightly through pH 3. Color was the only parameter positively effected as it was reduced by 35% at pH 3. Hydrogen peroxide oxidation, with or without pH adjustment, failed to produce any noteworthy results other than color removal.

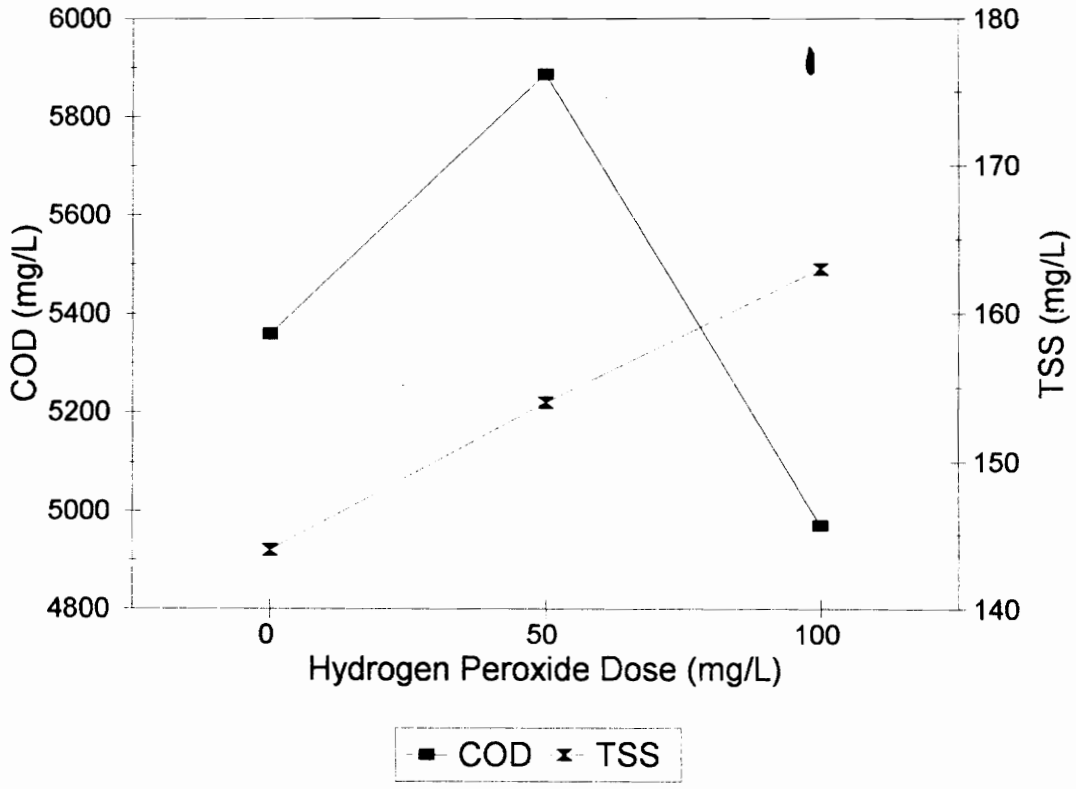


Figure 7. Effect of oxidation with hydrogen peroxide on soluble COD and TSS of bleach and finish, Experiment 4

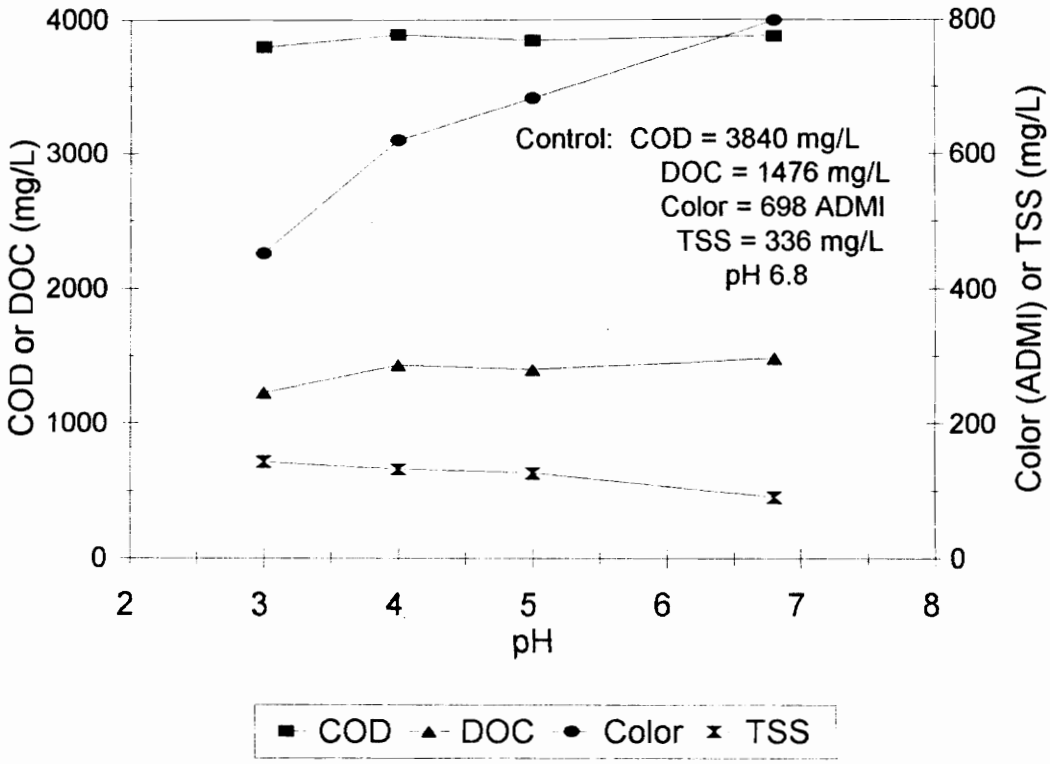


Figure 8. Effects of pH adjustment and hydrogen peroxide oxidation on soluble COD, DOC, color and TSS of bleach and finish, Experiment 5

4.1.3 Experiments 6 and 8 $_{(O,CC)}$

The next set of experiments was conducted to determine the effects of pH adjustment, oxidation and chemical coagulation on the bleach and finish samples. The pH values of samples in Experiment 6, excluding the control and one sample, were reduced in a range from the original value of 6.8, then dosed with 100 mg/L and 785 mg/L of hydrogen peroxide and AL220, respectively. This form of pretreatment produced samples which were more clear than any treated samples had been previously. The sample at pH 5 was fairly transparent with floating and sunken floc. The sample at pH 4 was extremely transparent with mostly floating floc. Figure 9 illustrates the results of the analyses. A minimum soluble COD value of 3055 mg/L, which represents a 20% reduction, was recorded at pH 5. A 19% reduction occurred in DOC concentrations at pH values of 4 and 5. Again, color was the most highly reduced parameter with removal of 82% at pH 4. A similar trend regarding TSS concentrations can be seen in Figure 9 when compared to Figure 8, oxidation only, but overall TSS concentrations were an average 11% higher with the addition of the polymer AL220.

Figure 10 compares analytical results from Experiments 5 and 6. Addition of AL220 after oxidation produced increased removals of color at every pH level. Removals of soluble COD and DOC were found at all pH levels except 3. Removals of COD, DOC and color averaged 10%, 9% and 58%, respectively.

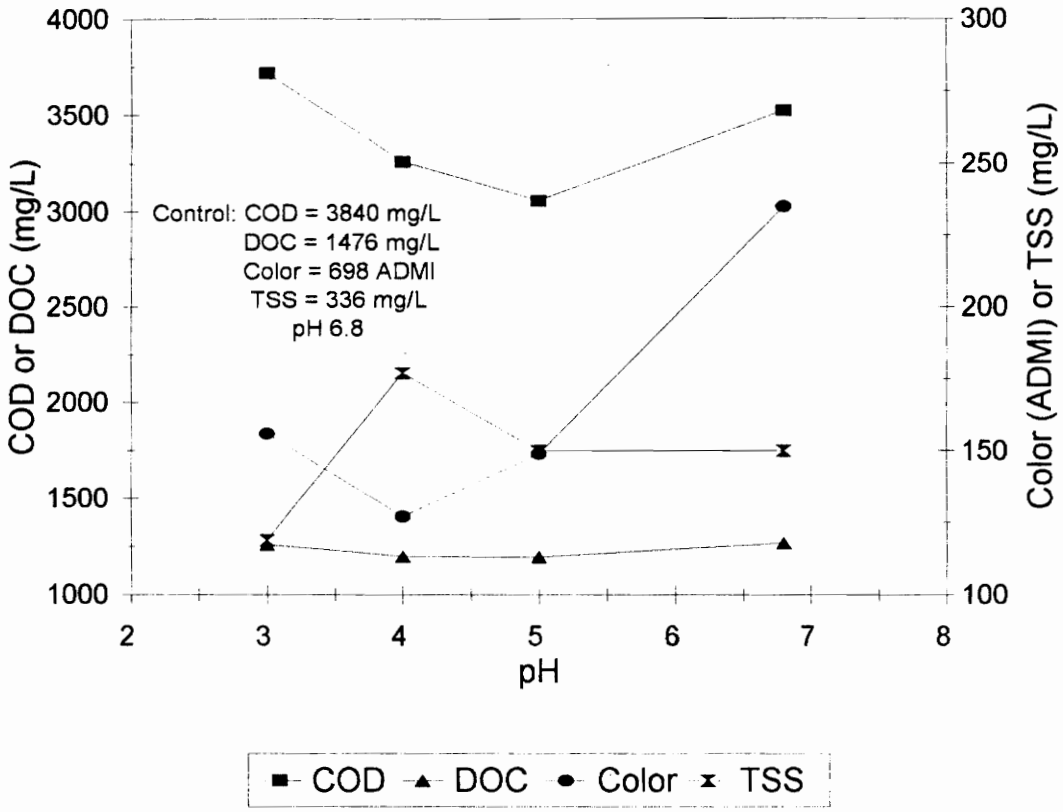


Figure 9. Effects of oxidation with hydrogen peroxide and coagulation with AL220 on soluble COD, DOC, color and TSS of bleach and finish, Experiment 6

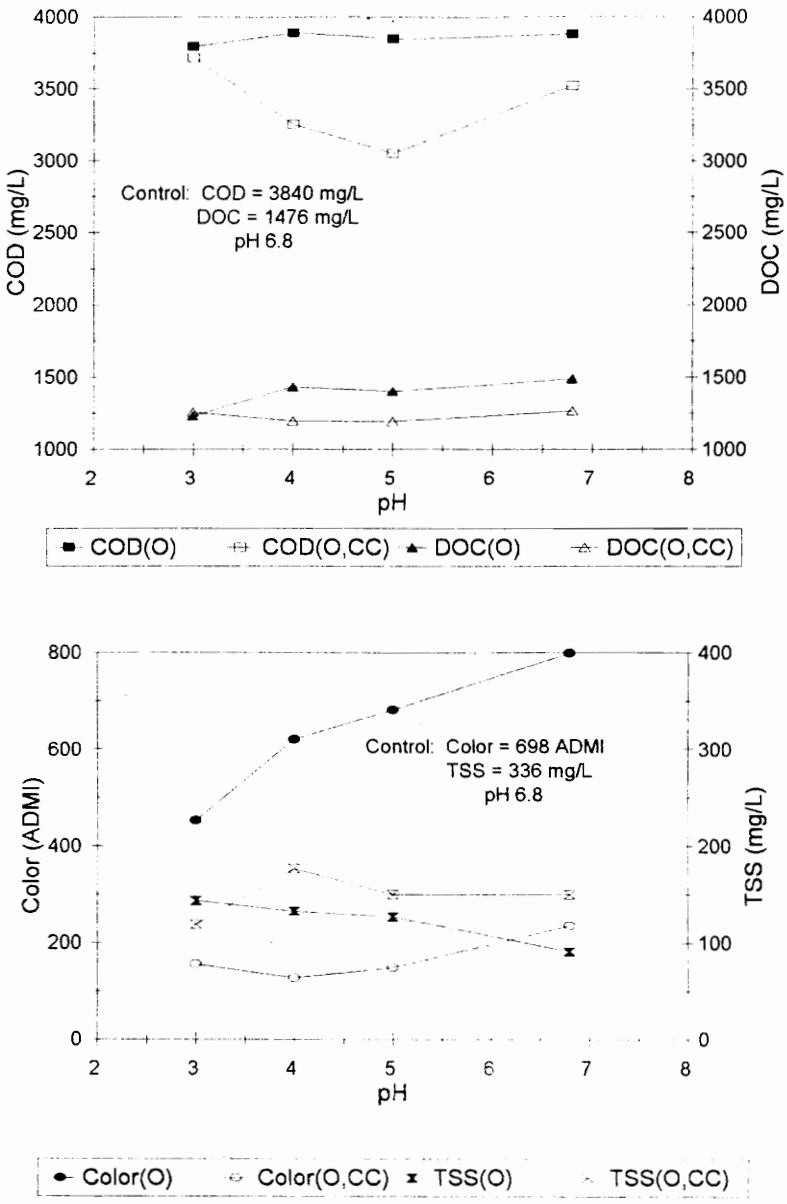


Figure 10. Comparison of effects of oxidation with hydrogen peroxide only, and coupled with coagulation with AL220, on soluble COD, DOC, color and TSS of bleach and finish, Experiments 5 and 6

Experiment 8 reversed the order following pH adjustment to chemical coagulation followed by oxidation, and also tested samples dosed with AL220 only. A different batch of bleach and finish, with an initial pH of 9.75 as opposed to the usual range of 6.5 to 7, was used for this experiment. The same concentrations of oxidant and polymer were used as were used previously, 100 mg/L and 785 mg/L, respectively. Figure 11 illustrates the results for this experiment. Soluble COD and DOC were variable, but responded more favorably to AL220 addition alone. Color removal was 68% at pH 4.5 as a result of both coagulation/oxidation and coagulation alone. TSS concentrations also increased in both applications at pH 4.5. The increased solids that formed probably contained color that was consequently filtered out prior to color measurement. Not all chemical coagulation plus oxidation samples were analyzed.

Based on the results of Experiments 5, it appeared that oxidation provided some color removal at low pH levels. Oxidation followed by chemical coagulation in Experiment 6, appeared to further enhance the color removal. In the case of experiment 8, chemical coagulation preceding oxidation provided the same results concerning color removal as did chemical coagulation alone. It appears that if oxidation is used to remove color, the oxidant may need to be applied prior to a chemical coagulant and at pH values at or below 4.5. Experiments 6 and 8 cannot be directly compared because the bleach and finish

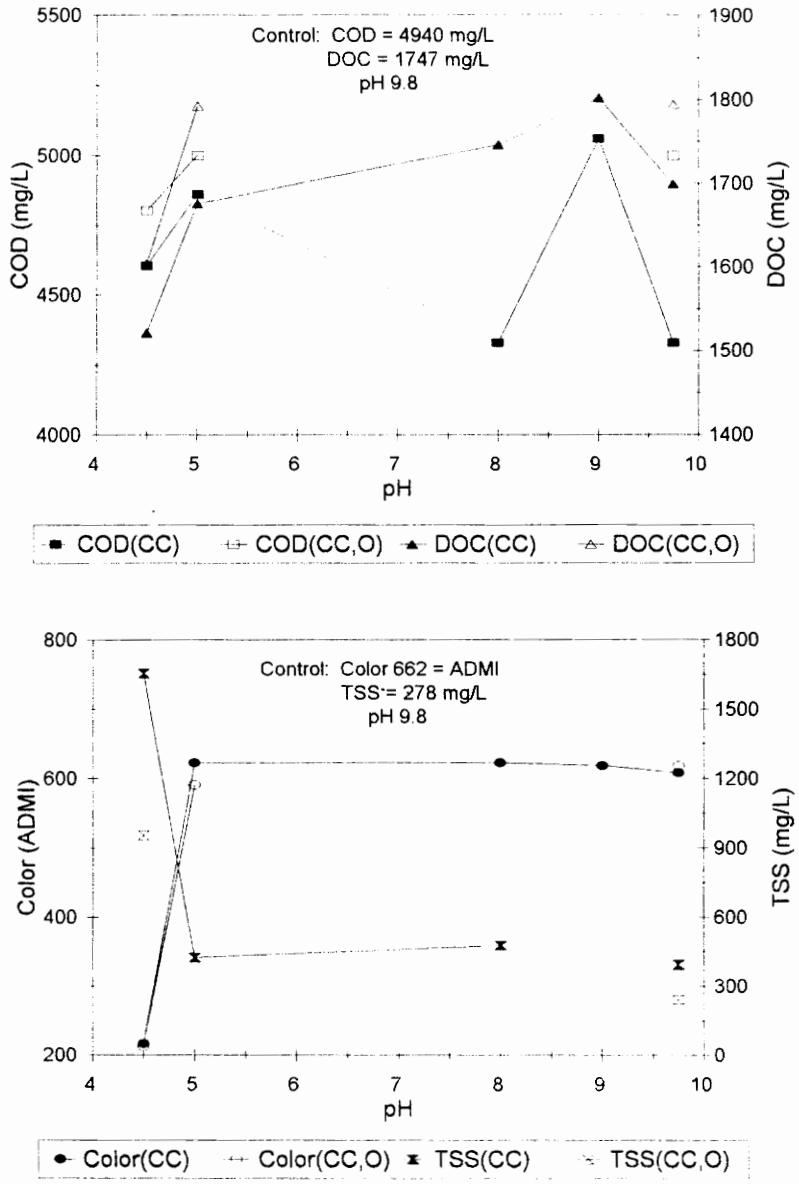


Figure 11. Comparison of effects of coagulation with AL220 only, and coupled with oxidation with hydrogen peroxide on soluble COD, DOC, color and TSS of bleach and finish, Experiment 8

that was tested in each case was not from the same delivery.

4.1.4 Experiments 7, 9, 10 and $11_{(CC)}$

Figure 12 illustrates the results of Experiment 7. This experiment focused on AL220 addition at two different concentrations and pH levels. The maximum soluble COD, DOC and color reductions occurred at a pH of 4.5 and AL220 dose of 400 mg/L. The reductions in the parameters were 15%, 30% and 84%, respectively. All of the TSS concentrations decreased an average of 46% from the control concentration of 336 mg/L. It was expected that TSS concentrations would increase due to addition of the polymer as they did in other experiments.

Experiment 9 built on the results of previous experiments by incorporating the pH value of 4.5 for all samples and a range of AL220 polymer doses of 250 to 785 mg/L. The organic polymer A130 was added in concentrations of 5, 10 and 20 mg/L, as indicated on Figure 13. The results of Experiment 9 are shown on Figure 13 where soluble COD, TOC and color reductions were 9%, 27% and 34%, respectively. DOC values increased an average of 8%.

Experiment 10 utilized Nalco polymers 7135 and 9764. Results are shown in Figure 14. As expected from results of earlier pH adjustment tests, the sample which was adjusted to pH 2.5 resulted in a color reduction; in this case, the reduction was 49%. The sample dosed with 100 mg/L of 7135 had 55% of the color removed, while the same dose of 9764 only removed 34% of the color.

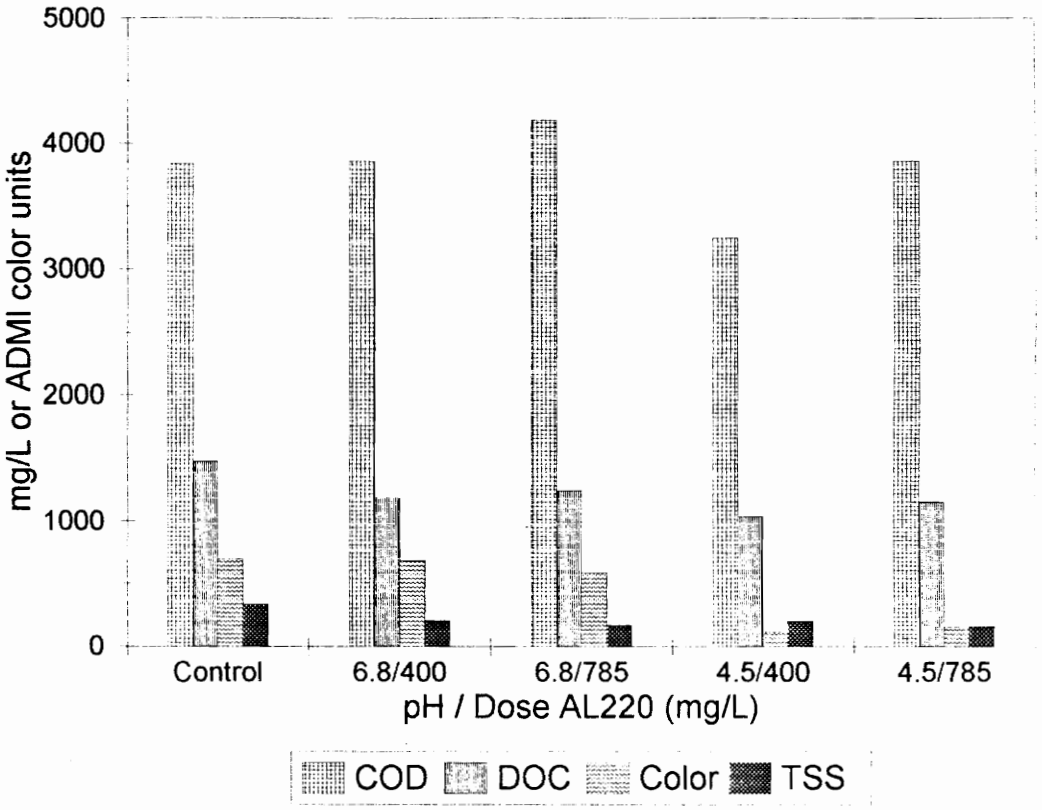


Figure 12. Effects of pH adjustment and coagulation with AL220 on soluble COD, DOC, color and TSS of bleach and finish, Experiment 7

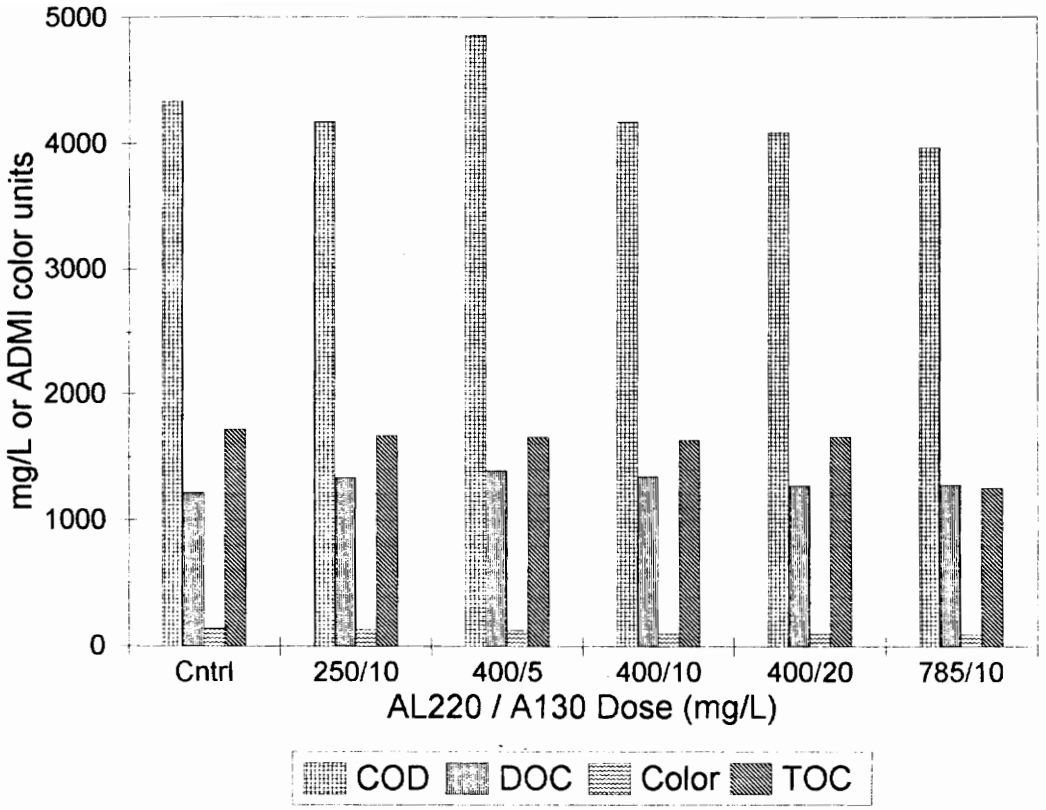


Figure 13. Effect of coagulation with AL220 and A130 on soluble COD, DOC, color and TSS of bleach and finish, Experiment 9

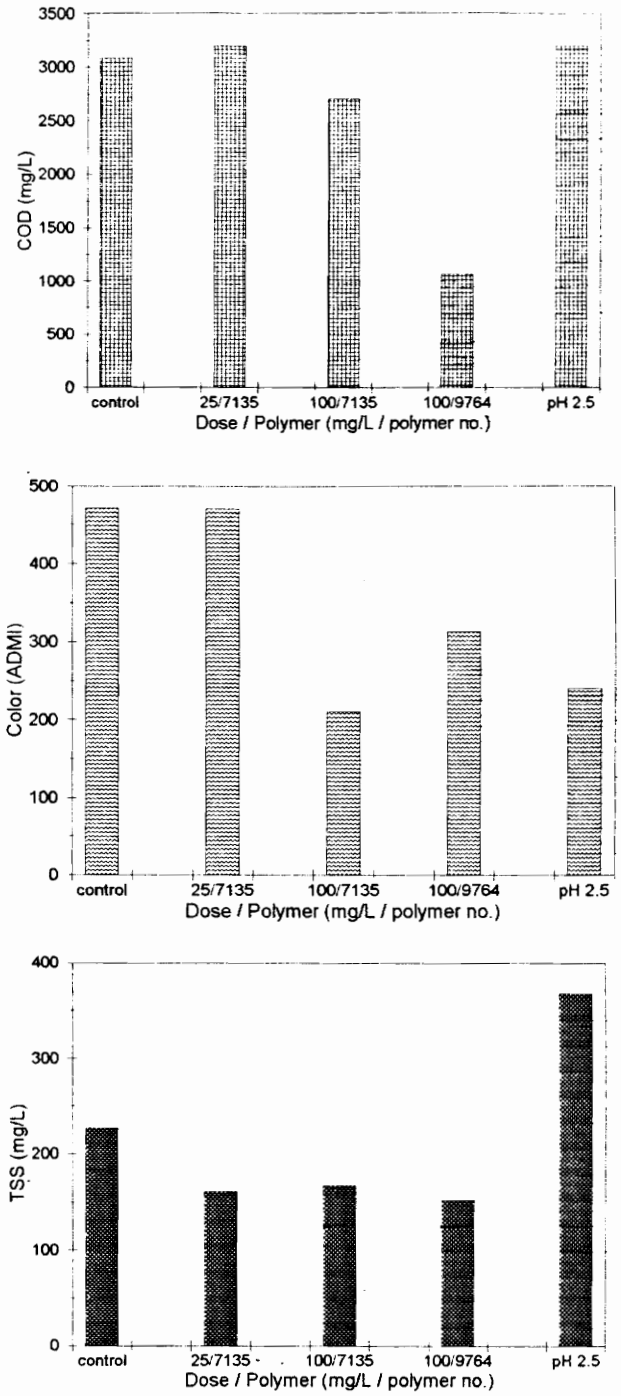


Figure 14. Comparison of effects of coagulation with polymers 7135 or 9764, or pH adjustment on soluble COD, color and TSS of bleach and finish, Experiment 10

Conversely, the 100 mg/L dose of 9764 was able to remove 65% of the soluble COD, but only 12% of the COD was removed with 100 mg/L of 7135. The pH 2.5 sample and 25 mg/L dose of 7135 sample resulted in a 4% increase in COD. As in earlier experiments, reduction of pH resulted in an increase in TSS. In this case, a 62% increase in TSS occurred. Polymer applications resulted in TSS reductions ranging from 26-33%.

Weber (1994) applied concentrations of 50 to 300 mg/L of various other organic polymers to samples of bleach and finish. Reported color, DOC and TSS removals ranged from 84 to 94%, 8 to 11% and 70 to 86%, respectively. As with Weber's results regarding the bleach and finish, color appeared to be the only parameter which was able to be repeatedly removed through various pretreatment attempts. Organic content was the most troublesome characteristic of the bleach and finish. The organic content was large and, as evidenced by the pretreatment attempts, very difficult to remove. Nalco polymer 9764 was able to remove soluble COD, but the variability of the waste could cause COD removals to be less than 65% in any subsequent experiments.

Nalco polymers were utilized again in Experiment 11. In this case, the polymers were applied to the thermosol dye and print waste streams to determine whether soluble COD, color and TSS would be affected. Pretreatment with the Nalco polymers was also compared to the standard pretreatment scheme, which used AL220 and A130 to treat the dye and print and

is described in section 3.2.1 of Methods and Materials. This comparison was performed to determine whether pretreatment using polymers 7135 or 9764 would provide greater removals of organic matter, color and solids than the standard pretreatment scheme.

Figure 15 illustrates the results of Experiment 11. On Figure 15, Cntrl2 and stndprt are used as abbreviations for the standard pretreatment scheme control and sample, respectively, as those two samples were tested on a different day than the other samples . The results are mixed, as they were in Experiment 10. The 50 mg/L dose of 9764 was able to remove 78% of the soluble COD present, while the 25 and 50 mg/L doses of 7135 were able to remove 55%. The 100 mg/L dose of 7135 and 25 mg/L dose of 9764, with removals of 6% and 11%, respectively, were ineffective at removing COD compared to the other dose combinations discussed above. None of the soluble COD present was removed using the AL220 and A130 combination of the standard pretreatment scheme. In that case, control and pretreated sample COD concentrations were each measured to be 202 mg/L. According to data reported by Weber (1994), the standard pretreatment scheme removed 73 to 78% of the total COD, but was ineffective at removing soluble COD. Weber reported removals of soluble COD ranging from 0 to 33%. Therefore, it was not surprising that none of the soluble COD was removed in the standard pretreatment scheme samples tested in Experiment 11. The 100 mg/L dose of

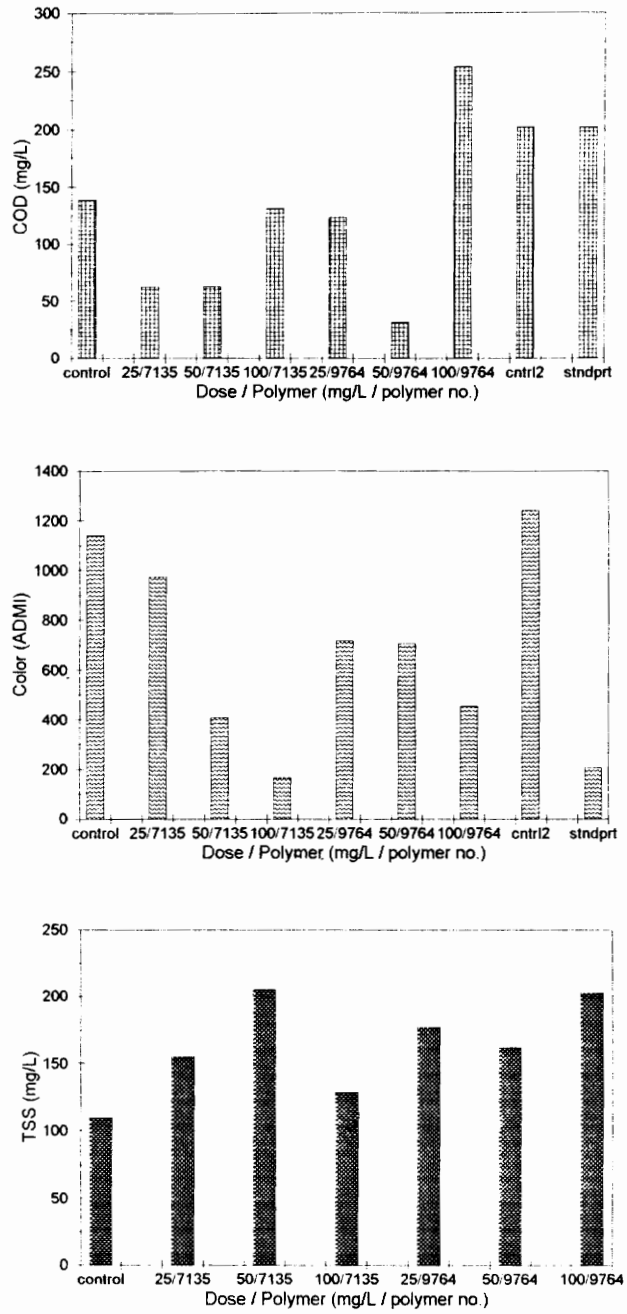


Figure 15. Comparison of effects of coagulation with polymers 7135 or 9764 on soluble COD, color and TSS of thermosol dye and print, Experiment 11

7135 removed 85% of the color, while the standard pretreatment using AL220 and A130 removed 83% of the color when compared to the control used in that experiment. All remaining samples had some color removed with removals ranging from 15 to 64%. Concentrations of TSS increased in every case with increases ranging from 17 to 86%. TSS concentrations were not determined for the samples that were dosed with the AL220/A130 combination.

4.2 CONTINUOUS FLOW REACTOR OPERATION

Discussions and comparisons of both the 4 day and 7 day HRT operation results are included in the following sections: steady state monitoring, kinetic coefficient determination, organic removal, nutrient removal and metal and ion removal. Toxicity evaluations were performed on 7 day HRT samples only. Figures 16 through 28 are included to illustrate the results of the reactor studies. Pertinent data are tabulated in Tables 7 through 17. All data collected from CFR operations are tabulated and included in Appendix C. All COD measurements were soluble except where otherwise noted. Results of the 3 day HRT operation (Weber, 1994) are included and compared to the 4 and 7 day HRT operations throughout the following sections.

4.2.1 Steady State Monitoring Parameters

Steady state parameters MLSS, effluent TSS, COD and color were

measured three times per week, on average, during the 4 day HRT operation. The reactors had been operating at a 4 day HRT for 101 days when parameter measurements began. Operation and data collection at this level continued until day 160.

Following 4 day HRT operation, the HRT was adjusted to 7 days and the same parameters plus DOC were again measured. Measurements began on day 30 of the 7 day HRT operation. Measurements began earlier in this case due to time constraints and the fact that the biomass was already generally acclimated to this type of waste since the reactors had been in operation for nearly one year from the time operation was begun by Weber (1994). The parameters were measured an average of two times per week until operation stopped on day 123.

Figures 16 through 20 summarize the parameters listed above for 4 day HRT operation. The data was analyzed and steady state was determined to have started on day 101 and ended on day 123. Effluent became difficult to filter after day 123. On day 126, the effluent was still difficult to filter so samples were viewed under a microscope. Large populations of filamentous organisms were visible. When decreased aeration did not promote a reduction in the filamentous population, bleach (Wonder Chemical Corp., Fairless, PA) was added to kill the unwanted organisms. Minor signs of recovery, including increased COD and color removal, were evident by day 140, but the reactors never fully recovered to

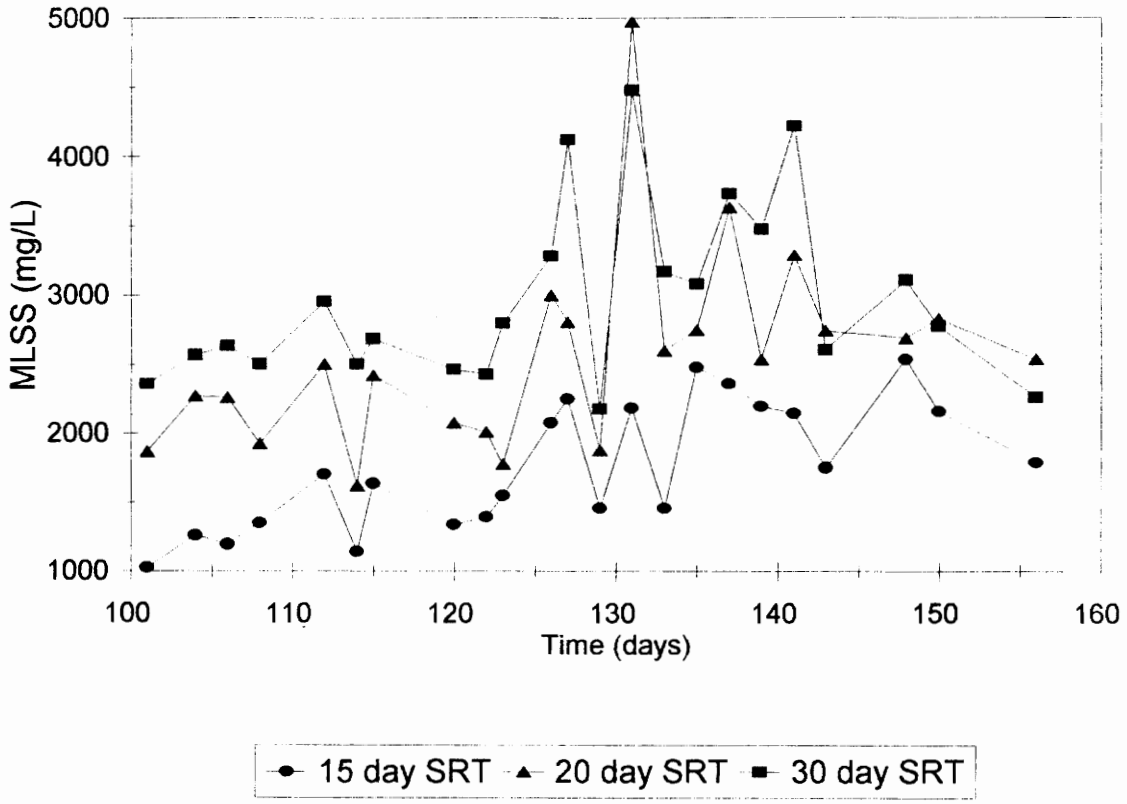


Figure 16. MLSS for 4 day HRT CFR operations

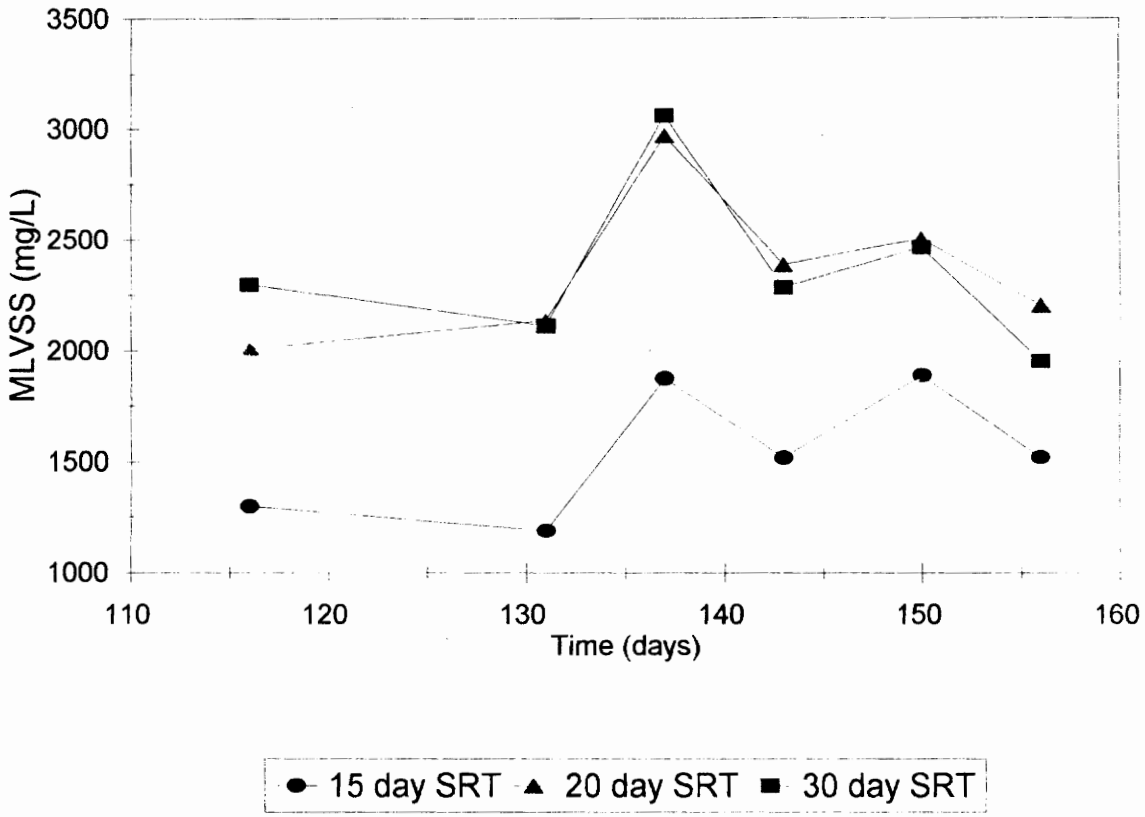


Figure 17. MLVSS for 4 day HRT CFR operations

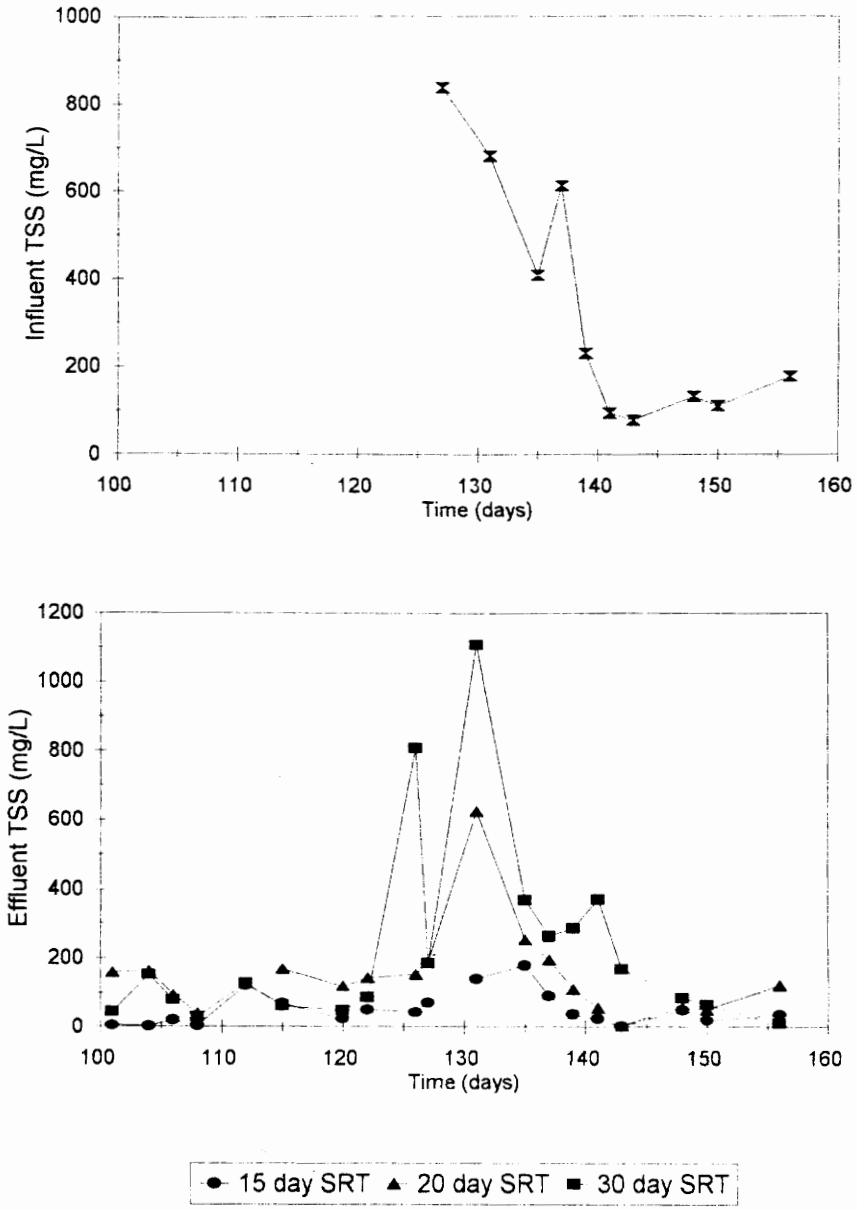


Figure 18. Influent and effluent TSS for 4 day HRT CFR operations

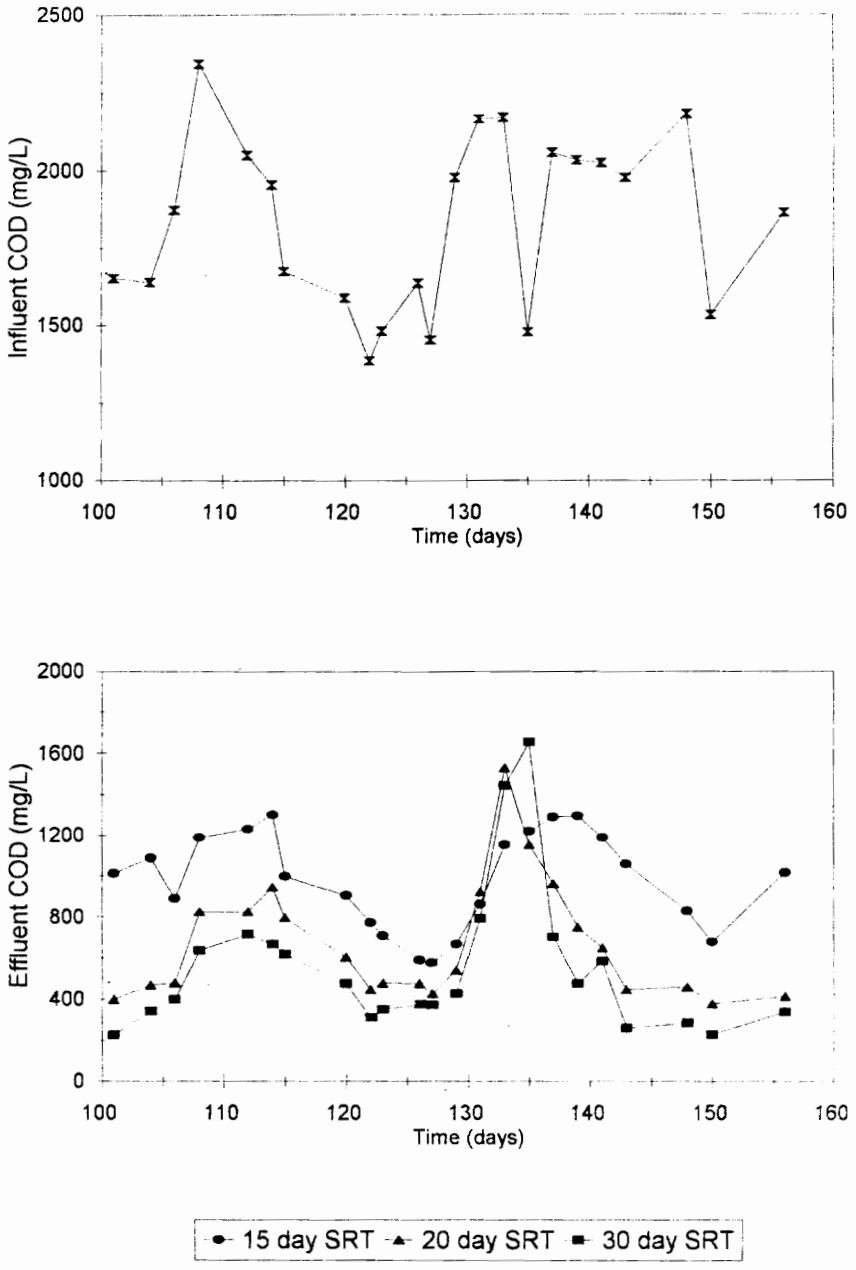


Figure 19. Influent and effluent soluble COD for 4 day HRT CFR operations

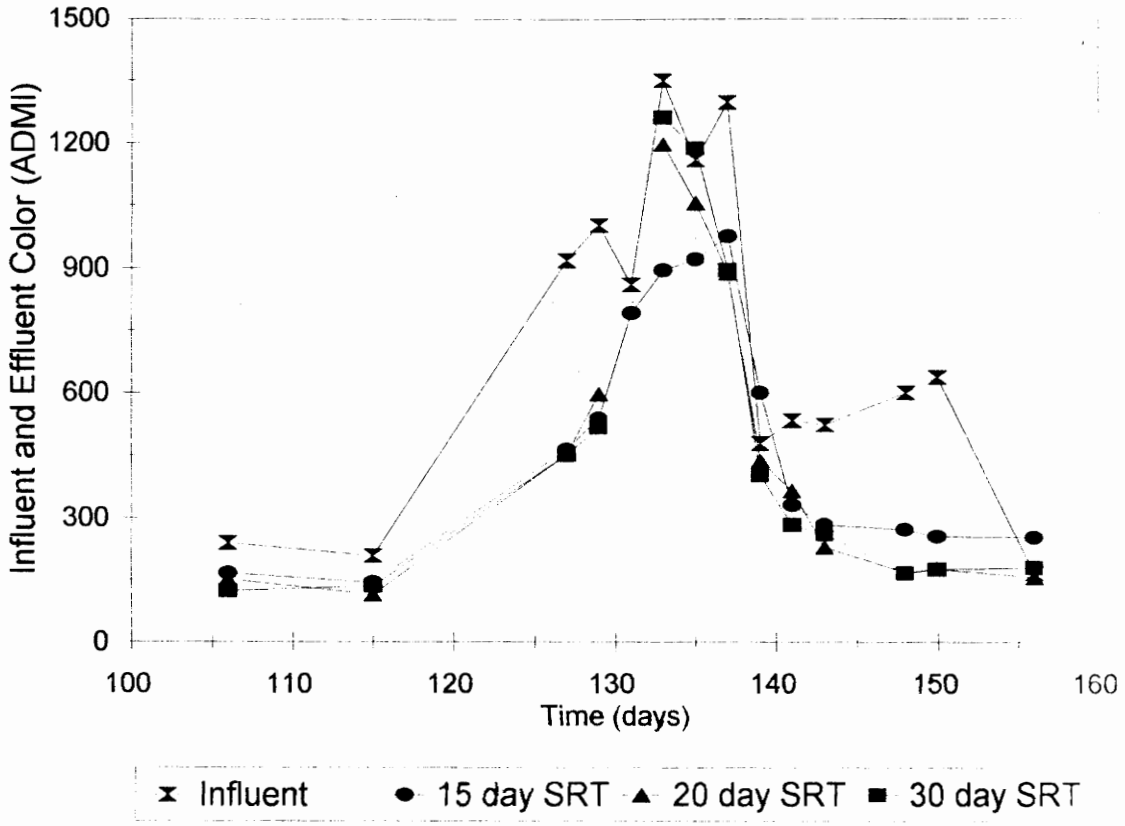


Figure 20. Influent and effluent color for 4 day HRT CFR operations

steady state conditions before the HRT was increased to 7 days. Therefore, it was decided to end the steady state period at day 123.

Figures 21 through 26 summarize the steady state monitoring parameters for the 7 day HRT operation. Following analysis of the data, steady state was determined to have existed in the reactors from day 62 through day 101 for the 15 and 30 day θ_c reactors. The same time period was used for the 20 day θ_c reactor, except that days 69 and 73 were excluded from the value averaging. Figure 21 illustrates that the MLSS population in the 20 day θ_c reactor declined over days 69 and 73 to levels below those of the 15 day reactor. Also apparent, on Figure 24, is that the COD concentrations in the 20 day θ_c reactor rose from day 62 through day 73 to a value that does not appear on the graph because it was greater than the influent concentration on that day . Due to the upset nature of the 20 day θ_c reactor during this time period, corresponding parameter values were not included in steady state averaging. The reactor recovered by day 83. Table 7 lists the average steady state parameter values along with percent removals in parentheses for both the 4 day and 7 day HRT operations, and the 3 day HRT operation which resulted from the work performed by Weber (1994).

Figures 16 and 21 illustrate the MLSS concentrations for the 4 and 7 day HRT studies. At each HRT level, MLSS concentrations increased with increasing θ_c value. MLSS concentrations, including those from the 3 day HRT study, ranged from 1358 to 3353 mg/L. The increase in HRT from 3 days to 7

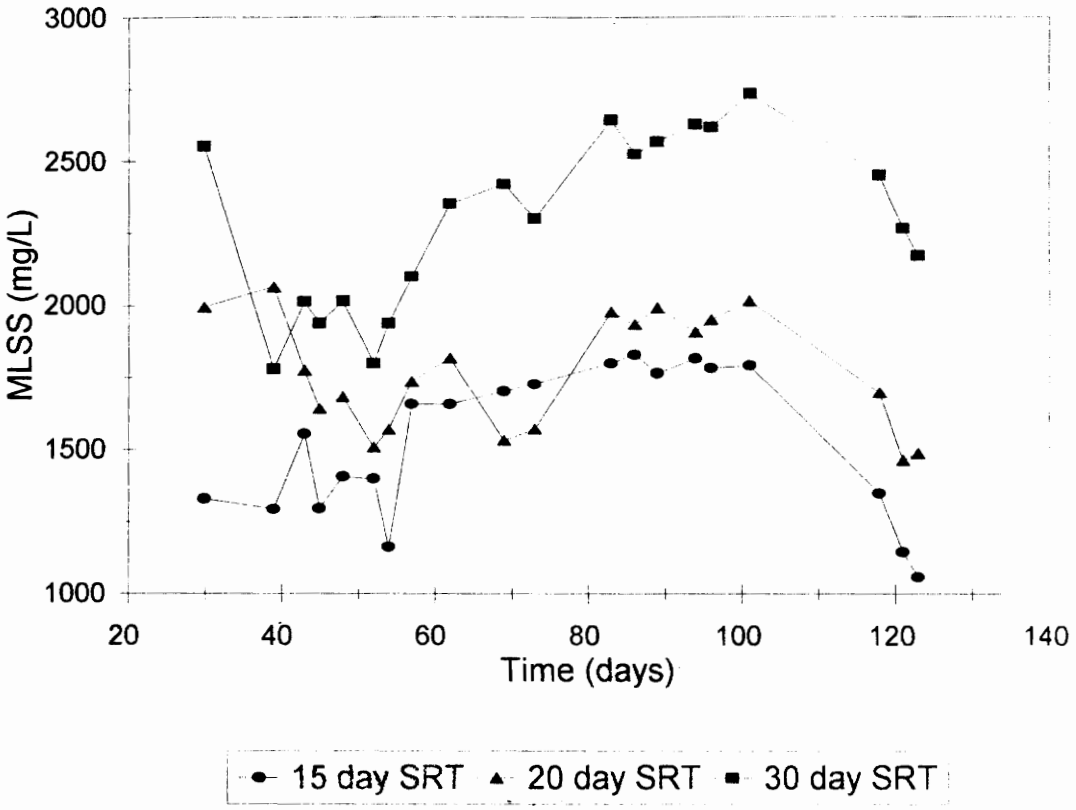


Figure 21. MLSS for 7 day HRT CFR operations

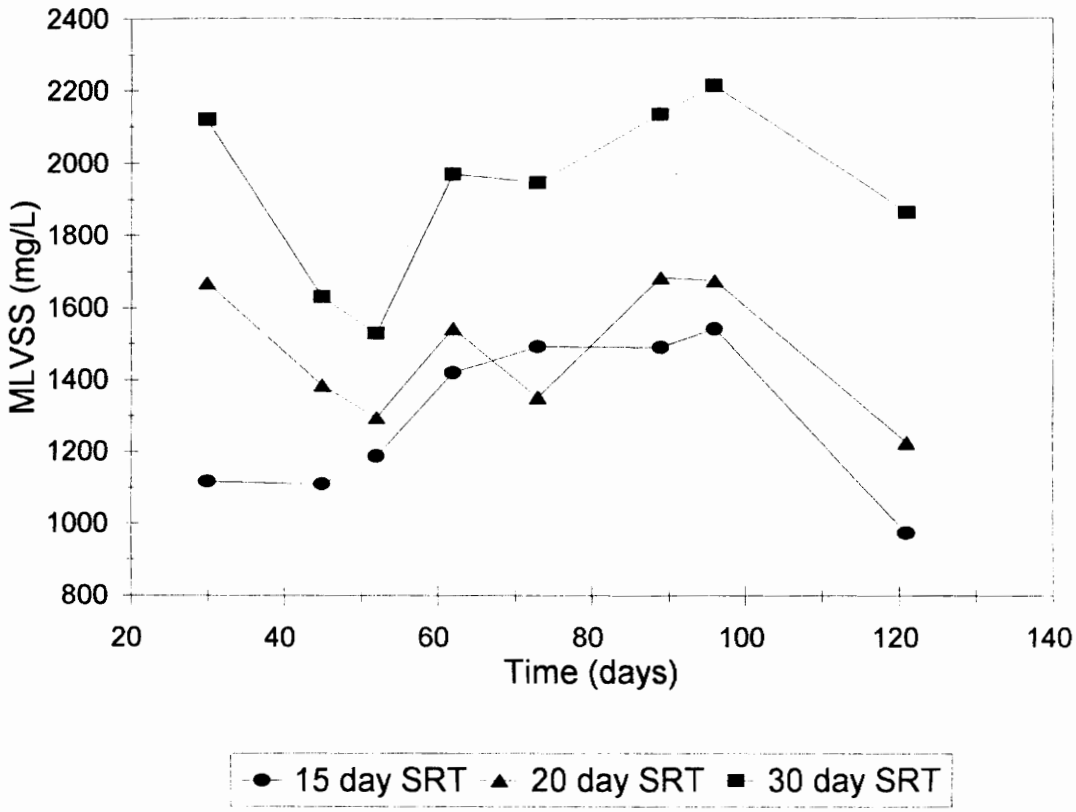


Figure 22. MLVSS for 7 day HRT CFR operations

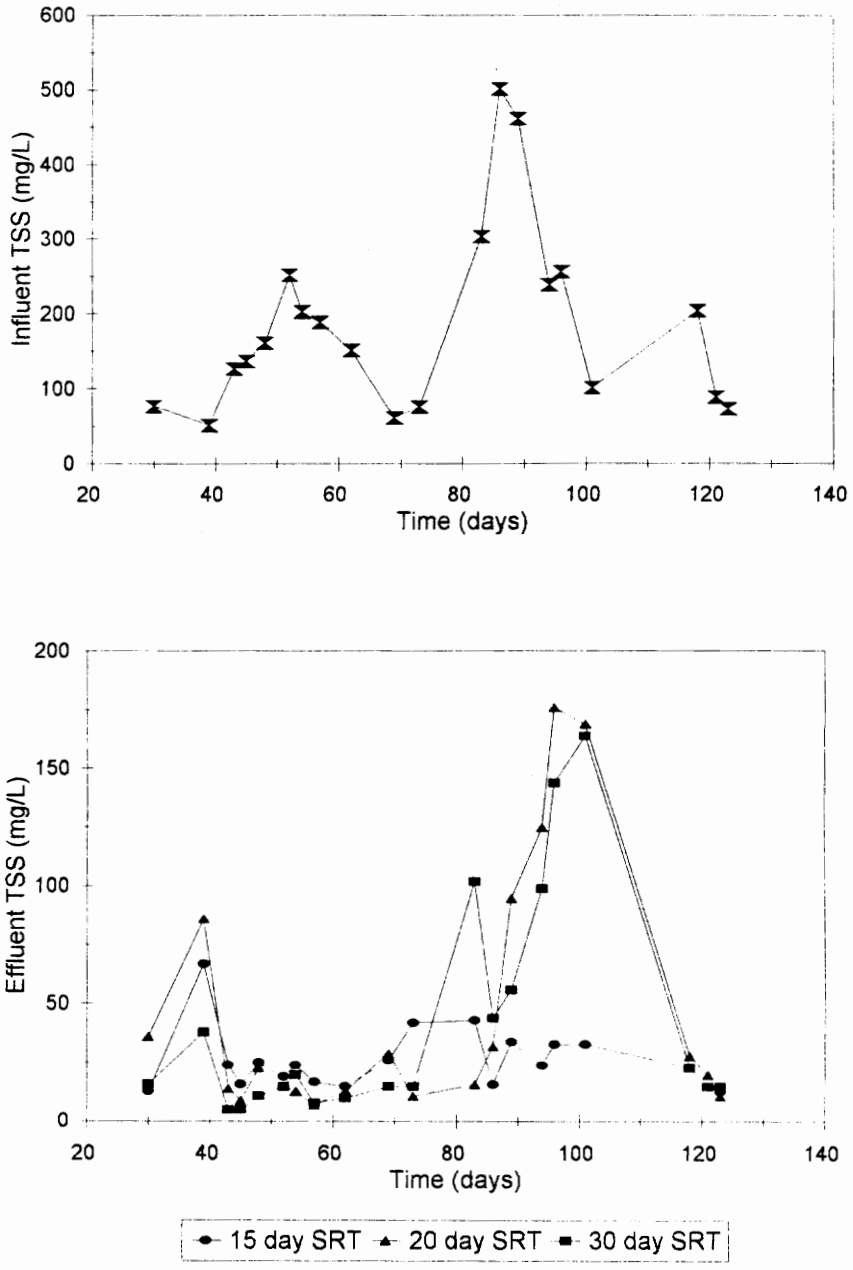


Figure 23. Influent and effluent TSS for 7 day HRT CFR operations

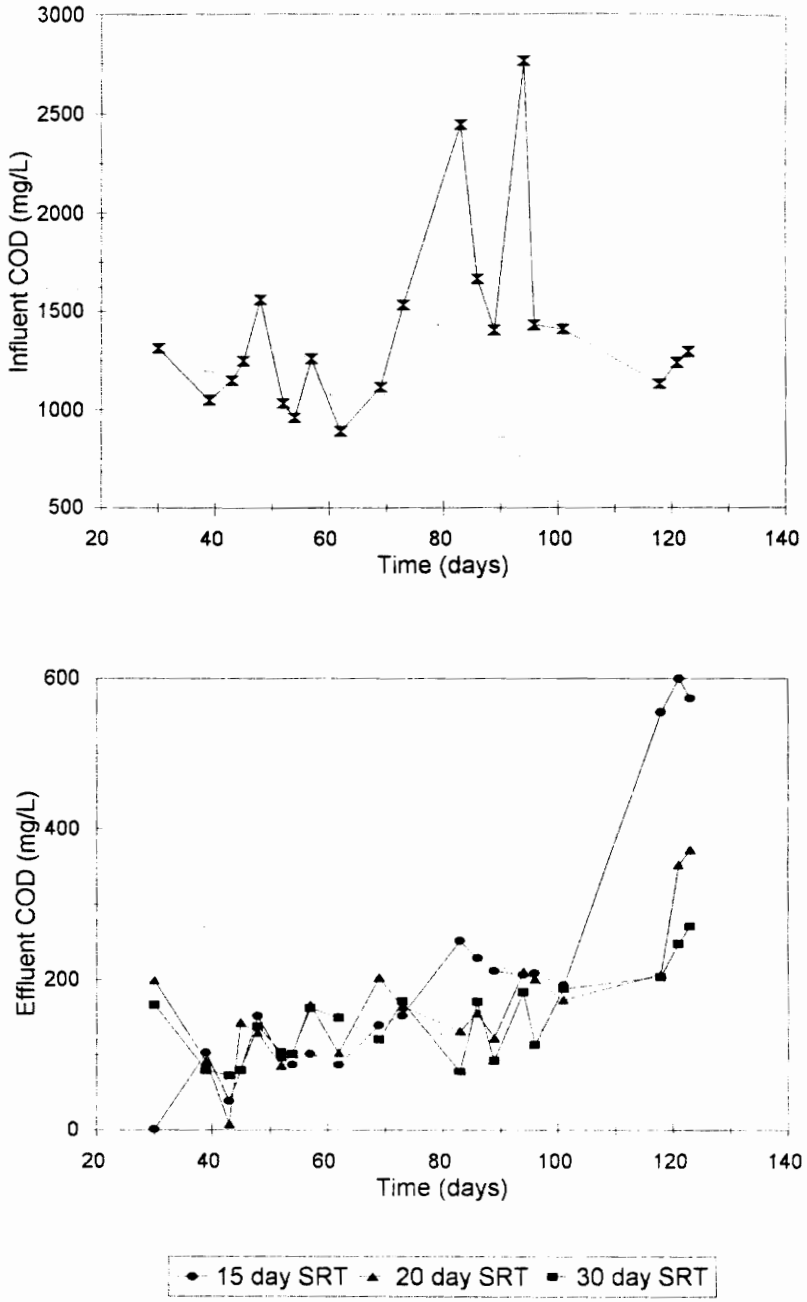


Figure 24. Influent and effluent soluble COD for 7 day HRT CFR operations

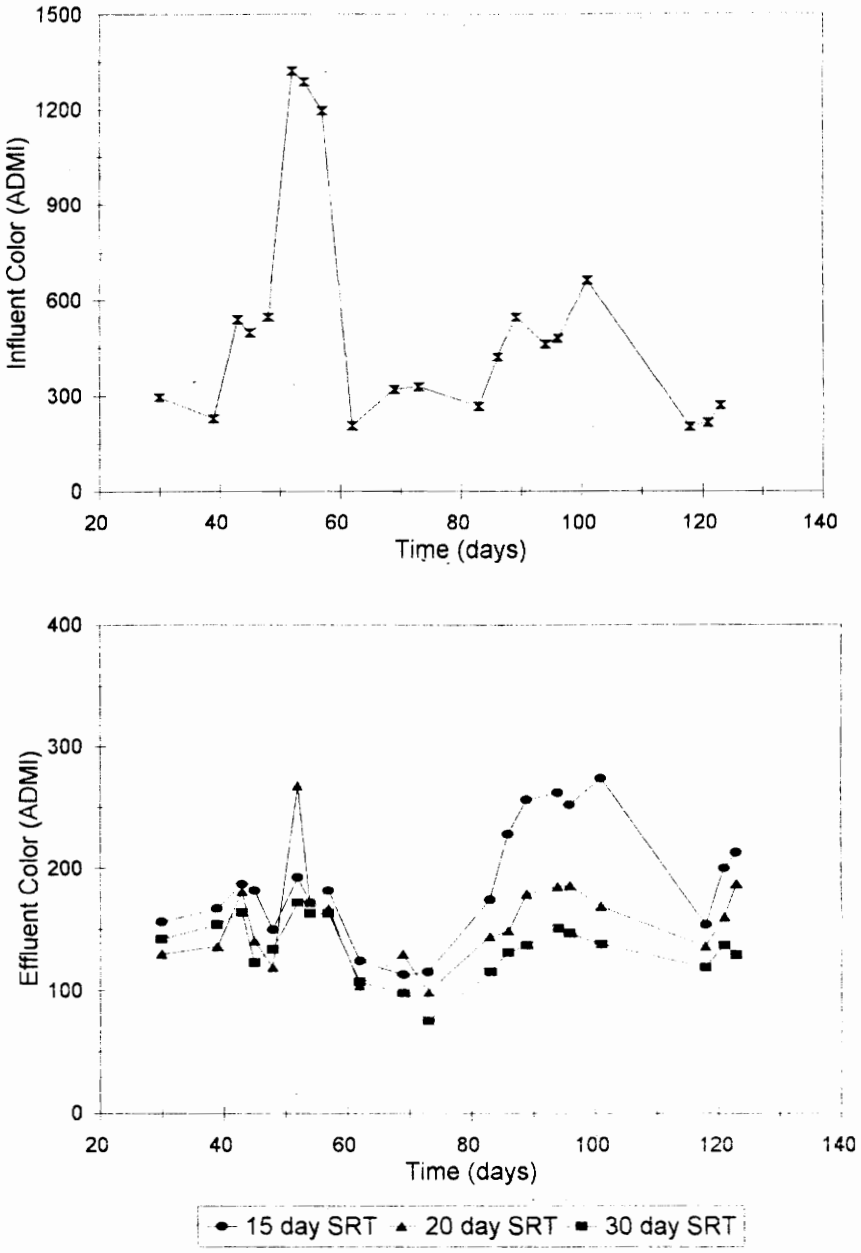


Figure 25. Influent and effluent color for 7 day HRT CFR operations

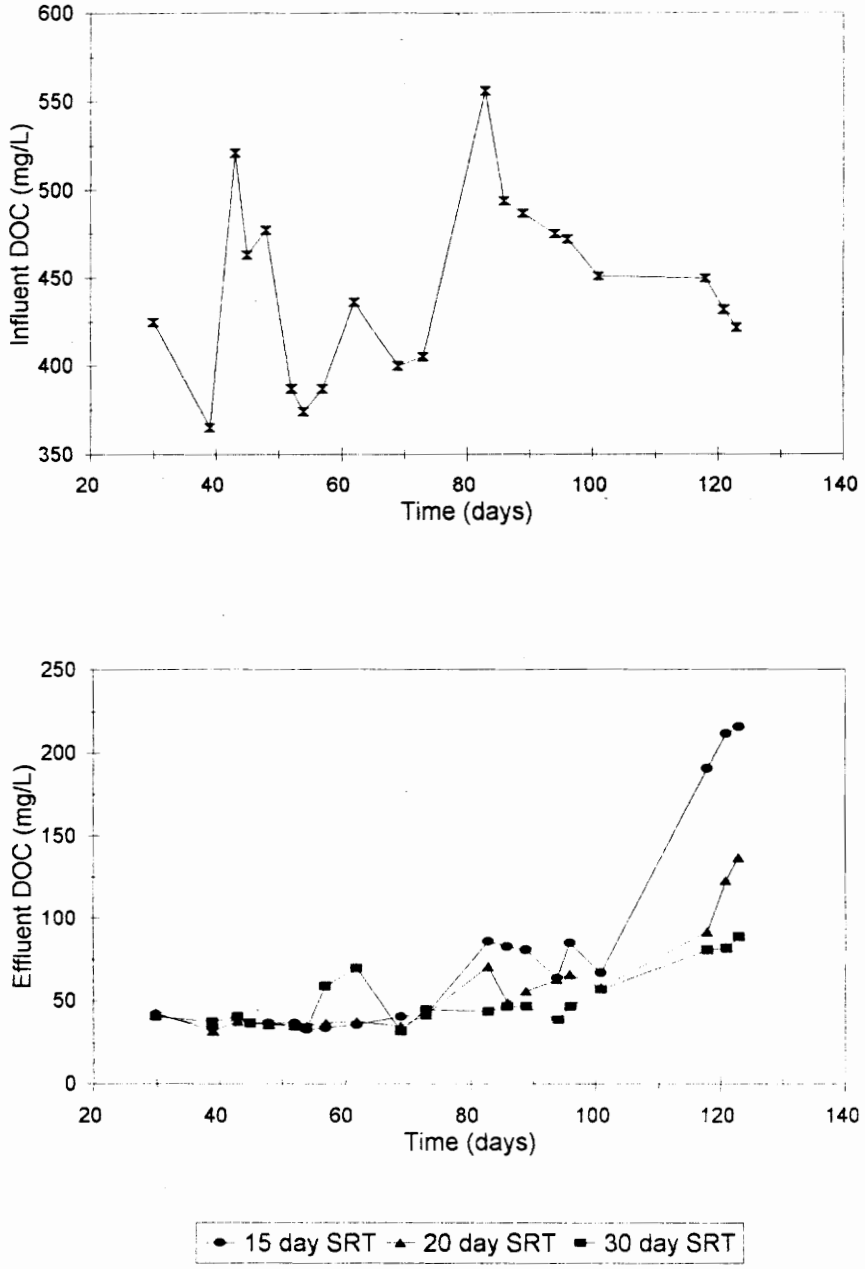


Figure 26. Influent and effluent DOC for 7 day HRT CFR operations

Table 7. Average steady state parameter values and percent removals

θ_c (days)	Steady State Period (days)	MLSS (mg/L)	MLVSS (mg/L)	TSS** (mg/L)	Soluble COD (mg/L)	Color (ADMI)	DOC*,** (mg/L)
3 day HRT							
8	28-48	1076	959	--	664(55%)	230(43%)	--
15	22-104	1805	1598	--	605(59%)	188(42%)	--
20	30-104	2345	2117	--	496(66%)	170(52%)	--
30	46-104	3353	2913	--	472(68%)	170(53%)	--
4 day HRT							
15	101-123	1358	1074	38	1010(43%)	156(31%)	--
20	101-123	2073	1721	127	628(64%)	135(40%)	--
30	101-123	2590	2227	80	475(73%)	131(42%)	--
7 day HRT							
15	62-101	1764	1508	30(79%)	187(89%)	200(51%)	65(84%)
20	62, 83-101	1942	1651	89(53%)	157(91%)	159(61%)	57(86%)
30	62-101	2533	2134	72(59%)	141(92%)	122(70%)	48(88%)

* Did not perform DOC on 4 day HRT samples.

** Weber (1994) did not include summary of TSS or DOC average concentrations.

days corresponded to a decrease in the rate of substrate introduction into the reactors and produced a predicted decrease in MLSS concentration for all sludge ages except the 7 day HRT 15 day θ_c reactor. A large decline, 11 to 24%, was evident between MLSS concentrations from the 3 day to 4 day operation in the 20 and 30 day θ_c reactors, but very slight, 2 to 6%, from the 4 day to 7 day operation. It is possible, due to the complexity of the waste, that reactors operated at an HRT of greater than approximately 4 days will not display a reduction in MLSS concentrations along with the reduction in substrate feed rate.

Figures 17 and 22 illustrate MLVSS concentrations for the 4 day and 7 day HRT operations. MLVSS ranged from 79 to 86% of MLSS for the 4 day HRT study and 84 to 85% for the 7 day HRT study. Once the reactors recovered from the filamentous infestation, during the latter part of the 4 day HRT study which was not included as part of steady state analysis, MLVSS averaged 87 to 88% of the MLSS. MLVSS was steady throughout the 7 day HRT operation. Weber (1994) reported that volatile suspended solids accounted for 89% of MLSS.

In both the 4 and 7 day HRT operations, effluent TSS was variable. Effluent TSS is often hard to predict because it can be affected by a number of factors including an air stone slipping toward the front of the reactor and disrupting settling in the clarifier. Effluent TSS concentrations for the 4 day HRT operation ranged from 38 to 127 mg/L, while 7 day concentrations ranged from

30 to 89 mg/L. Percent removals of effluent TSS are not available for the 4 day HRT operation, but 7 day removals ranged from 53 to 79%.

During days 93 through approximately 103 of the 7 day study, a build up of some compound was evident in the 20 and 30 day θ_c reactors initially, then in the 15 day θ_c reactor. This buildup caused the effluent TSS concentrations to rise sharply. An analysis was performed to attempt to identify the type of compound that was causing the problem. Initially, the assumption was some type of silicate, because the effluent was cloudy in appearance, and difficult to filter. Samples from each reactor effluent were acidified to pH 4, then to pH 2.5, before a precipitate formed. The precipitate was puffy and cloud-like in appearance. Samples of the precipitates were then baked in the muffle furnace for 20 minutes at 550 °C to determine the volatile portion. Over 80% of the substance was volatile. Silicic acid may have formed when the pH was decreased to 2.5 and the volatile portion may have been the water associated with the acid formation. Silicates are not volatile at temperatures of 550 °C. Another possibility was that some type of organic compound, possibly PVA, had built up in the reactors. Personnel at the Plant were questioned, but were unable to identify any changes that would explain the problem that was encountered.

Influent and effluent COD concentrations are illustrated in Figures 19 and 24. Influent COD averaged 1765 mg/L for the 4 day HRT study and 1672 mg/L

for the 7 day study. Variability of the influent COD concentrations is evident in both figures. Biomass operating at the 7 day HRT removed 89 to 92% of the COD, while only 43 to 73% was removed by the biomass operating at the 4 day HRT. Weber (1994) reported a COD removal range for the 3 day HRT operation of 59 to 68%. This range is similar to the range of 43 to 73% seen at the 4 day HRT. Since average influent COD and reactor MLSS concentrations did not differ significantly between either the 4 day or 7 day HRT operations, one possible explanation for the increased COD removal is adsorption of organic matter to the biomass as opposed to a pure biodegradation mechanism.

Influent and effluent color for 4 day and 7 day HRT operation is illustrated in Figures 20 and 25. Removals ranged from 42 to 52% for the 3 day (Weber, 1994), 31 to 42% for the 4 day, and 51 to 70% for the 7 day HRT operations. Although biological treatment is often most noted for removal of organic matter, biological treatment is, according to Gardiner and Borne (1978), often beneficial in terms of color removal due to oxidation of the color by the biomass or sorption of the color to the bacterial solids prior to removal from the system. Reactive and disperse dyes are used by the Plant and according to Grau (1991), the "adsorption behavior of activated sludge is similar to that of activated carbon for reactive and disperse dyes". As noted by Weber (1994) for reactors operated at a 3 day HRT, influent color fluctuations for the 4 and 7 day HRT operations were reflected in effluent color levels. Influent and effluent COD also exhibited

comparable patterns. Incorporation of some type of equalization basin would help to smooth the peaks and likely produce lower, more consistent effluent concentrations.

Influent and effluent DOC for the 7 day HRT operation is illustrated in Figure 26. DOC was not measured in the 4 day HRT study. Removals range from 84 to 88% and are comparable to the COD removals exhibited by the reactors in the 7 day operation which were 89 to 92%.

Operation of the reactors with a 7 day HRT produced significantly higher COD and DOC removal than operation with a 4 day HRT. More color was also removed by operation at the 7 day HRT, but removal of color was not as great as the removals of COD and DOC. The increased removals were accomplished with almost identical MLSS concentrations. Influent organic and color concentrations did not vary significantly between the two HRT levels; therefore, no measurable degradation occurred in the influent over the additional three days of treatment provided by the 7 day HRT operation.

Due to the various chemicals and auxiliaries used by the textile industry, the influent was likely composed of three levels of organic matter; easy, moderately difficult and very difficult to degrade materials. In allowing three additional days for the biomass to be in contact with the influent, further opportunity for degradation of the moderately difficult organic matter was provided. The biomass concentrations may have remained stable due to their

ability to degrade a larger fraction of substrate. Theoretically, biomass populations that treat more readily biodegradable waste, such as domestic waste, would decline in response to an increase in HRT.

Dilution was a mechanism that may have been acting to produce greater degradation in the 7 day HRT reactor operations. A form of equalization was occurring in the reactor's contents due to dilution of the high strength influent by the lower strength of the reactor's contents. The 7 day HRT operation influent concentration averaged 1672 mg/L and the average reactor COD concentrations ranged from 141 to 187 mg/L; therefore, dilution factors ranged from 9 to 12. Influent COD in the 4 day HRT operation averaged 1765 mg/L, while average reactor COD concentrations ranged from 475 to 1010 mg/L. Dilution factors for the 4 day HRT operation were therefore significantly lower, in the area of 2 to 4. Because the concentration of organics and other inhibitory matter that was felt by the biomass was less during the 7 day HRT operation due to dilution, it is possible the biomass reacted to the dilution and were able to further degrade the substrate.

Sorption of organic matter, as opposed to pure biodegradation, may account for a part of the reduced effluent organic levels seen in the 7 day HRT reactor operation. Table 8 illustrates a comparison of effluent TSS and differences between effluent total and soluble COD (ΔCOD) for the 3 day and 7 day HRT operations. This table may show that sorption was a mechanism that

Table 8. Relationship of COD to effluent TSS

7 DAY HRT						
θ_c (days)	Sol. COD (mg/L)	Tot. COD (mg/L)	Δ COD (mg/L)	Eff. TSS (mg/L)	ΔCOD / Effluent TSS	MLSS (mg/L)
15	39	151	112	24	4.7	1555
	80	200	120	16	7.5	1298
	153	204	51	42	1.2	1728
Average	91	185	94	27	3.5	1527
20	8	77	69	14	4.9	1775
	144	184	40	9	4.4	1642
	--	165	--	11	--	1572
Average	76	142	66	11	6	1663
30	73	147	74	5	14.8	2013
	80	180	100	5	20	1938
	172	169	0	15	0	2300
Average	108	165	57	8	11.6	2084
3 DAY HRT						
θ_c (days)	Sol. COD (mg/L)	Tot. COD (mg/L)	Δ COD (mg/L)	Eff. TSS (mg/L)	Avg ΔCOD / Avg TSS	MLSS (mg/L)
	836	1164	328	--	---	1735
15	838	1472	634	--	--	1610
	881	1818	937	--	--	1750
	1332	1572	240	--	--	--
Average	972	1507	535	--	--	1698
	554	641	87	--	--	2620
	560	680	120	--	--	2570
20	661	669	8	--	--	2660
	664	688	24	--	--	2605
	516	556	40	--	--	2140
Average	591	647	56	80	0.8	2039
	649	765	116	--	--	3390
	600	688	88	--	--	3355
30	775	816	41	--	--	3325
	672	752	80	--	--	3380
	198	278	80	--	--	3450
Average	579	660	81	78	1.0	3380

occurred during the 7 day HRT operation based on the values of ΔCOD and the small values of TSS, however, sufficient data does not exist to completely support the theory. The ΔCOD to TSS ratios were greater during the 7 day HRT operation than during the 3 day HRT operation for both the 20 and 30 day θ_c reactors. These ratios may additionally signify levels of treatment, with larger values signifying better treatment than smaller values. The ΔCOD value for the 30 day θ_c, 7 day HRT operation contradicted the theory described above. Effluent TSS values for the 3 day HRT were not identifiable for the exact time period that the total and soluble COD values were determined. The values that appear in the table for the 3 day HRT operation were average TSS values reported by Weber (1994). Batch tests would have provided further insight into sorption.

Average pH, temperature and dissolved oxygen concentrations appear in Table 9. No distinction was made between 4 and 7 day HRT operation due to the fact that no significant differences appeared in these parameters during those two operations. Influent pH was maintained between 7 and 8 with additions of 1 N sodium hydroxide, when necessary. Effluent pH levels ranged from 7.7 to 8.4 and averaged 7.9 to 8.0. Dissolved oxygen (DO) levels ranged from 4.1 to 7.5 mg/L and averaged 5.8 to 6.9 mg/L. Temperatures ranged from 21 to 26 °C and averaged 24.1 to 24.3 °C. The reactors were located on a bench top next to windows in a laboratory that was not temperature controlled.

Weber (1994) performed the 3 day HRT operation in a temperature controlled environment, away from natural light. Weber reported average effluent temperatures, pH and DO concentrations of 18.5±1 to 18.8±1 °C, 7.35 to 7.45, and 4.5 to 6.0 mg/L, respectively.

Table 9. Average pH, temperature and DO for CFRs

θ_c, days	pH	Temperature, °C	DO, mg/L
15	7.9	24.1	5.8
20	8.0	24.3	6.9
30	8.0	24.2	6.7

4.2.2 Kinetic Coefficient Analysis

The steady state operation kinetic coefficients calculated for the 4 day and 7 day HRT treatment operations for this waste were determined using the method outlined in Appendix H, Determination of Kinetic Coefficients, (Metcalf and Eddy, Inc., 1991). Kinetic coefficients were calculated for each of the HRT operations. The coefficients are necessary for the design of biological kinetic models and are defined by Metcalf and Eddy (1991) as;

(1) K_s - half velocity constant, the substrate concentration at one half of the maximum growth rate, mass/unit volume

(2) k - maximum rate of substrate utilization per unit mass of microorganisms, $time^{-1}$

(3) Y - maximum yield coefficient, mass/mass

(4) k_d - endogenous decay coefficient, time^{-1}

The first step in the determination of kinetic coefficients involved plotting the specific utilization rate U, versus the substrate concentration S, and then S versus the sludge age or mean cell residence time, θ_c. Average steady state values from Table 7 were used.

$$= \frac{S_0 - S}{\theta X}$$

where: S_0 = average influent COD, mg/L

S = average effluent COD, mg/L

θ = hydraulic residence time, HRT, days

X = average mixed liquor volatile suspended solids, MLVSS, mg/L

The nonbiodegradable substrate concentration S*, was estimated from these graphs. Figures D1 and D2 illustrate S* and are included in Appendix D. This non-biodegradable fraction was subtracted from the averaged values of substrate concentration in all the following equations in order to account for only the degradable substrate in determination of the kinetic coefficients. Tables D1 and D2 list all of the parameters that were used in determination of the kinetic coefficients, including those described below.

To determine K_s and k, $\frac{1}{U}$ was plotted against $\frac{1}{S-S^*}$ for each θ_c. The slope of the line that resulted is $\frac{K_s}{k}$ and the intercept is $\frac{1}{k}$.

$$\frac{1}{U} = \frac{X\theta}{S_0 - (S-S^*)} = \frac{K_s}{k}\frac{1}{S-S^*} + \frac{1}{k}$$

To determine Y and k_d, $\frac{1}{\theta_c}$ was plotted against U. The slope of the line that resulted is Y and the intercept is $-k_d$.

$$\frac{1}{\theta_c} = YU - k_d$$

Linear regressions were performed to determine the best fit line through the data points. These regressions are included in Tables D1 and D2. The results of the kinetic coefficient analysis are listed in Table 10. The graphs of the best fit lines used for kinetic coefficient determination are illustrated on Figures 27 and 28. Coefficient determination was sensitive to the choice of steady state time period. K_s and k were more sensitive to variations in steady state time period assumptions than Y and k_d. Table 10 includes additional results from the 3 day HRT study (Weber, 1994), and results from a study by Ghosh *et al.* (1978) concerning aerobic treatment of effluent from a textile dyeing and finishing mill alone (Mill), and in combination with municipal waste effluent

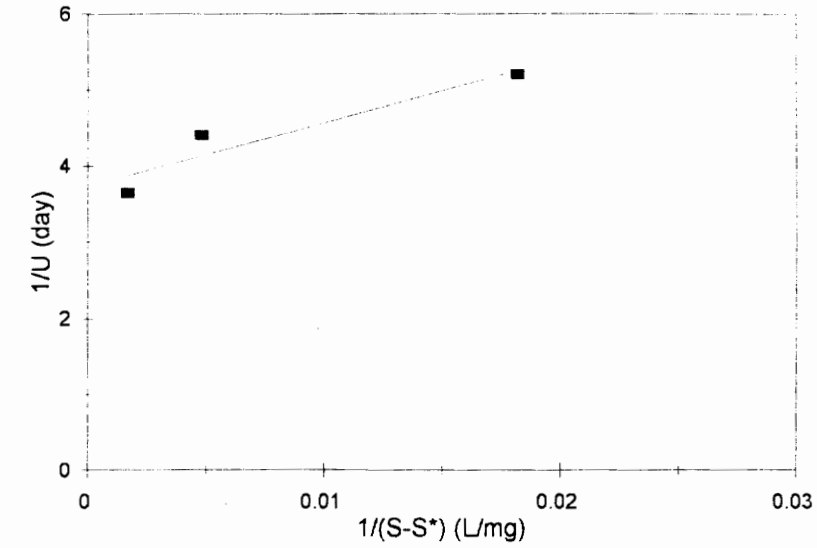
(Mill plus Municipal). Also included for comparison purposes is the maximum specific growth rate, μ_m. Maximum specific growth rate is equal to the product of the utilization rate constant, k, and the maximum yield coefficient, Y:

$$\mu_m = kY$$

Table 10. Kinetic coefficient results and comparative values

Study or Type	K_s, mg/L	k, day^{-1}	Y	k_d, day^{-1}	μ_m, day^{-1}
3 Day HRT	--	--	0.62	0.03	--
4 Day HRT	22	0.27	0.41	0.04	0.11
7 Day HRT	2.6	0.16	0.74	0.05	0.12
Mill	not reported	0.19	0.52	0.013	0.10
Mill plus Municipal	40	0.24	0.53	0.024	0.13

Similarity exists between coefficients k, Y and k_d, but the value of K_s for the 7 day HRT operation is low compared to the other values of K_s. That value may be a result of the inherent variability in estimating S*, or the value may indicate the type of degradation that occurred during the 7 day HRT operation. Maximum specific growth rates for the 4 and 7 day HRT CFR operations were nearly identical, 0.11 and 0.12 day^{-1}. The values for the Mill and Mill plus Municipal are also similar at 0.10 and 0.13 day^{-1}. That similarity may be representative of the fact that all the waste streams were from textile manufacturing processes.



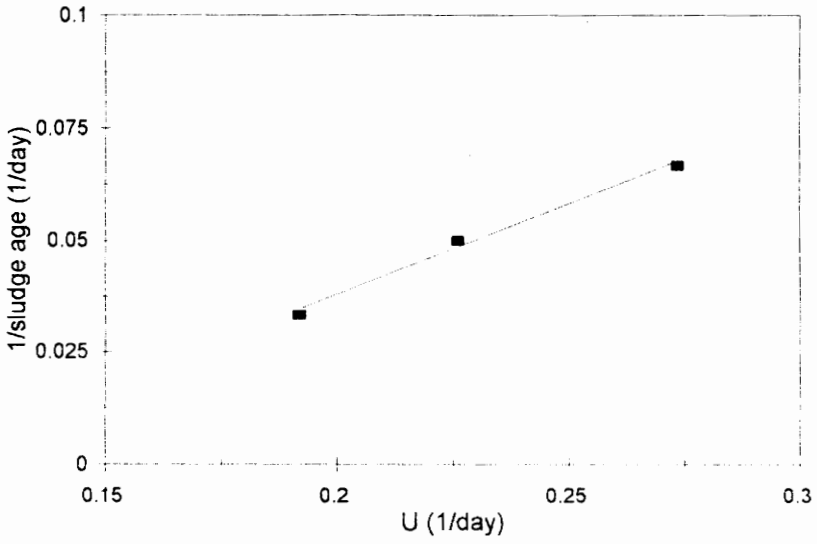
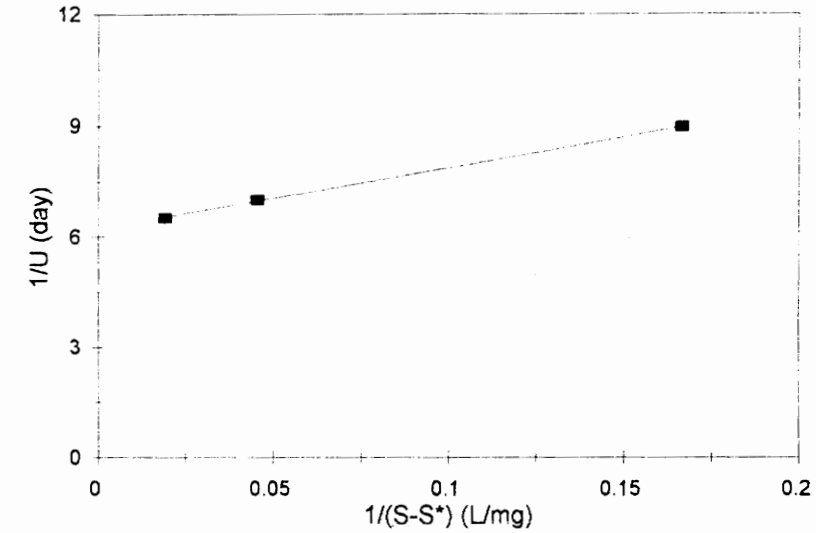


Figure 27. Kinetic coefficients K_s, k, Y and k_d for 4 day HRT CFR operations



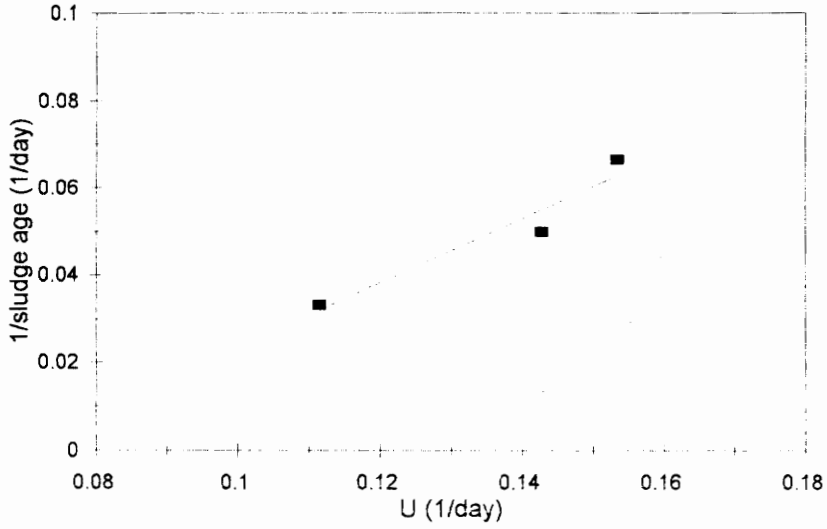


Figure 28. Kinetic coefficients K_s, k, Y and k_d for 7 day HRT CFR operations

The maximum yield coefficient, Y, is often corrected to account for the loss of biomass through death and decay. According to Metcalf and Eddy (1991), the "effects of endogenous respiration on the net bacterial yield are accounted for by defining the observed yield as a ratio of the net rate of bacterial growth (mass/unit volume·time) and the substrate utilization rate (mass/unit volume·time) ". The following equation was used in determining the measured observed yield, Y_{obs}, for each HRT operation and θ_c. All parameters are as described in section 3.2.2, Biological Treatment, and previously in this section.

$$Y_{obs} = \frac{\Delta X}{\Delta S} = \frac{XQ_w + QX_e}{(S_0 - S)Q}$$

Table 11 and Figure 29 illustrate the results of the observed yield calculations. The 7 day HRT operation produced the largest measured observed yield when compared to the observed yields of the 3 and 4 day HRT operations. The larger observed yield displayed by the 7 day HRT CFR operation relates to the improved treatment seen during that operation, with biodegradation evidently enhanced.

Table 11. Measured observed yields for 3, 4, and 7 day HRT CFR operations

3 day HRT (Y = 0.620)	15 day θ_c	20 day θ_c	30 day θ_c
MLVSS, X (mg/L)	1598	2117	2913
Δ COD, S (mg/L)	870	980	1051
TSS, X_e (mg/L)	88	100	66
Flow, Q (L/day)	3.33	3.33	3.33
Wastage, Q_w (L/day)	0.483	0.343	0.256
Measured Y_{obs}, (mg/mg)	0.37	0.33	0.28
4 day HRT (y = 0.41)	15 day θ_c	20 day θ_c	30 day θ_c
MLVSS, X (mg/L)	1074	1721	2227
Δ COD, S (mg/L)	755	1137	1290
TSS, X_e (mg/L)	38	127	80
Flow, Q (L/day)	2.5	2.5	2.5
Wastage, Q_w (L/day)	0.58	0.32	0.24
Measured Y_{obs}, (mg/mg)	0.38	0.30	0.23
7 day HRT (Y = 0.74)	15 day θ_c	20 day θ_c	30 day θ_c
MLVSS, X (mg/L)	1508	1651	2134
Δ COD, S (mg/L)	1485	1515	1531
TSS, X_e (mg/L)	30	89	72
Flow, Q (L/day)	1.43	1.43	1.43
Wastage, Q_w (L/day)	0.64	0.42	0.29
Measured Y_{obs}, (mg/mg)	0.47	0.38	0.33

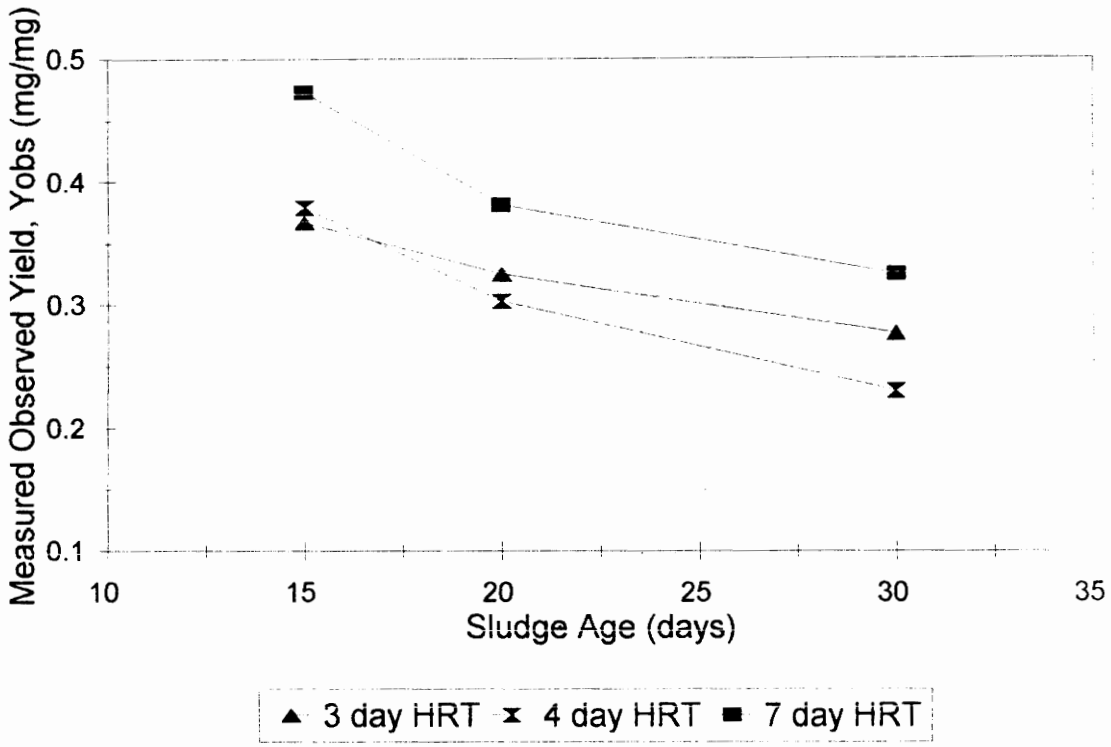


Figure 29. Measured observed yields for 3, 4, and 7 day HRT CFR operations

4.2.3 Organic Removal

BOD analyses were limited in the 4 and 7 day HRT operations. A summary of BOD_5, COD and DOC for 3 (Weber, 1994), 4 and 7 day HRT operations is provided in Table 12. Included in Table 13 are the corresponding BOD/COD ratios and additional data representing a combination BOD_{20}/BOD_5 analysis. A BOD_{20} analysis was conducted, then BOD_5 concentrations were determined for samples from the BOD_{20} bottles.

Average influent COD's for both 4 and 7 day HRT operation, 1765 and 1672 mg/L, were greater than the average value for 3 day operation, 1464 mg/L. Soluble COD removal was nearly equal for the 3 day (Weber, 1994) and 4 day HRT operations with removals ranging from 43 to 73%. The greatest average removals resulted from 7 day operation and ranged from 89 to 92%.

DOC analyses were not performed for the 4 day operation, but average influent values for 3 and 7 day operation were closer at 418 and 475 mg/L, respectively. The influent DOC range at 3 day HRT operation, 238 to 779 mg/L, was greater than the 7 day operation range which was 400 to 556 mg/L. Removals were again greater at 7 day operation, ranging from 86 to 90%. Removal ranges from 54 to 69% were reported by Weber (1994) for 3 day HRT operation.

BOD analyses were conducted during operation periods which were not ultimately included in steady state periods. BOD_5 samples and corresponding

Table 12. Organic removals for 3,4 and 7 day HRT operations

3 DAY HRT								
TEST (mg/L)	Influent Range	Ave	15 day sl. age Range	Ave	20 day sl. age Range	Ave	30 day sl. age Range	Ave
Sol. BOD5	203-318	237	30-158	90	52-100	67	42-105	72
% Removal			29-85	63	69-75	72	64-82	70
# Trials	5		5		5		5	
Tot. BOD5	287-695	435	158-184	171	207-254	231	88-288	214
% Removal			36-57	47	27-64	48	40-71	57
# Trials	7		4		5		5	
Sol. COD	809-1960	1464	220-881	588	60-808	498	40-775	563
% Removal			18-76	59	45-94	66	44-96	69
# Trials	15		23		43		45	
DOC	238-779	418	97-272	174	117-234	190	95-197	136
% Removal			43-63	54	42-75	56	62-78	69
# Trials	20		5		6		6	
	4 DAY HRT							
TEST (mg/L)	Influent Range	Ave	15 day sl. age Range	Ave	20 day sl. age Range	Ave	30 day sl. age Range	Ave
Sol. BOD5		172		62		67		84
% Removal				64		61		51
# Trials	1		1		1		1	
Sol. COD	1386-2345	1765	710-1300	1010	400-948	628	225-670	475
% Removal			34-53	43	52-76	64	63-86	73
# Trials	10		10		10		10	
DOC								
% Removal								
# Trials	0		0		0		0	
	7 DAY HRT							
TEST (mg/L)	Influent Range	Ave	15 day sl. age Range	Ave	20 day sl. age Range	Ave	30 day sl. age Range	Ave
Sol. BOD5			<12		<12		<12	
% Removal								
# Trials	0		1		1		1	
Tot. BOD5	<80		<12		<12		<12	
% Removal			>85		>85		>85	
# Trials	1		1		1		1	
Sol. COD	891-2763	1672	87-252	187	103-211	157	78-189	141
% Removal			85-92	89	86-95	91	83-97	92
# Trials	9		9		7		9	
DOC	400-556	475	36-86	65	35-71	57	32-70	48
% Removal			82-92	86	86-91	88	84-92	90
# Trials	9		9		7		9	

Table 13. BOD/COD ratios for 4 and 7 day HRT CFR operations

4 DAY HRT				
TEST (mg/L)	Influent	15 day sl. age	20 day sl. age	30 day sl.age
Sol. BOD5	172	62	67	84
% Removal		64	61	51
Sol. COD	2171	1153	1531	1443
% Removal		47	29	34
BOD5/COD	0.08	0.05	0.04	0.06
7 DAY HRT				
TEST (mg/L)	Influent	15 day sl. age	20 day sl. age	30 day sl.age
Tot. BOD5	<80	<12	<12	<12
% Removal		>85	>85	>85
Sol. BOD5	--	<12	<12	<12
% Removal		--	--	--
Sol. COD	1050	103	92	80
% Removal		90	91	92
BOD5/COD	--	<0.12	<0.13	<0.15
7 DAY HRT*				
TEST (mg/L)	Influent	15 day sl. age	20 day sl. age	30 day sl.age
Sol. BOD20	1194	<60	<60	<60
% Removal		>95	>95	>95
Sol. COD	1312	107	199	167
% Removal		92	85	87
BOD20/COD	0.91	0.56	0.3	0.36
Sol BOD5	<120	<3	<3	<3
% Removal		>98	>98	>98
Sol. COD	--	9	9	8
% Removal		--	--	--
BOD5/COD	--	<0.33	<0.33	<0.37

*See text for description of this section of table

results from the 4 day HRT operation period were collected during the time of the filamentous problem which existed in the reactors and is described in section 4.2.1. Weber (1994) reported average effluent soluble BOD_5 concentrations for the 15, 20 and 30 day θ_c reactors, respectively, of 90, 67 and 72 mg/L at the 3 day HRT operation. Corresponding effluent soluble BOD_5 concentrations for the 4 day operation were 62, 67 and 84 mg/L, respectively. The 15 day θ_c reactor was the least affected by the filamentous growth and consequently produced the lowest effluent BOD_5 concentration. If the 20 and 30 day reactors had been operating without trouble, effluent soluble BOD_5 concentrations for the 4 day HRT operation would have most likely been less than 62 mg/L. BOD samples from the 7 day HRT operation were analyzed prior to day 62, which was the start of steady state operation. The total and soluble BOD_5 analysis results indicate that the 7 day operation produced a reduction of BOD_5 to levels less than 12 mg/L for all reactors. A total BOD_5 effluent limit of 15 mg/L is currently being proposed for the Plant.

Table 13 illustrates the results of the various BOD analyses which were performed on reactor influents and effluents coupled with BOD/COD ratios. Ratios of soluble BOD_5/COD for the 4 day operation effluents, 0.04 to 0.06, are less than those reported by Weber (1994), 0.14 to 0.16. As described above, effluent soluble BOD_5 concentrations for 3 and 4 day HRT operations were similar. Effluent COD values that were used to produce the BOD_5/COD ratios for

the 3 day HRT operation ranged from 498 to 588 mg/L (Weber, 1994). Effluent COD values for the 4 day operation ranged from 1153 to 1531 mg/L, therefore causing the calculated ratios for the 4 day operation to be less than those of the 3 day operation. Ratios resulting from the 7 day HRT operation were more similar to Weber's (1994) results, ranging from less than 0.12 to less than 0.15. In this case, effluent BOD_5 values were low, as were corresponding COD values. All BOD_5/COD ratios were below 0.5. Wastes with low BOD_5/COD ratios are often difficult to degrade and can contain a residual fraction that is non-degradable. BOD_5/COD ratios are often misleading as low values can indicate toxic or refractory material, or material that is just slower to biodegrade.

Table 13 also contains results from the combination BOD_{20}/BOD_5 analysis. Influent BOD_{20} was 1194 mg/L, while effluent BOD_{20} concentrations were less than 60 mg/L. The subsequent BOD_5 analysis, performed on samples from the BOD_{20} analysis, produced concentrations of less than 120 mg/L for the influent and less than 3 mg/L for all reactor effluents. BOD_{20}/COD ratios ranged from 0.91 for the influent to 0.56, 0.3 and 0.36 for the 15, 20 and 30 day θ_c reactors, respectively. The BOD_5/COD analysis performed on effluent from the BOD_{20}/BOD_5 test produced ratios of 0.33, 0.33 and 0.37 for the 15, 20 and 30 day θ_c reactors, respectively. Apparently, degradable material was present, due to the fact that COD concentrations were reduced significantly to 8 and 9 mg/L, although a longer time period of greater than 20 days was required to more

completely degrade the samples.

4.2.4 Nutrient Removal

Table 14 lists the concentrations of total phosphorus (Total P), orthophosphate (Ortho P), total Kjeldahl nitrogen (TKN), and ammonia nitrogen (NH_3-N) that were measured in the influents and effluents of the 4 and 7 day HRT operations.

Weber (1994) reported a range of removals of Total P from 69 to 76% for the 3 day HRT operation. A similar range of 59 to 76% removal resulted from the 4 day operation. An average of 90% was removed in each reactor during the 7 day HRT operation. Ortho P concentrations were not measured in the effluents from the 4 day operation, but Ortho P was not detected in any of three tests which were conducted on effluents from the 7 day operation. Likewise, Weber (1994) detected only a trace amount of Ortho P in one reactor and reported removals ranging from 80 to 100%.

TKN removals ranged from 58 to 71% for the 4 day operation, while Weber (1994) reported lower average removals of 39 to 56%. The 7 day HRT operation TKN removals ranged from 82 to 85%. According to Argaman (1991), increased nitrogen removal by assimilation can be achieved by maximizing the net sludge production. Although the largest net sludge production occurred in the 15 day θ_c reactor during the 7 day HRT operation, the effluent TKN

Table 14. Nutrient removals for 4 and 7 day HRT CFR operations

4 DAY HRT				
TEST mg/L	Influent Range Av	15 day sl. age Range Ave	20 day sl. age Range Ave	30 day sl. age Range Ave
Total P	3.4	1.1	0.8	1.4
% Removal				
# Trials	1	1	1	1
Ortho P	ND			
% Removal				
# Trials	2	0	0	0
TKN	31	11	13	9
% Removal		65	58	71
# Trials	1	1	1	1
NH3 - N	16.2			
% Removal				
# Trials	1	0	0	0
7 DAY HRT				
TEST mg/L	Influent Range Av	15 day sl. age Range Ave	20 day sl. age Range Ave	30 day sl. age Range Ave
Total P	4-8 6	0.4-0.7 0.6	0.3-0.8 0.6	0.3-1 0.6
% Removal		82-95 90	79-96 90	85-96 90
# Trials	3	3	3	3
Ortho P	ND-1.2 0.8	ND	ND	ND
% Removal				
# Trials	6	3	3	3
TKN	30-46 39	4-9 7	5-10 7	5-9 6
% Removal		74-91 82	76-84 82	78-88 85
# Trials	4	4	4	4
NH3 - N	15-28 21	0	0	0
% Removal		100	100	100
# Trials	4	4	4	4

concentrations were nearly equal for all reactors. Although effluents from 4 day operation were not analyzed for NH_3-N concentrations, NH_3-N was not detected in any of the four tests that were conducted to determine NH_3-N concentrations in effluents from the 7 day operation. It would be reasonable to assume that none or very low levels existed in 4 day effluents, especially since Weber (1994) reported NH_3-N levels of 2 to 4 mg/L in the 3 day HRT effluents. The corresponding removals for the 3 day HRT operation were 82 to 92%.

Weber (1994) reported a BOD_5:N:P ratio of 100:9:0.7, and cited similarity to the ratio suggested for use by Shriver and Daugue (1978), of 100:5:1. The 100:5:1 ratio is often used to achieve optimal performance when treating dye wastewater. Sufficient BOD_5 data to use in ratio estimation was not collected during the 4 and 7 day operation, but it is reasonable to assume that average influent BOD_5 values would have been similar to those reported by Weber (1994), since the same type of waste was delivered over the course of the entire study. Average influent Total P and TKN values for 4 and 7 day operation, 3.4 and 31, and 6 and 39 mg/L, respectively, were similar to those values, 2.9 and 36 mg/L, reported by Weber (1994) for 3 day operation. The BOD_5:N:P ratio for 4 and 7 day operation should therefore be similar to the value of 100:9:0.7 that was reported by Weber (1994).

4.2.5 Metal and Anion Removal

Soluble cation and anion concentrations (μg/L and mg/L, respectively) which resulted from analyses described in sections 3.3.8.1 and 3.3.9 are shown in Tables 15 and 16. Table 15 presents the results of the analyses that were performed on the waste streams (dye, print, pretreated dye and print, and bleach and finish) during the chemical pretreatment step described in section 3.2.1. Color was the only other parameter that was determined for the waste streams during pretreatment due to the extent of the work done previously by Weber (1994). Color data appears in Table C5 in Appendix C. Table 16 presents the results of the metal and anion analyses that were conducted on the reactor influent and effluents over the course of the CFR operation at both 4 and 7 day HRT levels. Value ranges and averages are shown in both tables. Following the results and discussion of the soluble cations and anions shown in Table 16 are the results of the total chromium and soluble hexavalent chromium analyses that were performed on reactor influent and effluents. The analysis methods are described in sections 3.3.8.2 and 3.3.8.3. Total chromium and soluble hexavalent chromium were analyzed during the 7 day HRT operation only.

The Plant faces proposed monthly average discharge limits for total recoverable copper, zinc and silver, dissolved hexavalent chromium and total chromium of 4.63, 32.8, 0.59, 8.4 μg/L and 5.2 kg/day, respectively. Based on an average flowrate at the Plant of 1 million gal/day (MGD), the total

Table 15. Cation and anion concentrations in waste streams prior to CFR treatment

WASTE STREAMS	Thermosol Dye	Print	Pretreated Dye/Print	Bleach and Finish
CATIONS ug/L	Range Ave	Range Ave	Range Ave	Range Ave
Chromium	1.3-11 5	2-4 2	0.7-7 3	ND-7 3
# Trials	8	8	8	8
Copper	12-266 68	12-324 91	10-137 39	ND-146 73
# Trials	8	8	8	8
Silver	ND-0.4 0.1	ND-0.2 0.04	ND-0.2 0.03	ND
# Trials	8	8	8	8
Zinc	30-150 69	70-850 301	50-130 78	ND-690 225
# Trials	8	8	8	8
ANIONS mg/L				
Chloride	9-18 12	9-19 12	12-20 15	ND-47 26
# Trials	7	7	8	8
Nitrate-N	0.4-1.0 0.6	ND-0.6 0.3	ND-1.0 0.6	ND-1.2 0.3
# Trials	7	7	8	8
Ortho P	ND-0.2 0.04	ND	ND	2-4 3
# Trials	5	5	5	5
Sulfate	354-905 539	8-59 30	292-1242 730	ND-73 37
# Trials	7	7	8	8

Table 16. Cation and anion concentrations in the influent and effluents for 4 and 7 day HRT CFR operations

		4 DAY HRT		
CATIONS ug/L	Influent Range Ave	15 day sl. age Range Ave	20 day sl. age Range Ave	30 day sl. age Range Ave
Chromium	ND-3 2	3	2	3
# Trials	5	1	1	1
Copper	ND-170 69	15	37	20
# Trials	5	1	1	1
Silver	ND	ND	ND	ND
# Trials	5	1	1	1
Zinc	ND-230 128	130	340	340
# Trials	5	1	1	1
ANIONS mg/L				
Chloride	20-40 26	24-45 35	27-992 510	25-128 77
# Trials	5	2	2	2
Nitrate-N	ND-0.6 0.3	0.4	0.4-0.6 0.5	0.3
# Trials	5	2	2	2
Ortho P	ND			
# Trials	2	0	0	0
Sulfate	292-561 470	268-767 518	270-747 509	264-768 516
# Trials	5	2	2	2
		7 DAY HRT		
CATIONS ug/L	Influent Range Ave	15 day sl. age Range Ave	20 day sl. age Range Ave	30 day sl. age Range Ave
Chromium	2-12 5	3-4 3	2-16 7	2-4 3
# Trials	7	3	3	3
Copper	11-126 48	5-33 20	3-63 26	4-57 23
# Trials	7	3	3	3
Silver	ND-0.2 0.03	ND-0.2 0.07	ND-1.5 0.5	ND
# Trials	7	3	3	3
Zinc	80-790 273	160-420 280	160-410 297	180-390 310
# Trials	7	3	3	3
ANIONS mg/L				
Chloride	21-27 23	24-27 26	23-27 25	25-32 29
# Trials	6	3	3	3
Nitrate-N	0.1-0.6 0.4	0.2-1 0.6	0.3-3 2	1-8 5
# Trials	6	3	3	3
Ortho P	ND-1.2 0.8	ND	ND	ND
# Trials	6	3	3	3
Sulfate	327-664 506	516-742 664	526-744 655	557-804 704
# Trials	6	3	3	3

chromium concentration limit translates to 1.4 mg/L.

Silver was not detected (ND) in the reactor effluents during 4 day HRT operation, but very low levels were detected once in the 15 day and 20 day θ_c reactor effluents during 7 day HRT operation. Average soluble silver concentrations remained below discharge limits. On average, both copper and zinc concentrations present in the dye and print streams were reduced by 50% through chemical pretreatment. Reactor effluent concentrations of both soluble zinc and soluble copper from both 4 and 7 day HRT operations are above the proposed limits. If the proposed limits are enacted, the Plant will need to enhance removals of these metals. Copper was removed more readily through biological treatment than was zinc. Measured zinc concentrations increased from the influent to the effluent stage. Results show that the range of total soluble chromium levels in the reactor effluents, 2 to 7 μg/L, was consistently below the discharge limit for soluble hexavalent chromium which was 8.4 μg/L . This result indicates that the limit for soluble hexavalent chromium was met throughout the 7 day HRT operational period of the reactors.

Concentrations of chloride, nitrate-N, Ortho P and sulfate in mg/L are shown in Tables 15 and 16. Sulfate levels rose as a result of pretreatment due to the presence of aluminum sulfate in the polymer AL220. Nitrate-N levels remained fairly constant in the 4 day HRT operation, but increased from influent to effluent in the 7 day HRT operation. Ortho P was not detected in the influent

of the 4 day operation, possibly due to the fact that only two measurements were conducted. Ortho P was found in the 7 day HRT influent, averaging 0.8 mg/L. Conversely, none was evident in the reactor effluents.

As described in section 3.3.8.2, total chromium was measured to determine if compliance with the discharge limits was possible. Total chromium was measured twice during the 7 day HRT operation. Average concentrations for the influent, 15 , 20 and 30 day θ_c reactors were 6.3, 2.6, 0.8 and 1.7 μg/L, respectively. All concentrations were determined to be below the proposed limit of 1.4 mg/L, which was calculated based on the permit specified load limit of 5.2 kg/day and an average flow of 1 MGD.

During 7 day HRT operation, a standard additions curve experiment was performed to directly determine concentrations of soluble hexavalent chromium that were present in the reactor influent and effluents. This type of experiment was performed due to the color of the waste interfering with the colorimetric method for determining soluble, hexavalent chromium concentrations. The color of the samples interfered in the standard additions experiment also. Results from the total unfiltered and total soluble analyses detailed above for the bench scale treatment were averaged over the number of tests that were performed. Although all effluent total and soluble chromium averages were less than proposed soluble hexavalent chromium monthly average limits, upper range results for total soluble chromium did at times exceed soluble hexavalent

chromium limits. As the chromium limits are with respect to monthly averages and average results from the 7 day HRT operation were below those permitted averages, soluble hexavalent chromium concentration limits should not be exceeded since hexavalent chromium is only a part of the total chromium concentrations which were measured.

Efforts to reduce the input of metals like chromium and others that are regulated are currently underway through pollution prevention programs that are being implemented by the Plant.

4.2.6 Toxicity Evaluation

The results of the short term chronic and acute toxicity tests that were conducted on 15 and 30 day θ_c effluents from the 7 day HRT operation are shown in Table 17. Also included in the table are the results of the short term toxicity tests performed on waste samples from the 3 day HRT operation (Weber, 1994).

The Plant's proposed NOEC limit for chronic toxicity is 68% (chronic toxicity unit, TU_c=1.46). Although the State has not stipulated an acute toxicity limit for the Plant, LC50 values of greater than 100% in acute tests are usually necessary for compliance with the biomonitoring requirements in typical NPDES permits. All toxicity tests that were conducted on samples from the 7 day HRT operation were passed with NOEC values of 100% and LC50 values greater

Table 17. Effluent toxicity results

θ_c, days	NOEC STCPp*, % 3 day HRT	LOEC STCPp*, % 3 day HRT	NOEC STCPp*, % 7 day HRT	NOEC STCDp#, % 3 day HRT	LOEC STCDp#, % 3 day HRT	LC50 ACd•, % 7 day HRT
15	25	50	100	50	75	>100
20	50	75	--	50-75	75-100	--
30	<25	25	100	50-75	75-100	>100

*Short term chronic toxicity tests with *Pimephales promelus*
#Short term chronic toxicity tests with *Daphnia pulex*
•Acute toxicity tests with *Ceriodaphnia dubia*

than 100%. Table 17 illustrates that operation at the 3 day HRT resulted in test failure as NOEC values were less than 100% in every case. At the time toxicity analyses were performed on the effluents from the 3 day HRT operation, the Plant's NOEC limit for chronic toxicity was 100%. The increased HRT value appeared to provide the additional treatment which was necessary to reduce the toxicity of the samples to a level which does not cause test failure.

Levels of COD and color, and percent removals of these parameters, may be possible indicators of toxicity. Average 7 day HRT operation effluent COD and color concentrations (percent removals in parenthesis) were 121 (89%) to 150 (83%) mg/L and 98 (69%) to 107 (48%) ADMI units during tests with the 30 day θ_c reactor effluent. The COD and color values for the tests with the 15 day θ_c effluent were 153 (90%) to 252 (90%) mg/L and 115 (65%) to 174 (35%) ADMI units. Conversely, Weber (1994) reported average COD and color values of 831

mg/L and 250 ADMI units during the time period that 3 day HRT samples were tested for chronic toxicity with *Pimephales promelus*, and 515 mg/L and 93 ADMI units when samples were tested for chronic toxicity with *Daphnia pulex*. Average COD and color removals were 52 and 36%, and 56 and 61%, during *Pimephales promelus* and *Daphnia pulex* chronic testing, respectively. The average color value of 93 ADMI units would be higher if data for the 15 day θ_c reactor had been available for inclusion in the averaging process. Only data from the 20 and 30 day θ_c reactors was available. COD levels, more than color levels, may serve as indicators of effluent toxicity, as COD levels were much higher during the 3 day HRT operation toxicity analyses.

CHAPTER V. SUMMARY and CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY and CONCLUSIONS

The thermosol dye, print and bleach and finish waste streams have been analyzed and treated at Virginia Tech from May of 1993 through November of 1994. Waste characterization was performed initially, followed by pretreatment experiments with individual and combinations of the waste streams. A pretreatment scheme was adopted for a combination of the thermosol dye and print waste, which in combination with the bleach and finish stream, was subsequently treated aerobically and biologically with bench scale reactors. That portion of the research is described fully by Weber (1994). The research described herein began in early 1994. The focus was successful treatment of the bleach and finish waste stream, further work with the bench scale reactors using identical sludge ages but higher HRT levels than Weber, and further toxicity testing due to the fact that the effluents from Weber's research had failed toxicity tests.

The conclusions drawn from this research are described below.

(1) Pretreatment of the bleach and finish waste stream did not produce promising results. The organic content of the waste stream was difficult to remove and, in almost every case, was unaffected by any of the pretreatment methods considered. On one occasion, Nalco polymer 9764 was able to remove

65% of the COD from the bleach and finish wastewater, but that instance was the only time more than 20% was removed. Although color is not a major component of the bleach and finish, it was readily affected by many of the pretreatment method combinations used. Removals were regularly greater than 35% at pH levels less than 6, in conjunction with either oxidation or oxidation and chemical coagulation. Color was most readily removed by coagulation with AL220, (84%).

(2) The bench scale biological reactor system operating at the 4 day HRT produced effluent that was nearly identical to the effluent produced by a 3 day HRT operation. Removals of COD ranged from 50 to 70% in both systems. Color removals were slightly better at the 3 day HRT operation, (42 to 53%), than the 4 day HRT operation, (31 to 42%). Coefficients, K_s, k, Y and k_d, were determined to be 22 mg/L, 0.27 day^{-1}, 0.41, and 0.04 day^{-1} , respectively, for the 4 day HRT operation.

(3) Reactors operating at the 7 day HRT level produced far better results than were noted in either the 3 or 4 day HRT operations. Interestingly, the MLSS concentrations did not decrease as a result of the reduced feed rate. COD removals ranged from 89 to 92%, whereas color removal ranged from 51 to 70%. Average effluent COD values ranged from 141 to 187 mg/L and color ranged from 122 to 200 ADMI. Kinetic coefficients, K_s, k, Y and k_d, were determined to be 2.6 mg/L, 0.16 day^{-1}, 0.74, and 0.05 day^{-1} , respectively, for the

7 day HRT operation. The increased levels of treatment may be the result of increased sorption by the biomass, or a type of equalization occurring in the reactors due to dilution of the high strength influent by the lower strength reactor contents. Although the biomass concentrations that were present during the 4 day and 7 day HRT operations did not differ significantly, the biomass present during the 7 day HRT operation was able to produce effluent with much lower COD. It is most likely that the increased time allotted during the 7 day HRT operation and dilution of organic matter allowed the biomass to achieve enhanced degradation of the more difficult to degrade organic matter that remained undegraded during the 4 day HRT operation.

(4) Effluents from both the 15 day and the 30 day θ_c reactors, during the 7 day HRT operation, were tested for chronic and acute toxicity with *Pimephales promelus* and *Ceriodaphnia dubia*, respectively. In each case, chronic tests resulted in NOEC values of 100% and acute tests resulted in LC50 values of greater than or equal to 100%. Effluents from the 3 day HRT reactor operation failed chronic tests; acute tests were not performed. The data suggested that COD level might serve as an indicator of toxicity. COD concentrations were between 121 and 252 mg/L and removals ranged from 83 to 90% during the 7 day HRT effluent toxicity tests. Conversely, average COD concentrations and removals during the 3 day HRT operation were 515 to 831 mg/L and 52 to 56%, respectively.

(5) Copper and zinc levels pose a problem as the 7 day HRT operation failed to reduce concentrations of these metals to levels below those mandated in the Plant's permit. The bleach and finish waste stream contributed the highest concentration of these metals, on average, when compared to the pretreated dye and print streams.

5.2 RECOMMENDATIONS

The following suggestions are listed as possible areas of further study concerning these waste streams and as possible operational changes for the Plant to incorporate into the treatment of the waste streams.

(1) Based on the results of the 7 day HRT biological reactor operation, pretreatment of the bleach and finish waste stream may not be necessary.

(2) The Plant, despite current operation at the recommended 7 day HRT level, should strive to better control the on-site activated sludge basin. System parameters, like MLSS and wastage, should be carefully monitored to produce optimum system performance. Incorporation of an equalization basin, prior to pretreatment of the dye and print streams, would help dampen surges into the aerated lagoon and improve the overall system performance.

(3) Although toxicity tests performed with effluent from the 7 day HRT bench scale operation were passed, effluent metals violations still pose a problem. Further work should be performed to determine ways in which metal

levels can be reduced to levels that are below those in the Plant's permit. Additional treatment or incorporation of a pollution prevention strategy may be necessary for further reduction of metal concentrations.

CHAPTER VI. REFERENCES

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APPENDIX A

Abbreviations

LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers Institute
BOD_5	5 day biological oxygen demand
BOD_{20}	20 day biological oxygen demand
CFR	continuous flow reactor
COD	chemical oxygen demand
EC50	concentration required to effect 50% of the test organisms
DAF	dissolved air flotation
DO	dissolved oxygen
DOC	dissolved organic carbon
HRT	hydraulic residence time
LC50	concentration required to kill 50% of the test organisms
MGD	million gallons per day
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
N	normality, chemical equivalence per liter
NH_3-N	ammonia nitrogen
NOEC	no observed effect concentration
Ortho P	orthophosphorus
POTW	publicly owned treatment works
ppm	parts per million, mg/L
SRT	sludge retention time, sludge age

Theta$_c$, θ_c	sludge age, sludge retention time
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
Total P	total phosphorus
TSS	total suspended solids

APPENDIX B

Waste Stream Pretreatment Data

Table B1. Experiments 1, 2 and 3

Experiment 1 (F): Bleach and finish particle size range determination, pH 6.9

Filter Size (um)	TSS (mg/L)	Color (ADMI)
Control	–	2032
>20-25	54	1791
>11	71	1591
>8	32	1477
>2	8	1454
1.5	104	1199
1.2	110	918

Experiment 3 (pH, F): Bleach and finish pH adjustment, then filtration through range of filters

Filter Size (um)	pH 5 TSS (mg/L)	pH 3 TSS (mg/L)
Control: See Experiment 1		
>20-25	20	95
>11	76	108
>8	48	111
>2	54	119
1.5	111	228
1.2	66	173

Experiment 2 (pH): effects of pH alteration on bleach and finish, color is unfiltered, apparent

pH	COD (mg/L)	Color (ADMI)
Control (6)	4197	814
5.5	4340	761
5	4242	875
4.5	4470	788
4	4047	794
3.5	3891	660
3	3898	615
2.5	2798	440
2	3703	306

Table B2. Experiments 4 and 5

Experiment 4 (O): Hydrogen peroxide addition, bleach and finish pH 6.1

Dose H2O2 (mg/L)	COD (mg/L)	TSS (mg/L)
0	5359	144
10		143
30		153
50	5887	154
75		149
100	4970	163

Experiment 5 (pH, O): pH alteration of bleach and finish with H2O2 doses of 100 mg/L

pH	COD (mg/L)	Color (ADMI)	DOC (mg/L)	TSS (mg/L)
Control (6.8)	3840	698	1476	336
6.8	3879	799	1489	91
5	3849	683	1401	127
4	3889	620	1433	133
3	3800	453	1234	144

Table B3. Experiments 6 and 8

Experiment 6 (pH, O, CC): repeat of Experiment 5 plus addition of 785 mg/L AL220

pH	COD (mg/L)	Color (ADMI)	DOC (mg/L)	TSS (mg/L)
Control (6.8)	3840	698	1476	336
6.8	3522	235	1268	150
5	3055	149	1195	150
4	3258	127	1197	177
3	3719	156	1260	119

Experiment 8 (pH, CC, O): reversed order of Experiment 6, not same shipment of bleach and finish, pH 9.8
Also tested samples with pH adjustment and AL220 addition only

	COD (mg/L)		Color (ADMI)		DOC (mg/L)		TSS (mg/L)	
	Control = 4940		Control = 662		Control = 1747		Control = 278	
pH	AL220	AL220/h.px.	AL220	AL220/h.px.	AL220	AL220/h.px.	AL220	AL220/h.px.
10.5	4861	--	625	--	1806	--	--	--
9.8	4330	4999	609	619	1699	1794	394	241
9	5058	--	619	--	1801	--	--	--
8	4330	--	623	--	1746	--	477	--
5	4861	4999	623	591	1676	1792	423	--
4.5	4605	4802	217	213	1522	1604	1656	955

Table B4. Experiments 7, 9 and 10

Experiment 7 (pH, CC): tested two AL220 doses and two pH levels on bleach and finish, based on results of Experiment 6

pH/ AL220 dose (mg/L)	COD (mg/L)	Color (ADMI)	DOC (mg/L)	TSS (mg/L)
Control	3840	698	1476	336
6.8/785	4186	585	1242	166
6.8/400	3861	683	1185	201
4.5/785	3861	154	1148	158
4.5/400	3251	114	1033	203

Experiment 9 (pH, CC): used polymer A130 following application of AL220 to bleach and finish, pH was adjusted to 4.5 for AL220, 7 for A130

AL220/A130 dose (mg/L)	COD (mg/L)	Color (ADMI)	DOC (mg/L)	TOC (mg/L)
Control	4335	139	1215	1724
250/10	4168	126	1335	1671
400/5	4856	123	1389	1657
400/10	4168	99	1346	1636
400/20	4085	99	1269	1660
785/10	3960	92	1280	1254

Experiment 10 (CC): bleach and finish pH at 7.5, used Nalco organic polymers 7135 and 9764, plus sample at pH 2.5, no polymer

Dose/Polmr (mg/L)/ID	COD (mg/L)	Color (ADMI)	TSS (mg/L)
Control	3084	471	227
25/7135	3199	470	161
100/7135	2704	210	167
100/9764	1066	313	152
pH 2.5	3199	240	368

Table B5. Experiment 11

Experiment 11 (pH, CC): used same Nalco polymers from Experiment 10, but tested dye and print at an adjusted pH of 7, also tested dye and print with standard pretreatment used with AL220 and A130

Dose/Polmr (mg/L)/ID	COD (mg/L)	Color (ADMI)	TSS (mg/L)
Control	139	1143	110
25/7135	62	974	155
50/7135	62	406	205
100/7135	131	166	129
25/9764	123	717	177
50/9764	31	704	162
100/9764	254	454	203
Control2	202	1240	--
Stndrd Prt.	202	207	--

APPENDIX C

Continuous Flow Reactor Operation Data

Table C1: 4 day HRT CFR operation data

Day	Date	MLSS (mg/L)			MLVSS (mg/L)				TSS (mg/L)		
		15 day	20 day	30 day	15 day	20 day	30 day	Influent	15 day	20 day	30 day
101	5/12	1025	1870	2360					5	160	45
104	5/15 P	1260	2270	2570					2	163	153
106	5/17	1194	2260	2636					21	95	81
108	5/19	1350	1925	2504					4	41	31
112	5/23	1700	2500	2955					123	--	128
113	5/24 P										
114	5/25	1140	1620	2500							
115	5/26	1637	2423	2684	1300	2010	2299		69	170	62
120	5/31	1336	2074	2465					25	119	49
122	6/2	1390	2010	2430					51	144	87
123	6/3 P	1550	1776	2796							
126	6/6	2074	3000	3280					44	154	810
127	6/7	2250	2806	4122				837	71	190	186
129	6/9	1456	1880	2174							
130	6/10 P										
131	6/11	2184	4978	4480	1192	2133	2110	682	141	626	1109
133	6/13	1460	2600	3170							
135	6/15	2480	2745	3083				410	180	255	370
137	6/17 P	2360	3633	3736	1873	2973	3061	614	92	197	265
139	6/19	2197	2538	3477				232	38	112	288
141	6/21	2144	3289	4224				96	25	57	372
143	6/23 P	1750	2742	2605	1518	2386	2283	79	2	5	170
148	6/28	2539	2688	3106				133	50	59	86
150	6/30 P	2156	2826	2776	1888	2500	2462	112	20	52	66
156	7/6	1789	2535	2261	1520	2201	1950	179	37	123	11

P = pretreated

Table C1. Continued

Day	Date	Sol. COD (mg/L)				Color ADMI				DOC (mg/L)			
		Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day
101	5/12	1652	1012	400	225								
104	5/15 P	1640	1088	468	341								
106	5/17	1875	890	480	400	240	166	153	125				
108	5/19	2345	1190	827	638								
112	5/23	2050	1230	826	718								
113	5/24 P												
114	5/25	1955	1300	948	670								
115	5/26	1673	999	798	620	209	145	116	136				
120	5/31	1588	906	608	476								
122	6/2	1386	774	449	310								
123	6/3 P	1482	710	480	349								
126	6/6	1637	592	478	376								
127	6/7	1453	577	428	373	919	465	452	452				
129	6/9	1980	669	543	428	1004	540	598	518				
130	6/10 P												
131	6/11	2167	865	924	793	861	793						
133	6/13	2171	1153	1531	1443	1352	896	1200	1263				
135	6/15	1477	1221	1155	1656	1160	922	1058	1190				
137	6/17 P	2056	1291	964	705	1299	977	889	896				
139	6/19	2032	1296	752	476	478	601	438	402				
141	6/21	2024	1190	651	587	534	330	364	282				
143	6/23 P	1976	1060	450	259	524	282	230	260				
148	6/28	2181	829	461	284	601	271	168	166				
150	6/30 P	1533	680	378	227	638	254	177	176	589	213	61	62
156	7/6	1862	1017	415	338	166	252	156	180	491	314	143	121

P = pretreated

Table C2. 7 day HRT CFR operation data

Day	Date	MLSS (mg/L)			MLVSS (mg/L)			TSS (mg/L)			
		15 day	20 day	30 day	15 day	20 day	30 day	Influent	15 day	20 day	30 day
27	8/5 P										
30	8/8	1332	1996	2553	1118	1669	2120	77	13	36	16
39	8/17	1295	2065	1780				51	67	86	38
41	8/19 P										
43	8/21	1555	1775	2013				127	24	14	5
45	8/23	1298	1642	1938	1110	1386	1630	137	16	9	5
48	8/26	1407	1684	2016				161	25	23	11
51	8/29 P										
52	8/30	1400	1510	1800	1188	1296	1529	252	19	15	15
54	9/1	1163	1571	1938				203	24	13	20
57	9/4	1657	1737	2100				189	17	7	8
60	9/7 P										
62	9/9	1657	1818	2353	1419	1542	1969	151	15	13	10
69	9/16	1702	1533	2420				61	26	29	15
73	9/20	1728	1572	2300	1492	1352	1946	76	42	11	15
74	9/21 P										
81	9/28 P										
83	9/30	1800	1978	2645				303	43	16	102
86	10/3	1829	1934	2525				502	16	32	44
89	10/6	1765	1993	2569	1489	1683	2135	462	34	95	56
93	10/10 P										
94	10/11	1816	1907	2630				238	24	125	99
96	10/13	1783	1950	2620	1540	1674	2214	256	33	176	144
101	10/18	1792	2016	2734				101	33	169	164
102	10/19 P										
115	11/1 P										
118	11/4	1351	1698	2450				204	23	28	23
121	11/7	1146	1464	2266	974	1225	1863	89	15	20	15
123	11/9	1059	1489	2173				73	13	11	15

P = pretreated

Table C2. Continued

Day	Date	Sol. COD (mg/L)				Color ADMI				DOC (mg/L)			
		Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day
27	8/5 P												
30	8/8	1312	1	199	167	296	156	130	142	425	42	43	41
39	8/17	1050	103	92	80	229	167	136	154	365	34	32	38
41	8/19 P												
43	8/21	1151	39	8	73	541	187	181	164	521	40	38	41
45	8/23	1248	80	144	80	500	182	141	123	463	37	37	37
48	8/26	1557	152	130	138	548	150	119	134	477	37	36	36
51	8/29 P												
52	8/30	1033	96	86	104	1324	193	268	172	387	37	36	35
54	9/1	960	87	102	102	1290	172	172	163	374	33	35	34
57	9/4	1260	102	167	163	1198	182	167	163	387	34	37	59
60	9/7 P												
62	9/9	891	87	103	150	207	124	104	107	436	36	38	70
69	9/16	1114	140	203	121	320	113	130	98	400	41	35	32
73	9/20	1529	153	165	172	328	115	99	75	405	42	42	45
74	9/21 P												
81	9/28 P												
83	9/30	2444	252	132	78	267	174	144	115	556	86	71	44
86	10/3	1664	229	156	171	421	228	149	131	494	83	49	47
89	10/6	1404	212	123	93	546	256	179	137	487	81	56	47
93	10/10 P												
94	10/11	2763	207	211	184	462	262	185	151	475	64	63	39
96	10/13	1429	209	201	114	480	252	186	147	472	85	66	47
101	10/18	1408	193	174	189	662	274	169	138	451	67	58	57
102	10/19 P												
115	11/1 P												
118	11/4	1130	555	208	204	203	154	136	119	450	191	92	81
121	11/7	1239	600	352	248	215	200	160	137	432	212	123	82
123	11/9	1293	573	372	271	269	213	187	129	422	216	137	89

P = pretreated

Table C3: Reactor influent and effluents TKN, Ammonia-N and Total Phosphorus

4 day HRT

Day	TKN mg-N/L				Ammonia-N mg-N/L				Total Phosphorus mg-P/L			
	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day
149									3.42	1.06	0.76	1.39
158	30.7	11.3	13.2	9	16.2	--	--	--				

7 day HRT

Day	TKN mg-N/L				Ammonia-N mg-N/L				Total Phosphorus mg-P/L			
	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day
11	40.2	8.5	9.8	9	16.5	0	0	0				
18									3.9	0.7	0.8	0.6
21	41.4	7.5	7.2	6.7	26	0	0	0				
26									7.3	0.8	0.6	1
27	45.7	3.9	7.1	5.3	27.8	0	0	0				
35									7.5	0.4	0.3	0.3
45	30.4	7.8	5.4	4.6	14.7	0	0	0				

Table C4. Reactor influent and effluent BOD

4 day HRT

Day	Sol. BOD5 (mg/L)			
	Influent	15 day	20 day	30 day
134	172	62	67	84

7 day HRT

Day	Sol. BOD5 (mg/L)				Tot. BOD5 (mg/L)			
	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day
39	--	<12	<12	<12	<80	<12	<12	<12

Day	Sol. BOD20 (mg/L)				*Sol. BOD5 (mg/L)			
	Influent	15 day	20 day	30 day	Influent	15 day	20 day	30 day
31	1194	<60	<60	<60	<120	<3	<3	<3

*BOD5 was conducted on BOD20 samples at end of test

Table C5. Waste stream metals, anions and color

Cation and color analyses

Date	Thermosol: Cu (ug/L)	Cr (ug/L)	Ag (ug/L)	Zn (mg/L)	Color (ADMI)	Print: Cu (ug/L)	Cr (ug/L)	Ag (ug/L)	Zn (mg/L)	Color (ADMI)	Pretreated Thermosol/Print: Cu (ug/L)	Cr (ug/L)	Ag (ug/L)	Zn (mg/L)	Color (ADMI)
May 25	ND	ND	ND	ND	--	ND	ND	ND	ND	--	ND	ND	ND	ND	--
June 10	266	8	ND	0.06	1007	324	3.5	ND	0.1	2414	137	4.4	ND	0.09	471
June 17	61	1.3	ND	0.03	1820	98	2.4	ND	0.19	3791	34	0.7	ND	0.06	822
July 10	39	3.2	ND	0.04	792	37	1.7	ND	0.07	2132	18	4	ND	0.09	151
July 22	21	7.6	ND	0.05	1834	54	1.7	ND	0.13	1726	10	4.3	ND	0.06	120
August 19	20	3.6	ND	0.04	1325	24	2.2	ND	0.39	3412	11	2.8	ND	0.13	241
Septem. 7	12	1.8	0.4	0.15	456	124	1.8	0.2	0.85	1525	15	1	0.2	0.08	132
Septem 28	80	11.4	0.2	0.09	834	58	3.3	ND	0.3	2647	61	6.5	ND	0.06	508
October 31	48	3.4	0.3	0.09	--	12	1.7	0.1	0.38	--	29	0.7	ND	0.05	--

Date	Bleach and Finish: Cu (ug/L)	Cr (ug/L)	Ag (ug/L)	Zn (mg/L)	Color (ADMI)	Combination (Influent): Cu (ug/L)	Cr (ug/L)	Ag (ug/L)	Zn (mg/L)	Color (ADMI)
May 25	ND	ND	ND	ND	--	ND	ND	ND	ND	--
June 10	ND	ND	ND	ND	1796	170	2.9	ND	0.17	761
June 17	129	2.7	ND	0.14	1269	135	1.3	ND	0.23	527
July 10	70	3.3	ND	0.14	425	30	2.9	ND	0.11	199
July 22	26	6.8	ND	0.16	698	11	3.1	ND	0.13	214
August 19	36	2.4	ND	0.28	763	12	3	ND	0.17	392
Septem. 7	146	2.4	ND	0.69	1002	17	3.2	ND	0.41	228
Septem 28	101	2.1	ND	0.15	651	76	5.3	ND	0.08	606
October 31	72	3	ND	0.24	--	24	1.7	ND	0.1	--

-- = no data
ND = not detected

Table C5. Continued

Anion Analysis

Date	Thermosol: Cl (mg/L)	NO3-N (mg/L)	PO4-P (mg/L)	SO4 (mg/L)	Print: Cl (mg/L)	NO3-N (mg/L)	PO4-P (mg/L)	SO4 (mg/L)	Pretreated Thermosol/Print: Cl (mg/L)	NO3-N (mg/L)	PO4-P (mg/L)	SO4 (mg/L)
May 25*	6.7	0.4	ND	20.6	6.7	0.4	ND	20.6	12.4	0.6	ND	292
June 10	11.6	0.6	--	905	9.1	0.2	ND	7.6	14.2	0.5	ND	1242
June 17	9.7	0.6	--	374	9.8	0.6	ND	59.2	13.4	0.5	ND	530
July 10	11	1	ND	354	19	ND	ND	26	18	1	ND	565
July 22	15	1	ND	642	15	ND	ND	24	20	ND	ND	860
August 19	9.5	0.4	0.2	690	10.6	0.4	ND	29.2	13.7	0.8	ND	1090
Septem 7	10.4	0.4	ND	397	10.7	0.2	ND	25.2	13.5	0.4	ND	773
Septem 28	17.8	0.5	ND	408	9	0.6	ND	38.3	15.7	0.6	ND	484

* Figures represent a combination of thermosol and print prior to pretreatment.

Date	Bleach and Finish: Cl (mg/L)	NO3-N (mg/L)	PO4-P (mg/L)	SO4 (mg/L)	Combination (Influent): Cl (mg/L)	NO3-N (mg/L)	PO4-P (mg/L)	SO4 (mg/L)
May 25	ND	ND	ND	ND	20.1	0.6	ND	292
June 10	ND	ND	ND	ND	39.9	0.6	ND	792
June 17	35.7	0.4	ND	46.8	20.7	0.5	ND	322
July 10	32	ND	3	45	23	ND	ND	383
July 22	36	ND	2	73	25	ND	ND	561
August 19	34.4	0.4	4.4	42.8	23.6	0.4	1.2	664
Septem 7	47	0.2	3.2	51.5	22	0.4	0.7	470
Septem 28	33.3	1.2	2.7	37.5	21.7	0.6	0.6	327

-- = no data
ND = not detected

Table C6. Reactor influent and effluent cations, anions and total chromium

Influent Date	Cl (mg/L)	NO3-N (mg/L)	PO4-P (mg/L)	SO4 (mg/L)	Cu (ug/L)	Cr (ug/L)	Ag (ug/L)	Zn (mg/L)	Tot. Cr (ug/L)
August 21	22.8	0.3	0.6	641	72	12.3	ND	0.24	
Septem 17	21.1	0.1	0.9	569	11	2.5	0.2	0.12	
Octob 10	27.2	0.4	ND	363	126	5.6	ND	0.79	
Octob 20									5.1
Nov 10									4.5
15 day Sludge Age Date	**Cl (mg/L)**	**NO3-N (mg/L)**	**PO4-P (mg/L)**	**SO4 (mg/L)**	**Cu (ug/L)**	**Cr (ug/L)**	**Ag (ug/L)**	**Zn (mg/L)**	**Tot. Cr (ug/L)**
May 25	24	0.4	--	268	--	--	--	--	
June 18	44.5	0.4	--	767	15	2.6	ND	0.13	
August 21	--	--	--	--	33	4.2	ND	0.26	
August 24	26.8	1.1	ND	742	--	--	--	--	
Septem 17	23.7	0.2	ND	734	5	2.6	0.2	0.16	
Octob 10	26.5	0.5	ND	516	21	3.5	ND	0.42	
Octob 20									2
Nov 10									1.1
20 day Sudge Age Date	**Cl (mg/L)**	**NO3-N (mg/L)**	**PO4-P (mg/L)**	**SO4 (mg/L)**	**Cu (ug/L)**	**Cr (ug/L)**	**Ag (ug/L)**	**Zn (mg/L)**	**Tot. Cr (ug/L)**
May 25	27	0.4	--	270	--	--	--	--	
June 18	992	0.6	--	747	37	2.3	ND	0.34	
August 21	--	--	--	--'--	63	16	ND	0.32	
August 24	27.1	2.6	ND	744	--	--	--	--	
Septem 17	22.6	0.3	ND	696	3	2.2	ND	0.16	
Octob 10	26.4	2.2	ND	526	11	3.9	1.5	0.41	
Octob 20									0.9
Nov 10									0.5
30 day Sludge Age Date	**Cl (mg/L)**	**NO3-N (mg/L)**	**PO4-P (mg/L)**	**SO4 (mg/L)**	**Cu (ug/L)**	**Cr (ug/L)**	**Ag (ug/L)**	**Zn (mg/L)**	**Tot. Cr (ug/L)**
May 25	24.9	0.3	--	264	--	--	--	--	
June 18	128	0.3	--	768	20	2.6	ND	0.35	
August 21	--	--	--	--	57	3.8	MD	0.39	
August 24	30.7	8.2	ND	804	--	--	--	--	
Septem 17	24.9	1.1	ND	750	4	2.4	ND	0.18	
Octob 10	31.7	4.4	ND	557	8	3.1	ND	0.36	
Octob 20									1.5
Nov 10									1.2

APPENDIX D

Kinetic Coefficient Analysis Data

Table D1. Kinetic coefficient data for 4 day HRT

Sludge Age (days)	So, inf COD (mg/L)	S-S*, eff COD (mg/L)	X, MLVSS (mg/L)	So-(S-S*) (mg/L)	X*HRT (mg/L*d)	1/U (day)	1/(S-S*) (L/mg)	1/sldg age (1/day)	U (1/day)
15	1765	590	1074	1175	4296	3.65617	0.001695	0.066667	0.27351
20	1765	208	1721	1557	6884	4.421323	0.004808	0.05	0.226177
30	1765	55	2227	1710	8908	5.209357	0.018182	0.033333	0.191962

S*=420 mg/L steady state determined to be days 101 through 123 of reactor operation

Regression Statistics - Ks and k

Multiple R	0.943927475
R Square	0.890999079
Adjusted R Square	0.781998158
Standard Error	0.362609689
Observations	3

Analysis of Variance

	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*
Regression	1	1.074795639773	1.0747956398	8.174234393	0.21420060737
Residual	1	0.131485786695	0.1314857867		
Total	2	1.206281426468			

	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95.00%*	*Upper 95.00%*
Intercept	3.740345785	0.319119381287	11.720835539	0.007200659	-0.3144504069	7.795142
x1	83.68890814	29.27145823065	2.8590618029	0.103660214	-288.24023292	455.618

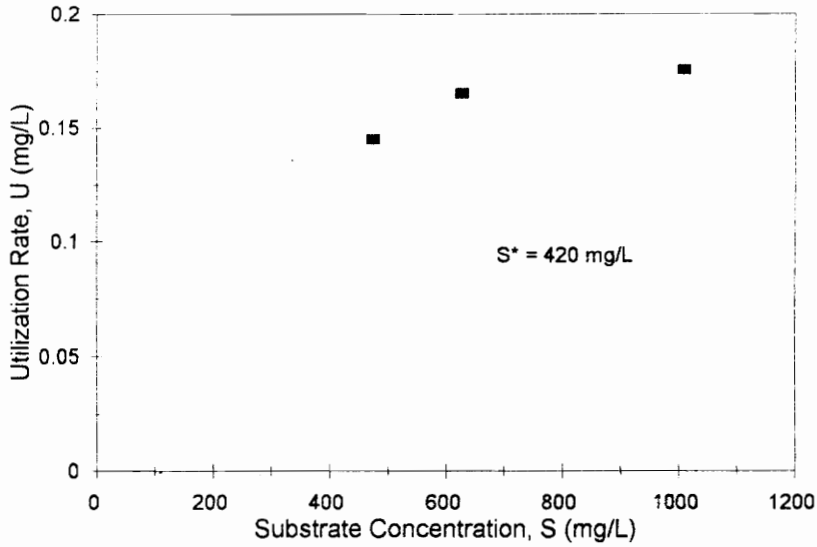
Regression Statistics - Y and kd

Multiple R	0.995714111
R Square	0.991446591
Adjusted R Square	0.982893183
Standard Error	0.002179884
Observations	3

Analysis of Variance

	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*
Regression	1	0.000550803662	0.0005508037	115.9124539	0.05896180933
Residual	1	4.75189372E-06	4.751894E-06		
Total	2	0.000555555556			

	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95.00%*	*Upper 95.00%*
Intercept	-0.043432843	0.008769082357	-4.9529519085	0.038429114	-0.1548545989	0.067989
x1	0.405261141	0.037641759252	10.766264621	0.008517139	-0.0730227586	0.883545



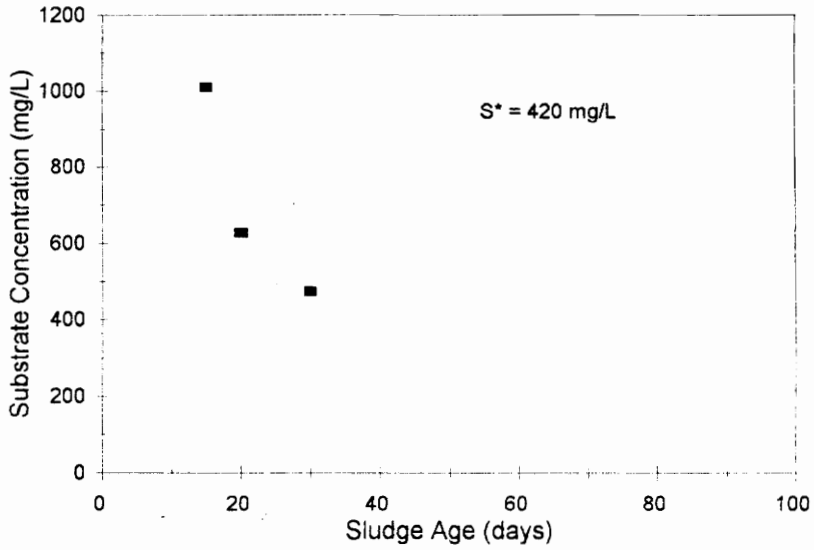


Figure D1. Utilization rate versus substrate concentration and substrate concentration versus sludge age, 4 day HRT CFR operations

Table D2. Kinetic coefficient data for 7 day HRT

Sludge Age (days)	So, inf COD (mg/L)	S-S*, eff COD (mg/L)	X, MLVSS (mg/L)	So-(S-S*) (mg/L)	X*HRT (mg/L*d)	1/U (day)	1/(S-S*) (L/mg)	1/sldg age (1/day)	U (1/day)
15	1672	52	1508	1620	10556	6.516049	0.019231	0.066667	0.153467
20	1672	22	1651	1650	11557	7.004242	0.045455	0.05	0.142771
30	1672	6	2134	1666	14938	8.966387	0.166667	0.033333	0.111528

S*=135 mg/L, steady state data determined to be days 62 through 101 of reactor operation, days 69 and 73 are omitted from 20 day sludge age avera

Regression Statistics - Ks and k

Multiple R	0.999761323
R Square	0.999522702
Adjusted R Square	0.999045405
Standard Error	0.040071287
Observations	3

Analysis of Variance

	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*
Regression	1	3.362559055383	3.3625590554	2094.12858	0.01390943008
Residual	1	0.001605708017	0.001605708		
Total	2	3.3641647634			

	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95.00%*	*Upper 95.00%*
Intercept	6.224228175	0.036153182623	172.16266242	3.3737E-05	5.76485843512	6.683598
x1	16.48567613	0.360250913911	45.761649702	0.00047718	11.9082542603	21.0631

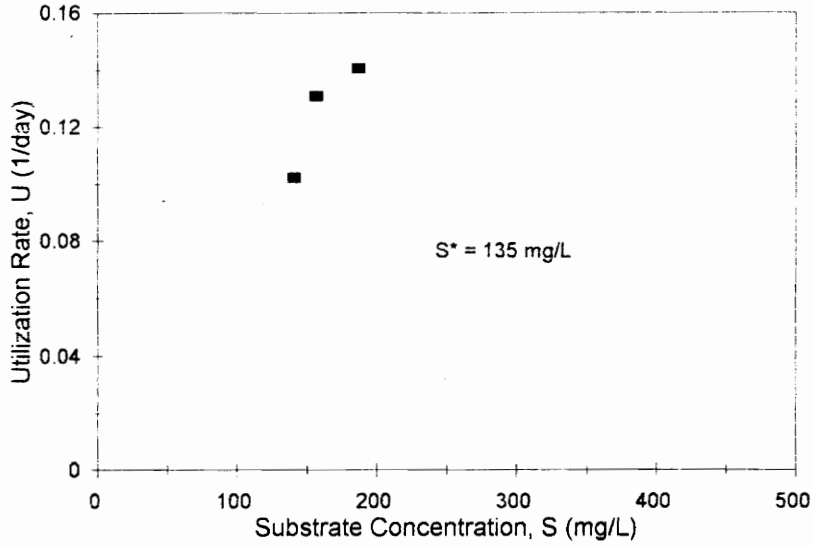
Regression Statistics - Y and kd

Multiple R	0.962249586
R Square	0.925924265
Adjusted R Square	0.851848531
Standard Error	0.006415075
Observations	3

Analysis of Variance

	df	*Sum of Squares*	*Mean Square*	*F*	*Significance F*
Regression	1	0.00051440237	0.0005144024	12.4996974	0.17548167424
Residual	1	4.11531859E-05	4.115319E-05		
Total	2	0.000555555556			

	Coefficients	*Standard Error*	*t Statistic*	*P-value*	*Lower 95.00%*	*Upper 95.00%*
Intercept	-0 0500275	0 028533788711	-1 7532721	0.22164867	-0.4125836568	0.312529
x1	0 735919291	0 208151928167	3 5354911087	0.07152486	-1.9089017232	3.38074



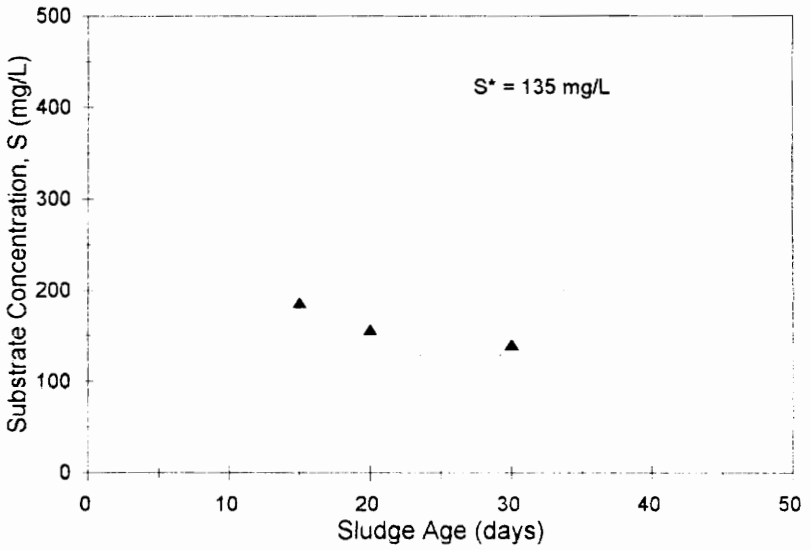


Figure D2. Utilization rate versus substrate concentration and substrate concentration versus sludge age, 7 day HRT CFR operations

APPENDIX E

Toxicity Evaluation Reports

BIOLOGICAL MONITORING, INC.
Toxicity Test Condition Summary

Client: Tetra Tech, Inc./Bibb Prepared by: Jennifer Maloney

VPDES Permit #: N/A

Experiment ID#: BIB092394-1

Test Organism: Pimephales promelas

Test Type: Short Term Chronic

Organism Age at Start of Test: < 24h

Sample Tested: $\theta_c = 15d$

Sample Type: Composite

Sample Collection Dates and Times: 09/22-23/94 1100-1300, 09/23-24 1300-1145, 09/24-25 1130-1130, 09/25-26 1130-0830, 09/26-27 0930-1030, 09/27-28 1030-1000, 09/28-29 1030-1030.

Sample Collector: Mary Opdycke Delivered by: Mary Opdycke

Test Solution Renewal Frequency: Daily

Dilution Water Used: MHRW

Test Temperature: 25 ± 1°C

No. of Replicates per conc.: 2 No. of Organisms per Replicate: 10

Chamber Size: 100x50 mm

Feeding prior to test: None Feeding Regime:3x Daily Test Volume: 200mL

Photo Period: 16h light/8h dark Test Duration: 7d

Start of Test: Date: 09/23/94 Time: 1445

End of Test: Date: 09/30/94 Time: 1425

Equipment: pH Meter: SA 720 (c)
DO Meter: YSI 58 (A)
SCT Meter:YSI 33 (c)
°C Measurement: Calibrated Thermometer
Salinity: SCT Meter
Chlorine: Fisher/Porter Amperometric Titrator

Test Method Reference: U.S. EPA. 1989. Short-term methods for estimating the Chronic toxicity of effluents and receiving waters to freshwater and marine organisms. EPA/600/4-89/001.

BIOLOGICAL MONITORING, INC.
Chronic Toxicity Test Data Summary

Client	Tetra Tech, Inc./Bibb	NPDES Permit #	N/A	
Test Organism	Pimephales promelas		Date	Time
Experiment ID	BIB092394-1	Start Test	09/23/94	1445
Sample Tested	θc= 15 day reactor	End Test	09/30/94	1425

RESULTS

Water Chemistry Analyses (Range) — Survival and Reproduction

Conc. (%)	Temp. (°C)	D.O. (mg/l)*	pH	Initial Alkalinity mg/l as $CaCO_3$	Initial Hardness mg/l as $CaCO_3$	Cond. (µmhos)	Survival (%) 96h / 7d	Mean Weight (mg)
0	24-25	6.7-7.9	7.2-8.1	67	91	285-330	100/95	0.390
50	24-25	5.0-7.6	7.8-8.6			1250-1300	100/95	0.512
75	24-25	4.1-7.4	7.9-8.6			1700-1800	100/100	0.487
100	24-25	3.7-7.1	8.0-8.9	430	60	1900-2300	100/100	0.387

STATISTICAL ANALYSES

Test Method	End Point		
Dunnett's	Survival	NOEC= 100%	LOEC= N/A
Dunnett's	Growth	NOEC= 100%	LOEC= N/A

NOEC = No Observed Effect Concentration LOEC = Lowest Observed Effect Concentration

SURVIVAL DATA

1. Arc Sine Transformation was used.
2. Data PASS normality using Shapiro-Wilks test.
3. Data FAIL homogeneity using Bartletts test.
4. Fathead Minnow survival in all effluent concentrations was not significantly lower than survival in the control using Dunnett's Test, (p>0.05).

GROWTH DATA

1. No transformation was used.
2. Data PASS normality using Shapiro-Wilks test.
3. Data PASS homogeneity using Bartletts test.
4. Fathead Minnow growth in all effluent concentrations was not significantly lower than growth in the control using Dunnett's Test (p>0.05).

Comments:

* = See bench sheets for notes on aeration.

BIOLOGICAL MONITORING, INC.
Toxicity Test Condition Summary

Client: Tetra Tech, Inc./ Bibb Prepared by: Jennifer Maloney

NPDES Permit #: N/A

Experiment ID#: BIB092794-1

Test Organism: Ceriodaphnia dubia

Test Type: Static Acute Screen

Organism Age at Start of Test: < 24 h

Sample Tested: θc= 15 day reactor

Sample Type: Composite

Sample Collection Dates and Times: 09/26-27 0930-1030

Sample Collector: Mary Opdycke Delivered by: Mary Opdycke

Test Solution Renewal Frequency: N/A

Dilution Water Used: DMW

Test Temperature: 20 ± 1°C

No. of Replicates per conc.: 2 No. of Organisms per Replicate: 10 Chamber Size: 60ml

Feeding prior to test: None Feeding Regime: None Test Volume: 35mL

Photo Period: 16h light/8h dark Test Duration: 48h

Start of Test: Date: 09/27/94 Time: 1305

End of Test: Date: 09/29/94 Time: 1350

Equipment:
pH Meter: SA 720 (c)
DO Meter: YSI 58 (A)
SCT Meter:YSI 33 (c)
°C Measurement: Calibrated Thermometer
Salinity: SCT Meter
Chlorine: Fisher/Porter Amperometric Titrator

Test Method Reference: U.S. EPA. 1989. Short-term methods for estimating the Chronic toxicity of effluents and receiving waters to freshwater and organisms. EPA/600/4-89/027.

BIOLOGICAL MONITORING, INC.
Acute Toxicity Test Data Summary

Client	Tetra Tech, Inc./ Bibb	NPDES PERMIT # N/A		
Test Organism	Ceriodaphnia dubia		Date	Time
Experiment ID	BIB092794-1	Start Test	09/27/94	1305
Sample Tested	θc= 15 day reactor	End Test	09/29/94	1350

RESULTS

Water Chemistry Analyses

(Range)

Conc. (%)	Temp. (°C)	D.O. (mg/l)	pH	Initial Alkalinity mg/l as $CaCO_3$	Initial Hardness mg/l as $CaCO_3$	Cond. (µmhos)	Survival (%) 48h
0	20-21	7.5 - 7.7	7.2 - 7.3	94	90	160 - 185	100
100	20-21	6.4 - 6.7	8.0 - 8.4			1900 - 2000	100

STATISTICAL ANALYSES

Test Method	LC50 (%)	95% Fiducial (Confidence) Limits
N/A	>100	N/A

COMMENTS:

BIOLOGICAL MONITORING, INC.
Toxicity Test Condition Summary

Client: Tetra Tech, Inc./Bibb Prepared by: Greg Turner

VPDES Permit #: N/A

Experiment ID#: BIB090894-1

Test Organism: Pimephales promelas

Test Type: Short Term Chronic

Organism Age at Start of Test: < 24h

Sample Tested: θ_c=30d

Sample Type: Composite

Sample Collection Dates and Times: 09/07-08/94 1330-1030, 09/08-09 1030-1030, 09/09-10 1030-1030, 09/10-11 1030-1130, 09/11-12 1130-1000, 09/12-13 0930-1015, 09/13-14 930-930

Sample Collector: Mary Opdycke Delivered by: Mary Opdycke

Test Solution Renewal Frequency: Daily

Dilution Water Used: MHRW

Test Temperature: 25 ± 1°C

No. of Replicates per conc.: 2 No. of Organisms per Replicate: 10

Chamber Size: 300ml

Feeding prior to test: None Feeding Regime:3x Daily Test Volume: 200mL

Photo Period: 16h light/8h dark Test Duration: 7d

Start of Test: Date: 09/08/94 Time: 1255

End of Test: Date: 09/15/94 Time: 1155

Equipment: pH Meter: SA 720 (c)
DO Meter: YSI 58 (A)
SCT Meter:YSI 33 (c)
°C Measurement: Calibrated Thermometer
Salinity: SCT Meter
Chlorine: Fisher/Porter Amperometric Titrator

Test Method Reference: U.S. EPA. 1989. Short-term methods for estimating the Chronic toxicity of effluents and receiving waters to freshwater and marine organisms. EPA/600/4-89/001.

BIOLOGICAL MONITORING, INC.
Chronic Toxicity Test Data Summary

Client	Tetra Tech, Inc./Bibb	NPDES Permit #	N/A	
Test Organism	Pimephales promelas		Date	Time
Experiment ID	BIB090894-1	Start Test	09/08/94	1255
Sample Tested	θc= 30 day reactor	End Test	09/15/94	1155

RESULTS

Water Chemistry Analyses (Range) — Survival and Reproduction

Conc. (%)	Temp. (°C)	D.O. (mg/l)*	pH	Initial Alkalinity mg/l as $CaCO_3$	Initial Hardness mg/l as $CaCO_3$	Cond. (µmhos)	Survival (%) 96h / 7d	Mean Weight (mg)
0	24-26	6.1-7.9	7.4-7.9	66	80	275-300	100/100	0.465
50	24-26	5.8-7.9	7.7-8.8			1300-1350	100/100	0.509
75	24-26	5.0-8.0	7.9-8.7			1850-1900	100/100	0.622
100	24-26	4.3-7.9	8.1-8.9	392	54	2200-2450	100/100	0.480

STATISTICAL ANALYSES

Test Method	End Point		
N/A	Survival	NOEC= 100%	LOEC= N/A
Dunnett's	Growth	NOEC= 100%	LOEC= N/A

NOEC = No Observed Effect Concentration LOEC = Lowest Observed Effect Concentration

SURVIVAL DATA

1. Arc Sine Transformation was used.
2. Data FAIL normality using Shapiro-Wilks test.
3. Data FAIL homogeneity using Bartletts test.
4. Fathead Minnow survival in all effluent concentrations was not significantly lower than survival in the control. There was 100% survival in all test concentrations.

GROWTH DATA

1. No transformation was used.
2. Data PASS normality using Shapiro-Wilks test.
3. Data PASS homogeneity using Bartletts test.
4. Fathead Minnow growth in all effluent concentrations was not significantly lower than growth in the control using Dunnett's Test ($p>0.05$).

Comments:

* = See bench sheets for notes on aeration.

BIOLOGICAL MONITORING, INC.
Toxicity Test Condition Summary

Client: Tetra Tech, Inc./ Bibb Prepared by: Valerie Rasnake

NPDES Permit #: N/A

Experiment ID#: BIB090994-2

Test Organism: Ceriodaphnia dubia

Test Type: Static Acute Screen

Organism Age at Start of Test: < 24 h

Sample Tested: θc= 30 day reactor

Sample Type: Composite

Sample Collection Dates and Times: 09/08-09 1030-1030

Sample Collector: Mary Opdycke Delivered by: Mary Opdycke

Test Solution Renewal Frequency: N/A

Dilution Water Used: DMW

Test Temperature: 20 ± 1°C

No. of Replicates per conc.: 1 No. of Organisms per Replicate: 5 Chamber Size: 30ml

Feeding prior to test: Normal Feeding Regime: None Test Volume: 25mL

Photo Period: 16h light/8h dark Test Duration: 48

Start of Test: Date: 09/09/94 Time: 1325

End of Test: Date: 09/11/94 Time: 1235

Equipment:
pH Meter: SA 720 (c)
DO Meter: YSI 58 (A)
SCT Meter:YSI 33 (c)
°C Measurement: Calibrated Thermometer
Salinity: SCT Meter
Chlorine: Fisher/Porter Amperometric Titrator

Test Method Reference: U.S. EPA. 1989. Short-term methods for estimating the Chronic toxicity of effluents and receiving waters to freshwater and organisms.
EPA/600/4-89/027.

BIOLOGICAL MONITORING, INC.
Acute Toxicity Test Data Summary

Client	Tetra Tech, Inc./ Bibb	NPDES PERMIT # N/A		
Test Organism	Ceriodaphnia dubia		Date	Time
Experiment ID	BIB090994-2	Start Test	09/09/94	1325
Sample Tested	θc= 30 day reactor	End Test	09/11/94	1235

RESULTS

Water Chemistry Analyses

(Range)

Conc. (%)	Temp. (°C)	D.O. (mg/l)	pH	Initial Alkalinity mg/l as $CaCO_3$	Initial Hardness mg/l as $CaCO_3$	Cond. (µmhos)	Survival (%) 48h
0	19.5-20.5	7.7 - 7.9	7.7 - 7.9	92	86	160 - 175	100
100	19.5-20.5	7.5 - 7.8	8.2 - 8.7	392	54	2050 - 2200	95

STATISTICAL ANALYSES

Test Method	LC50 (%)	95% Fiducial (Confidence) Limits
N/A	>100	N/A

COMMENTS:

VITA

Mary Ellen Opdycke was born in St. Louis, Missouri on March 5, 1966. She was raised in Maryland and attended Chesapeake Senior High School. After graduation, she attended the University of Maryland, College Park for three semesters and studied Aerospace/Mechanical Engineering. Deciding that particular engineering discipline was not very interesting, she changed her major to Civil Engineering when she enrolled at California State University, Long Beach in the fall of 1988. She graduated in May of 1991 with a Bachelor of Science in Civil Engineering.

After two years of employment with a civil engineering firm in Huntington Beach, California, she enrolled at Virginia Polytechnic Institute and State University in Blacksburg, Virginia. After three semesters, she received a Master of Science in Environmental Engineering. That degree was completed in the Spring of 1995.

Mary E. Opdycke