PRETREATMENT AND BIODEGRADATION OF WASTEWATER FROM A TEXTILE DYEING AND FINISHING INDUSTRY

by

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(ABSTRACT)

Pretreatment is a common approach for removing color and reducing the organic load of textile dyeing and finishing wastewater. Subsequent aerobic treatment is often employed to complete organic removal as well as remove toxicity and metals. The wastewater from the textile dyeing and finishing industry studied was not treated efficiently and often failed effluent toxicity and metals tests. In this research project, various pretreatment alternatives were studied in an attempt to identify the most efficient and economical method(s). Also, aerobic, biological treatment was performed in bench-scale reactors to determine the biological kinetic coefficients of the wastewater so that the overall efficiency and performance of the biological treatment system might be improved. Effluent toxicity of the wastewater was also evaluated in hopes that improved treatment efficiency would yield subsequent improved effluent toxicity. The performance of a sequencing batch reactor was compared to that of the continuous-flow reactors.

In regard to pretreatment with various polymers, coagulation with a blend of inorganic aluminum and a

polyamine (AL220, Polymer Systems, Inc.) produced the most economical and efficient results. Subsequent addition of an anionic polymer improved the settling characteristics of the chemical flocs. Color removal ranged from 71-90% and DOC removal averaged 25% with AL220 doses between 400-600 mg/L.

Increased sludge ages (θ_c) of the continuous-flow reactors produced improved removal efficiencies. Sludge ages of 8-30 days resulted in an average of 55-68% COD removal. Kinetic analysis produced values of 0.032 d^{-1} and 0.619 for k_d and Y, respectively. K_s and k could not be determined accurately. This difficulty was attributed to possible inhibitory effects and a residual, biorefractory COD that was not quantified in this study.

The SBR, operated with a cycle time of one day and an average MLSS concentration of 4,266 mg/L, achieved an average 69% COD removal and 59% color removal. Addition of nutrients did not appear to improve these efficiencies. Settling characteristics of the sludge were excellent.

Preliminary acute toxicity testing of the SBR effluent and effluent from the 8 day θ_c reactor produced encouraging results. Subsequent chronic toxicity testing of the 15, 20 and 30 day θ_c reactors yielded a maximum No Observed Effect Concentration of 50-75%.

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1.0 INTRODUCTION

As concern for the environment increases, the discharge limits for industrial effluents get stricter. In the case of the textile dyeing industry, consumer demands for increased color stability has led to the generation of wastewater high in color and organics. It is necessary to remove the majority of these contaminants prior to discharge to a receiving water.

The chemical dyes used by the textile industry are one of their main causes of pollution. The discolored wastewater is aesthetically displeasing and has potential to block the path of the sunlight to organisms in the receiving water. This discoloration can make the water unacceptable to public water supplies and recreational waters.

Color may be imparted to fibers during the dyeing process by several types of dyes including vat, disperse, reactive, pigment and sulfur dyes. For certain types of dyes, 90% of the dye is fixed to the fabric while the remaining 10% leaves in the wastewater effluent. There exist several methods to remove color from wastewater. Carbon adsorption, ultrafiltration, oxidation, reduction and chemical coagulation will all remove some degree of color, depending on the type of dye in use.

Not only is textile dyeing wastewater highly colored,

but toxicity and metals concentrations may also be high due to the sophisticated dyes and auxiliaries in use. Also, the level of organics is high due to the addition of chemicals and the bleaching of natural fibers. It is necessary to reduce these concentrations so the environment will not be adversely impacted. Biological treatment is the most commonly used method for the previously mentioned pollutants.

Treatment alternatives for wastewater from a textile dyeing and finishing plant (to be referred to as "the Plant") were studied. The types of fabric typically handled at the Plant include 100% cotton, 50/50 polyester/cotton blend or a 70/30 polyester/cotton blend. Among the operations at the Plant are two bleaching and finishing ranges, a thermosol dyeing process and a printing facility.

The two bleaching and finishing ranges at the Plant use the hydrogen peroxide bleaching procedure to remove dirt and sizing from the fabric prior to dyeing. Silicate is added during the bleaching operation as a stabilizer. Surfactants are also used. The finishes used include stiffening and weighting agents, oil and water repellents and flame retardants. Approximately 300,000 gal/day of bleach/finish wastewater leave the Plant each day containing natural organics as well as excess chemicals and sizing.

Thermosol dyeing is performed at the Plant on one

dyeing range. Vat, disperse, reactive, pigment and sulfur dyes are used. The fabric is dried, cured, and then exposed to hydrosulfite and 50% caustic for reduction. Oxidation with peroxide and acetic acid is the next step, followed by a wash with detergent. Approximately 400,000 gal/day of thermosol wastewater are produced. The wastewater contains excess dyes and various chemicals, as indicated above.

There is one printing range at the Plant. Chemicals used in the printing process include print concentrate (acrylic polymer), pigment dye, print binder (acrylic latex copolymer) and print softener (petroleum oils). The fabric is dried and cured following printing.

The Plant presently treats its print and thermosol wastewaters on-site using chemical coagulation and dissolved air flotation (DAF) for color removal and some organic removal, followed by an aerated lagoon and secondary sedimentation for final removal of organics, toxicity and metals (Figure 1, as prepared by Harry R. Diz). Bleach and finish wastewater flows directly to the aerated lagoon. Sludges removed by the DAF and from the secondary clarifier are presently managed through aerobic digestion, belt filter press and landfilling. The Plant has often failed effluent toxicity limits and there is some concern that removal of metals will soon have to be enhanced. Additionally, there is regard that the costs associated with treating the

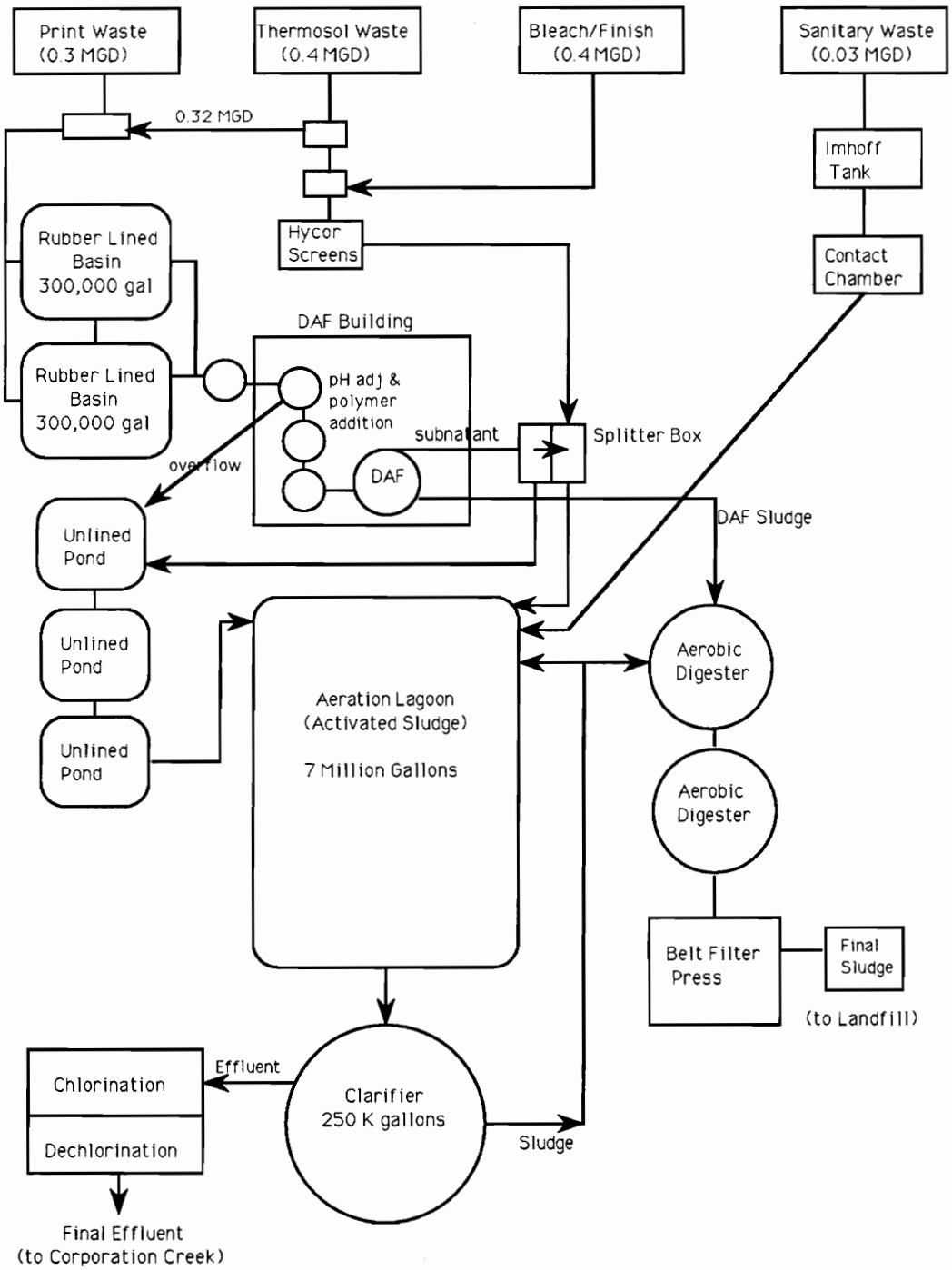


Figure 1. Flow Diagram of the Plant's Wastewater Treatment Facility

various waste streams is excessive.

Thus, the objectives of this study were to:

(1) experiment with various physicochemical methods in an attempt to determine a more cost effective and efficient pretreatment process for the Plant's wastewater;

(2) determine, using a bench-scale system, the biological kinetic coefficients of the textile mill wastewater so that the overall efficiency and performance of the biological treatment system might be improved;

(3) compare the performance of a sequencing batch reactor to continuous-flow reactors; and,

(4) evaluate the effluent toxicity of the treated wastewater using *Pimephales promelas* and *Daphnia pulex*.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

Water is a necessary ingredient in the textile dyehouse and "successful results in the dyehouse depend on the quality of the process water." The three main uses of water in the textile industry are (1) process water (50-60%), (2) cooling water (25-35%) and (3) boiler steam (5-10%). (Park and Shore, 1984) It is inevitable that this water leaves the plant containing some dye and chemical wastes, as well as natural organic waste.

Total dye consumption each year is more than 100,000,000 pounds. Approximately 10% of this is discharged as waste (Porter, 1973). Along with the dyes, auxiliary chemicals such as detergents, starch, oils, softeners and many inorganic chemicals are discharged in the effluent (Gardiner and Borne, 1978). Organic impurities, extracted from the natural fibers, also contribute to the wastewater effluent.

Due to the increased concern for the environment and tighter regulations, improved treatment of textile wastewater is needed. Even as far back as 1952, Nemerow suggested that the predominant pollutional characteristics of textile wastewater included:

(1) intense color and surface unsightliness

(2) high pH and alkalinity

(3) high chemical oxygen demand (COD)

(4) high chlorine demand

(5) high temperature

(6) extreme toxicity of sulfur dye wastes.

All of these characteristics must be treated to some extent before the wastewater can be discharged to the environment.

Regulations often involve limits for biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), fats, oils and greases (FOG) and color (Davis, 1991). Toxicity and metal limits must also be met. Assuming a flow of 1 million gallons per day (MGD), the present Plant limits are 98 mg/L (372 kg/day), 1,493 mg/L (5,650 kg/day) and 266 mg/L (1,005 kg/day) for effluent BOD_5, COD and TSS, respectively.

Typically, treatment of textile dye wastewater is difficult. Since the dyes are made to be tough and long lasting, it is no surprise that they are difficult to degrade.

Pretreatment and biological treatment systems are specific to the particular wastewater being treated. Bench and pilot-scale tests must be performed on the wastewater to determine the most appropriate method (Tunay *et al.*, 1990).

The following literature review will outline the

processes performed at the Plant. General toxicity problems will be discussed and physical, chemical and biological treatments alternatives will be presented.

2.2 PLANT FUNCTIONS

A plant which functions as a textile dyeing and finishing plant would perform the following operations.

2.2.1 Bleaching

Bleaching is typically performed only on natural fibers and/or blends of natural fibers such as cotton, flax or wool (Nettles, 1983). The purpose of the bleaching procedure is to remove naturally occurring proteins, pectins, waxes and ash prior to application of the dye.

The procedure involves first removing sizes, starches and adhesives from the fabric. Scouring is the next step in which oil and wax are removed to ensure uniform penetration of the dye onto the fiber. Bleaching is performed next. There are several bleaching mechanisms available, each with its own advantages and disadvantages: peroxide, peracetic acid, sodium chlorite and sodium hypochlorate (Nettles, 1983). Surfactants are added during the wetting step to "help ensure the success of the process" (Nettles, 1983). The surface active agents help to lower the surface tension of the water in relation to the fiber so the water will wet

the substrate (Needles, 1986).

The wastewater from this bleaching process is typically high in organics and must be treated prior to discharge to the environment. The waste is often alkaline and sometimes has a high temperature. It will also contain residues from the oxidizing agent used in the bleaching step.

2.2.2 Printing and Dyeing

The printing and dyeing processes involve the application of dyes to fabric. Dyes are "colored molecules soluble or dispersable in water or solvent media which can penetrate the fiber on coloration" (Needles, 1981). Dyes are typically classified according to chemical constitution or basis of application. Dyes containing anionic functional groups include acid, direct, mordant and reactive dyes. Basic dyes contain cationic groups. Vat dyes, azoic dyes and sulfur dyes all require chemical reactions before application. Disperse dyes, solvent dyes and pigments are all in a class of special colorants.

Printing is a specialized dyeing technique (Needles, 1981). The dye used in the process is thick and viscous to limit migration of the dye on the fabric so a design or pattern can be formed. It is also necessary to apply a paste to help the dye adhere to the fabric. The dye is transferred onto the fabric using a block or engraved roller

or a rotary screen and squeegee system.

Dyeing is a process where a dye of one particular color is applied to the fabric. Several methods can be used to accomplish this, including range dyeing, foam dyeing, jet dyeing and thermosol dyeing. Often, heat must be applied to the fabric to ensure complete application of the dye.

During both the printing and dyeing processes, it is necessary to add auxiliary chemicals to aid or alter the operation. Addition of acids and bases will induce a charge formation in the fabric and help to increase the diffusion of the dyes. Bases are also used to aid in dissolving vat and sulfur dyes. Inorganic salts can act as a leveling agent, as well as help provide more even dyeing. Surface active agents are also used as leveling agents and help to complete fiber wetting.

The dyeing and printing wastes contain dye residues as well as residues of the various auxiliary chemicals employed. In addition, the print waste stream will contain the paste and thickeners that were added to prevent migration.

2.2.3 Finishing

"Finishing provides a method whereby deficiencies in the textile can be corrected or specific properties can be introduced" (Needles, 1981).

Physical finishing techniques or dry finishing processes involve the production of formed textile substrate, such as yarn. Chemical finishing methods or wet finishing are the application of "chemical reagents or polymeric materials to the textile structure" (Needles, 1981). Methods for application include padding, spraying, printing or vapor techniques. Examples of chemical finishes affecting aesthetics and comfort are optical finishes, softeners and abrasion resistant fibers, stiffening and weighting agents and crease resistant and stabilizing finishes. Some protective finishes include oil and water repellents, antistatic agents and flame retardants.

Waste liquors from the finishing process contain primarily various starch fillings. Many of the other finishes are expensive and used more sparingly.

2.3 TOXICITY OF DYE WASTEWATER

Textile dyes and the auxiliary chemicals used in the dyeing process have come under close scrutiny regarding their toxic effects on the environment. Effluent toxicity limits are becoming more strict and adhesion to the limits is necessary.

2.3.1 Toxicity Reduction Evaluation (TRE)

An industry or municipality is required to monitor its

effluent for toxicity, chemically and biologically. Typically, the industry would hold a permit with certain chemical and biological toxicity limits. Biological toxicity limits are defined as "the capacity of the wastewater to cause death (acute toxicity) or to reduce normal growth or reproduction (chronic toxicity) of sensitive aquatic organisms" (Diamond, 1993). If the industry fails to meet these limits, it is usually necessary to perform a Toxicity Reduction Evaluation (TRE). "The major objectives of the TRE are to identify and reduce or eliminate the toxic substances in the effluent within a mandated time frame" (Diamond, 1993).

A flowchart of the TRE process can be seen in Appendix B. The first step usually taken in a TRE is assessment of chemical use, facility housekeeping and treatment systems at the particular plant. A Toxicity Identification Evaluation (TIE) is performed next in an attempt to characterize and identify the toxicants. The TIE involves three phases. Phase I is a Toxicity Characterization Procedure intended to aid in determining the physical/chemical nature of the constituents causing toxicity (EPA 600/3-88/034, 1988). Phase II is the Toxicity Identification Procedure which involves methods to identify the toxicants if they are non-polar organics, ammonia, chlorine or metals (EPA 600/3-88/035, 1988). Toxicity Confirmation Procedure is Phase III

and involves confirming the suspected toxicant (EPA 600/3-88/036, 1988). Of course, these procedures can be altered according to the specific site situation. They are only meant to act as guidelines.

Once the toxicants have been identified, their source must be located. If the source can not be eliminated or replaced, attempts are then made to remove or reduce the toxicants through various treatment schemes. The appropriate treatment must be implemented with follow up monitoring.

The Plant is presently undergoing a TRE, following an inconclusive TIE. Attempts are being made to reduce toxicity through proper chemical and biological treatment. The toxicity limit at the Plant is 100% No Observed Effect Concentration (NOEC) in the effluent.

2.3.2 Sources of Toxicity

Several experiments have been performed in an attempt to determine the toxicity of some dyes. ICI America, a dye manufacturer, performed such tests and found that 75% of their dyestuffs are not toxic at concentrations of 100 mg/L, while 3.5% were toxic between 0.1 and 1 mg/L. In another survey performed by Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), 2% of the 3,000 dyes tested were found to be toxic at a level less

than 1 mg/L. (Brown, 1987)

A TIE was performed on the effluent from another dye manufacturing plant (DiGiano *et al.*, 1991). It was suspected that chloride was the primary cause of toxicity in the effluent since large quantities of sodium chloride were used at the plant. Phase I of the TIE determined that chloride accounted for 33-50% of the sample toxicity. The remainder of the toxicity was due to the more polar organic compounds.

Wells *et al.* (1991) performed a TIE on textile wastewater effluents. Three textile plants were involved in the study. Each operated it own wastewater treatment facility with a flow of about one million gallons per day (MGD). It was concluded that organics did not contribute to the LC_{50} value (the concentration that will cause the death of 50% of the organisms). An anionic speciated form of zinc was discovered as the major contributor to the toxicity. McKay (1979) agreed that heavy metals in dye wastewater, such as copper and chromium, were toxic to the microorganisms in a biological treatment system and should be removed to a large extent.

Walsh *et al.* (1980) measured the toxicity of textile mill effluents to freshwater and estuarine algae, crustaceans and fishes. Twenty three samples were examined,

and they all affected the growth of the freshwater alga, *Selenastrum capricornutum*. Thirty five percent were inhibitory while 65% were stimulatory. Fourteen of the samples were tested with the marine alga, *Skeletonema costatum*. "Overall, 71% of the samples were inhibitory and 71% were stimulatory to the marine alga." They also found that fish were generally less responsive to the waste than the crustaceans. Sixty one percent of the wastes were toxic to *Daphnia pulex*, 40% were toxic to *Pimephales promelus* and 53% were toxic to *Palaemonetes pugio* and *Cyprinodon variegatus*.

Abo-Elela *et al.* (1988) attributed the toxicity of a particular textile wastewater to organic contaminants, pH value or unionized ammonia.

Huber (1984) investigated surfactants as a cause of toxicity. Cationic surfactants were highly toxic to *Daphnia magna* and fish species. However, aerobic biochemical treatment was capable of degrading these toxic chemicals.

Ankley and Burkhard (1992) performed a TIE on primary effluent from a Publicly Owned Treatment Works (POTW). Phase I and II procedures indicated that surfactants were the cause of toxicity. Further testing revealed that sufficient amounts of anionic and nonionic surfactants existed to be concerned. Chlorine also contributed to the acute toxicity.

2.4 PRETREATMENT OPTIONS

Prior to biological treatment, it is often desirable to pretreat an industrial wastewater to prevent shocks and excessive organic loading to the treatment system. Many pretreatment alternatives exist and ultimately accomplish a variety of things. Each wastewater has different pretreatment needs, and bench studies must be performed to determine the site specific remedy.

2.4.1 pH Adjustment

The wastewater from a textile mill can sometimes be alkaline in nature. In this situation, it is necessary to reduce the pH for proper pretreatment and to ensure optimum operation of the biological system.

Addition of sulfuric acid (H_2SO_4) is a common, yet expensive method of neutralization (Nemerow, 1978). The storage and feeding requirements of H_2SO_4 are low due to its high acidity, but it is corrosive and difficult to handle. It costs $0.10/pound (Plant, personal communication, 1993).

A newer method, which is more economical, is to blow waste boiler-flue gas through the alkaline wastes (Nemerow, 1978). There is about 14% carbon dioxide (CO_2) in stack gases. Carbonic acid will form when the CO_2 is dissolved in the wastewater. The carbonic acid then reacts with the

alkaline wastes to neutralize it. The hydrogen sulfide which is developed in the stack gas must be eliminated by burning, absorbing, or venting to the upper atmosphere to prevent excess odors.

Bottled CO_2 can also be applied to alkaline wastewater in much the same way that flue gas is used, yet there are fewer operating difficulties. If the quantity of waste to be treated is large, though, treatment with CO_2 may not be economical. In 1956, a textile plant with a flow of six MGD discovered that CO_2 treatment would cost $275 each day in operating costs. Capital cost was estimated at $150,000. (1956 as cited by Nemerow 1978).

A textile plant in South Carolina recently switched from H_2SO_4 to CO_2 neutralization (Pierce, 1988). The plant cut chemical costs by 40% while eliminating some of the safety, environmental and maintenance concerns associated with acid.

Schwarzlmuller and Brissie (1988) are advocates of neutralization using flue gas. Some of the advantages pointed out include:

(1) no acidification of the wastewater

(2) flue gas is available in excess at no cost

(3) no danger of corrosion

(4) the process is easy and not hazardous.

A rough cost estimate was performed by Schwarzlmuller and Brissie (1988) to compare neutralization treatment using H_2SO_4, CO_2 and flue gas. Total costs for the use of H_2SO_4 were estimated at $205,000 per year. The use of pure CO_2 was estimated at $185,800 per year, while the use of flue gas was approximately $25,200 per year.

2.4.2 Anaerobic Treatment

Several experiments have been performed on textile dye waste using anaerobic treatment. In an anaerobic system, CO_2, hydrogen and simpler organics suitable for energy are formed from the more complex organics in the waste. The simpler organics are oxidized to acetate and hydrogen which are later converted to methane by methanogens (Metcalf & Eddy, 1991).

Anaerobic treatment of textile dye wastewater has achieved substantial color removal. Decoloration with anaerobic treatment has been seen primarily in the case of a specific type of dye - an azo dye - which contains an azo bond that is broken during the anaerobic treatment process, thereby eliminating the color.

Ghosh *et al.* (1978) performed an anaerobic experiment on the effluent from a textile mill. The wastewater was sealed in containers for several days where substantial

color reduction was observed. Experiments in an upgraded anaerobic reactor with a 12 hour detention time resulted in 10% BOD reduction and 40% color reduction.

Meyer (1981) observed that decoloration occurred readily in an anaerobic system treating azo structures. Besides color, though, the wastewater was not decomposed in any other way.

Loyd *et al.* (1992) performed experiments on a specific azo dye wastewater to investigate anaerobic treatment. It was concluded that the anaerobic treatment helped substantially in decoloration but little biodegradation was seen. Also, "anaerobic pretreatment enhanced succeeding aerobic biodegradation."

According to Wuhrmann *et al.* (1980) the decoloration of the azo dyes by anaerobic treatment is not a final degradation step. It simply changes the composition and characteristics of the wastewater, but further treatment of the waste is still required.

2.4.3 Oxidation

Pretreatment using chemical oxidation is a popular method for color removal and organic reduction. Chlorine (Cl_2), ozone (O_3) and hydrogen peroxide (H_2O_2) are among the common oxidants used.

According to Gardiner and Borne (1978), Cl_2 is the least expensive oxidant in use. However, when it is used in high concentrations, non-biodegradable matter can be produced through various chemical reactions. Halliday and Beszedits (1986) noted that Cl_2 oxidation is a simple operation and no sludge is produced. It is possible for the color that is initially removed to return and chlorinated hydrocarbons can form.

Hydrogen peroxide is not used as much as Cl_2 and O_3, yet it has been found very advantageous. Halliday and Beszedits (1986) sited one japanese publication that reported better color removal with H_2O_2 than with Cl_2.

Hickman (1993) described H_2O_2 as a "versatile oxidizing agent." It is a very stable compound which is good for long periods of storage. It may be necessary, when using H_2O_2 as an oxidizer, to add an activator such as Fenton's reagent to overcome the stability. Hickman (1993) also experimented with H_2O_2 in addition to iron (II) sulfate which was being added for coagulation of a wastewater. The H_2O_2 improved the color removal being achieved with the iron (II) sulfate alone.

According to Michelsen *et al.* (1992), the use of Fenton's reagent with H_2O_2 was effective for removing color from highly colored wastewaters that did not contain

substantial dissolved organics. The presence of sizing, organic auxiliaries or natural cotton impurities reduced the effectiveness and increased the cost. Treatment of a copper phthalocyanine dye that had a DOC concentration of 870 mg/L required 3,000 mg/L of H_2O_2. Another less organic dye required only 180 mg/L. Ozonation was selected over Fenton's reagent for those wastes high in organics.

McCurdy *et al.* (1991) found that pretreatment of a textile dye wastewater with 150 mg/L of H_2O_2 yielded less than 5% color reduction and did not improve biodegradation. Waste reduced with 225 mg/L of hydrosulfite was inhibitory to the biological treatment system. Reduction followed by oxidation with 150 mg/L of H_2O_2 produced a less inhibitory environment.

Ghosh *et al.* (1978) attempted to reduce the color in wastewater with H_2O_2, but got no results at pH 7. At a pH of 12, there was significant decoloration but only after a 24 hour detention time. Brower and Reed (1987) bleached the color out of dye wastes through addition of 100-300 mg/L of Cl_2 or H_2O_2. This treatment was only effective on some of the dyes studied.

Color was removed from a textile wastewater in less than 10 minutes through the use of O_3 (Lin and Lin, 1993). The ozonation broke the highly structured molecules into

smaller more easily degradable ones. The O_3 was ineffective as far as COD removal. Some residual COD was produced by the O_3, but it was removed easily by the activated sludge process.

2.4.4 Coagulation and Flocculation

Coagulation and flocculation are often used as a form of pretreatment, primarily for color removal, although some COD, nutrients and BOD can be removed as well. "Coagulation is a process for combining small particles into larger aggregates" (AWWA, 1990). Coagulation takes place through chemical particle destabilization or through a sweep mechanism where large flocs encompass the dyes. Flocculation is the physical process where the flocs are allowed to contact one another and increase in size. Some popular coagulants include aluminum sulfate (alum), ferric salts, lime and organic polymers.

Chemical coagulation is one of the most effective and economical techniques for color removal, especially for disperse, vat and sulfur dyes (Halliday and Beszedits, 1986). Alum, lime and ferric sulfate will remove 75-90% of the color with doses in the range of 300-600 mg/L. Subsequent addition of organic polymers will help to form larger, faster settling flocs.

Tunay *et al.* (1990) reported that "chemical coagulation typically removes 40-70% of the COD depending on the wastewater composition." Tunay *et al.* (1990) concluded that pretreatment requirements must be determined on a case by case basis.

McKay (1979) noted that lime was the most popular coagulant, capable of achieving up to 90% color removal, followed by alum. According to McKay (1979), disadvantages of these chemical coagulants include the extensive initial testing required in order to determine the dosing needs and the poor sludge that is produced. Tunay *et al.* (1990) agreed that the sludge produced through chemical processes was 30 times that in a biological system. Halliday and Beszedits (1986) also noted that the sludge produced from the addition of alum is more voluminous than that produced through the use of lime or ferric sulfate.

Porter and Sargent (1977) reported on the removal efficiencies for different treatment methods applied to textile wastewater. Coagulation with alum removed anywhere from 60-95% BOD and COD and 60-90% of the color. Temperature, pH and suspended solids were all important factors in the removal efficiencies.

An example was given by Nemerow (1952) in which dye waste from Salisbury Cotton Mill was combined with a municipal wastewater. Coagulation with alum produced the

best results with 86% color removal and 67% BOD reduction. At a pH of 8.3, the required alum dose was 200 mg/L while the dose could be lowered to 140 mg/L at a pH of 7.0. The use of alum was superior to chlorination, acidification and coagulation with lime or ferrous sulfate. When the chemical treatment was followed by biological treatment a total of 86% BOD was removed and 83% of the color was reduced.

Removal of COD and BOD through the addition of lime and ferrous sulfate was examined by Abo-Elela *et al.* (1988). Lime doses of 750-2000 mg/L reduced the COD from 974 mg/L to as low as 111 mg/L. BOD was reduced from 396 mg/L to 22 mg/L. The effluent pH following treatment with lime was greater than 12 which did not comply with effluent standards. Ferrous sulfate doses of 200-450 mg/L achieved results similar to the lime with an effluent pH of 8.8. Treatment with a combination of lime and ferrous sulfate produced the best results. Doses were in the range of 750-2,000 mg/L. Effluent COD was 99 mg/L and effluent BOD was 19 mg/L. Also, a more compact sludge was produced.

Similarly, Nicolaou and Hadjivassilis (1992) tested several coagulants on the wastewater from an actual textile dyeing plant located in Cypruss and found that a combination of ferrous sulfate and hydrated lime at a dose of 720 mg/L produced optimum results. Addition of a small amount of organic polymer improved the sludge quality. Overall, 50%

of the BOD was removed and 70% of the COD.

Woldman (1974) cited one case history of a textile dyeing mill which dyed synthetics and blends. Chemical coagulation with lime and ferric chloride removed 82.5% of the color, biological treatment removed 57% of the color and a combination of the two produced a 93.6% reduction in color (Pt-Co Units).

Another case history (Woldman, 1974) reported on color removal from a textile dye wastewater prior to discharge to a municipality. Cl_2 was tested, but was not consistently effective. An alum dose of 500 mg/L followed by 1 mg/L of an organic polymer produced 76% color removal as well as 29% COD removal. Addition of 400 mg/L of ferric chloride followed by 1 mg/L of an organic polymer achieved 73%, 77% and 73% reduction of color, COD and BOD, respectively. Up to 275 mg/L of lime were added to maintain neutral pH.

The use of lime as a coagulant was compared to alum in treatment of a textile wastewater (Shelley *et al.*, 1976). The optimum dose for each was found using the jar testing procedure. A dose of 4,500 mg/L of lime at a pH of 11.9 reduced the COD by 62% and the color by 81.5%. Six hundred mg/L of alum removed 44% of the COD and 62.8% of the color.

Rodman (1971) studied coagulation with lime and alum as well as pretreatment using activated carbon, reverse

osmosis, radiation and biological treatment. Four dyes were tested: direct blue 106, acid black 26A, disperse blue 3 and reactive red 3. Coagulation with 60 parts lime/100,000 parts dye produced 90% color removal with the acid black 26A. Twenty-four percent and 50% of the color was removed from the disperse and reactive dyes, respectively, while the direct blue 106 yielded 12% color removal. Coagulation with 40 parts alum/100,000 parts dye yielded 90% color removal of the acid black and 100% color removal of disperse blue dyes. Sixty percent color removal was obtained with the reactive red, while a maximum of 18% color removal of the direct blue 106 was seen. Rodman (1971) found biological treatment essentially ineffective for color removal of the dyes. The radiation achieved 100% color removal except with the disperse blue 3 in which case only 50% of the color was removed. Reverse osmosis yielded 95-100% color removal with all the dyes tested.

Hatton and Simpson (1986) tested alum, ferric sulfate and polyaluminum chloride for color removal from raw sewage containing textile wastewater. Effluents from four different treatment works were examined with the jar testing procedure and chemical coagulant doses ranging from 10-30 mg of M_2O_3/L. Alum was found to be the most effective, although different doses were required in the different plants and

varying results achieved. About 75% of suspended solids were removed after treatment with alum as well as 10-40% of COD. These results were applied to a plant trial. The waste contained 60% industrial waste, primarily textile. A dose of 30 mg/L of Al_2O_3 was added to achieve color removal ranging from 48-59%. Seventy one percent of solids were removed, 40.7% of COD and 23.5% BOD.

Olthof and Eckenfelder (1976) compared coagulation with lime, alum and ferric sulfate. A dose of 500 mg/L of ferric sulfate required a high pH to achieve 80-90% color removal. Five hundred mg/L of alum similarly removed 80-90% of the color at a neutral pH. Lime was required at 1.5-4 times the dosage of ferric sulfate or alum to achieve the same color removal. All three coagulants achieved similar organics removal: 30-60% COD, 23-62% BOD and 20-50% TOC. The sludge produced by addition of lime settled faster and dewatered easier than both the alum and ferric sludges. The ferric sludge behaved significantly better than the alum sludge.

The advantages of coagulation with organic polymers was reviewed by Davis (1991). Although polymers are much more expensive than inorganic salts, a much smaller volume is used, less sludge is produced and it can be applied over a much broader pH range. Experiments were performed with waste from a dyeing and finishing plant. Organic polymer

doses ranging from 200-1,200 mg/L were tested. The lowest dose gave similar results to the highest dose. On a larger scale test, waste was treated with 400 mg/L of the first polymer. A second polymer was added to increase floc size and the flocs were removed via dissolved air flotation (DAF). Additional clean up was performed with a sand filter and carbon adsorption. Overall, 85% of the color was removed, 96% of suspended solids, 99% of FOG and 34% of the dissolved solids. Most of the color removal occurred through the activated carbon while the rest was removed by the sand filter. The DAF did not aid in color removal, although that is where substantial organic reduction occurred.

The coagulation of disperse dyes with polymers was researched by Crowe *et al.* (1977). Neither nonionic nor anionic polymers were effective. Cationic polymers were effective in the range of 15-50 mg/L. It was found that minimum polymer dose was required with the polymer of the highest cationic charge. Also, increased molecular weight decreased the dose due to the large area available for adsorption. Alum coagulation of the disperse dyes was possible at a pH of 4 with doses of 30-60 mg/L Al_2O_3; yet, much lower doses (3-5 mg/L) could achieve similar results at pH 5.5-7.0.

Stahr *et al.* (1980) studied the addition of alum and organic polymers. Alum doses of 100-500 mg/L were examined using a jar testing apparatus and wastewater from three different textile plants. The alum was found to be ineffective by itself, and the sludge produced was voluminous and difficult to dewater. Addition of a low molecular weight, cationic polymer following the addition of alum produced the best results. Color standards were met with alum doses ranging from 100-500 mg/L and a polymer dose of 10 mg/L. Experiments using the polymer alone required large quantities and was very expensive. The pH of the waste being treated had a large effect on the amount of polymer needed. At a pH of 8, five times as much polymer was needed than at a pH of 4 due to the polymer charge density.

Kreye *et al.* (1972) also studied the coagulation of textile dyeing and finishing wastes using alum and polymer. Jar tests were performed and an alum dose of 350 mg/L achieved 90% color removal. Adjustments in pH did not affect COD or TOC removal efficiencies, but color removal could be improved. Optimum pH range was 5-6.5. Addition of 2-5 mg/L of organic polymer following alum addition produced good color and organic removal as well as reduced the amount of alum needed. Settling time of the floc was reduced and the treatability of the sludge was improved.

Kace and Linford (1975) investigated organic polymer coagulation of a simulated textile wastewater with and without the addition of a primary coagulant. Five organic polymers were screened at a pH of 7. The three cationic polymers achieved greater than 90% color removal. The remaining anionic polymers were ineffective. The cationic polymer which performed the best, PEI 400, had an average molecular weight of 60,000. Attempts were made to decrease the necessary dose by decreasing the pH. This was possible, although only within a small pH range, below which redispersion of the dye occurred. Treatment with alum was tried alone and achieved an acceptable color reduction although a voluminous sludge was produced. Therefore, treatment with alum and organic polymer was tried in combination and a 95% color reduction was seen with little redispersion.

As previously mentioned, Lin and Lin (1993) examined the use of ozonation followed by chemical coagulation. Color was reduced in less than 10 minutes using O_3 at a rate of 13.25-20.49 g/h. Chemical coagulation with alum following ozonation reduced 70% of the COD. Treatment with alum alone reduced more COD than if the waste were treated with O_3 then alum, but not as much of the color was removed. Lin and Lin (1993) also found that as the COD of the

wastewater increased, treatment became more difficult.

2.4.5 SEDIMENTATION AND DISSOLVED AIR FLOTATION

"Sedimentation is the separation from water, by gravitational settling, of suspended particles that are heavier than water" (Metcalf and Eddy, 1991). In the case of chemical pretreatment, the suspended particles would be the chemical floc formed. In addition to producing a clear effluent, it is desired to produce a sludge that is easy to handle and treat.

Dissolved air flotation (DAF) is "a unit operation used to separate solid or liquid particles from a liquified phase" (Metcalf and Eddy, 1991). Air is dissolved in the wastewater under several atmospheres of pressure, then the pressure is released to atmospheric level. The fine air bubbles in the liquid phase attach to the flocs and the buoyant force causes the flocs to rise to the surface. Flocs collected on the surface are removed via a skimming operation.

Sedimentation is a far simpler process with fewer operational problems. In some cases though, settling may be too slow or the flocs formed could be lighter than water, in which case use of a DAF would be necessary.

Grau (1991) cited Kalus (1986) who reported that dissolved air flotation was becoming more attractive. The

detention time in the DAF is about 10-30 minutes while 2-3 hours are needed for settling. Also, the sludge produced from the DAF has a solids concentration of 2-7% while that for settling is typically in the range of 0.8-2.5%.

As previously mentioned, Davis (1991) used DAF for removal of chemical flocs formed. Initially, a polymer was added to the waste and allowed to flocculate. Addition of a second polymer increased the floc size. The treated water then entered the DAF where it was combined with water pressurized at 60 psi. The chemical flocs floated to the surface and were removed by a skimmer. While no color was removed, 70% of the BOD and COD were reduced, 60% suspended solids and 87% FOG using a 47 minute detention time.

2.5 AEROBIC BIOLOGICAL TREATMENT

The aerobic biological treatment process involves degradation of the waste through the supply of oxygen to microorganisms. More often than not in the textile industry, this type remedy is chosen for some portion of the treatment system. It has proven effective for reducing the organic load as well as toxicity. Also, some color reduction is achieved by degradation and by adsorption of dyes onto activated sludge.

2.5.1 Biodegradability of Textile Dye Wastewater

Textile dye wastewater is partially biodegradable and contaminants can be removed through biological treatment. The characteristics of the particular wastewater will dictate to what extent the waste will degrade. In the process of treating the waste biologically, many of the dyes and chemicals are also removed by adsorption to the activated sludge.

Typically, longer aeration periods are needed to deal with textile wastewater (Alspaugh, 1973). High alkalinity, trace metals, toxicity and seasonal changes all contribute to the difficulty of treating textile waste. Also, surfactants present in the wastewater reduce the rate of adsorption of oxygen from the air into the water.

Weeter and Hodgson (1977) studied a wastewater treatment plant that received waste from three textile mills. Experiments indicated a low oxygen uptake rate. This signified that the dyes or chemicals were difficult to degrade. It was concluded that the structures which give the dyes their color were not affected biologically. Singer and Little (1975) as cited by Weeter and Hodgson (1977) concluded that the observed difference in TOC and BOD of the effluent from 21 day BOD tests on 20 textile dyes would indicate that a nonbiodegradable portion existed. According to Gardiner and Borne (1978), the chemical structure of a

dye or chemical has a lot to do with the extent to which it will biodegrade.

Porter and Snider (1976) conducted long term BOD tests on textile chemicals, eight of which were dyes. The textile dyes used in the study degraded slowly and continued to degrade and consume oxygen after 30 days. It was recommended that the BOD test be coupled with a COD test so that total organics in the waste could be compared to degradable organics.

Porter and Sargent (1977) reported that 84% of the BOD in a particular textile wastewater could be removed through biological treatment while about 33% of the COD remained unless it was held up in the sludge. A maximum of 20% of the color could be removed by biological processes. It was concluded that biological treatment alone was insufficient for cleaning the wastewater.

2.5.2 Continuous Flow Reactors (CFR)

A continuous-flow reactor is a reactor or tank that is continuously fed wastewater and treated effluent is continuously leaving the reactor. This is in contrast to a batch reactor which receives waste and releases treated water at certain time intervals. In the case of a completely-mixed, continuous-flow reactor, clarification of the effluent is an important part of the system. Cells from

the reactor are separated and a portion is recycled back to the reactor. Continuous-flow aerobic treatment systems include activated sludge, aerated lagoons, trickling filters and rotating biological reactors.

Shriver and Daugue (1977) studied aerobic biological treatment of a wastewater from a textile dyeing mill in North Carolina. The waste consisted of sizing, dyes, soaps and oils. The high ratio of COD to BOD of the influent indicated that the organic waste would degrade at a much slower rate than most wastes. Four bench scale reactors were operated with detention times of 12, 24, 36 and 48 hours. The reactor contained an aeration chamber, air supply, clarifier and sludge return. BOD, COD, color and SS were measured every day for a one month period. Some conclusions drawn from the results of the study include:

(1) The waste was deficient in nitrogen and phosphorus.

(2) Foaming was apparent, but posed no problem and was reduced as the MLSS increased.

(3) Substantial COD and color removal could be seen with increased detention time.

(4) 85% COD removal was easily achieved at detention times of 36 and 48 hours.

Overall, the activated sludge process was successful with this particular textile dye wastewater.

Abo-Elela *et al.* (1988) also studied treatment of

textile wastewater with a bench-scale, activated sludge unit. Influent COD of the wastewater ranged from 422-1,876 mg/L, and influent BOD was in the range of 117-735 mg/L. Prior to treatment, the textile waste was combined with 50% domestic wastewater for nutrients. A detention time of 6 hours and an MLSS of 3,000 mg/L yielded an effluent COD of 82 mg/L and an effluent BOD of 20 mg/L.

Woldman (1974) reviewed a situation in which treatment of waste from a cotton manufacturing and finishing mill was done using the activated sludge process and compared to treatment by an aerated lagoon. The wastewater had an average flow rate of three MGD, an average influent BOD of 500 mg/L and an average influent color of 1300 mg/L. The activated sludge unit, operated with a one day detention time, removed 65-91% of the color and 90-98% of BOD. The aerated lagoon, operated with a five day detention time, removed 0-50% of the color and 65-87% of the BOD. Another case cited by Woldman (1974) dealt with wastewater from a plant that dyed and finished synthetics. When the waste was chemically pretreated with high doses of lime, 12% of the BOD was removed and 72% of the color. An aerated lagoon with a three day detention time followed the chemical treatment and removed an additional 64% of the BOD and 9.3% of the color.

Shelley *et al.* (1976) compared chemical-biological

treatment to chemical-physical treatment. The textile wastewater was pretreated in two manners: (1)alum and (2) excess lime. The two waste streams were then treated either biologically in a batch activated sludge unit or physically with 40 mg/L of $HgCl_2$ to prevent biological growth prior to being pumped through an activated carbon unit. Following pretreatment with alum and biological treatment, COD was reduced by 80%. Biological treatment and pretreatment with lime yielded a COD removal of 86%. The pretreated wastes that were sent through activated carbon yielded 55% TOC removal with alum and 66% TOC removal with lime.

Loyd *et al.* (1992) studied Navy 106 wash water combined with 25% domestic sewage. Aerobic treatment in bench scale activated sludge units produced 38% reduction of TOC, 75% BOD_5 reduction and 35% COD reduction. Anaerobic treatment of the wastewater had little effect on the BOD_5 and COD. Loyd *et al.* (1992) also examined the reduction of toxicity through aerobic and anaerobic treatment, as well as a combination of anaerobic and aerobic treatment. Untreated wastewater had an LC_{50} of 7%. Anaerobic treatment did not change this value, but subsequent aerobic treatment resulted in an LC_{50} of 56%. Aerobic treatment alone increased the LC_{50} to 26%.

Little and Lamb (1973) believed that toxicity was

reduced by biological treatment via adsorption onto the sludge. Abo-Elela *et al.*(1988) were able to reduce the toxicity of a textile wastewater by first combining it with 50% domestic sewage, then treating the waste with activated sludge.

Continuous-flow, bench-scale, biological reactors are often used to determine the kinetic coefficients of a particular wastewater. These coefficients can be used in biological kinetic models for design of a full size biological treatment system. The parameters that need to be determined include the endogenous decay coefficient (k_d), maximum yield coefficient (Y), substrate concentration at half the maximum growth rate (K_s), and maximum rate of substrate utilization per unit mass of microorganisms (k). By varying the sludge age in several reactors and measuring various kinetic parameters such as MLSS, effluent SS, influent COD, and effluent COD, plots can be constructed and values for kinetic coefficients can be estimated.

Gayle *et al.* (1986) operated a pilot plant study for the activated sludge treatment of a wastewater from a nylon-producing textile plant. A chemostat was operated at 20, 30 and 40 day detention times. TOC removal ranged from 93-95% and TKN removal ranged from 28-56%. An attempt was made to determine the kinetic coefficients, although variations of

the influent wastewater made comparisons between the different sludge ages difficult. Y and k_d could be reported with some confidence, while values for K_s and k were more difficult to evaluate (Gayle *et al.* 1986). The values reported are given below:

Y= 0.7 mg VSS/mg TOC

k_d = 0.05 day^{-1}

k = 0.3-1 mg/mg-day

K_s = 600-4,050 mg/L

Brown *et al.* (1984) operated three continuous-flow, activated sludge units at hydraulic retention times (HRT) of 5, 10 and 15 days to develop the biokinetic coefficients of a textile wastewater containing primarily caprolactam, the cyclic monomer for nylon-6. Greater than 85% removal of organic carbon could be achieved with an HRT greater than or equal to 10 days. The following kinetic coefficients were obtained assuming 40 mg/L of residual COD.

Y = 0.17 mg/mg

k_d = 0.3 day^{-1}

k = 1.0 mg/mg-day

K_s= 223 mg/L

Ghosh *et al.* (1978) performed treatability studies on textile waste alone and on a combination of textile and domestic wastewater. Four continuous-flow, bench-scale

reactors were used with sludge ages ranging from 9-50 days. The combination wastewater achieved a higher BOD removal. Sludge settling characteristics were better and the oxygen requirement was less. The kinetic data obtained can be seen in Table 1.

Table 1. Kinetic coefficients of textile wastewater (Ghosh *et al.*, 1978).

Coefficients	Mill	Mill & Domestic
K (1/mg-day)	0.002	0.004
K (1/day) maximum rate of substrate uptake	0.19	0.24
K_t (true cell yield coefficient)	0.52	0.53
K_d (decay coefficient) 1/day	0.013	0.024

Additional studies have been performed on the removal of color from textile wastewater by adsorption to activated sludge. Hitz *et al.* (1978) made several broad comments regarding the behavior of various dye groups in an activated sludge process. It was reported that the high solubility of acid dyes lead to low adsorption. Very little adsorption occurred with reactive dyes. Disperse dyes reportedly had high to medium adsorption, while high adsorption occurred with both direct and basic dyes.

Dohanyos *et al.* (1978) studied the removal of 20 organic dyes by adsorption onto activated sludge. Removal of the dyes by activated sludge was found to be considerably different from the removal of degradable organic matter. The controlling processes include diffusion, adsorption and chemical linkages. The ability of the dyes to be removed by activated sludge is a function of the dye properties, as well as the activated sludge properties. Also, the quantity of dye removed was directly proportional to the amount of sludge in the system.

Ganesh *et al.* (1993) performed batch sludge digestion studies using aerobic and anaerobic treatment. "Sorption and aerobic color degradation of Navy 106 wash water increased with increased biomass concentration in the reactors." High color to biomass ratios resulted in less color degradation.

2.5.3 Sequencing Batch Reactor (SBR)

"A sequencing batch reactor is a fill-and-draw activated sludge treatment system" (Metcalf and Eddy, 1991). The main difference between SBRs and CFRs is that the SBR process is a batch process. All unit processes take place in the same reactor, sequentially. The typical five step process carried out is (1) fill - addition of substrate to the reactor, (2) react - aeration and reaction period, (3)

settle - solids separation by gravity, (4) draw - removal of clarified water and (5) idle - the time after drawing from tank, before refilling.

According to Irvine and Busch (1979) "The SBR provides in time what the CFR provides in space." An SBR is often used by the food processing industry or small rural communities. SBRs were abandoned for a time due to operational difficulties and demand of attention. But today, with improved process technology, the SBR "calls for reevaluation" (Irvine *et al.*, 1977).

Arora *et al.* (1985) reported several advantages of the SBR: (1) it can handle fluctuations, (2) the discharge can be held until it meets effluent limits, (3) the length of the cycle can be kept the same while the levels in the tank can be manipulated, (4) no return activated sludge is necessary (5) filamentous growth can be controlled, and (6) nitrogen and phosphorus removal can be achieved without chemicals.

Wanner (1992) compared CFRs to SBRs. He reported that the two were comparable as far as COD, phosphorus and nitrogen removal were concerned. The activated sludge in the SBR performed nitrification and denitrification at a slightly higher rate than the CFR. The settling properties of the sludge from the CFR were acceptable with medium-sized, irregular flocs, while the SBR sludge exhibited a

high settling velocity by giant flocs.

Al-Harazin *et al.* (1991) studied the use of an SBR for treatment of toxic wastewater. An SBR with MLSS concentration of 3,000 mg/L effectively treated a wastewater with up to 800 mg/L of phenol with no signs of inhibition. Effluent phenol concentration was 0.5 mg/L. The SBR also responded well to shock loading. Seventy five percent removal was achieved with loadings up to 1,600 mg/L of phenol and a 1 day detention time.

The treatment of hazardous waste using an SBR was studied by Herzbrun *et al.* (1985). Substantial energy and costs savings were seen by use of an SBR rather than activated carbon for removal of the organic compounds from the hazardous waste. Nine, bench-scale reactors were operated with detention times ranging from 1.25-10 days. Reactors at colder temperatures operated less effectively, yet still met the effluent limits. A full-scale operation achieved 76% TOC removal and 99% phenol removal.

McCurdy *et al.* (1991) studied biological degradation of pretreated textile wastewater in an SBR. A mixture of 75% textile waste and 25% municipal waste was pretreated with hydrosulfite and hydrogen peroxide. Following this pretreatment, the waste was treated in an SBR with a cycle time of 1 day. Overall, removals of color, COD, TOC and BOD were 77%, 60%, 61% and 66%, respectively.

3.0 METHODS AND MATERIALS

The following chapter presents the methods and materials used in the pretreatment and biological treatment of the textile dye wastewater. The analytical procedures used to characterize the wastewater are also introduced. The "waste streams" in the subsequent chapter refers to wastewaters from the following operations at the Plant: printing, thermosol dyeing, and bleaching/finishing.

3.1 PRETREATMENT OF TEXTILE DYE WASTEWATER

Several studies were conducted in an attempt to determine the most efficient means of pretreatment. Color removal and organic reduction were the primary concerns in the pretreatment step. Table 2 provides an outline of the experiments performed.

3.1.1 Anaerobic Degradation

The three waste streams were treated separately in an experiment to determine if the color could be degraded through anaerobic treatment. A batch test was conducted using 99 (33 per waste stream) BOD bottles prepared with the wastewater, Blacksburg primary effluent (BPE), and sludge from the secondary clarifier at the Plant in the proportions shown in Table 3. The test was modeled after an experiment

Table 2. Pretreatment alternatives.

Pretreatment	Waste Stream Treated	Tests Performed*
Anaerobic Degradation	Print Thermosol Bleach/Finish	Color
Hydrogen Peroxide Addition	Print/Thermosol Bleach/Finish	Color, DOC
Aeration	Print Thermosol Various Combos	Color, TSS
Polymer Addition	Print Thermosol Bleach/Finish	Color, DOC, TSS
Carbon Dioxide Addition	Print/Thermosol	pH, Color, DOC

*See Appendix A for definition of abbreviations

Table 3. Preparation of test bottles for each of the waste streams in the anaerobic pretreatment study.

Number of Bottles#	Waste* (mL)	BPE (mL)	Secondary Clarifier Sludge (mL)	%Waste: %BPE
7x3	295	0	5	100:0
13x3	222	73	5	75:25
13x3	148	148	5	50:50

*Waste refers to print, thermosol, or bleach/finish, all treated separately.
#x3 represents the number of bottles in triplicate

performed by Loyd *et al.* (1992). The pH of the waste was adjusted to 7.0 prior to treatment. The bottles were water-sealed and incubated at 34°C. Each bottle was shaken daily during the first 14 days of the experiment.

Color of the treated waste was measured on days 0, 2, 4, 6, 10, 14, and 21 to determine the extent of color removal over time. One bottle from each group was used for the initial color measurement. Two bottles were used from each of the 75:25 and 50:50 groups and one bottle from the 100:0 group for subsequent color measurements. On each day that color was measured, a new set of five bottles from each waste stream was used since the previously used bottles would have been exposed to the air.

Aerobic treatment would follow this anaerobic step if it were used at the Plant, so the bottles were aerated for 15 minutes prior to color measurement to take into account possible changes that could occur due to exposure to the air.

3.1.2 Hydrogen Peroxide Addition

Hydrogen peroxide (H_2O_2) was added to the waste streams in a series of jar tests to determine if color and/or organics could be reduced. A standard Phipps and Bird (Richmond, VA), six-paddle jar test apparatus was used. The

bleach/finish waste stream was the focus in this experiment although a qualitative test was done on a combination of the print/thermosol waste streams.

A 3% H_2O_2 solution was added to 500 mL samples of bleach/finish waste in concentrations ranging from 10-400 mg/L. A two minute rapid mix period (120 rpm) was followed by a 15 minute flocculation period (30 rpm). After removing the paddles, the samples were allowed to settle for 20 minutes at which time samples were taken for color and DOC measurements.

Three parts print and four parts thermosol were combined and treated with 3% H_2O_2 in concentrations of 50-500 mg/L. No quantitative measurements were taken due to the lack of apparent reaction.

3.1.3 Aeration

An experiment was performed to determine if aeration would have any effect in changing the color and/or suspended solids of the print and thermosol waste streams.

One liter (L) each of print, thermosol, and three different combinations of print and thermosol were aerated for one hour. A 1:1 ratio of print:thermosol was used to represent what was occurring at the Plant (blend). Three parts print were combined with four parts thermosol to

represent the wastewater that would be treated if the Plant facilities were large enough to accommodate all of the waste for pretreatment (combo). Three parts print were combined with two parts thermosol to represent a possible enlarged printing capacity at the Plant (future). Color and total suspended solids measurements were taken before and after treatment.

3.1.4 Polymer Addition

Presently, the Plant is using polymer addition as a means of pretreatment. Several jar tests were performed using various polymers, as described in the subsequent section, to determine if a more effective, cost efficient polymer existed.

3.1.4.A Jar Testing

The three waste streams, print, thermosol, and bleach/finish, were initially tested separately with several different polymers. The polymers tested were: Nalco 8105, Magnifloc 577-C, Polymer C377, Polymer C381, and Polymer C372. Table 4 summarizes the relative molecular weights and charge densities of these polymers. The polymer used at the Plant, AL220, was also included in the testing. A 1%, by weight, polymer solution of each of these was prepared.

Jar tests were performed as previously described in

Table 4. Summary of polymer characteristics.

Polymer	Molecular Weight	Charge Density
Nalco 8105	low	very high cationic
Magnifloc 557-C	medium	very high cationic
C377	medium	very high cationic
C381	high	very high cationic
C372	low	very high cationic
AL220	low	high cationic
A130	very high	medium anionic

section 3.1.2. Prior to polymer addition, the waste streams were neutralized with 1 N sulfuric acid (H_2SO_4). Polymer was added in concentrations ranging from 25-800 mg/L. Following settling, samples were taken for color, TSS and DOC analysis.

In addition to testing the three waste streams separately, several different combinations were studied: (1) 1:1:1 print:thermosol:bleach/finish (mix), (2) 1:1 print:thermosol (blend), (3) 3:4 print:thermosol (combo), and (4) 3:2 print:thermosol (future). Color measurements were made following treatment.

The most effective polymer, as decided from color and organics reduction, was chosen for further polymer testing and compared to the polymer presently used at the Plant, AL220. Using the previously determined optimum polymer dose, the pH of the samples was varied from 4-8 and jar testing was performed to find the best pH at which coagulation would occur.

Using the optimum pH and polymer dose, an anionic polymer (A130) was added following the addition of each of the cationic polymers to determine if coagulation/settling could be improved. Prior to addition of the anionic polymer, the sample was neutralized to pH 7. Flocculation time for the anionic polymer was 10 minutes at a speed of

30 rpm. Concentrations from 2-20 mg/L of A130 were considered.

3.1.4.B Separation of Chemical Flocs

It was necessary to decide how to separate the flocs produced in the pretreatment step. The Plant presently uses dissolved air flotation (DAF) which is effective, yet much more costly and labor intensive than settling.

Based on results to this point, a decision was made to pretreat the print and thermosol waste streams only. The bleach/finish waste stream would go without pretreatment to biological treatment. Print, thermosol, and a 1:1 combination of print and thermosol (blend) were studied. Settling and DAF experiments were performed with the waste streams after treatment with polymers C377 and AL220/A130. Previous experiments eliminated all other polymers for use in this final testing.

To measure the efficiency of settling, 1 L of the waste was treated as previously discussed using jar testing apparatus. The optimum pH and polymer dose were used. Following flocculation, the sample was transferred to a 1 L graduated cylinder and allowed to settle for two hours. The level of the settling sludge in the cylinder was measured every five minutes for the first half hour, every 15 minutes for the next half hour, and every 30 minutes after that.

Measurements were taken to determine color and organics reduction and effluent solids.

The efficiency of DAF was measured using a bench-scale DAF unit (Figure 2). Three L of the waste stream were placed in a 5 L circular, plastic container and treated with the appropriate polymer dose. A mixer with a variable speed motor was used. The flocculated sample was pumped into the DAF unit where separation occurred. Again, measurements were taken to determine color and organics removal and effluent solids.

3.1.5 pH Adjustment

The polymer eventually chosen for pretreatment, AL220, required a pH of about 4 to be most effective. If the pH of the waste was adjusted to about 6, subsequent addition of the acidic AL220 would allow a final pH of 4. During the preliminary jar testing, H_2SO_4 was used to reduce the pH. In an effort to reduce potential hazards due to acid storage/use at the Plant, the ability of carbon dioxide (CO_2) to decrease pH was evaluated versus the capacity of acid additions.

Three L of the print/thermosol (3:4 combination) waste was treated with CO_2. The amount of CO_2 was measured using a flow meter and a stop watch. The pH was measured over time.

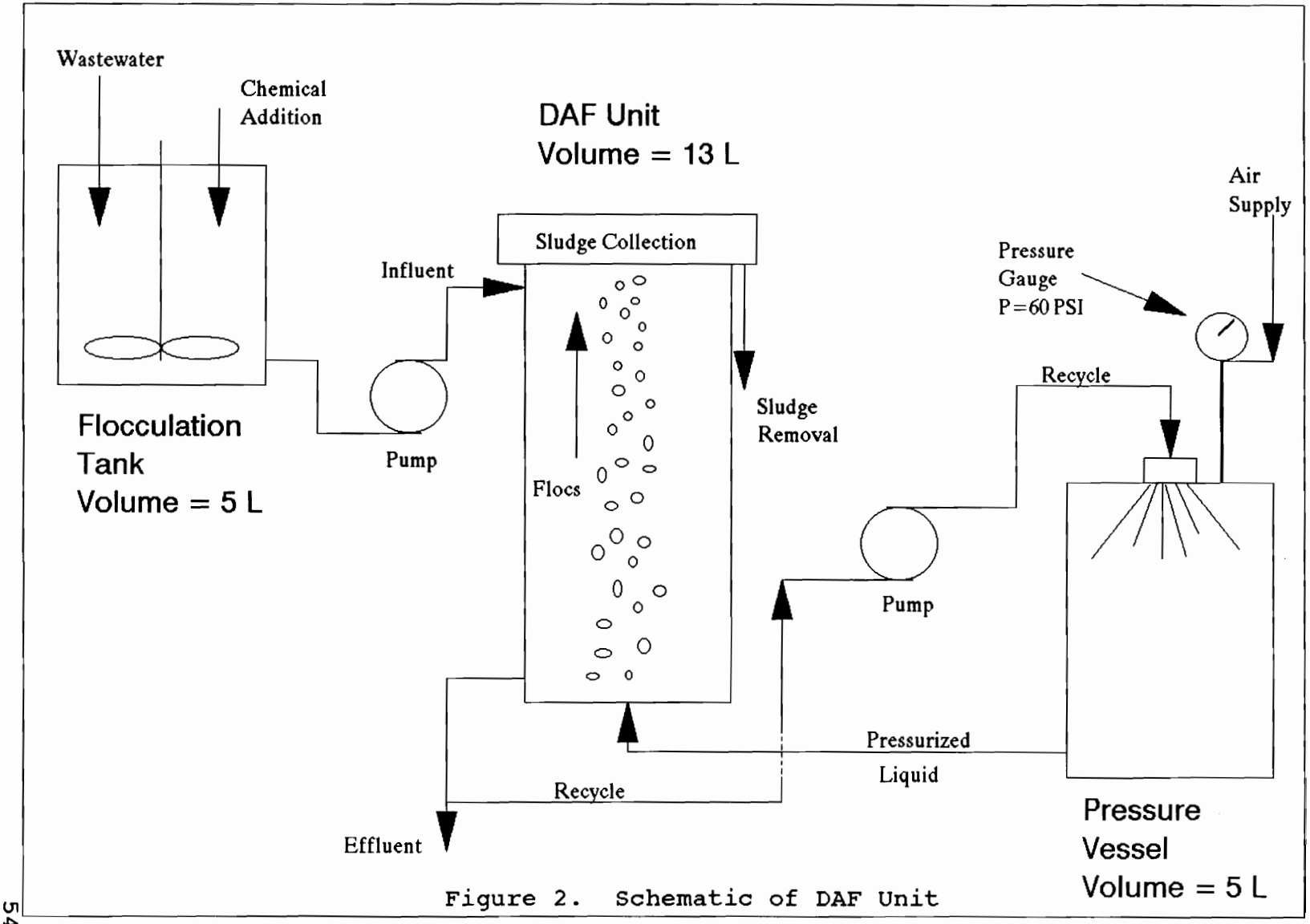


Figure 2. Schematic of DAF Unit

After pH adjustment, the waste was treated with C377 and AL220/A130 as previously discussed using the jar testing apparatus. Polymer concentrations of 0, 400, 500 and 600 mg/L were examined. The effluent color and DOC were measured and compared to those values obtained when the pH of the waste was adjusted with acid.

3.1.6 Bench Scale Pretreatment Apparatus

Prior to bench-scale, biological treatment, up to 25 gallons of combined print and thermosol waste had to be pretreated on a batch basis. A 30-gallon Nalgene tank was used for coagulation, flocculation, and settling purposes. An American Model LR-41C variable speed stirrer was used for mixing. Three parts print and four parts thermosol were added to the tank and the pH of the waste was adjusted to about 6 using 1 N H_2SO_4. AL220 was added during the two minute rapid mix period to provide for a concentration of 600 mg/L. Following a 15 minute flocculation period, the pH of the waste was adjusted to about 7 using 1 N NaOH. Anionic polymer, A130, was then added at a concentration of 5 mg/L and the sample was allowed to flocculate for 10 minutes. The mixer was then shut off and removed; and the waste was allowed to settle for one hour at which time the supernatant was removed through pumping with a Masterflex

peristaltic pump at a rate of 1.5 L/min. The settled sludge was disposed of. Analyses were performed on the influent and effluent of the pretreatment step. Table 5 outlines the types and frequency of the tests performed.

3.2 BIOLOGICAL TREATMENT

A biological treatability study was performed using the waste from the Plant in an attempt to determine the kinetic coefficients of the wastewater. Also, effluent toxicity was measured and efforts were made to eliminate or reduce it. Four continuous-flow reactors were used. A sequencing batch reactor was also studied to compare its efficiency to that of the continuous-flow reactors.

3.2.1 Continuous-Flow Reactors

Four, continuous-flow, biological reactors were set-up in a constant temperature room (20°C) under a hood. Each reactor was operated at a different sludge age: 8, 15, 20, and 30 days.

The volume of each reactor was about 9.65 L and each was divided into two compartments by a baffle as shown in Figure 3. The larger of the compartments served as the activated sludge reactor and occupied about 85% of the volume. Sufficient air from the lab air lines was provided

Table 5. Analyses performed on pretreatment influents and effluents.

Analyses*	Sampling Frequency
Color, DOC	Once a week
TKN, NH_3-N, Total P, OrthoP, COD, BOD_5, TSS, Zinc, Silver, Copper, Sulfate, Chloride, Nitrate, Nitrite	Minimum of three times

*See Appendix A for definition of abbreviations.

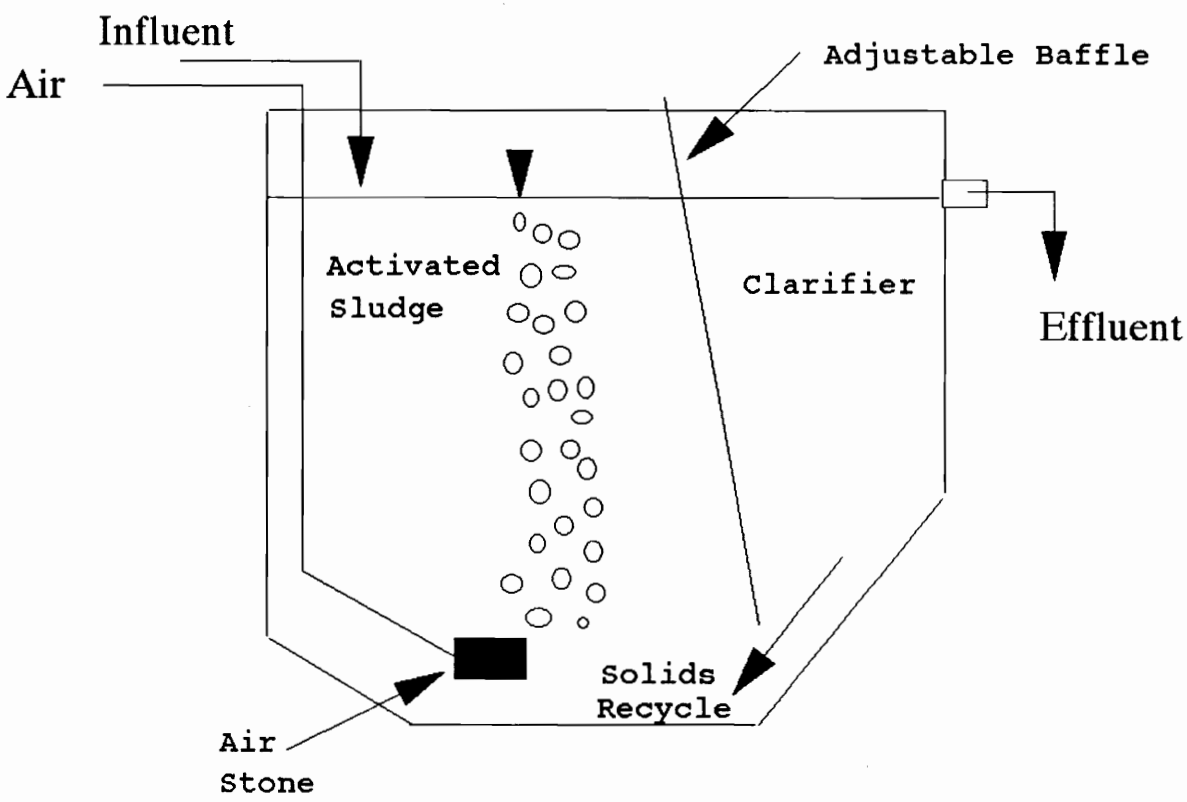


Figure 3. Schematic of Continuous-Flow Biological Reactor

to this compartment through an air stone to aerate, as well as mix the contents of the reactor.

The smaller compartment acted as a clarifier. Sludge was allowed to settle and biomass was recycled back to the activated sludge process.

The biological reactors were initially seeded with activated sludge from the aeration lagoon at the Plant. The seed was therefore already well acclimated to the wastewater.

Feed to the biological reactors consisted of actual waste from the Plant. Each week, fresh samples of print, thermosol, and bleach/finish waste were delivered to the lab at Virginia Tech. Approximately 0.3 MGD each of print waste and bleach/finish waste are produced at the Plant and 0.4 MGD of thermosol waste are produced. Sanitary waste produced on site is also treated in the biological treatment plant following partial treatment in an Imhoff tank. Therefore, based on relative flows and results of pretreatment work, print and thermosol waste were combined in a 3:4 ratio and pretreated as described in section 3.1.6. The effluent from the pretreatment process was combined with three parts bleach/finish waste. The amount of sanitary waste added was calculated assuming each of the 130 employees produced 30 gal/day of waste. These waste streams were combined in a 30 gallon plastic container. The

contents were stirred daily and the pH of the influent was maintained at about 7.5.

A Masterflex peristaltic pump with four heads supplied feed to the reactors. A hydraulic retention time (HRT) of three days was desired so a feed rate of 2.2 ml/min was maintained.

In order to maintain the desired sludge age, it was necessary to waste from the reactors daily. The mixed liquor suspended solids (MLSS) was measured and the amount to be wasted was calculated using the following equation:

$$\theta_c = \frac{V_r X}{Q_w} \qquad (1)$$

where θ_c = sludge age (days)
V_r = reactor volume (L)
X = mixed liquor suspended solids concentration (mg/L)
Q_w = mass of sludge wasted (mg/day)

The reactors were replenished with an equivalent amount of wastewater so the hydraulic retention time would not be affected.

3.2.2 Sequencing Batch Reactor (SBR)

One bench-scale, sequencing batch reactor (SBR) was used in the study of this wastewater. The reactor had a volume of 10 L. Eight L were occupied by the waste. The reactor was initially seeded with activated sludge from the

aerated lagoon at the Plant.

The mode of operation for the sequencing batch reactor was fill, react, settle, draw, and idle. Section 2.5.3 describes these steps in more detail.

The feed to the SBR was the same as the feed to the continuous flow reactors. Four L of the influent were pumped into the reactor each day at a rate of about 0.5 L/min. A Masterflex peristaltic pump with two pump heads was used. Air for the react period was supplied from the lab air lines through two, 6 inch, air stones. The react period for the SBR was 21 hours. The settle period was one hour, after which time 4 L of effluent were drawn from the reactor using the same pump described above at a flow rate of 0.5 L/min. Idle time was approximately one hour. Each complete cycle was therefore 24 hours long.

It was desired to maintain the MLSS of the SBR around 4,000 mg/L, so it was necessary to periodically waste from the reactor. The amount to be wasted was determined using a mass balance on the actual MLSS.

On day 30, the effect of nutrient addition on the SBR was examined. Ten mg/L of NH_4Cl as N were added with 1 mg/L of KH_2PO_4 as P during the fill period of the cycle. Effluent wastewater characteristics were measured following addition of the nutrients.

3.2.3 Analyses

MLSS, color, and COD were measured every other day in all the reactors to determine when steady state was reached. Once steady state was reached, several tests were performed in an attempt to characterize the waste as it went through the biological treatment process. The measurements made and their frequencies can be seen in Table 6.

3.3 ANALYTICAL PROCEDURES

Several analyses were performed on the influents and effluents of the pretreatment step and the biological treatment step to characterize the wastewater, as well as to determine the efficiency of the treatment being performed. *Standard Methods for the Examination of Water and Wastewater (*to be referred to as *Standard Methods, 1992)* was the source for the methods used in the analyses. Table 7 describes storage conditions of the samples collected.

3.3.1 Total/Dissolved Organic Carbon

Total and dissolved organic carbon (TOC and DOC) samples were analyzed on a DC-80 Dohrmann Automated Laboratory Total Organic Carbon Analyzer in conjunction with a Horiba PIR-2000 General Purpose Infrared Gas Analyzer. Dissolved organic carbon samples were filtered through 0.45 μm membrane filters prior to analyses. *Standard Methods*

Table 6. Analyses performed on biological treatment influents and effluents.

Analyses*	Sampling Frequency
Color, MLSS, COD, TSS	Every other day
MLVSS	Once a week
TKN, NH_3-N, Total P, OrthoP, BOD_5, Zinc, Silver, Copper, Sulfate, Chloride, Nitrite, Nitrate, DO	Minimum of three times
Chronic Toxicity	Twice
pH, Temperature	Once a week

*See Appendix A for definition of abbreviations.

Table 7. Storage and sampling conditions.

Analyses	Sample Volume Collected (mL)	Storage Conditions
TOC/DOC	>20	P*, -17°C < 2 weeks
Solids	>40	P, 4°C < 2 days
COD	>100	P, 4°C < 7 days, pH < 2
BOD	>1000	P, 4°C < 1 day
Total P	>500	P, 4°C < 7 days pH < 2
OrthoP	>50	G*, 4°C < 2 days
TKN/NH_3-N	>500	P, 4°C < 7 days pH < 2
Color	>50	P, 4°C < 2 days
Metals	>50	P, pH < 2, 20°C, 2 weeks
Ions	>50	P, 20°C < 2 weeks
Toxicity	>1000	P, 4°C < 2 days

*P = plastic, G = glass

(1992) method 5310 C, Persulfate-Ultraviolet Oxidation Method, was followed. Samples were analyzed with the instrument set on the appropriate range. The samples taken before and after pretreatment and samples of the bleach/finish stream contained particles that could have interfered with TOC measurements or possibly damaged the equipment. Therefore, TOC of these samples was not measured.

3.3.2 Solids

Total suspended solids (TSS) and mixed liquor suspended solids (MLSS) were measured according to *Standard Methods* (1992) method 2540 D (Total Suspended Solids Dried at 103-105°C). Samples for TSS analyses were taken from the effluent of each reactor. Samples for MLSS were taken following removal of the baffle and sufficient mixing of the entire contents of the reactor. Mixed liquor volatile suspended solids (MLVSS) were measured according to method 2540 E (Fixed and Volatile Solids Ignited at 500°C). Ten mL samples were analyzed and glass fiber filters were used.

3.3.3 Chemical Oxygen Demand

Soluble and total COD tests were performed. Samples were filtered through 0.45 μm membrane filters for soluble

COD analyses. *Standard Methods* (1992) method 5220 C (Closed Reflux, Titrimetric Method) was followed in the analysis.

3.3.4 Five Day Biological Oxygen Demand

Five day BOD (BOD_5) tests were performed on soluble samples filtered through 0.45 μm membrane filters and total samples. The samples were seeded when necessary with 1 mg/L of activated sludge from the bench-scale, activated sludge units. The BOD_5 test was performed as outlined in *Standard Methods* (1992), method 5210 B (5-Day BOD Test). Dilutions in the range of 0.01-0.1 were used, depending on the anticipated final BOD_5 value. Soluble BOD_5 measurements of the waste before and after pretreatment and the bleach/finish waste were not performed due to the difficulty in filtering the large quantities of waste required.

3.3.5 Total Phosphorus/Orthophosphorus

Total phosphorus (Total P) was measured according to *Standard Methods* (1992) Method 4500-P E (Ascorbic Acid Method) along with method 4500-P B (Sample Preparation-Persulfate Digestion Method). Rather than autoclaving, the samples were digested for 30 minutes in a block heater set between 120 and 130°C.

Orthophosphorus (OrthoP) was measured according to

method 4500-P E. Samples were stored for no more than two days and filtered through 0.45 μm membrane filters immediately following sample collection.

For both tests, colorimetric measurements were performed on a Beckman DU 640 Spectrophotometer.

3.3.6 Total Kjeldahl Nitrogen and Ammonia

Total Kjeldahl Nitrogen (TKN) was measured in accordance with *Standard Methods* (1992) method 4500-N_{org} B (Macro-Kjeldahl Method)and method 4500-NH_3 E (Titrimetric Method). One hundred mL samples were analyzed. Titrations were performed with 0.02 N H_2SO_4.

Ammonia (NH_3-N) was measured according to method 4500-NH_3 E as well, following distillation as outlined in section 4500-NH_3B (Preliminary Distillation Step). Sample size was 150 mL.

3.3.7 Color

Color was measured as outlined in method 2120 E, the ADMI Tristimulus Filter Method (Proposed), *Standard Methods* (1992). A Bausch and Lomb Spectronic 20 spectrophotometer was used for measurements. The Spectronic 20 was calibrated using platinum-cobalt color standards. Samples were filtered through 1.2 micron filters and pH adjusted to 7.6.

3.3.8 Metals

Copper, silver, and zinc were analyzed according to the method outlined in *Methods for Chemical Analysis of Water and Wastes* (EPA-600/4-79-020). Samples were filtered through 0.45 μm membrane filters prior to analysis on a Perkin-Elmer 703 Atomic Absorption Spectrophotometer. In cases where the level of detection required was low, the furnace was used for analysis. The flame was used when the concentration of the metal to be detected was high enough.

3.3.9 Ions

Chloride, nitrate, nitrite, and sulfate ions were measured using a Dionex 2010i Ion Chromatograph. Method 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity) of *Standard Methods* (1992) was used. Prior to analysis, samples were filtered through 0.45 μm membrane filters.

3.3.10 Toxicity

Short term chronic toxicity testing was performed at Biological Monitoring Incorporated (BMI), Blacksburg, VA. Procedures for the testing are outlined in *Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms* (EPA/600/4/89/001).

Effluents from the reactors with sludge ages of 15, 20 and 30 days were tested. Composite samples were taken over a 24 hour period. Samples were stored at 4°C for up to 36 hours. During the seven day toxicity test, solutions were renewed daily, and the temperature was maintained at about 25°C.

Short term chronic tests performed with the organism, *Pimephales promelas* (fathead minnow), were designed so that two replicates per concentration and 10 organisms per replicate were considered. The test volume used was 200-250 mL and the organisms were fed three times daily. It was necessary to aerate the samples throughout the testing period due to insufficient dissolved oxygen levels.

Toxicity testing with *Daphnia pulex* was performed with five replicates per concentration and one organism per replicate. The organisms were fed once each day and maintained in 15 mL of test solution.

3.3.11 pH/Temperature/Dissolved Oxygen

Temperature was measured using a thermometer graduated in celsius (°C). The pH was measured using either a portable Corning pH 106 meter or a bench-top, Fisher Accumet pH meter. The meters were calibrated with standards at pH 7.0 and 4.0 prior to use. A YSI Model 54 Oxygen Meter

(Yellow Springs, OH) was used to measure dissolved oxygen (DO). The DO in the activated sludge portion of the CFR was measured initially and at various times throughout the treatment.

4.0 RESULTS AND DISCUSSION

The following chapter presents the results of all the experiments that were performed in an attempt to treat the textile dye wastewater from the Plant. The chapter is divided into sections according to the method of treatment. A discussion follows each set of results.

Tables and figures are used throughout this chapter to aid the reader in understanding and visualizing the results. Supplementary tables and data can be seen in the appendices.

4.1 pH ADJUSTMENT

Figure 4 represents the results of treating a 3:4 combination of print:thermosol with carbon dioxide (CO_2). Carbon dioxide was bubbled into 3 L of the waste at a flowrate of 625 ml/min for 20 minutes. As can be seen in the figure, the pH of the waste was reduced from 9.2 to 5.5 in 10 minutes. The amount of CO_2 used was equivalent to 2,083 mL/L waste. No substantial pH reduction was seen beyond 10 minutes. Twenty minutes of treatment reduced the pH to 5.37 with an additional 2.1 L of CO_2/L waste.

An alkalinity titration was also performed on a 50 mL sample of the waste and 11.4 mL of 0.02 N sulfuric acid (H_2SO_4) decreased the pH from 9.12 to 5.37. An additional

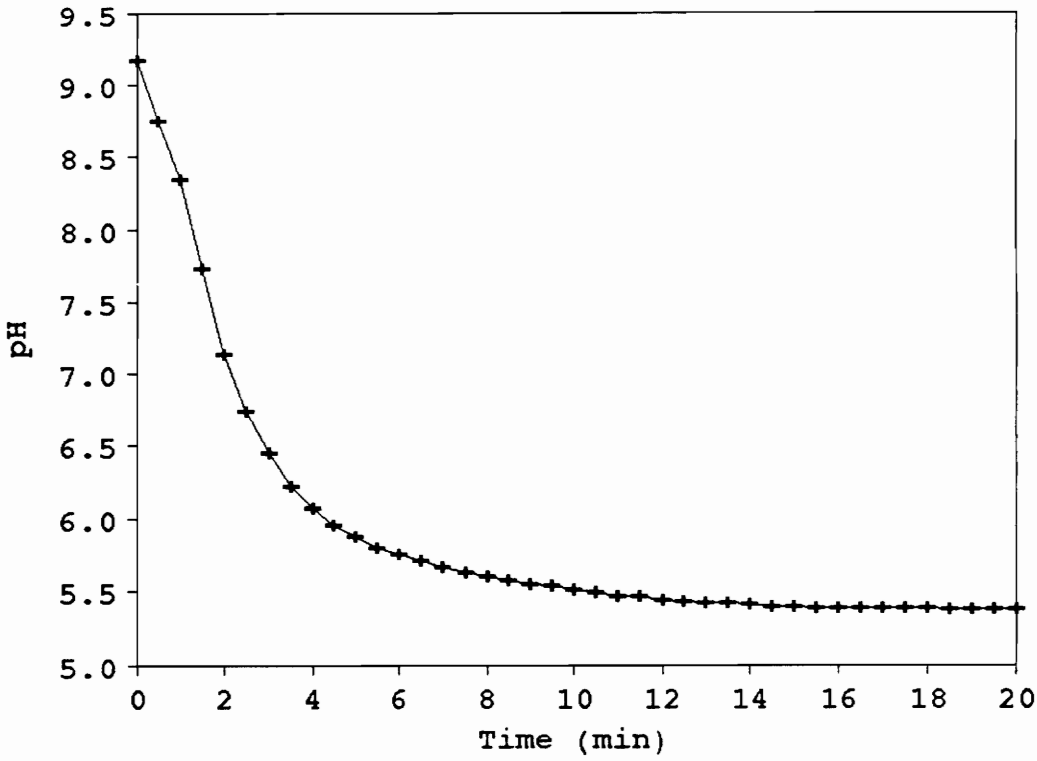


Figure 4. pH Adjustment with Carbon Dioxide - Titration Curve

0.7 mL of acid reduced the pH to 4.5. Theoretically, the number of equivalence of CO_2 and H_2SO_4 required to produce the same pH reduction should be equal. Any variations from this could be due to the inefficiency of the treatment systems.

The pH adjusted waste was then treated with an AL220 dose of 400, 500 and 600 mg/L, followed by 5 mg/L of A130 using a jar testing apparatus. Effluent color and DOC measurements can be seen in Figures 5 and 6.

Coagulation following pH adjustment with CO_2 resulted in 31-76% less color removal than the waste pH adjusted with acid. Also, as the polymer dose was increased, the effluent color of the CO_2 treated waste did not decrease as would be expected.

Effluent DOC of the two waste streams was very similar. Values ranged from 83-88 mg/L for the CO_2 treated waste and 74-97 mg/L for the acid treated waste.

The difference in the amount of color removed could be attributed to the initial pH of the waste. Prior to treatment with AL220, the waste adjusted with CO_2 had a pH of 5.4 while the waste adjusted with acid had a pH of 4.5. The lower pH of the acid treated waste could have been more amenable for the AL220 to perform and could account for the additional color removal.

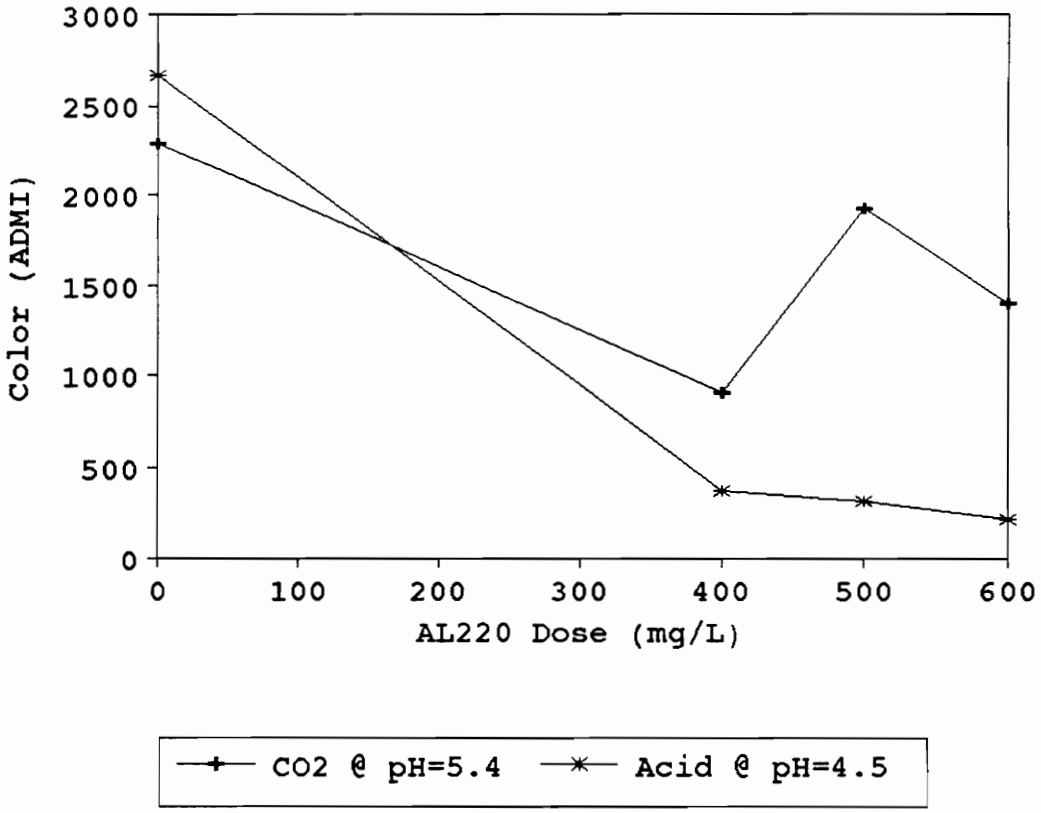


Figure 5. Comparison of color removal from waste pH adjusted with sulfuric acid and carbon dioxide

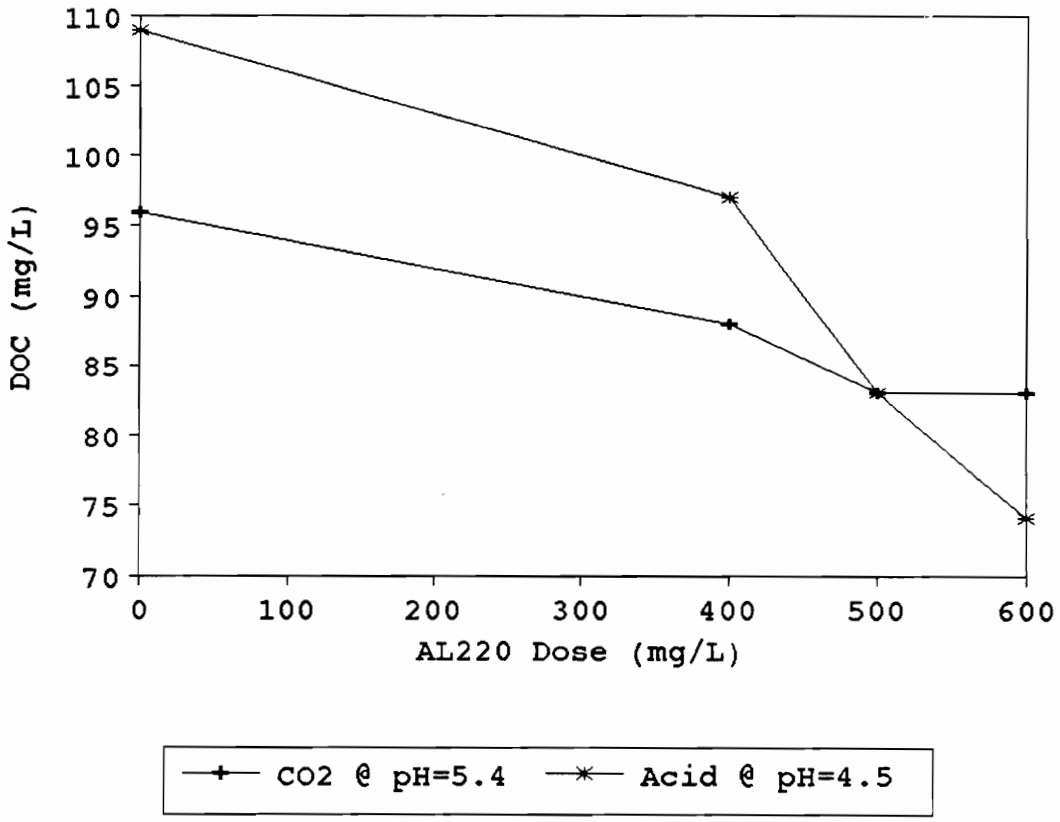


Figure 6. Comparison of DOC removal from waste pH adjusted with sulfuric acid and carbon dioxide

Attempts were made at the Plant to reduce the pH of the waste with CO_2. The waste was adjusted to a pH of 7 with CO_2 and further reduced to a pH of 4 with AL220. It was difficult to get the pH below 7 with CO_2 and the use of CO_2 interfered with the DAF process.

4.2 ANAEROBIC DEGRADATION

Figures 7-9 represent color removal by anaerobic degradation over time. The three ratios of wastewater to Blacksburg Primary Effluent (BPE) have been plotted for the print, thermosol and bleach/finish wastes. The duration of the tests and the ratios of waste to BPE used were modeled after an experiment performed by Loyd *et al.* (1992) in which substantial color removal was apparent in a textile wastewater after four days.

The color of all three combinations of print waste:BPE increased slightly upon anaerobic degradation. There were 17%, 20% and 28% increases in color for the 100:0, 75:25 and 50:50 ratios, respectively, after 21 days.

Combinations of thermosol and BPE, when anaerobically treated, showed reductions in color. After 10 days, an average of about 24% of the color was removed. Twenty one days of treatment reduced the color by an average of 22%. The samples with 100% thermosol waste achieved an average of

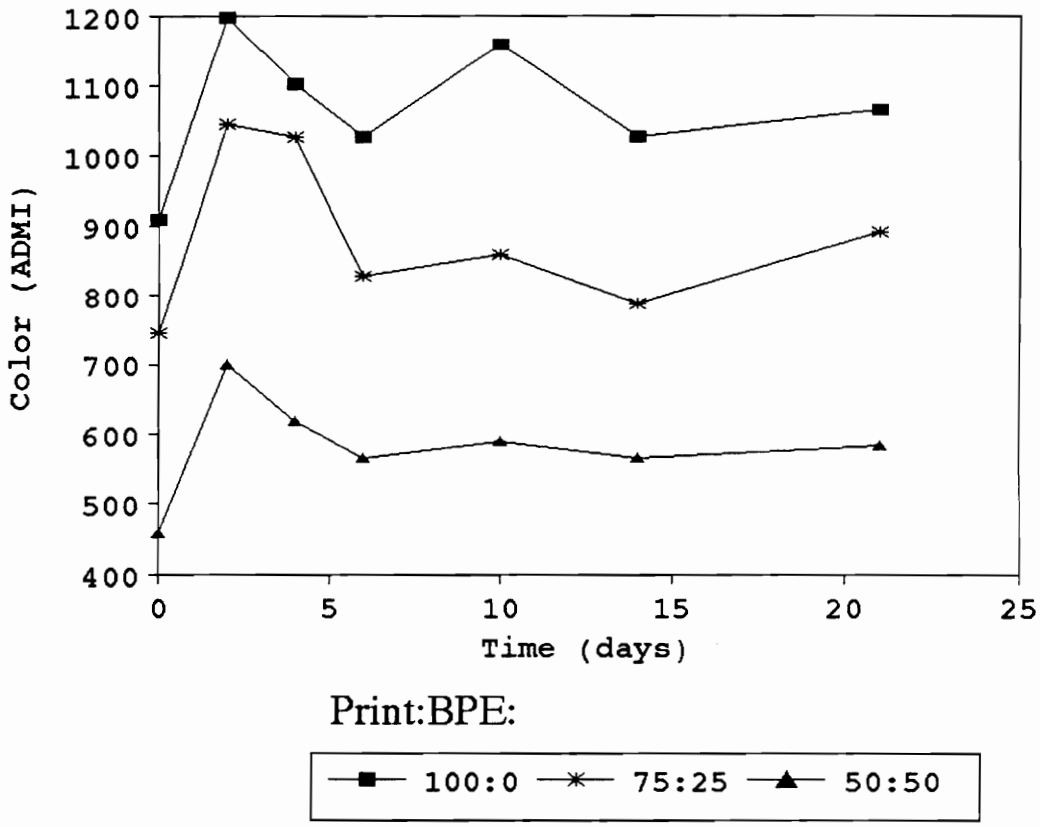


Figure 7. Color removal from print waste by anaerobic degradation

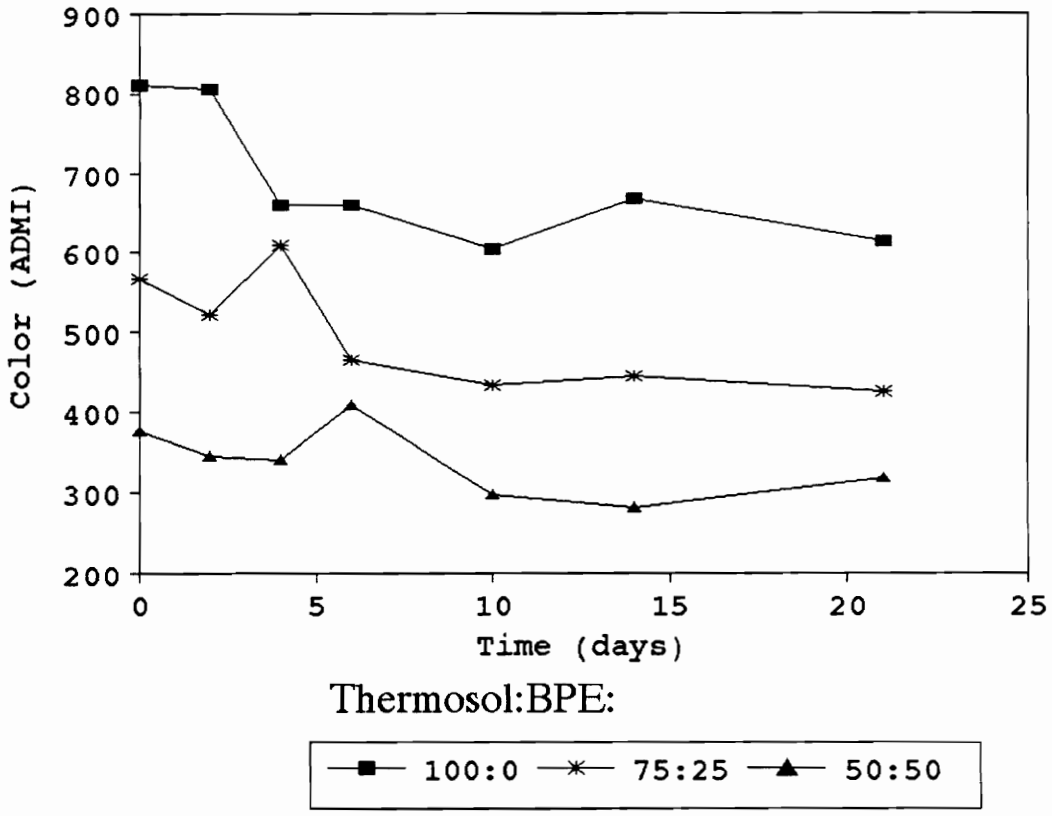


Figure 8. Color removal from thermosol waste stream by anaerobic degradation

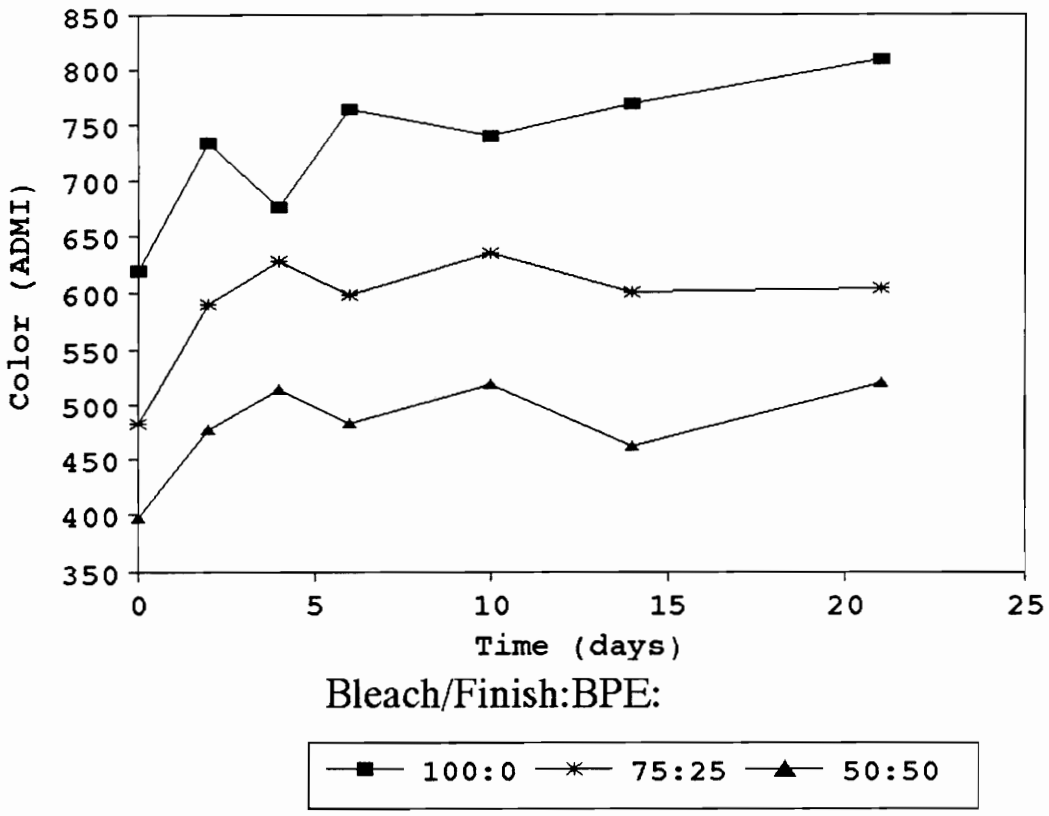


Figure 9. Color removal from bleach/finish waste stream by anaerobic degradation

1% less color removal than the sample containing 75% thermosol and 9% more color removal than the sample with 50% thermosol.

Anaerobic degradation of the bleach/finish waste resulted in an increase in color. Color increased 31% in 21 days with 100% bleach/finish waste being treated. A 25% color increase was seen when 75% of the bleach/finish waste was treated. When 50% bleach/finish waste and 50% BPE were treated anaerobically the color increased 31%.

According to Meyer (1981), Loyd *et al*. (1992) and Boe *et al*. (1993) color degradation by anaerobic treatment is often seen in wastewater containing azo dyes. The bleach/finish stream did not contain any dyes, only occasional pigments, which would account for the lack of color removal. Since the color in the print stream did not degrade, the dyes present may not be azo dyes, or they could be polyazo dyes which, according to Brown and Laboureur (1983), are more difficult to degrade than the mono and diazo dyes. The increase in color seen in both streams could be due to an increase of biomass or some other chemical reaction occurring during the treatment.
Azo dyes could have been present in the thermosol waste stream, accounting for the partial color removal.

Overall, the results of this screening test were not encouraging. The use of acclimated aerobic sludge as seed

instead of an anaerobic seed could account for some of the poor results. Although, the technique was promising in one case which would indicate that the necessary microbes must have been present to cause the color change. Due to the lack of results with two of the three waste streams tested, further experimentation with anaerobic degradation was not undertaken. Studies to determine if anaerobic treatment would enhance subsequent aerobic biological treatment were not performed.

4.3 OXIDATION WITH HYDROGEN PEROXIDE

Results of oxidation of the bleach/finish waste with hydrogen peroxide (H_2O_2) can be seen in Figure 10. Hydrogen peroxide concentrations ranging from 10-400 mg/L were tested using the jar testing apparatus. There were no visible changes in the appearance of the waste stream. Quantitative tests for color and DOC were only performed for dosages of 50-250 mg/L H_2O_2.

As can be seen in the figure, there was no substantial reduction in either color or DOC. A maximum of 8% color was removed at a dose of 50 mg/L and 6% DOC at a dose of 200 mg/L. According to Hickman (1993), because of the stability of H_2O_2, an activating agent is sometimes required. Since no activating agent was used in this experiment, stability of

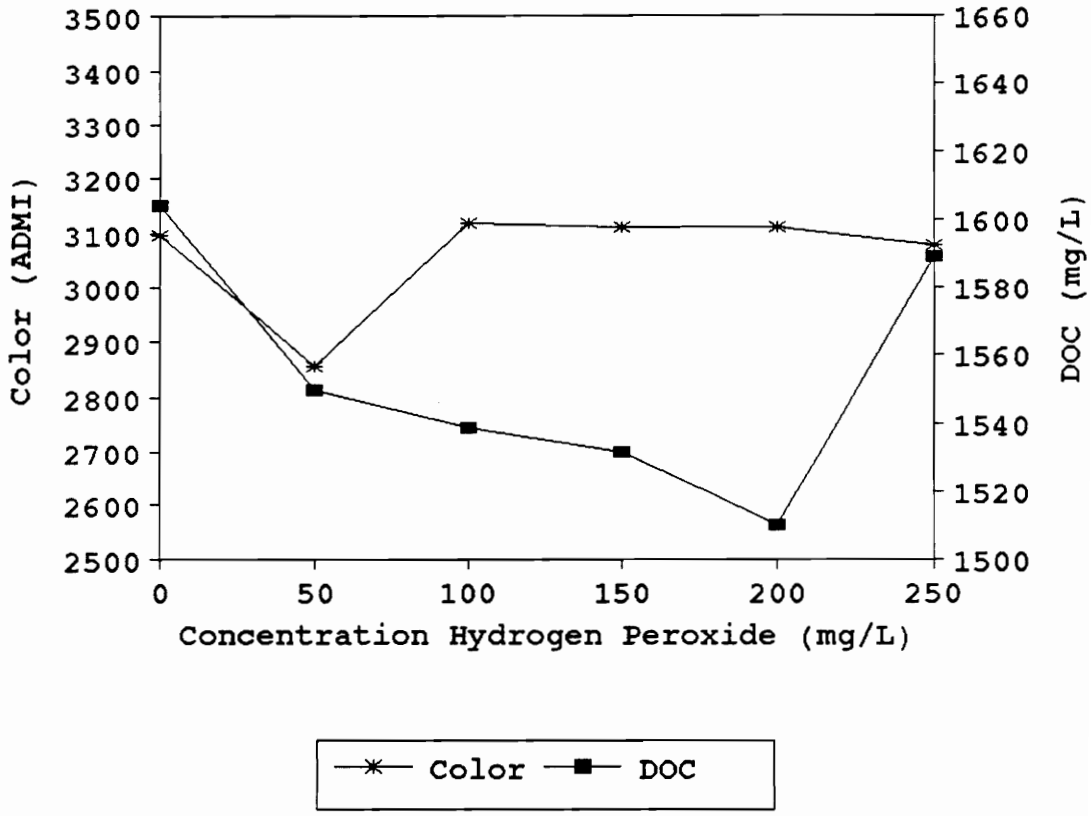


Figure 10. Color and DOC removal from bleach/finish waste stream following treatment with hydrogen peroxide

H_2O_2 could have contributed to the lack of results. Although, Michelsen *et al.* (1992) note that Fenton's reagent with H_2O_2 is not effective on wastes high in organics. The bleach/finish waste was very high in organics which could have been another reason that treatment with H_2O_2 produced no results. Whether or not the waste was more amendable to biological treatment following oxidation was not examined.

Hydrogen peroxide concentrations ranging from 50-500 mg/L were tested on a 3:4 combination of print and thermosol waste. This particular combination of waste was used because it represents the relative amounts of waste produced at the Plant. Qualitative results were not encouraging, so no further testing was performed.

4.4 AERATION

One L each of the five waste streams described in section 3.1.3 were aerated for one hour and allowed to settle for 20 minutes. Table 8 is the summary of color and TSS measurements before and after treatment.

All of the waste streams containing print waste formed a large amount of foam on the surface during aeration. The thermosol waste had some foam, but much less than the others. A thick, dark blue, paste-like material came to the

Table 8. Color and TSS measurements for aeration

Waste Stream*	Color Before (ADMI)	Color After (ADMI)	% Color Removal	TSS Before (mg/L)	TSS After (mg/L)
print	3154	2153	32	370	80
thermosol	1628	1535	6	0	0
blend	3622	2217	39	0	20
combo	3335	2624	21	0	0
future	3515	2806	20	140	0

*blend = 1:1 print:thermosol
combo = 3:4 print:thermosol
future = 2:3 print:thermosol

surface with the foam in all of the waste streams containing print waste.

After 1 hour of aeration, no color reduction was visible qualitatively. Quantitatively, though, there was some color reduction. Print, thermosol, blend, combo and future were associated with reductions of 32%, 6%, 39%, 21% and 20%, respectively. Those streams containing print waste experienced greater color reduction than the thermosol waste stream. There was no correlation between the amount of print in the waste and percent color removal.

The thick paste that rose to the surface probably attributed to the elimination of some color. There was no phase separation apparent in the thermosol waste stream and consequently, the lesser color removal was seen.

Some reduction in TSS was observed. Again, the separation of the paste-like material could have attributed to the decrease in TSS.

Overall, up to 39% of the color was removed by aeration. Although, the lowest effluent color value was 1535 ADMI, which is insufficient since regulations for effluent color limits will eventually be in the range of 200 ADMI. Therefore, although it appears that aeration alone would not be sufficient for color removal, it could be beneficial if it were implemented in combination with equalization of the waste prior to subsequent treatment systems.

4.5 POLYMER TREATMENT

Results of various polymer jar tests and chemical floc separation tests are presented in the following sections.

4.5.1 Preliminary Treatment

Preliminary jar tests were performed using several different polymers on the print, thermosol and bleach/finish waste streams, as explained in section 3.1.4. The doses used were chosen in order to compare the various polymers. Color of the waste varied with each batch, requiring that polymer doses be adjusted accordingly. This became apparent as the work progressed.

The print waste stream was highly colored and required high doses of polymer for coagulation and substantial color removal to occur. Color, DOC and TSS results for all six polymers tested can be seen in Figures 11-13. Color removal ranged from 20-65% at the maximum dose of 450 mg/L. DOC increased upon the addition of polymer. TSS removal was between 65% and 85% at the maximum polymer dose.

Results for color, DOC and TSS following the treatment of the thermosol waste stream are shown in Figures 14-16. All of the polymers except AL220 were tested and 72-89% of the color was removed at a dose of 75 mg/L. DOC was decreased by 37-44% and 77-86% of TSS was removed. Since the color of the thermosol was relatively low, only small doses of each of the polymers were needed for coagulation to occur. The AL220 polymer did not perform well at such low concentrations. AL220 is actually a blend of inorganic aluminum and a polyamine. Therefore, higher concentrations were required for coagulation to occur with AL220 than with the organic polymers. Higher doses were not tested during these preliminary experiments.

The bleach/finish waste yielded similar results for all the polymers tested in regards to color, DOC and TSS removal. Results can be seen in Figures 17-19. Color was reduced by 84-94%. DOC removal ranged from 8-11%, and TSS removal was in the range of 70-86%. Coagulation did not

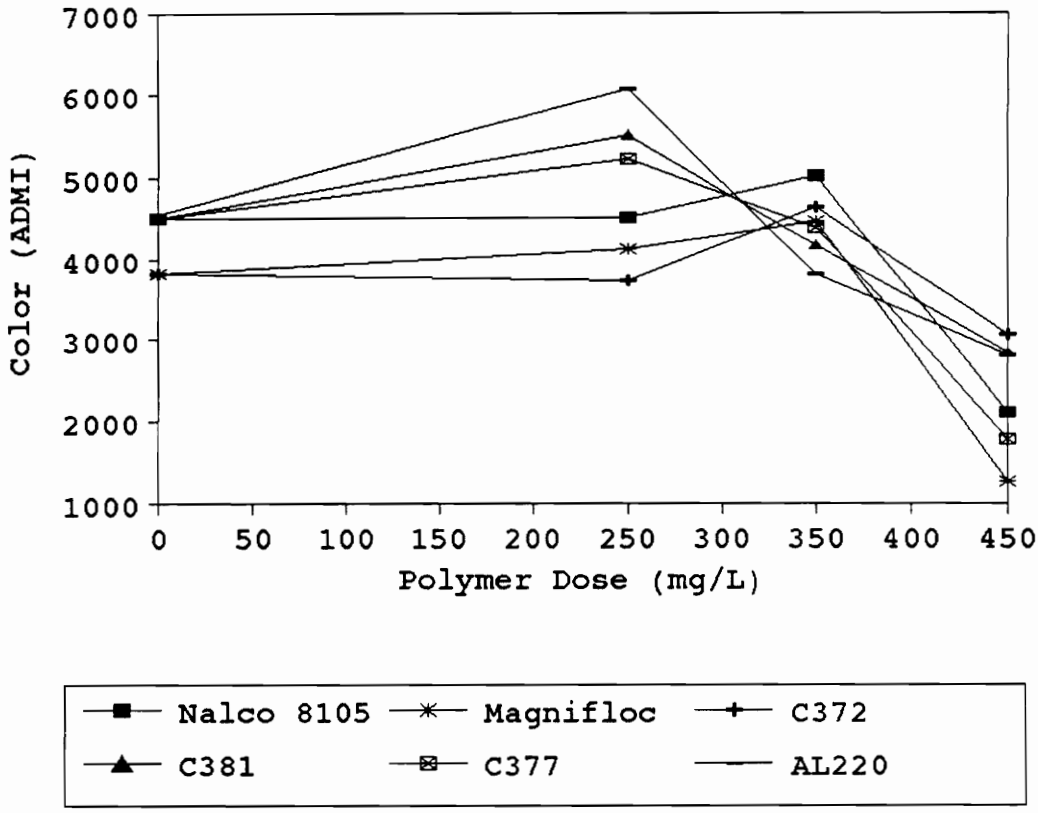


Figure 11. Preliminary jar tests - comparison of color removal from print waste stream following coagulation with various polymers

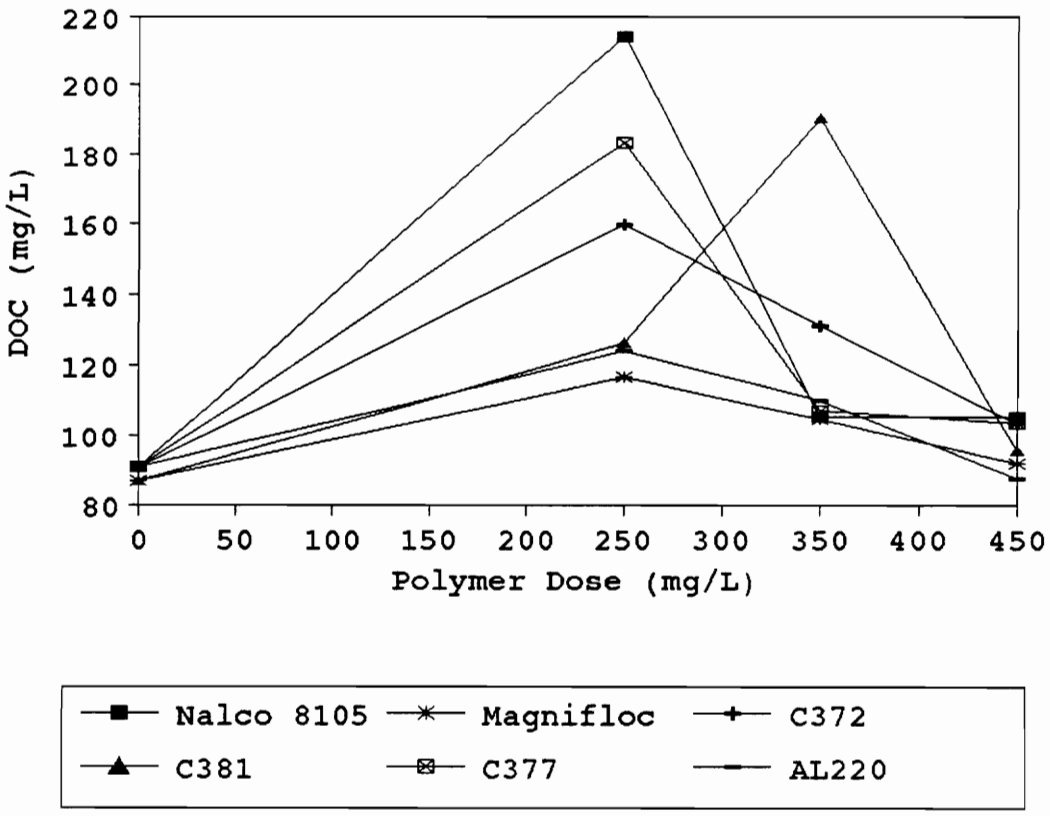


Figure 12. Preliminary jar tests - comparison of DOC removal from print waste stream following coagulation with various polymers

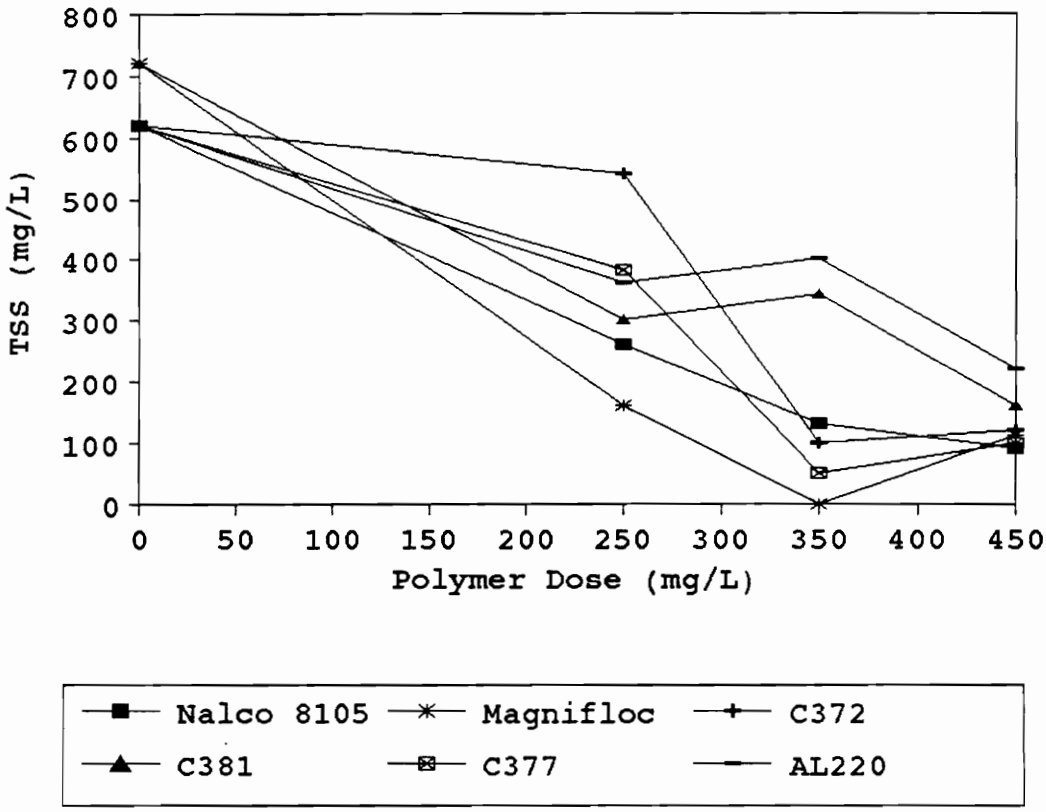


Figure 13. Preliminary jar tests - comparison of TSS removal from print waste stream following coagulation and settling with polymers

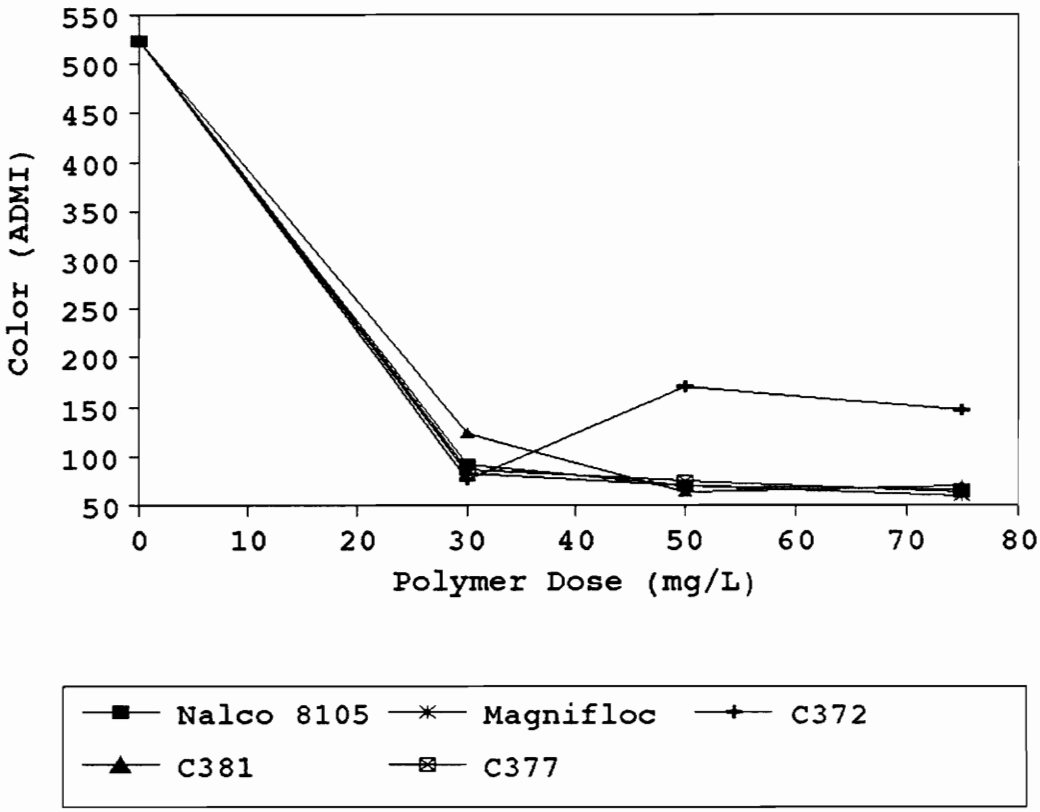


Figure 14. Preliminary jar tests - comparison of color removal from thermosol waste stream following coagulation with various polymers

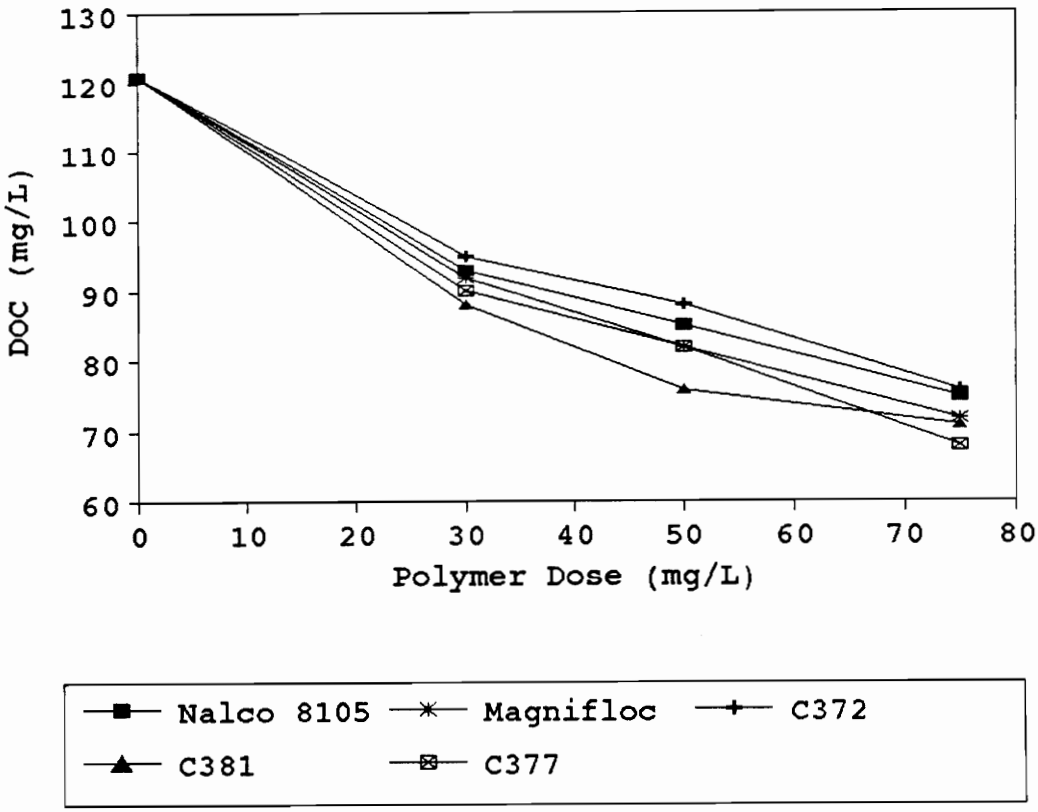


Figure 15. Preliminary jar tests - comparison of DOC removal from thermosol waste stream following coagulation with various polymers

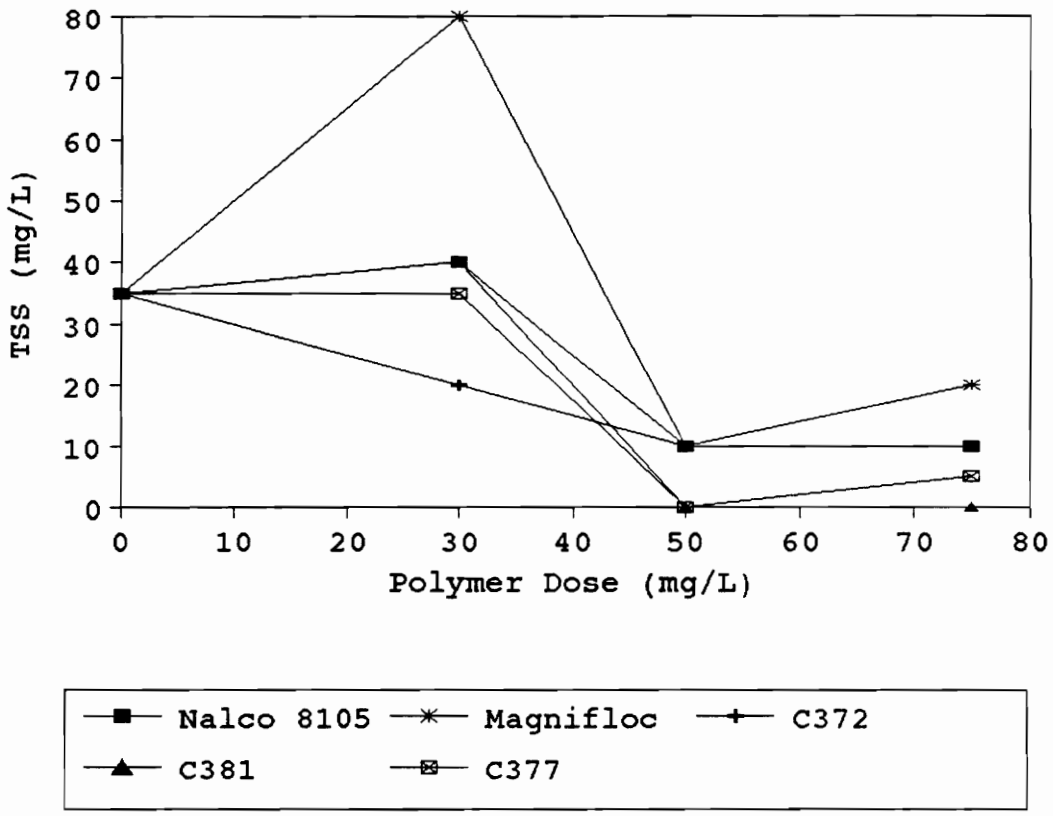


Figure 16. Preliminary jar tests - comparison of TSS removal from thermosol waste stream following coagulation and settling with various polymers

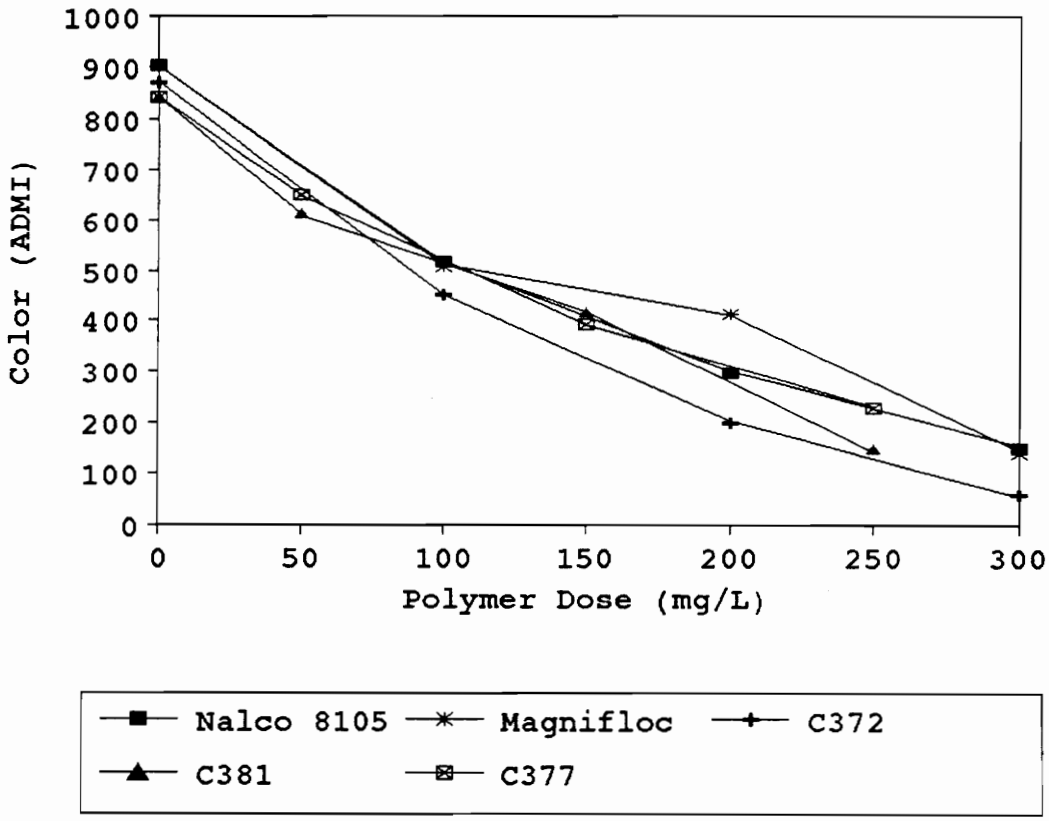


Figure 17. Preliminary jar tests - comparison of color removal from bleach/finish waste stream following coagulation with various polymers

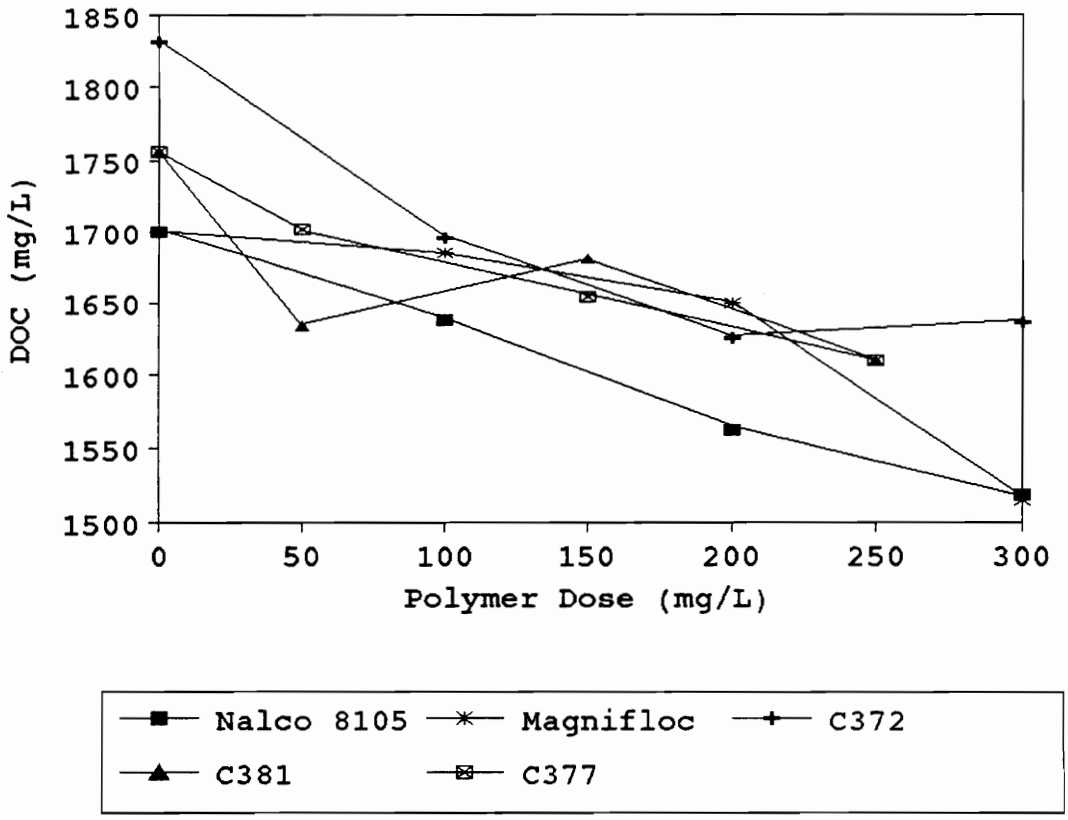


Figure 18. Preliminary jar tests - comparison of DOC removal from bleach/finish waste stream following coagulation with various polymers

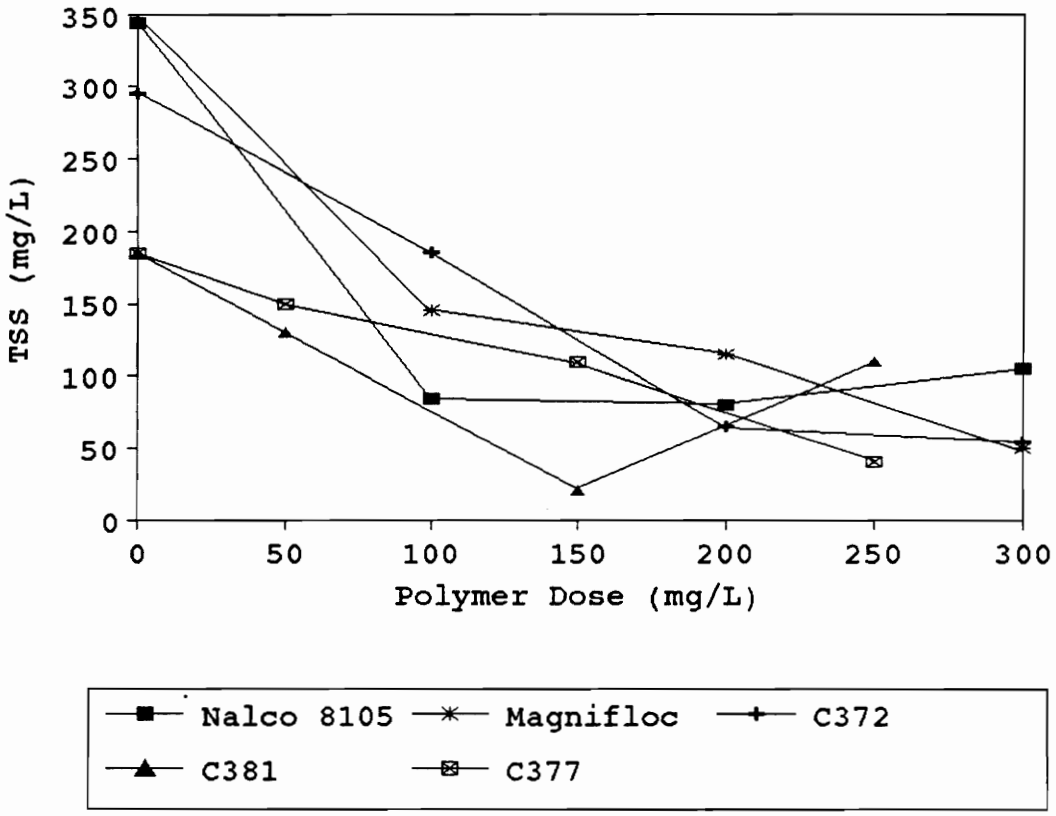


Figure 19. Preliminary jar tests - comparison of TSS removal from bleach/finish waste stream following coagulation and settling with various polymer

occur upon the addition of AL220 to the bleach/finish stream.

After reviewing these results, it was decided to compare the AL220 used at the Plant to polymer C377, which appeared to perform equally or better than all the others polymers tested.

4.5.2 AL220 vs. C377

Figures 20-22 compare the use of polymer C377 to AL220 on the print stream. Lower doses of C377 were applied since it is an organic polymer, while AL220 is a blend of an inorganic salt and an organic polymer. Effluent color, DOC and TSS are shown in the figures. A polymer dose was chosen for further testing from the jar tests performed on this batch of print waste. A dose of 200 mg/L of AL220 removed 41% of the color and 46% DOC, while 100 mg/L of C377 reduced the color by 67% and DOC by 44%. The TSS increased with the higher doses of C377. Two hundred mg/L of AL220 reduced the TSS from 270-60 mg/L.

Additional jar tests were done to determine the optimum pH range for coagulation to occur with the two polymers. pH was varied from 4-8, and the print waste was dosed with 200 mg/L AL220 and 100 mg/L C377. No measurements were taken, but qualitative results suggested that a pH between 5-6 was most appropriate for both polymers. AL220 was known to

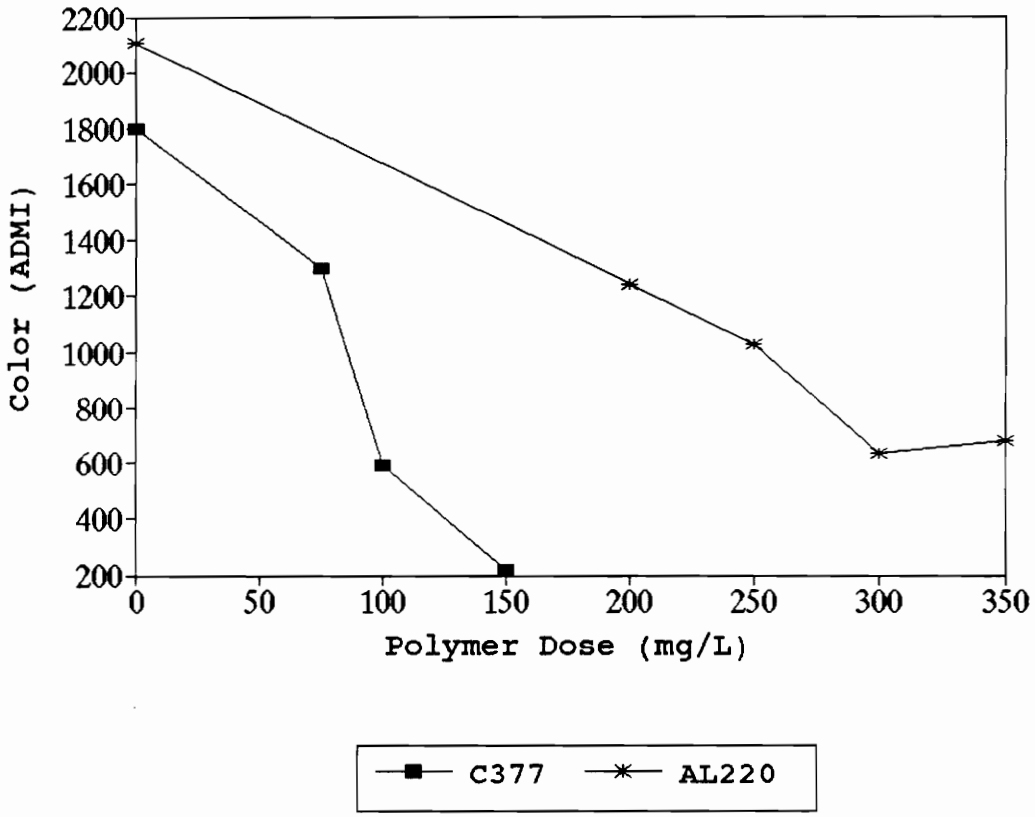


Figure 20. Comparison of color removal from print waste following coagulation with C377 and AL220

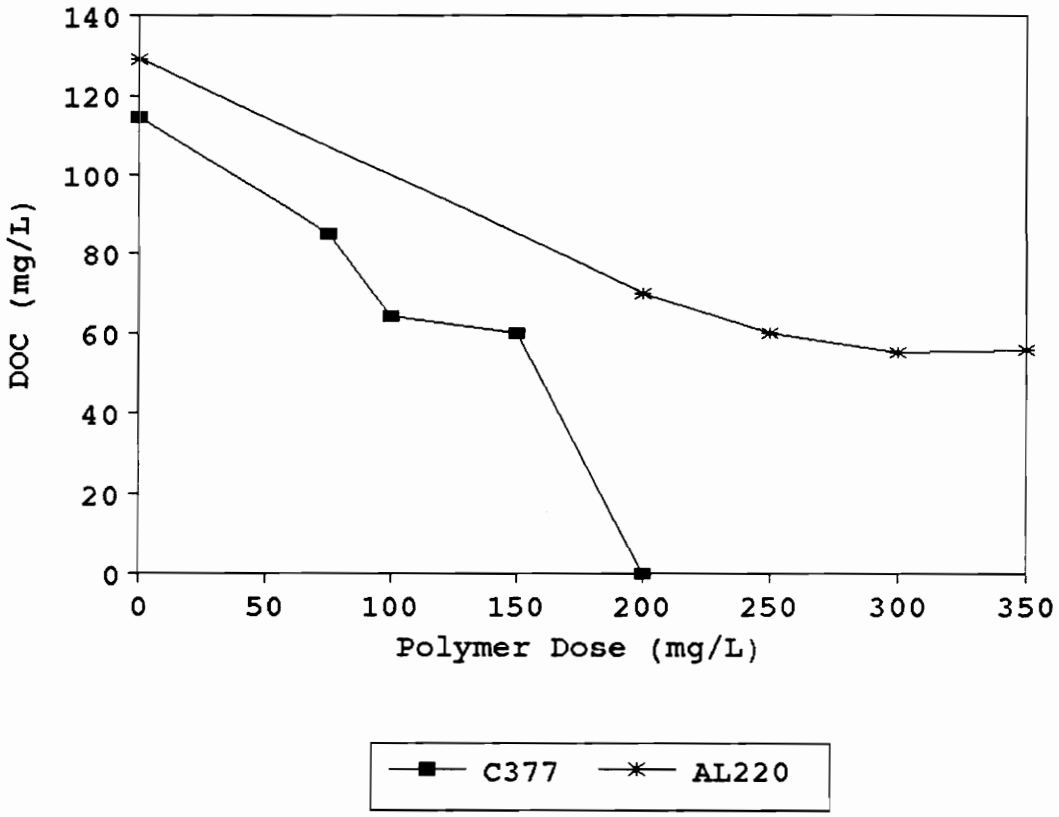


Figure 21. Comparison of DOC removal from print waste following coagulation with C377 and AL220

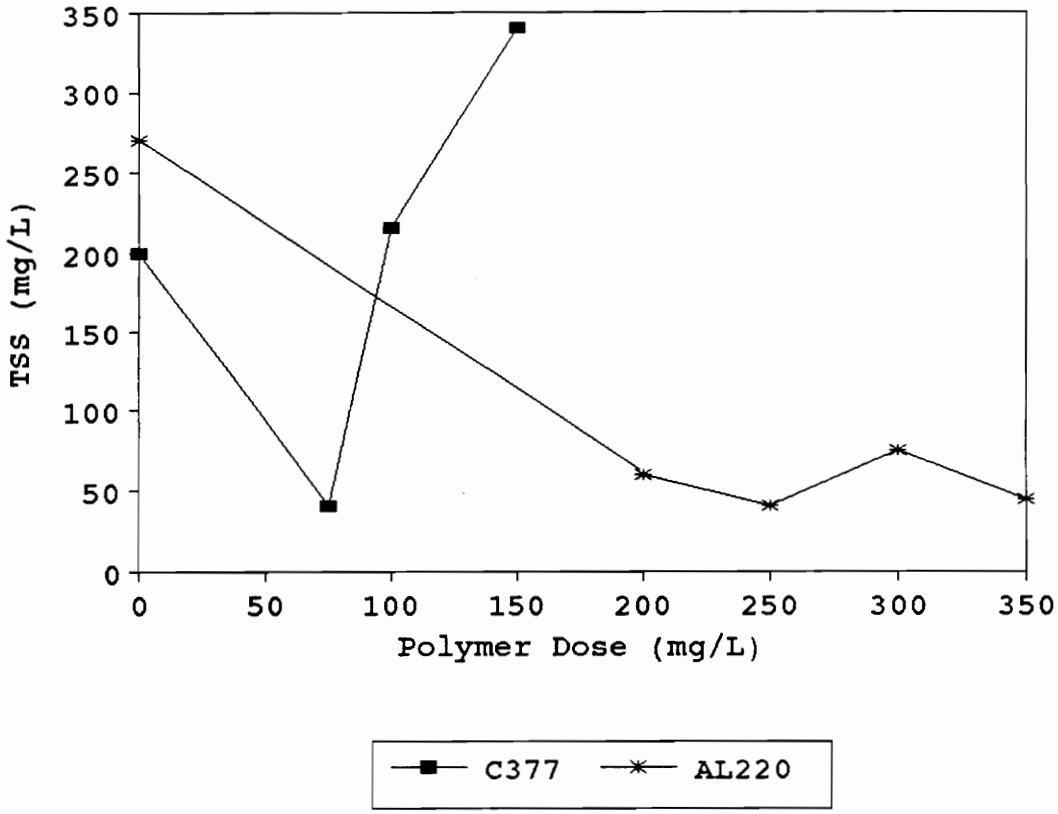


Figure 22. Comparison of TSS removal from waste following coagulation with C377 and AL220 and subsequent settling

perform best under acidic conditions (Miller, 1993). The acidity of AL220 decreased the pH of the waste from 5-6 to about 4 at a dosage of 200 mg/L.

Polymer A130 was added as a secondary coagulant to the print waste after treatment with AL220 and C377. Figures 23-25 compare the results for effluent color, DOC and TSS. Concentrations of A130 ranging from 2.5-15 mg/L were tested. Following the addition of 200 mg/L AL220, 2.5 mg/L of A130 reduced the color by 53%, the DOC by 15%, and increased the TSS by 117%. Increased concentrations of A130 did not produce markedly different results. C377 in combination with 2.5 mg/L A130 yielded a 6% color removal, 27% DOC removal and 25% increase in TSS. As with the AL220, increased doses of A130 did not significantly change these removal efficiencies.

Qualitatively, AL220 followed by A130 produced much larger flocs, which separated and settled better than the flocs formed by AL220, alone. Polymer C377 flocs did not change substantially upon addition of A130.

The use of AL220 and C377 with thermosol is compared in Figures 26-28. AL220 produced no results with thermosol in the preliminary tests because the dosage applied was insufficient for coagulation to occur. This thermosol batch contained substantially more color so higher polymer doses were applied which enabled coagulation with AL220.

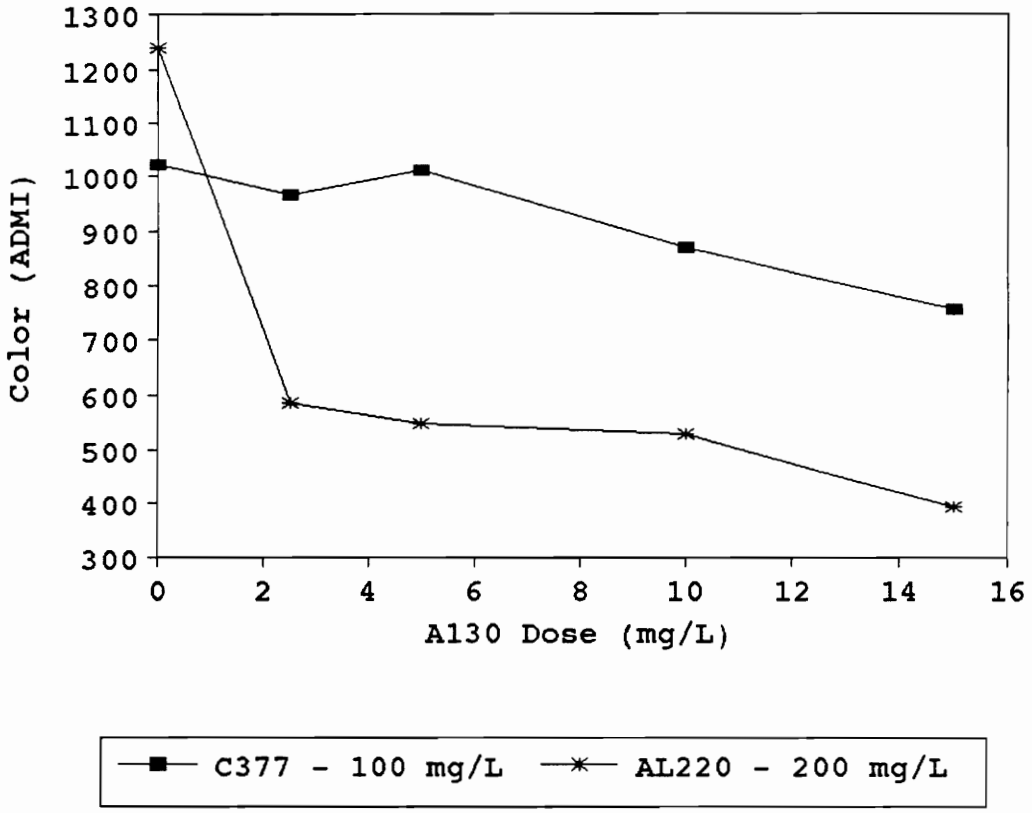


Figure 23. Color removal from print waste upon addition of A130 subsequent to AL220 and C377

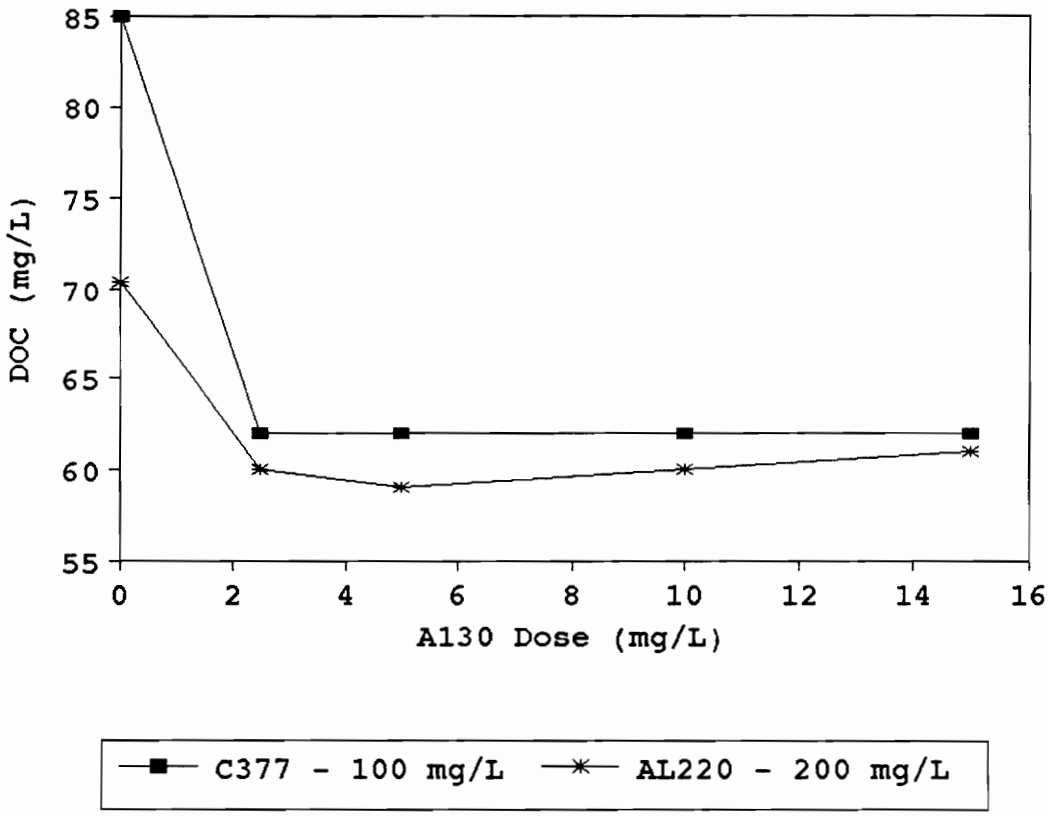


Figure 24. DOC removal from print waste upon addition of A130 subsequent to AL220 and C377

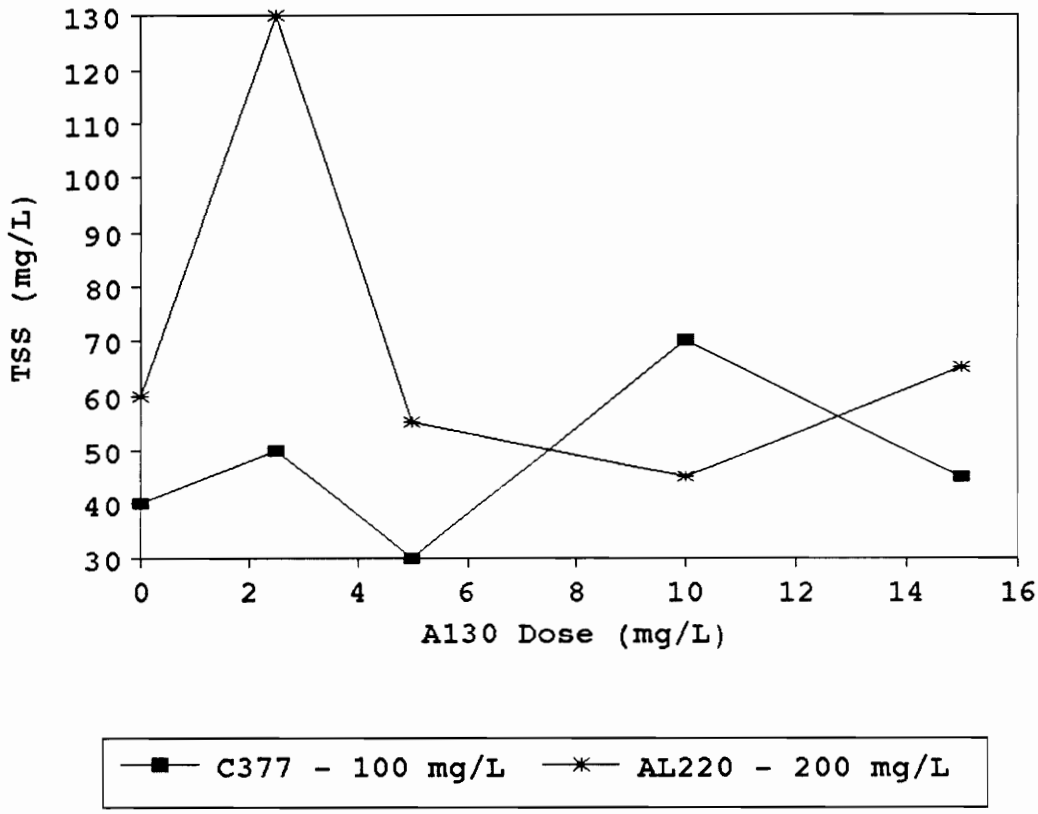


Figure 25. TSS removal from print waste upon settling and addition of A130 subsequent to AL220 and C377

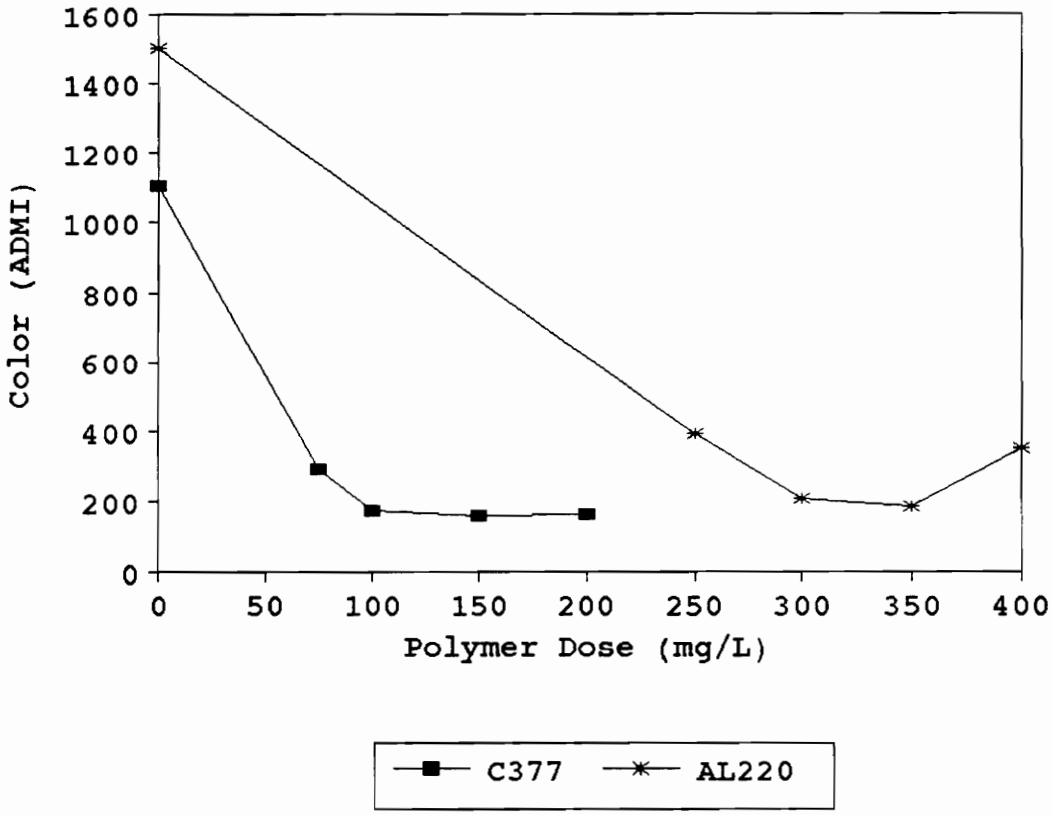


Figure 26. Comparison of color removal from thermosol waste following coagulation with C377 and AL220

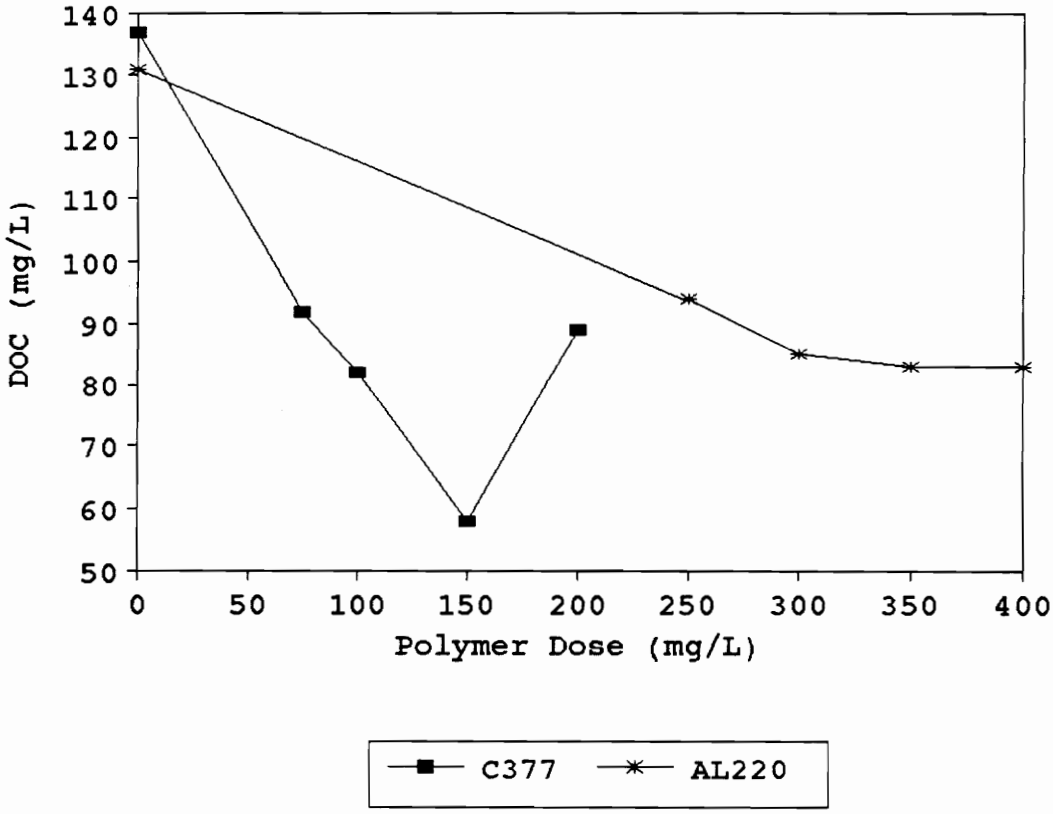


Figure 27. Comparison of DOC removal from thermosol waste following coagulation with C377 and AL220

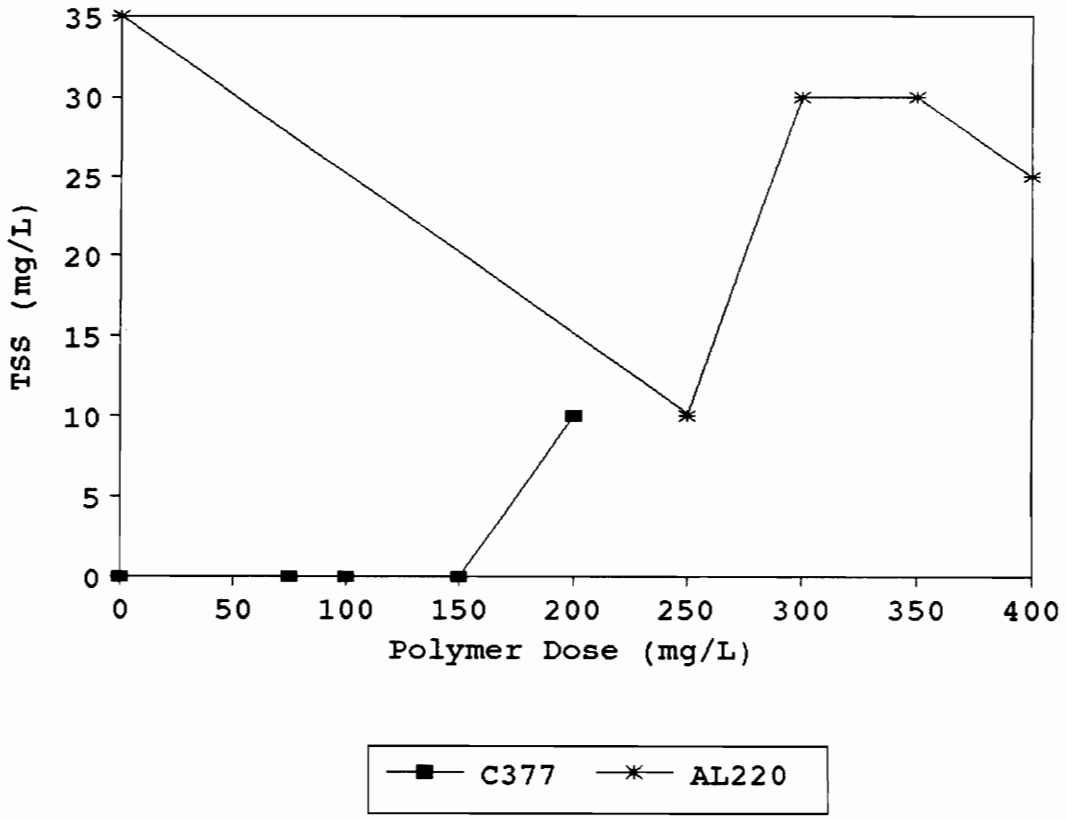


Figure 28. Comparison of TSS removal from thermosol waste following coagulation with C377 and AL220 and subsequent settling

Three hundred mg/L of AL220 performed well with the thermosol waste. Eighty-six percent and 35% of color and DOC were removed, respectively. Up to 400 mg/L AL220 were tested on this thermosol batch, but no substantial improvement over results with 300 mg/L was seen. Higher AL220 doses increased the effluent TSS. A dose of 150 mg/L of C377 reduced color by 86% and DOC by 58%. TSS did not change. A dose of C377 higher than 150 mg/L produced poorer results for both DOC and TSS removal.

Tests were performed on the thermosol waste, as mentioned with the print waste, to determine the optimum pH range for coagulation to occur. Qualitative results suggested that pH had little effect on the performance of C377. Further tests with C377 were performed with thermosol at a neutral pH. A pH range of 5-6 was optimum for the performance of AL220 in the thermosol waste stream.

Results of testing with A130 can be seen in Figures 29-31. Qualitatively, A130 in combination with AL220 produced large, rapidly settling flocs. There was a slight reduction in color, while DOC increased slightly. Effluent TSS decreased with lower doses of A130. Doses above 5 mg/L increased the TSS.

Addition of A130 following C377 yielded a slight increase in both color and DOC. TSS essentially did not change. The settling characteristics did not improve.

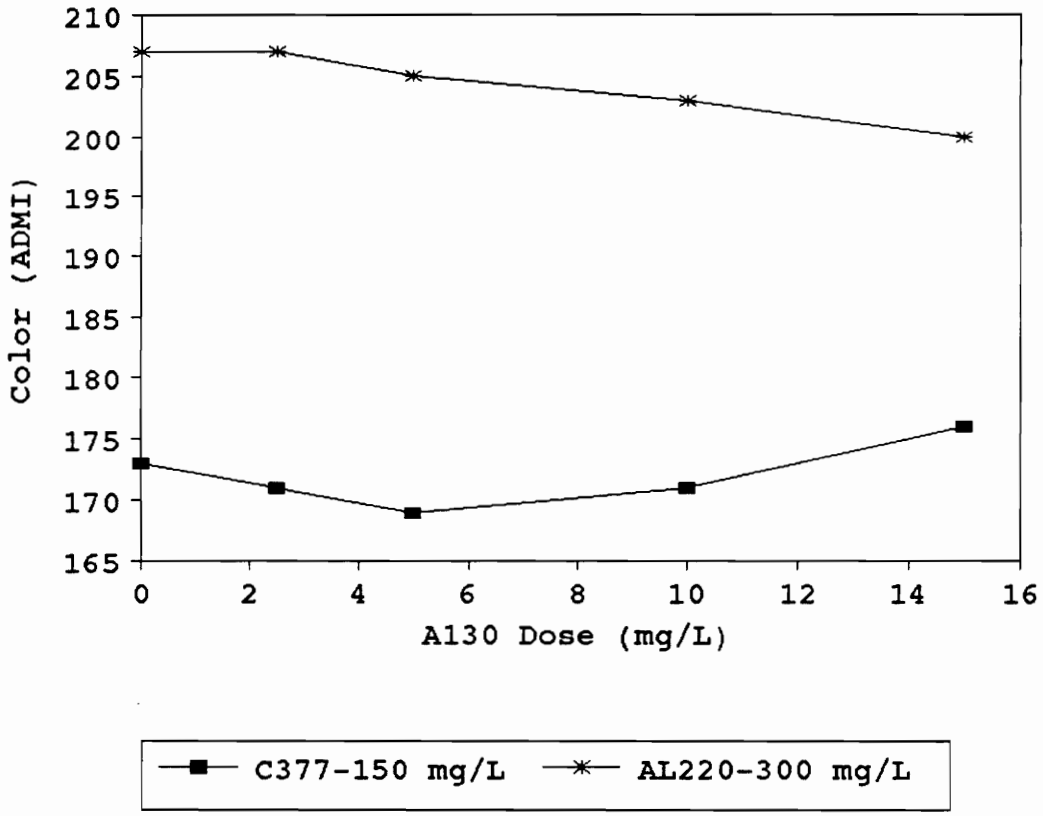


Figure 29. Color removal from thermosol waste upon addition of A130 subsequent to AL220 and C377

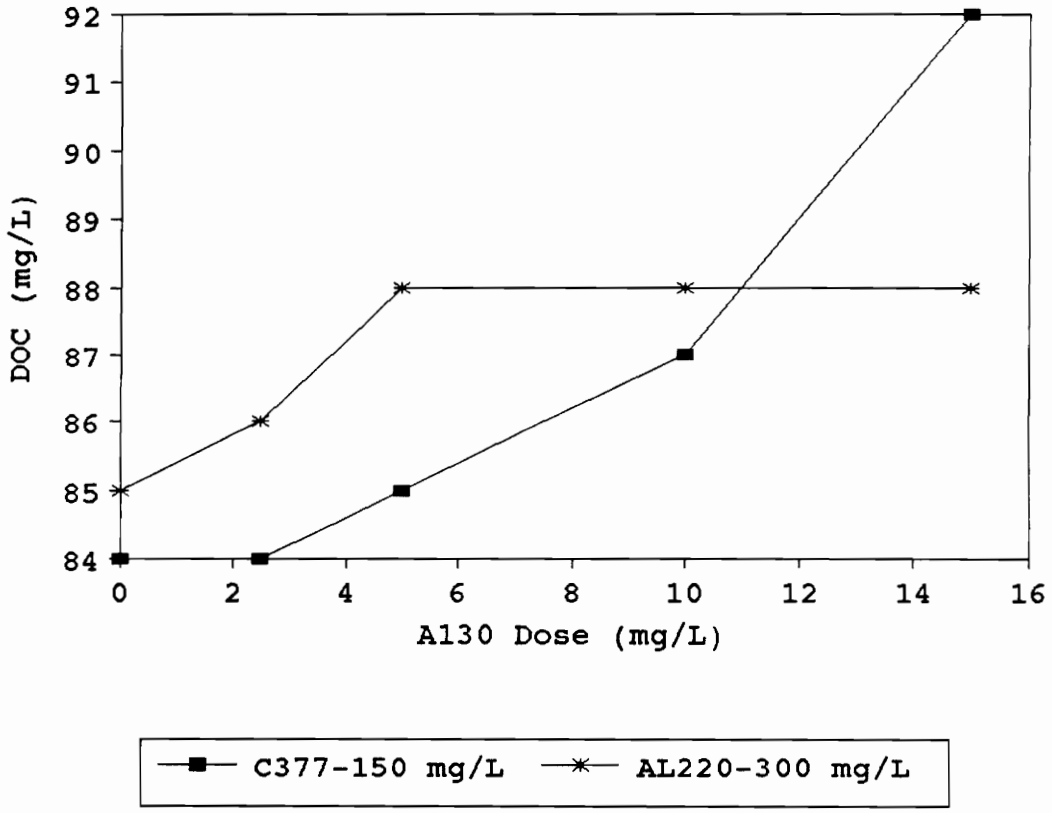


Figure 30. DOC removal from thermosol waste upon addition of A130 subsequent to AL220 and C377

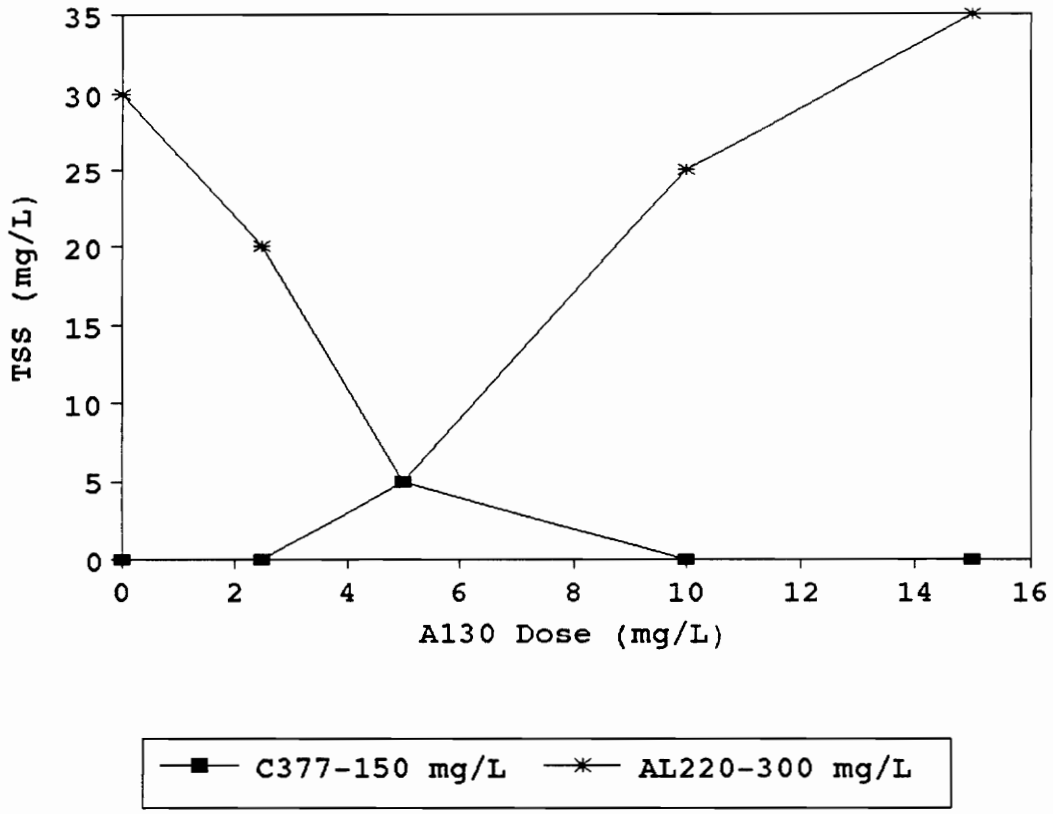


Figure 31. TSS removal from thermosol waste upon settling and addition of A130 subsequent to AL220 and C377

No results were obtained through addition of AL220 to the bleach/finish waste in the preliminary tests. AL220 was tried again with another batch of waste, and again no results were seen. Therefore, subsequent tests were performed only using C377. High doses were used because preliminary testing indicated that such doses were necessary. Figures 32-34 show the results of these jar tests. A C377 dose of 250 mg/L yielded an 86% reduction in color. Additional C377 improved this efficiency only slightly. Reductions in DOC ranged from 2-4%. TSS values increased with the addition of C377.

Experiments were performed to determine the optimum pH range for coagulation to occur when C377 was added to the bleach/finish waste. A pH range of 5-6 appeared, qualitatively, to be the most appropriate. Polymer A130 was added in combination with C377. Color and DOC of the effluent were not measured because no improvements in floc size or settling were seen.

A 1:1:1 mixture of print, thermosol and bleach/finish waste (mix), and a 1:1 mixture of print and thermosol (blend) were tested with AL220 and C377. Results of color tests can be seen in Figure 35. Two hundred mg/L of C377 reduced color by 84% and 90% for the mix and blend waste streams, respectively. Four hundred mg/L of AL220 were required to respectively remove 73% and 87% of the color.

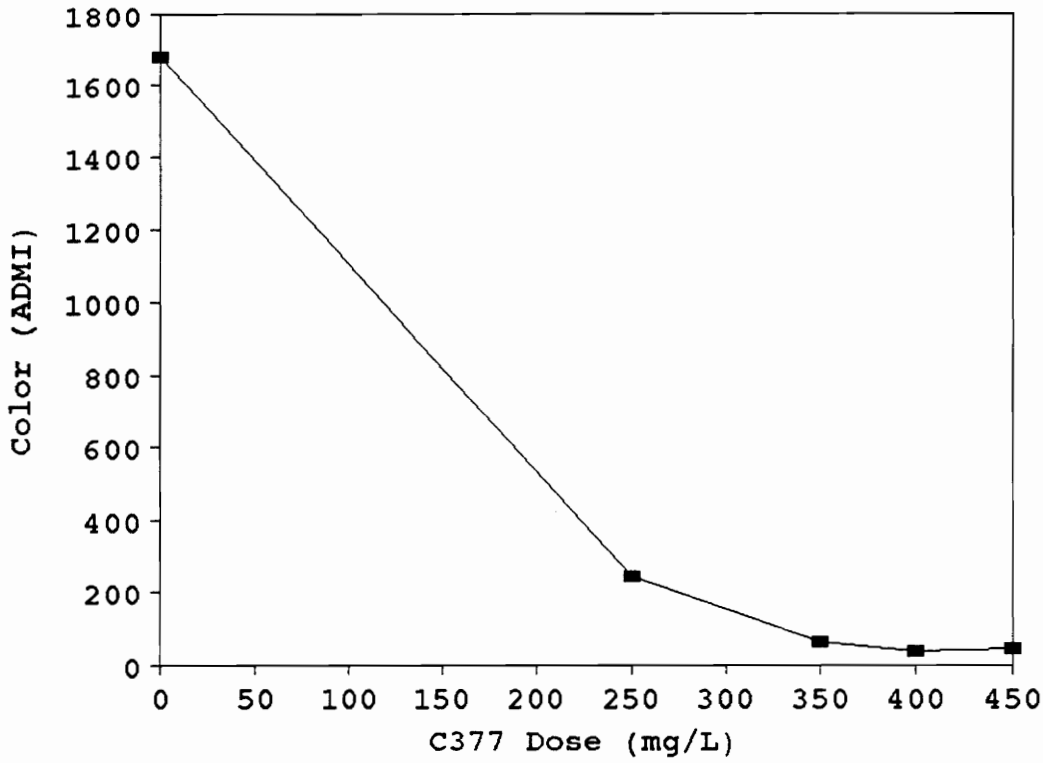


Figure 32. Color removal from bleach/finish waste following coagulation with C377

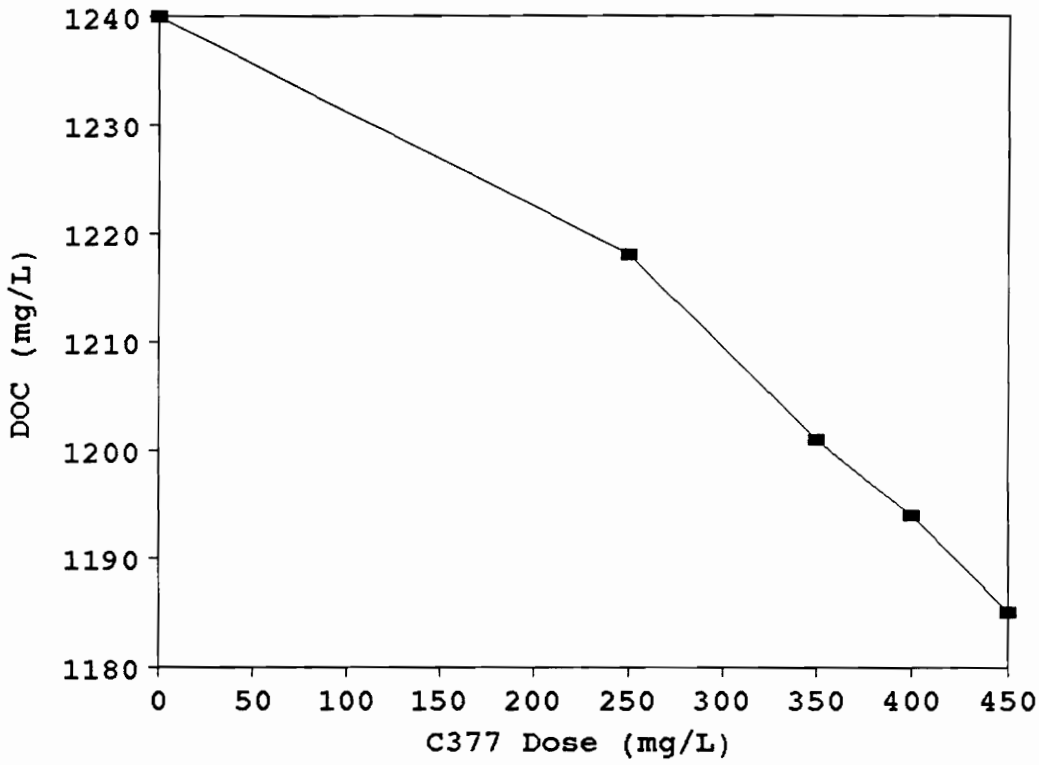


Figure 33. DOC removal from bleach/finish waste following coagulation with C377

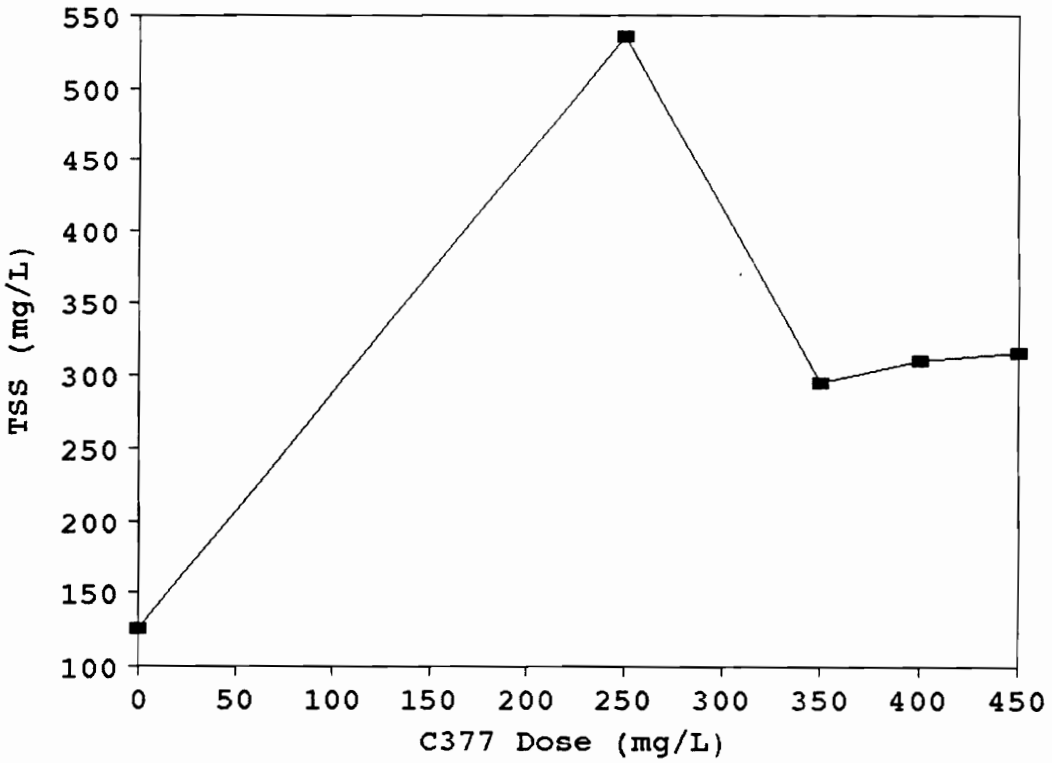


Figure 34. TSS removal from bleach/finish waste following coagulation with C377 and subsequent settling

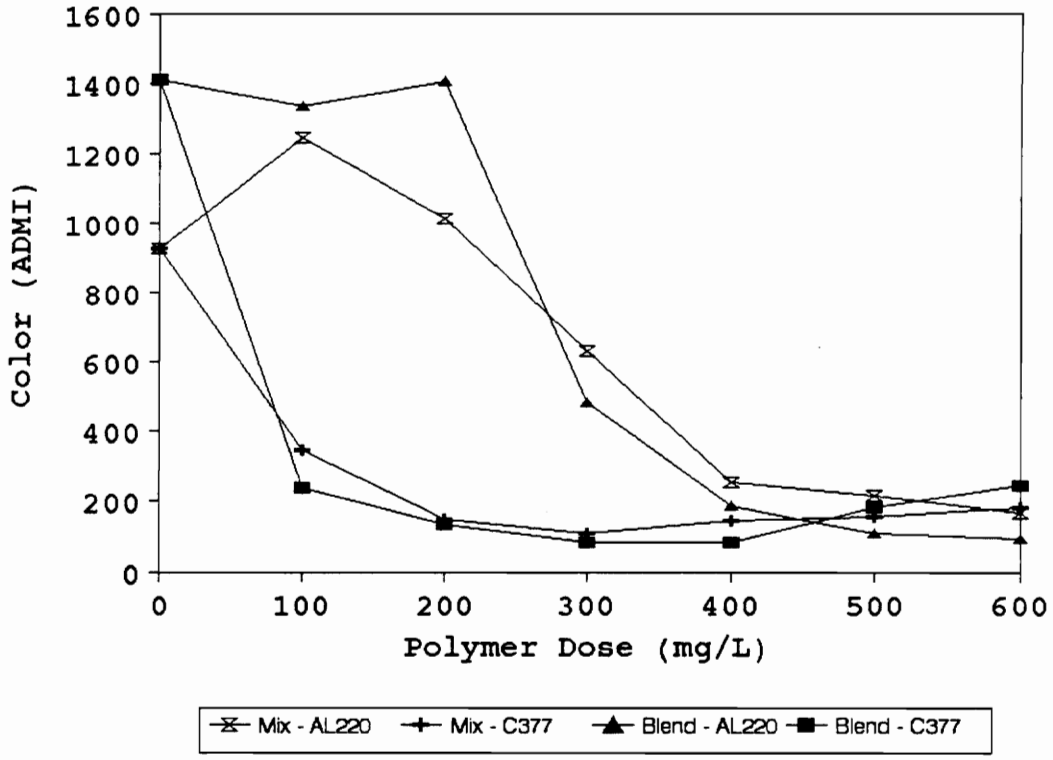


Figure 35. Comparison of color removal achieved through addition of C377 and AL220 to 1:1:1 print:thermosol:bleach/finish (mix) and 1:1 print:thermosol (blend)

In general, slightly better treatment of the blend stream was achieved.

With the print, thermosol and combination waste streams, C377 yielded results similar to AL220, but at different dosage levels. About half as much C377 as AL220 could be used to produce comparable results.

As previously mentioned, the AL220 is actually a combination of inorganic aluminum and a polyamine (Miller, 1993). Polymer C377 is a cationic, organic polymer. According to Davis (1991), an advantage of organic polymers over inorganic salts is the smaller volume needed to achieve equivalent removal efficiencies. However, organic polymers are more expensive than inorganic salts. In the case of these two coagulants, C377 costs six times as much as the AL220 blend (Miller, 1993). Therefore, in this case, it was still more economical to use AL220 even though twice as much was needed for coagulation.

For the most part, A130 did not help to remove additional color, DOC and TSS. On occasion, increases in DOC and TSS were seen. Qualitatively, addition of A130 greatly improved the AL220 flocs and settling characteristics. This is in agreement with Halliday and Beszedits (1986) and Niculaou and Hadjivarsilis (1992) who note that subsequent addition of organic polymers helps to form larger, faster settling flocs. The lack of improvement of the C377 treated

waste followed by A130 could simply be a function of the secondary coagulant used. Possibly a different anionic polymer would have yielded better results.

Polymer addition to the bleach/finish waste did not yield encouraging results. Even though a good percentage of color was removed, this stream does not always contain color. The DOC of the bleach/finish waste stream is very high and very little of it was reduced through coagulation. TSS increased with the addition of polymer.

When the mix stream was treated with AL220 and C377 and its color removal was compared to the blend stream, similarly treated, comparable results were achieved. Aside from initial dilution, the bleach/finish waste in the mix stream did not considerably alter the removal efficiencies. AL220 removed 73-87% of the color in the mix and blend streams, respectively, while C377 removed 84-90%. Since addition of bleach/finish did not increase or decrease the amount of polymer required, and polymer treatment of the bleach/finish waste alone was not beneficial, it was decided to continue testing with the print and thermosol waste streams only.

4.5.3 Settling vs. DAF for Chemical Floc Separation

Additional polymer testing was performed with AL220 and C377 on the print, thermosol and blend waste streams. Color

and DOC results can be seen in Figures 36-39. The purpose of these tests was to determine an adequate polymer dose for color and DOC removal for this batch of waste prior to performing settling and DAF tests. The polymer doses used can be seen in Table 9. Five mg/L of A130 were added following AL220 addition. Again, a smaller dose of C377 than AL220 was used. Higher doses than previously experimented with were applied due to the high influent color values.

Table 9. Polymer doses used for settling and DAF tests.

Waste	C377 (mg/L)	AL220 (mg/L)
print	300	600
thermosol	150	400
blend	300	700

Color, DOC and TSS results of the settling and DAF tests can be seen in Tables 10-12. When the treated waste was settled, color removal was slightly better with the use of AL220 for all 3 waste streams. Percent removals with AL220 ranged from 70-92%, while C377 treatment yielded 69-90% color removal. With use of DAF, the C377 treated waste removed only 2-3% more color than AL220 treated waste, except the blend waste where 1% less color was removed.

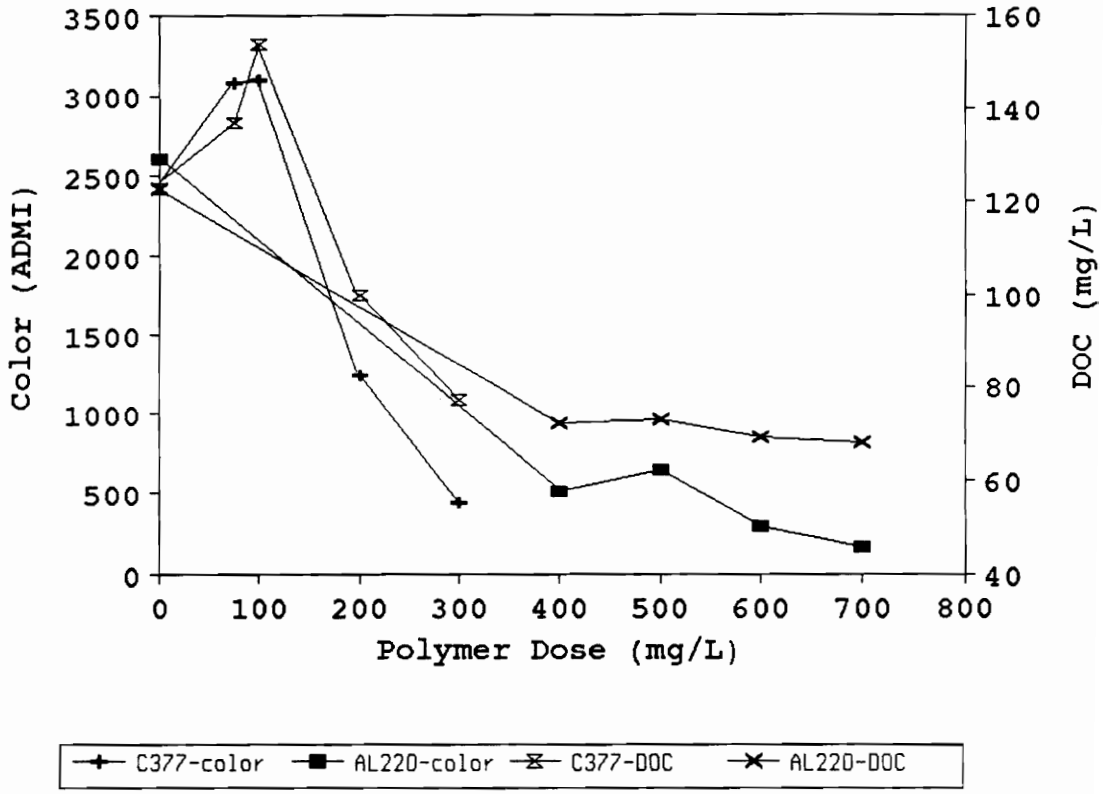


Figure 36. Color and DOC removal achieved through addition of AL220 and C377 to print waste

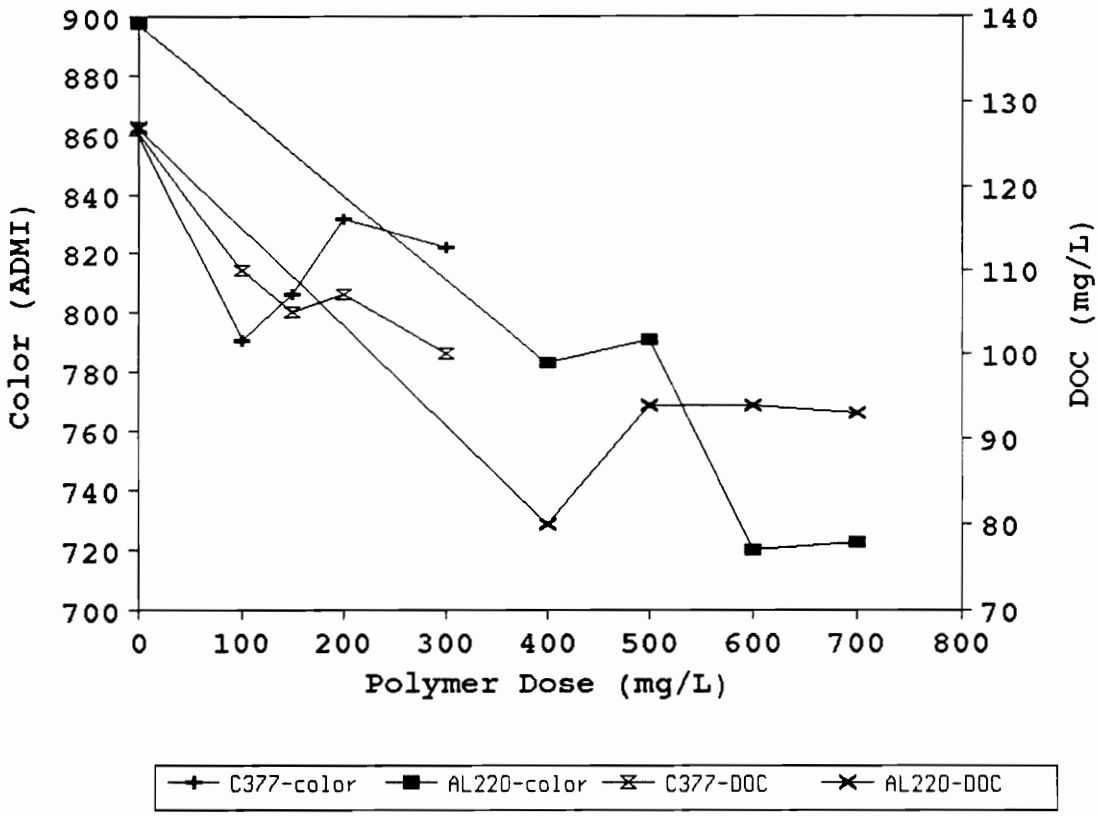


Figure 37. Color and DOC removal achieved through addition of AL220 and C377 to thermosol waste

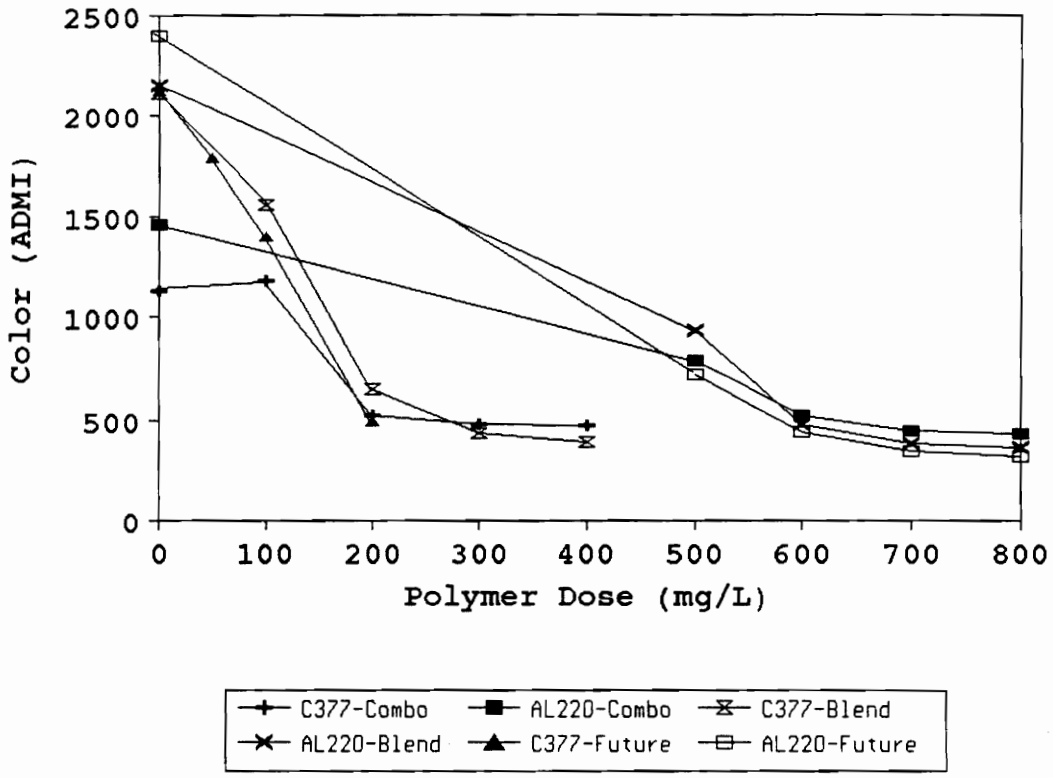


Figure 38. Color removal achieved through addition of AL220 and C377 to 1:1 print:thermosol (blend), 3:4 print:thermosol (combo) and 3:2 print:thermosol (future)

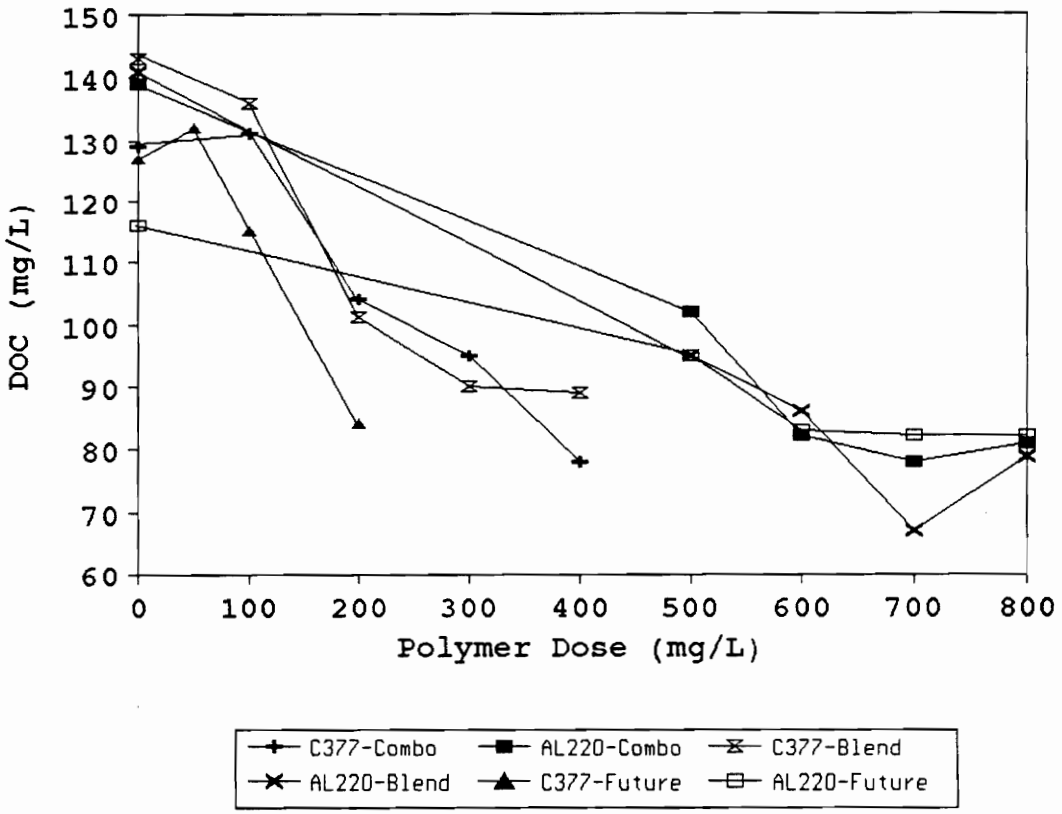


Figure 39. DOC removal achieved through addition of AL220 and C377 to 1:1 print:thermosol (blend), 3:4 print:thermosol (combo) and 3:2 print:thermosol (future)

Table 10. Color (ADMI) results for settling and DAF treatments.

Waste	Before	Settling w/C377	Settling w/AL220	DAF w/ C377	DAF w/ AL220
Print	2605	520	242	125	171
Therm	1857	584	557	364	422
Blend	3026	312	256	228	215

Table 11. DOC (mg/L) results for settling and DAF treatments.

Waste	Before	Settling w/C377	Settling w/AL220	DAF w/ C377	DAF w/ AL220
Print	143	82	72	75	73
Therm	157	109	105	78	89
Blend	141	95	83	84	81

Table 12. TSS (mg/L) results for settling and DAF treatments.

Waste	Before	Settling w/C377	Settling w/AL220	DAF w/ C377	DAF w/ AL220
Print	220	430	60	40	15
Therm	35	55	35	45	0
Blend	120	90	70	40	10

Overall, color removal achieved with DAF was better than that achieved with settling when the waste was treated with C377. This can be attributed to the size of the flocs that were formed. Upon coagulation, C377 formed very tiny flocs that were difficult to settle. DAF was better able to remove and separate them from the water. For the waste pretreated with AL220, settling and DAF were very comparable for color removal.

In all but one case, DOC removals were 1-8% higher when AL220 was used instead of C377. The difference between DOC removal of the settled waste and the DAF treated waste varied from 1-19%. The largest difference was seen with the thermosol waste. AL220 treated thermosol achieved 10% more DOC removal by DAF than settling. Likewise, thermosol treated with C377 achieved 19% more DOC removal when the DAF unit was used rather than settling. Other than these instances, removal efficiencies differed by only 1-7%.

Waste treated with AL220 resulted in higher TSS reductions than waste treated with C377. Overall, the DAF achieved better reductions, ranging from 67-100%. TSS removal efficiencies following settling were between 25-73%. On occasion, the TSS would increase upon addition of C377 or AL220.

Due to cost and performance, AL220 was chosen as the pretreatment option to be followed by A130. Although the

thermosol waste stream frequently required lower AL220 doses than the print waste stream to achieve sufficient coagulation, ease of operation and capital costs suggested that the print and thermosol streams be combined prior to treatment. Various combinations of print and thermosol were tested with the polymers. Since the Plant presently produces three parts print waste and four parts thermosol waste (combo), this ratio was considered in further testing and subsequent bench-scale pretreatment.

As far as chemical floc separation, the DAF did perform better in most cases, but the minimal difference and operational considerations suggested that settling would be more appropriate for a bench scale operation. The actual separation process to be used at the Plant would need to be determined on site with a pilot plant study. On two occasions at the Plant, a sample of pretreated waste was settled in a 900 mL glass jar for 1 hour while the bulk of the waste was passed through DAF. Effluent samples were taken from both operations. Results of various tests performed on the samples can be seen in Table 13. The first trial yielded better results when DAF was used. The second trial produced better results for two of the four tests when settling was used.

The characteristics of the flocs and the way they behave during separation is related to the type of dyes and

chemicals that are being used at the plant. On different days, different chemicals might be used thereby producing varied results.

Table 13. Character of effluents from settling and DAF trials at the Plant.

Trial	Process	COD (mg/L)	TSS (mg/L)	TOC (mg/L)	Color (ADMI)
1	Settling	280	40	80	89
1	DAF	320	0	65	123
2	Settling	261	0	80	192
2	DAF	224	50	80	157

4.6 BENCH-SCALE TREATMENT

The following sections present and discuss the results of the bench-scale pretreatment and biological treatability experiments that were performed.

4.6.1 Pretreatment

As previously discussed in section 4.5.3, it was decided to pretreat a combination of three parts print and four parts thermosol (combo) with AL220 and A130 prior to biological treatment. The chemical flocs were separated by gravity. Characteristics of the combo waste stream before and after treatment are discussed in sections 4.6.4-4.6.6.

Each week a new batch of wastewater (24 hr composite) was delivered to Virginia Tech and the color and characteristics of the wastewater differed. In order to determine the optimum AL220 dosage level, jar tests were performed on several different batches, and effluent color measurements were made. Figure 40 provides a summary of the results. Influent color ranged from 1060-2616 ADMI. AL220 concentrations of 300, 400 and 500 mg/L removed an average of 48%, 71% and 81% of the color, respectively. At AL220 and A130 doses of 600 mg/L and 5 mg/L, respectively, an average of 90% of the color was removed. Similarly, Kreye *et al.* (1972) was able to achieve 90% color removal with an alum dose of 350 mg/L and 2-5 mg/L of organic polymer. Kace and Linford (1975) treated a textile waste with alum and organic polymer to remove 95% of the color.

While removal efficiencies with AL220 doses of 300, 400 and 500 mg/L were sometimes adequate, occasionally, high influent color caused problems. Therefore, 600 mg/L was chosen as the amount of AL220 to dose during each bench-scale pretreatment. Since increased concentrations of AL220 were required, 5 mg/L of A130 were added, as opposed to 2.5 mg/L of A130 which was sufficient at the lower AL220 doses initially considered.

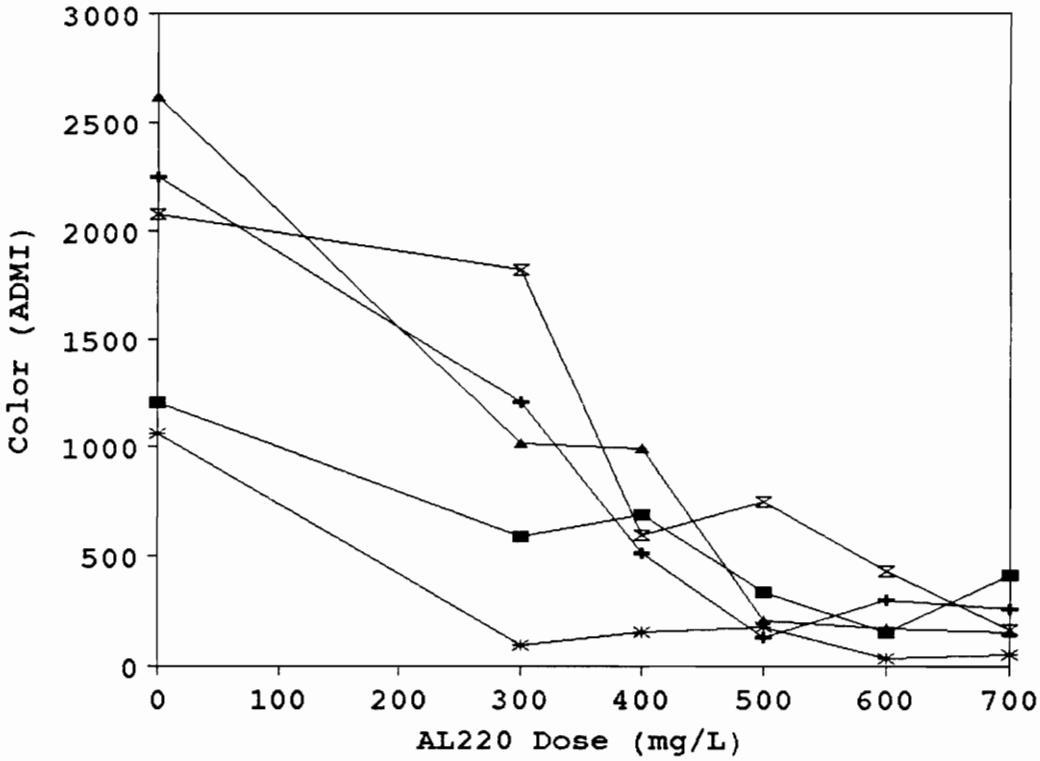


Figure 40. Comparison of color removal from different batches of print and thermosol waste streams

4.6.2 Sequencing Batch Reactor

Results of monitoring the SBR can be seen in Figures 41-44. Once the MLSS was built up (day 10), it was maintained at an average of 4,266 mg/L. Average MLVSS was 3,557 mg/L, yielding an average of 83% volatile solids. TSS of the effluent ranged from 10 to 100 mg/L. The addition of nutrients (section 3.2.2) during the last four days of operation had little effect on solids concentration.

Color removal in the SBR ranged from 17-79% with an average of 59%. Effluent color was typically below 200 ADMI which is sufficient for possible imposed limits in the future. Again, nutrient addition did not improve color removal.

The DOC of the effluent ranged from 69-278 mg/L, yielding an average of 59% removal. Effluent COD averaged 536 mg/L with an average percent removal of 69%. More thorough treatment could have possibly been achieved with a longer reaction period. DOC and COD removal efficiencies were not affected by nutrient addition.

Color and COD removal efficiencies were comparable to those reported by McCurdy *et al.* (1991) who obtained 77% color reduction and 60% COD removal with SBR treatment of a pretreated textile wastewater.

The settling behavior of the SBR sludge was very good. Sludge volume indices (SVI) ranged from 55-70 mL/L.

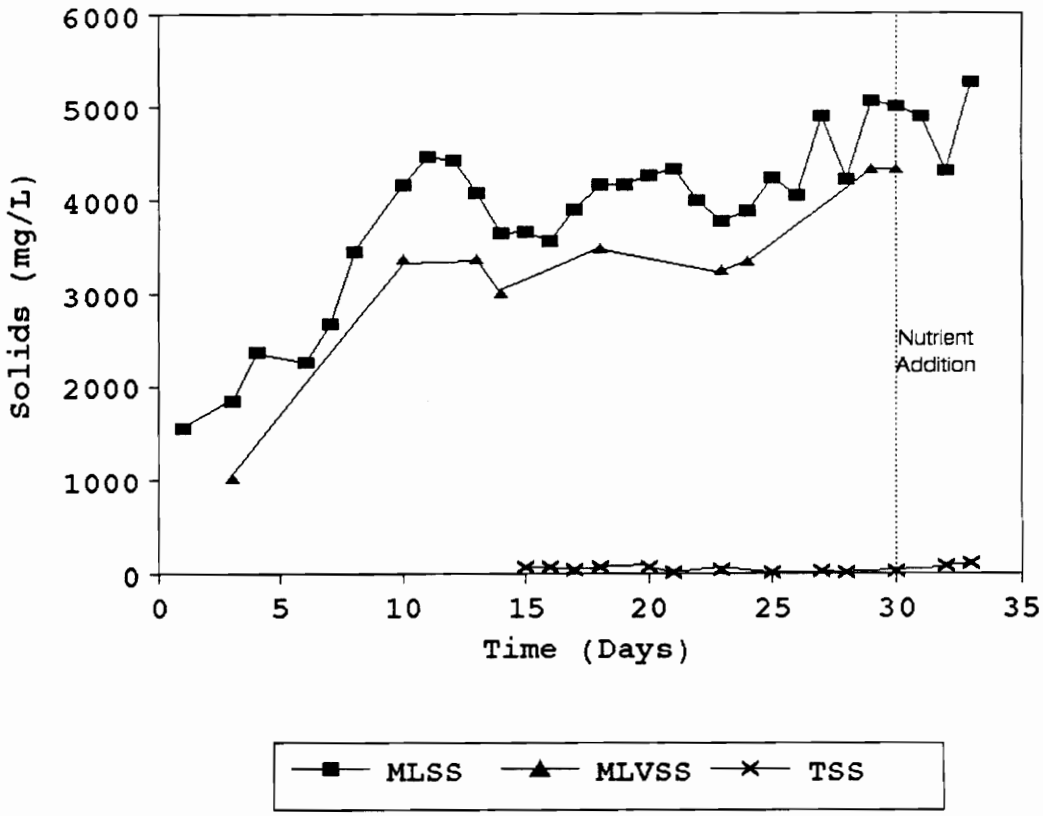


Figure 41. MLSS, MLVSS and effluent TSS for the sequencing batch reactor

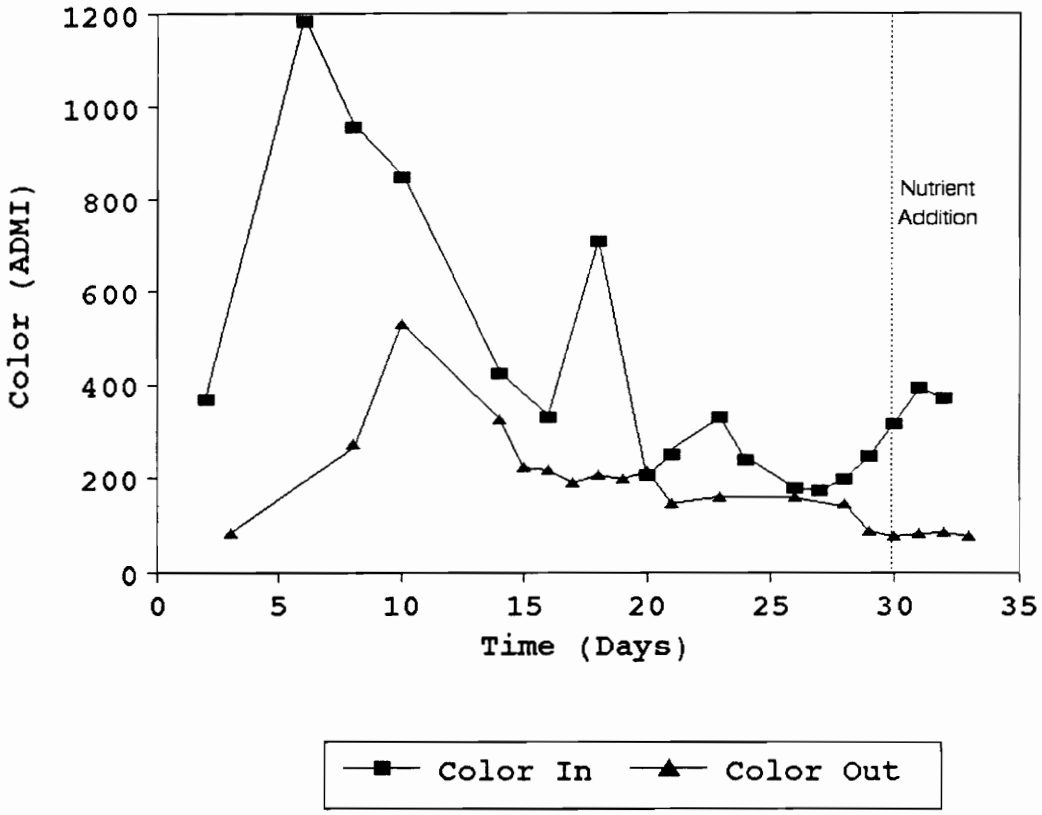


Figure 42. Effluent color and % color removal for sequencing batch reactor

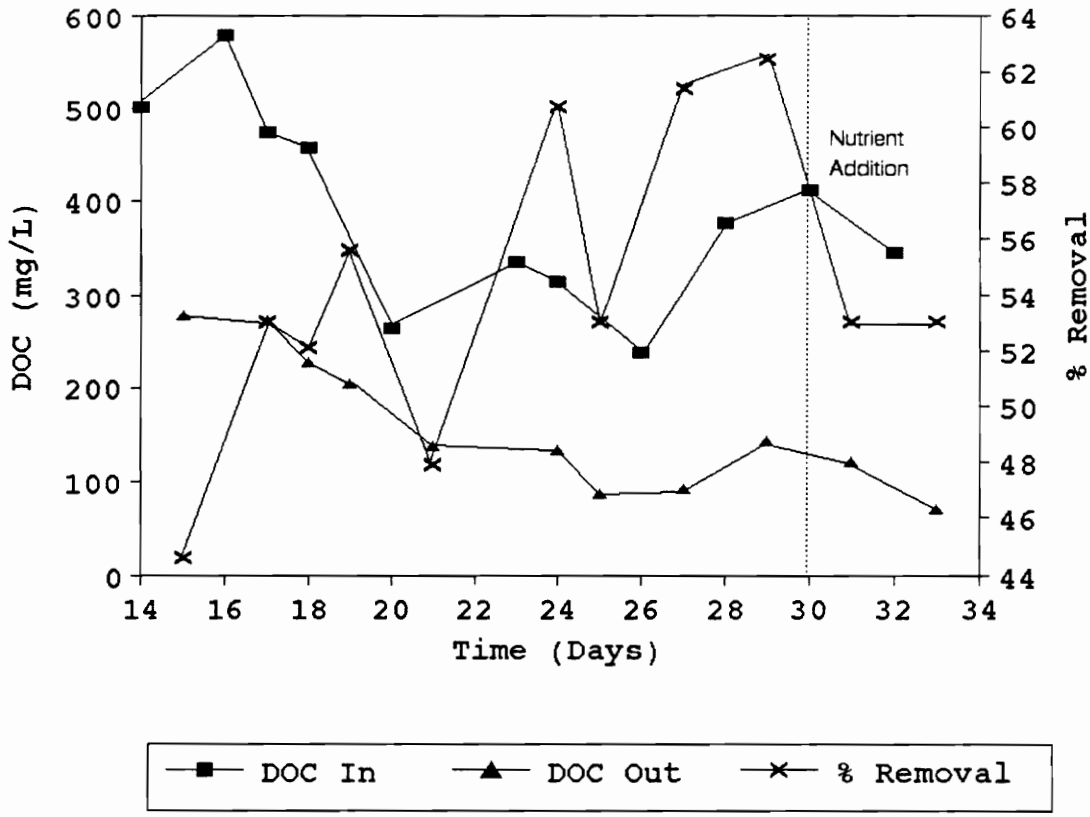


Figure 43. Influent and effluent DOC and % removal for sequencing batch reactor

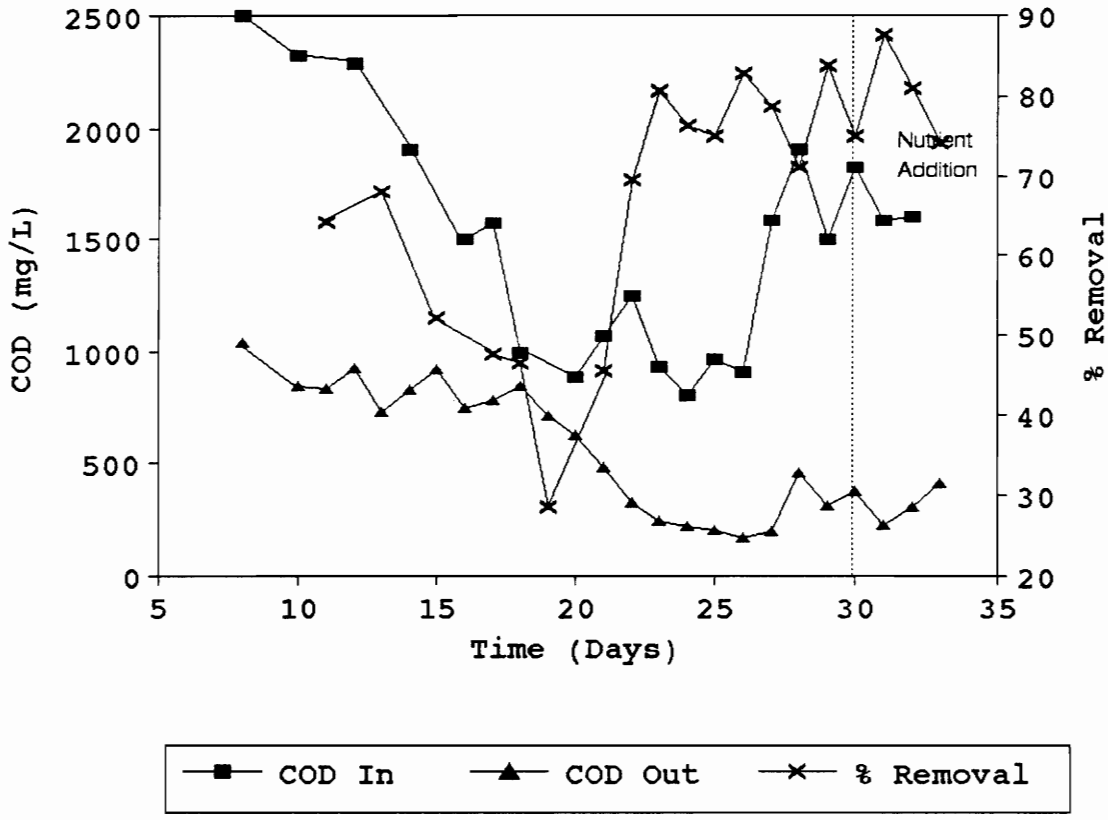


Figure 44. Influent and effluent COD and % removal for sequencing batch reactor

Typically, an SVI less than 100 mL/L is considered excellent. Additional characteristics of the SBR effluent are discussed in sections 4.6.4-4.6.6.

Effluent pH and temperature averaged 7.4 and 20°C, respectively. Average DO in the reactor was 8 mg/L.

Overall, SBR treatment of the wastewater was good, after an acclimation period of 23 days was allowed to achieve the best results.

4.6.3 Continuous Flow Reactors

Figures 45-48 summarize the monitoring of the four CFRs. MLSS, MLVSS, color and COD were used as a method of monitoring steady state. Review of MLSS, MLVSS and effluent COD helped to determine approximately when steady state was reached. Typically it is presumed that steady state of a CFR is achieved after it has operated for a time period equivalent to three sludge ages (θ_c). Therefore, each reactor was operated for at least three θ_cs and characterization of the waste was performed at that time. Tests performed before then were used if, upon final analysis, steady state had been achieved at the time of the test.

The 8 and 15 day θ_c reactors were operated for a shorter time period than the 20 and 30 day θ_c reactors.

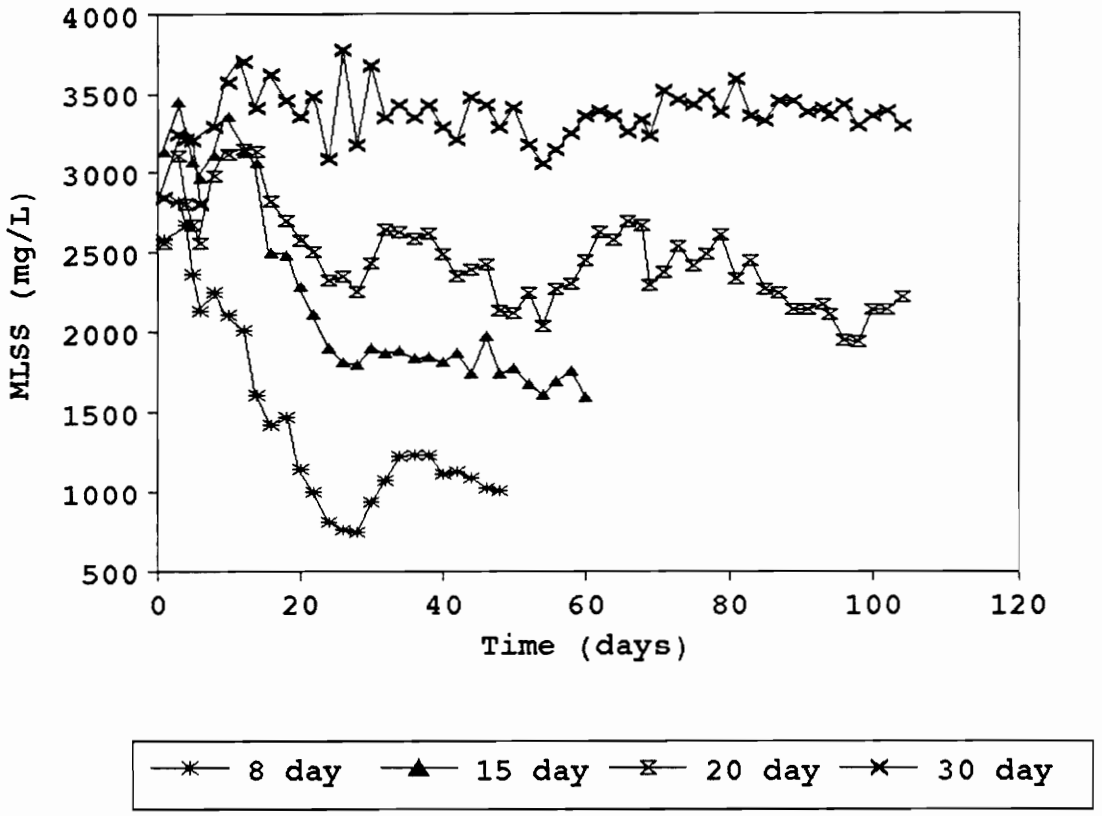


Figure 45. MLSS for continuous-flow reactors

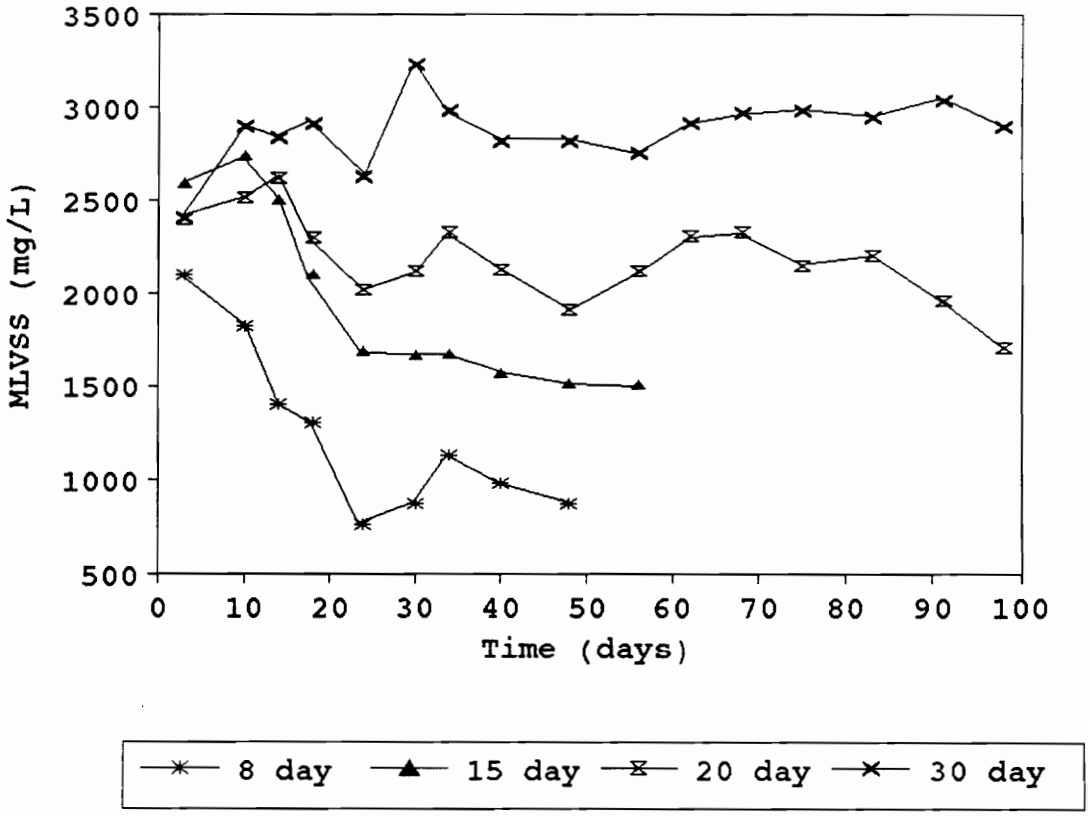


Figure 46. MLVSS for continuous-flow reactors

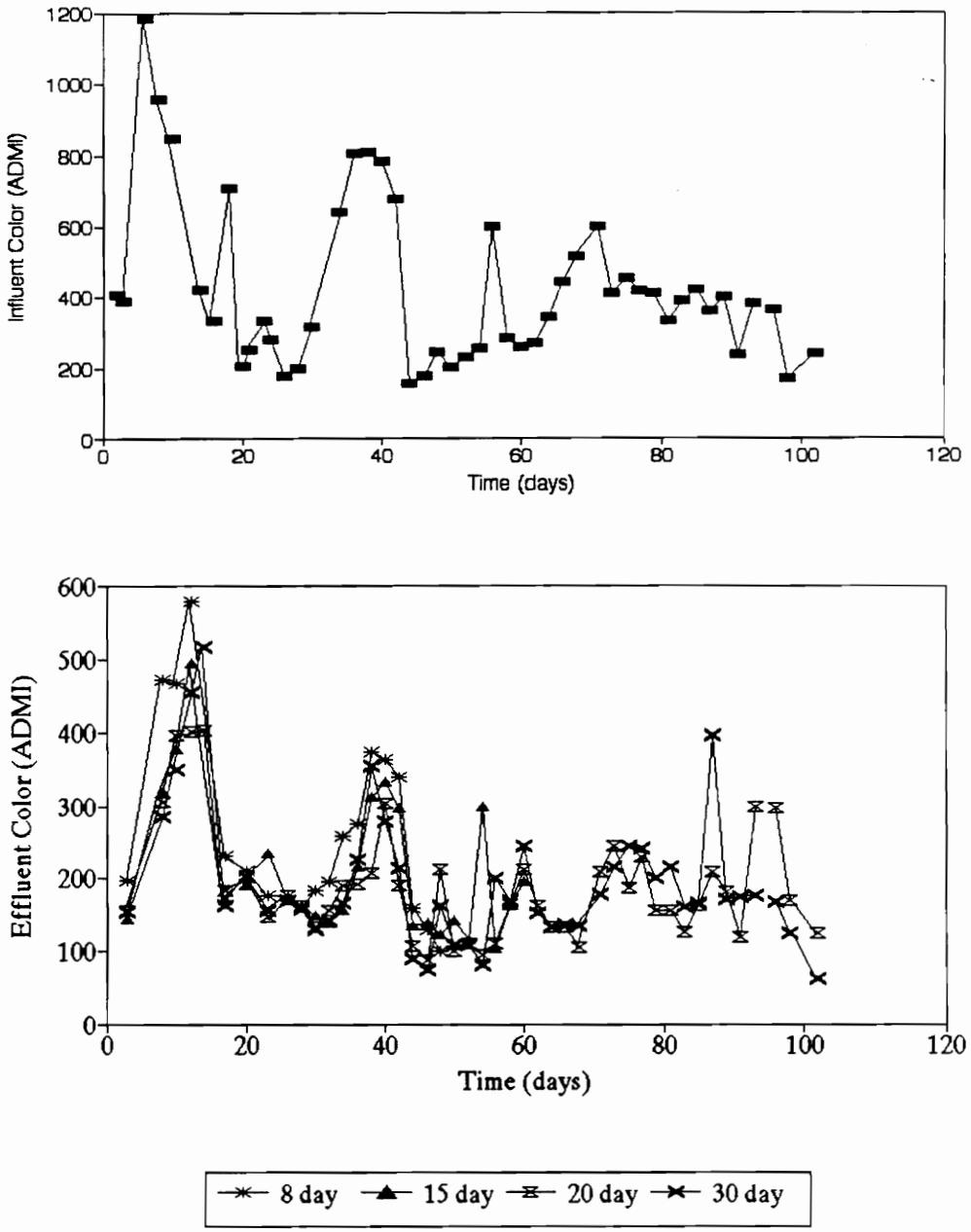


Figure 47. Influent and effluent color for continuous-flow reactors

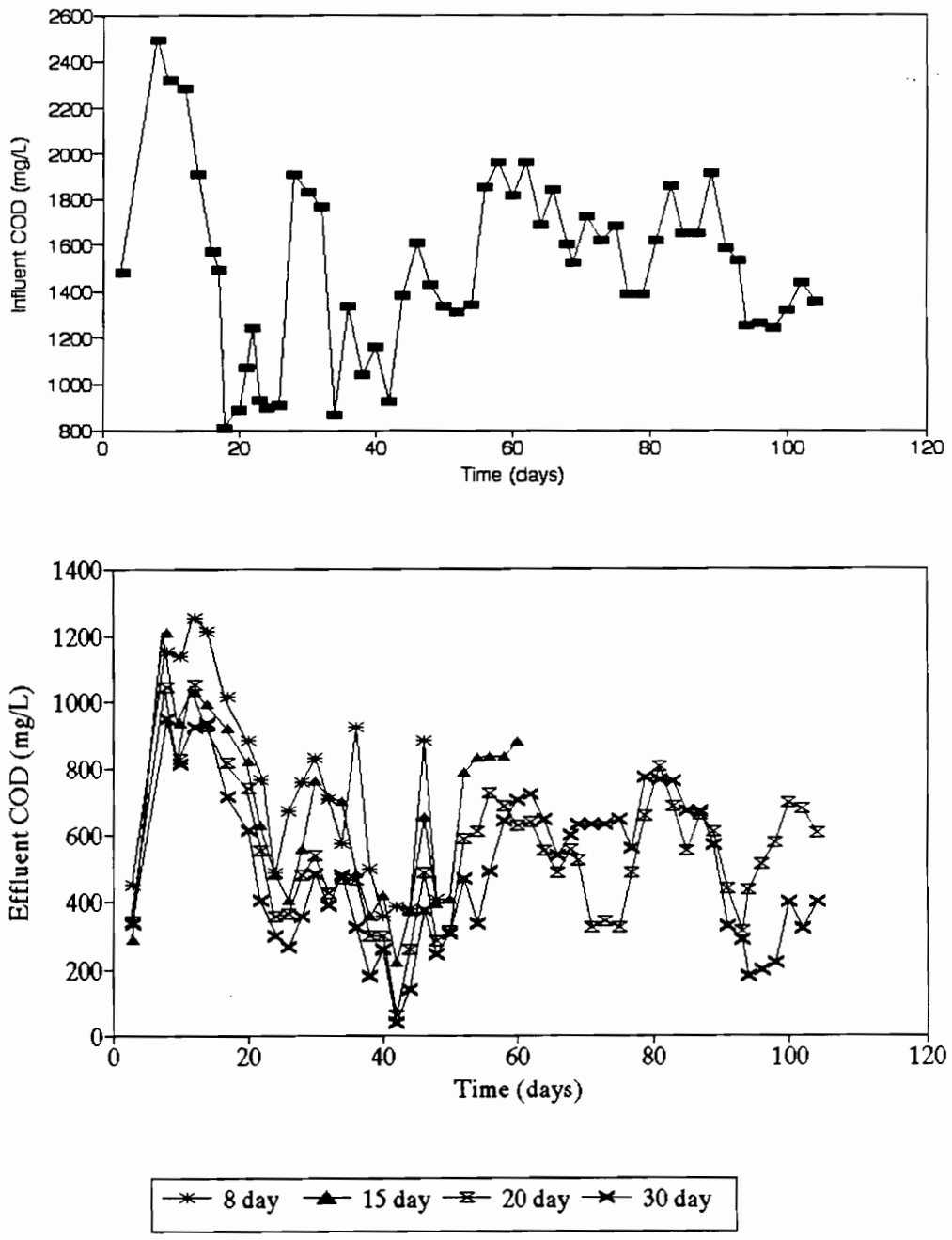


Figure 48. Influent and effluent COD for continuous-flow reactors

After day 50, the 8 day θ_c reactor was terminated. The 15 day θ_c reactor was shut down after 60 days of operation. Both the 20 and 30 day θ_c reactors were operated throughout the duration of the project.

Figures 45 and 48 were examined to determine when MLSS, COD and percent COD removal were relatively constant. Upon review of the final figures, steady state of the reactors with 15, 20 and 30 day θ_cs was reached before the time of three sludge ages had elapsed. Table 14 provides the days on which it was deemed that the reactors had achieved approximate steady state. Except for the 8 day θ_c reactor, steady state was estimated to have been reached at approximately 1.5 sludge ages in each of the other reactors.

Table 14. Approximate days on which steady state was achieved for the CFRs.

Reactor Sludge Age (days)	Day Steady State Achieved
8	28
15	22
20	30
30	46

Subsequent averages of effluent parameters were determined using the days in the table as the starting point and the

last day of operation as the final point.

The average values for MLSS, MLVSS, effluent color and COD for the four reactors can be seen in Table 15. Average color and COD removal are included as well.

Increased sludge age corresponded with increased MLSS and MLVSS. Figure 45 represents the amount of MLSS in each reactor over time. The initial MLSS of the four reactors

Table 15. Summary of CFR monitoring data for MLSS, MLVSS, COD and color.

Sludge Age (days)	MLSS (mg/L)	MLVSS (mg/L)	Color (ADMI)	% Removal	COD (mg/L)	% Removal
8	1,076	959	230	43	664	55
15	1,805	1,598	188	42	605	59
20	2,345	2,117	170	52	496	66
30	3,353	2,913	170	53	472	68

was in the range of 2,600-3,100 mg/L. Daily wasting of the reactors, as described in section 3.2.1, eventually steadied the MLSS. The 8, 15, and 20 day θ_c reactors all dropped from their initial MLSS values. The MLSS of the 30 day θ_c reactor increased slightly. MLVSS followed a trend similar to MLSS. Volatile solids accounted for an average of 89% of total solids.

Color removal in the CFR increased from 42-53% with

increased sludge age. Color removal in the SBR averaged 59% with an average MLSS of 4,266 mg/L. This trend in color removal is in agreement with Dohanyos *et al.* (1978) who noted that the quantity of dye removed was directly proportional to the amount of sludge in the system.

Effluent color from the CFRs followed the same trend as influent color. This may indicate that some form of equalization prior to biological treatment could be beneficial in producing a more constant effluent.

Increased sludge age also increased COD removal. Removals ranged from 55-68%. This range is above the COD removal achieved by Loyd *et al.* (1992). Aerobic treatment of textile wastewater in an activated sludge unit removed only 35% of the COD. On the other hand, Shriver and Daugue (1977) obtained 85% COD reduction using the activated sludge process and Abo-Elela *et al.* (1988) removed 81-96% COD.

Effluent COD values ranged from 472-664 mg/L, which is below the present Plant limit of 1,493 mg/L (at a flow of 1 MGD). Additional COD removal could possibly be achieved by increasing the sludge age or increasing the hydraulic retention time of the reactors.

TSS values of the effluent averaged 174, 88, 100 and 66 mg/L for the 8, 15, 20 and 30 day θ_c reactors, respectively. This particular data may not be representative of a full

scale operation. The settling chamber in the bench scale apparatus was easily disturbed by the mixing being performed in the activated sludge portion. Also, no aids or polymers were used to assist in settling. The Plant presently adds polymer to obtain effluent TSS within the limits.

Figure 49 represents average SVI (mL/L) versus sludge age. SVI is often used as a good representation of the settling characteristics of the sludge. As mentioned earlier, an SVI below 100 mL/L indicates an excellent settling sludge, while values of 100-200 mL/L represent a good settling sludge. Sludge ages of 15 and 20 days achieved the best SVIs, ranging from 127-143 mL/L. A higher θ_c of 30 days yielded a substantial increase in SVI to 282 mL/L. The average SVI for the SBR was 63 mL/L. This would indicate that the sludge in the SBR had better settling characteristics than those of the CFRs. Ability of the sludge to settle is related to the characteristics of the sludge and the biomass concentrations. Wanner (1992) compared SBRs to CFRs and found that while the settling properties of the sludge from the CFR were acceptable, the SBR sludge exhibited a high settling velocity.

Average temperature and pH values of the CFR's influent and effluents can be seen in Table 16 along with average DO values. The influent pH was held fairly constant at an

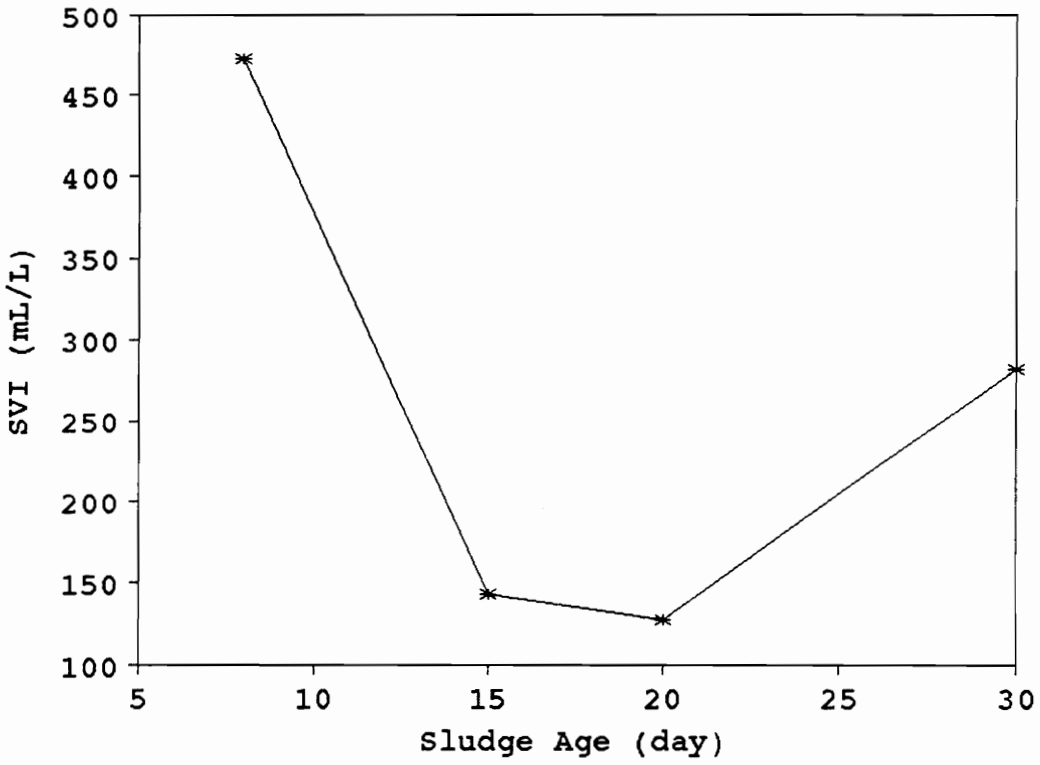


Figure 49. Comparison of sludge volume indices for the continuous-flow reactor

average of 7.5, which is within the required limits for efficient biological treatment. Occasionally, adjustment of the influent pH was necessary with 1 N NaOH. Average influent temperature was 19°C. Average effluent pH ranged from 7.3 to 7.5 which is within the effluent limits of 6-9. DO in the activated sludge portion of the reactors ranged between 2-8 mg/L, with an average of 5 mg/L.

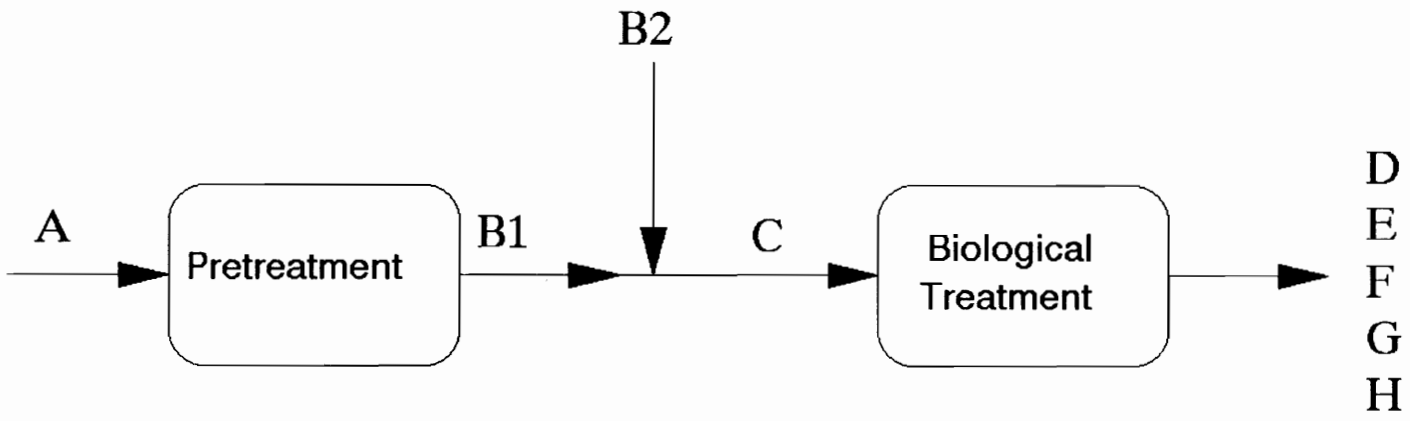
Table 16. Average pH, temperature and DO for CFRs.

Reactor Sludge Age (days)	pH	Temperature (°C)	DO (mg/L)
8	7.35	18.9±1	4.5
15	7.45	18.5±1	5.0
20	7.35	18.8±1	6.0
30	7.35	18.8±1	4.5

4.6.4 Organic Removal

Table 17 provides a summary of total and soluble BOD_5 and COD, TOC and DOC for each of the streams shown in Figure 50. A range of values and removal percentages, as well as the averages are shown. The number of trials performed is also tabulated.

Pretreatment of the print and thermosol waste achieved



A - 3: 4 combination of print:thermosol before pretreatment
B1 - 3:4 combination of print:thermosol after pretreatment
B2 - 3 parts bleach/finish
C - influent to biological reactors, 7 parts B1, 3 parts B2, sanitary waste
D - effluent SBR
E - effluent 8 day sludge age CFR
F - effluent 15 day sludge age CFR
G - effluent 20 day sludge age CFR
H - effluent 30 day sludge age CFR

Figure 50. Flowchart of Treatment Scheme

Table 17. Organic removal through treatment scheme

TEST	A	B1	B2	C	D	E	F	G	H
(mg/L)	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave
Total BOD	128	64	601	287-695 403	38-107 68	129-334 232	158-184 171	207-254 232	88-288 214
% Removal		50			67-87 79	16-61 39	36-57 47	27-64 48	40-71 57
# Trials	1	1	1	11	3	3	3	4	4
Soluble BOD				147-318 225	16-153 57	65-127 93	30-158 90	52-100 67	42-105 72
% Removal					34-90 74	41-56 46	29-85 63	69-75 72	64-82 70
# Trials				11	4	3	3	4	4
Total COD	860-1280 1105	220-320 273	5754-7017 6603	992-2984 2037	381-964 647	590-972 810	1164-1818 1485	556-688 647	278-816 660
% Removal		73-78 75			28-83 57	44-68 54	27-40 36	64-77 71	56-86 71
# Trials	3	3	3	15	9	3	3	5	5
Soluble COD	140-496 296	100-332 251	2367-6000 4850	809-1960 1464	303-841 556	360-925 618	220-881 588	60-808 498	40-775 463
% Removal		0-33 26			12-81 52	25-73 55	18-76 59	45-94 66	44-96 69
# Trials	7	7	6	15	8	20	23	43	45
TOC				389-698 544	54-301 158	297-378 338	216-323 270	147-160 154	152-166 159
% Removal					51-86 69	37-49 43	47-63 55	77-79 78	76-78 77
# Trials				6	3	2	2	2	2
DOC	58-396 132	46-112 81	951-1014 983	238-779 418	69-278 160	120-303 218	97-272 174	117-234 190	95-197 136
% Removal		19-84 25			44-80 59	36-49 54	43-63 54	42-75 56	62-78 69
# Trials	11	11	2	20	11	5	5	6	6

50% removal of total BOD_5. Seventy-five percent and 26% of total and soluble COD were removed, respectively. A higher percentage of total COD than soluble COD was removed because prior to pretreatment, the waste contained substantially more total COD than soluble COD. Following pretreatment, total and soluble COD differed by only an average of 22 mg/L. TOC could not be measured due to the quality of the samples. DOC removal was 25%. These removal efficiencies were slightly lower than those seen by Porter and Sargent (1977) upon coagulation with alum, but they were within the range achieved by Olthof and Eckenfelder (1976) after pretreatment with lime, alum and ferric sulfate. Overall, this pretreated waste stream was not a significant contributor to the organic matter in the influent wastewater to the biological reactors.

The bleach/finish stream was the primary contributor of organic matter to the influent waste stream. Total BOD_5 was 601 mg/L. Total COD, soluble COD and DOC averaged 6,603, 4,805 and 983 mg/L, respectively. Again, TOC could not be measured due to the poor quality samples.

Total and soluble BOD_5 values for the influent wastewater averaged 403 and 225 mg/L, respectively. Total COD averaged 2,037 mg/L, while soluble COD averaged 1,464 mg/L. Average TOC and DOC values of 544 mg/L and 418 mg/L

were obtained. The ratio of soluble BOD_5 to soluble COD for the influent was 0.154. Typical domestic wastewater has a BOD_5/COD ratio in the range of 0.4-0.8 (Metcalf & Eddy, 1991). The low ratio (0.154) indicates that the textile wastewater could be very difficult to degrade biologically.

Biological treatment removed 39-79% of total BOD_5 and 46-74% of soluble BOD_5. For the CFRs, treatment improved with increased sludge age. The SBR performed better than even the highest sludge age CFR in terms of BOD_5 removal possibly due to the larger population of microorganisms.

The CFRs removed a higher percentage of soluble BOD_5 than total BOD_5. The soluble BOD_5 was probably more easily degraded biologically. The SBR removed an average of 4% more total BOD_5 than soluble BOD_5.

Total COD removal ranged from 36-71% and soluble COD removal ranged from 52-68%. Total COD removal did not appear to follow any trend. The 20 and 30 day θ_c reactors removed an equal amount of total COD (71%), while the 8 day θ_c reactor removed 18% more than the 15 day θ_c reactor. Soluble COD removal did follow a pattern. Higher sludge ages achieved higher soluble COD removals. The SBR performed better than the 8 and 15 day θ_c reactors for total COD removal, but only slightly better than the 8 day θ_c reactor for soluble COD removal. The lack of any trend for

the total COD values could be attributed to the number of trials. If more samples had been taken a clearer trend may have established.

For the most part, TOC and DOC removal efficiencies for the CFRs increased as the sludge age increased. TOC removal ranged from 43-77%. The SBR achieved 69% TOC removal which is better than the 8 and 15 day CFRs. DOC percent removals were between 54% and 69%. The SBR removed 59% of DOC, second only to the 30 day reactor. In all but one case, greater percentages of TOC than DOC were removed.

It appears that the SBR achieved better BOD_5 removal than COD removal. High MLSS and a short acclimation period could account for this. The CFRs achieved fairly similar BOD_5 and COD removal efficiencies. The CFRs were operated for a longer period of time, so extended acclimation could have been the reason for improved COD removal.

Effluent ratios of soluble BOD_5 to soluble COD and TOC can be seen in Table 18.

Table 18. Effluent BOD_5/COD and BOD_5/TOC ratios.

Waste	BOD_5/COD	BOD_5/TOC
D	0.100	0.361
E	0.152	0.275
F	0.154	0.333
G	0.135	0.435
H	0.156	0.453

The four CFRs had BOD_5/COD ratios similar to the influent waste. The BOD_5/COD ratio for the effluent SBR is lower than the effluent CFR and the influent ratios. The SBR was better able to remove BOD_5 than COD which would account for this lower ratio following treatment.

The BOD_5/TOC ratio for typical untreated domestic wastes varies from 1.0-1.6. All effluent ratios of the treated waste were well below that typically found in domestic wastewater. Again, this is an indication that primarily non-biodegradable matter remained after biological treatment.

4.6.5 Nutrients

The range of values and removal percentages for Total P, OrthoP, TKN and NH_3-N for the waste streams shown in Figure 50 can be seen in Table 19. Average values and the number of trials are also included.

Prior to pretreatment, the combination print and thermosol waste stream contained an average of 1.3 mg/L of Total P and 0.4 mg/L of OrthoP. Coagulation removed an average of 66% and 75% of Total P and OrthoP, respectively. Thirty-three percent of TKN was removed along with 6% of NH_3-N. It is desirable to remove the nutrients in this portion of the treatment scheme if there are sufficient

Table 19. Nutrient removal through treatment scheme

TEST	A	B1	B2	C	D	E	F	G	H
(mg/L)	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave
Total P	0.2-2.2 1.3	0-0.8 0.5	6.4-12.7 9.4	2-3.7 2.9	0-0.7 0.4	0.7-1.4 1.0	0.3-1.3 0.9	0.1-1.6 0.7	0.4-1.0 0.8
% Removal		39-100 66			82-99 87	47-64 56	39-87 59	53-96 76	60-89 73
# Trials	6	6	3	11	6	4	4	6	6
Ortho P	0.1-0.6 0.4	0-0.3 0.1	1.3-3.5 2.2	0.1-1.1 0.5	0 0	0-0.1 0.1	0-0.1 0	0-0.3 0.1	0-0.1 0
% Removal		50-99 75			95-99 97	10-91 59	28-96 66	33-100 78	77-100 92
# Trials	4	4	3	11	3	4	4	4	4
TKN	13.7-41 25	12-21 16	38-54 48	22-65 36	7-22 15	11-15 13	7-49 16	12-33 22	11-25 18
% Removal		12-49 33			30-61 48	44-56 49	19-85 57	1-75 43	43-99 82
# Trials	6	6	3	14	8	4	6	7	6
NH3-H	7.5-14 11	7-12 10	5-13 7	5-36 15	0.1-10 1.5	0-0.6 0.3	0-18 3	0.1-9 2	0.1-13 4
% Removal		2-14 6			63-99 91	94-100 97	19-100 85	61-99 92	43-99 82
# Trials	5	5	3	14	7	4	6	7	6

nutrients available from other waste streams. However, if the waste is deficient in nutrients, their removal at this point would be undesirable, although unavoidable.

The bleach/finish stream contributed the bulk of phosphorus. Total P averaged 9.4 mg/L, and OrthoP averaged 2.2 mg/L. An average of 48 mg/L of TKN and 7 mg/L of NH_3-N were also contributed by the bleach/finish stream.

Total P of the influent stream averaged 2.9 mg/L, while OrthoP was 0.5 mg/L. Average influent TKN was 36 mg/L, and average influent NH_3-N was 15 mg/L. Combining the pretreated waste with the bleach/finish waste diluted the amount of nutrients available for use in biological treatment.

The amount of nitrogen and phosphorus needed for sufficient biological treatment is typically measured in terms of a ratio. According to Shriver and Daugue (1978), the ratio of BOD_5:N:P in textile dye wastewater should be 100:5:1 in order to achieve optimal treatment. LaGrega *et al.* (1994) agree, stating that this ratio is often used, based on general experience. Although, it is also suggested that the need for nutrients be determined through treatability tests. For this particular wastewater influent the average ratio of BOD_5:N:P was 100:9:0.7 which is not very different from the literature values. However,

availability of these nutrients in the wastewater was not determined.

Total P in the CFR effluents ranged from 0.7-1.6 mg/L and OrthoP ranged from 0-0.3 mg/L. TKN and NH_3-N effluent values ranged from 7-49 mg/L and 0.1-18 mg/L, respectively.

Section 3.2.2 explains that supplemental nutrients were added to the SBR during the last four days of operation to determine if they would have any effect on treatment efficiency. As previously discussed, color, COD, DOC and solids were not affected. Total P effluent was 0.6 mg/L, which was in the same range as had been previously recorded. Effluent OrthoP was 0.1 mg/L which was the same as the influent. Since 1 mg/L of KH_2PO_4 as P was added, it must have been used by the organisms. Effluent TKN and NH_3-N were 17.5 mg/L and 10 mg/L, respectively. The effluent TKN value was similar to effluent values previously obtained. Typical effluent NH_3-N values ranged from 0.1-0.2 mg/L. After addition of 10 mg/L of NH_3-N, the effluent value was 10 mg/L which would indicate that the nitrogen added was not used by the microorganisms. This test was performed over a short period of time. Influent variations were not taken into consideration and there was not a sufficient acclimation period. Further testing would need to be performed in order to draw valid conclusions.

4.6.6 Metals and Ions

Metal and ion analysis was performed on all the waste streams (see Table 20 and Figure 50). Zinc, copper and silver were measured because they were the metals of primary concern at the Plant. Silver was never detected in any of the waste streams. Zinc concentrations ranged form 0.1 to 0.6 mg/L. Copper ranged from 0 to 0.2 mg/L. Percent removals for zinc were not recorded due to the low values, and oftentimes, a slight increase rather than decrease was seen. Likewise, concentrations of copper were minimal throughout the treatment process. Any increase or decrease was also minimal.

Chloride, sulfate, nitrite and nitrate ions were also measured. Nitrite and nitrate were never detected in any of the streams. Chloride values ranged from 8.7 mg/L in the combined print and thermosol waste stream to 98.2 mg/L in the SBR effluent. Sulfate ranged from 90 mg/L in the bleach/finish stream to as high as 1,228 mg/L in the pretreated waste stream. Again, due to the large range and fluctuations, percent removals were not calculated.

4.6.7 Toxicity

Results of the short term chronic toxicity tests (STC) can be seen in Table 21. The No Observed Effect Concentration (NOEC) and the Lowest Observed Effect

Table 20. Metal and Ion removal through treatment scheme

TEST	A	B1	B2	C	D	E	F	G	H
(mg/L)	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave	Range Ave
Zinc	0.2-0.5 0.3	0-0.1 0.1	0.1-0.2 0.1	0.1-0.6 0.2	0.2	0.2-0.4 0.3	0.2-0.4 0.3	0.2-0.4 0.3	0.2-0.3 0.3
# Trials	4	3	2	8	3	3	5	3	3
Copper	0-0.2 0.1	0	0-0.1 0	0-0.1 0	0	0-0.1 0	0-0.1 0	0	0
# Trials	4	3	2	8	3	3	5	3	3
Chloride	8.7-10.2 8.3	13-26 19	33	19-25 23	22-98 49	20-27 23	23-31 25	19-26 22	21-26 23
# Trials	3	3	1	8	3	3	5	3	3
Sulfate	365-833 433	797-1228 1007	90	136-866 437+	149-322 207	327-396 364	408-674 487	425-671 606	497-517 660
# Trials	3	3	1	8	3	3	5	3	3

LOD Zinc = 0.01 mg/L
LOD Copper = 0.02 mg/L
LOD Silver = 0.01 mg/L

Concentration (LOEC) for the 20 day θ_c reactor were the highest (50% and 75%) when the *Pimephales promelas* (Pp) organisms were used. This is not surprising, considering that the 20 day θ_c reactor was treating the waste most efficiently at the time of the tests. All three reactors achieved an NOEC of at least 50% and an LOEC of at least 75% when the *Daphnia pulex* (Dp) organisms were tested. The Plant's NOEC limit for toxicity is 100%. The 15 and 30 day θ_c reactors were achieving better COD removal when these tests were performed than when the Pp tests were performed, which could account for the improved toxicity results. Thus, there is an indication that improved treatment will remove additional effluent toxicity. The Dp organisms appeared to be less sensitive to the waste than the Pp organisms at reactor θ_cs of 15 and 30 days.

Table 21. Effluent toxicity results.

Reactor Sludge Age (days)	NOEC STCPp*, %	LOEC STCPp, %	NOEC STCDp#, %	LOEC STCDp, %
15	25	50	50	75
20	50	75	50-75	75-100
30	<25	25	50-75	75-100

*Short term chronic toxicity tests with *Pimephales promelas*
#Short term chronic toxicity tests with *Daphnia pulex*

4.6.8 Kinetic Analysis

A kinetic analysis was performed as outlined by Metcalf & Eddy (1991). Average influent COD was calculated in two ways: (1) influent COD values were averaged over days 22-104 in order to include all the values within the four steady state ranges and (2) influent COD was averaged over the particular range of steady state for each reactor. Likewise, effluent COD was computed in two manners: (1) effluent COD was averaged over the particular steady state range for each reactor and (2) average percent COD removal was calculated and applied to influent COD as calculated in (1) above. The application of these different options to kinetic analysis can be seen in Appendix E.

The final analysis was performed using influent COD averaged over days 22-104 and effluent COD values were computed using the average percent COD removals. MLSS values were averaged over the particular steady state range for each sludge age. The average influent COD value was 1,475 mg/L. Average MLSS and COD values used in the analysis can be seen in Table 22.

A plot of $1/\theta_c$ versus the specific utilization rate, q (equation 2), yielded a line with an r^2 value of 0.993. Values for the kinetic coefficients Y and k_d were 0.619 and 0.032 d^{-1}, respectively.

Table 22. COD and MLSS values used in kinetic analysis.

Reactor Sludge Age (days)	Average Effluent COD (mg/L)	Average MLSS (mg/L)
8	664	1076
15	605	1805
20	496	2345
30	472	3353

$$q = \frac{S_o - S}{tX} \qquad (2)$$

where S_o=influent COD (mg/L)
S=effluent COD (mg/L)
t=hydraulic retention time (days)

The reciprocal of the specific utilization rate plotted against the reciprocal of effluent COD produced a line with an r^2 value of 0.853. The values for K_s and k determined from the graph were negative and therefore not reasonable.

With the values obtained for Y and k_d, further analysis was done to predict what may occur if the HRT of the reactors was increased.

$$X = \frac{\theta_c Y(S_o - S)}{t(1+k_d\theta_c)} \qquad (3)$$

Using equation 3, it was determined that by increasing the HRT of the 20 day θ_c reactor to 4 days, effluent COD could theoretically be reduced to 232 mg/L. An HRT of 4.5 days would theoretically produce an effluent COD as low as 77 mg/L. This prediction assumes that all of the COD can be biologically degraded. However, there appears to be a biologically refractive residual that needs to be quantified in future studies before reasonable estimates of K_s and k can be made. Mary Opdycke will continue to perform research in this area.

5.0 SUMMARY and CONCLUSIONS

Several methods of pretreatment were studied during this research project. Due to time and funding constraints, the various tests were conducted as screening trials. If encouraging results were not seen initially, further tests were not performed. It is possible that testing of some of the methods under different conditions could have yielded more positive results.

Furthermore, accurate conclusions can not always be drawn from the results of the pretreatment testing due to the variability in the characteristics of the wastewater. In this study, a difference in performance between two polymers of 75% one week decreased to 25% the following week, when a different batch of waste was studied.

The conclusions drawn from the results of this study are presented below.

(1) The waste treated with acid appeared somewhat more amenable to treatment with AL220 than the waste treated with CO_2. Therefore, it was recommended that acid be used for pH adjustment of this particular waste prior to addition of AL220. Previously, the Plant had been using AL220 to adjust pH as well as coagulate the waste. The suggestion to use acid in combination with AL220 has resulted in a savings of

$4,000-$5,000 per week.

(2) Several polymers were considered and compared in this study. It was more cost effective to use AL220 (a blend of inorganic aluminum and a polyamine) than the organic polymer, C377, for coagulation purposes, even though the organic polymer appeared to yield comparable effluents at a much lower dosage. Subsequent use of an anionic polymer (A130) improved settling characteristics of AL220, but not C377. Three parts print and four parts thermosol treated with 400-600 mg/L of AL220 and 5 mg/L of A130 removed 71-90% of the color and an average of 25% DOC. The bleach/finish waste stream did not respond well to any of the polymers used in the jar tests performed.

(3) The flocs formed through coagulation with AL220 and A130 were removed well through both DAF and settling.

(4) Increased sludge ages of the continuous-flow reactors improved treatment efficiencies. Sludge ages ranged from 8-30 days and effluent COD ranged from 472-664 mg/L. Kinetic analysis yielded Y and k_d values of 0.619 and 0.032 d^{-1}, respectively. Values for K_s and k could not be determined accurately with the data obtained.

(5) The 20 day θ_c reactor yielded the best results for effluent toxicity. An NOEC of 50-75% was achieved. Typical NOEC values at the Plant range from 0-24%.

(6) The SBR, operated with a cycle time of one day and an average MLSS concentration of 4,266 mg/L, achieved an average 69% COD removal and 59% color removal. Addition of nutrients did not appear to improve these efficiencies. Settling characteristics of the sludge were excellent.

(7) Aeration of waste streams containing print waste, removed 20-39% of the color. Although this would not alone be sufficient to meet future regulations, aeration might be beneficial if implemented in combination with equalization of the waste prior to subsequent treatment operations.

(8) Treatment of the bleach/finish waste by oxidation with H_2O_2 did not yield encouraging results. A maximum of 8% color and 6% DOC were removed at a dose of 250 mg/L.

(9) Based on color measurements alone, results of anaerobic degradation of the textile wastewater were not encouraging. Color decreased by up to 24% in the thermosol waste but color increased in the print and bleach/finish waste streams.

6.0 RECOMMENDATIONS

The following section is a series of suggestions for further studies to be performed with this textile dye wastewater.

(1) Pretreatment of the bleach/finish waste stream was not successful with the methods tried during this research project. Extremely high organic levels warrant further experimentation of ways to pretreat this waste stream and reduce some of the organic load to the biological treatment system or make the waste more amendable to biodegradation.

(2) Further on site studies should be performed to determine the most efficient and economical means of separation of the chemical flocs formed during coagulation of the print and thermosol waste.

(3) Additional studies should be performed to determine if this textile dye wastewater contains sufficient nutrients in the right ratio.

(4) Continuous-flow reactors should be operated at higher sludge ages and longer hydraulic retention times to determine if further biodegradation would occur.

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APPENDIX A

Abbreviations

ADMI	American Dye Manufacturers Institute
BOD_5	5-day biological oxygen demand
BPE	Blacksburg primary effluent
CFR	continuous-flow reactor
COD	chemical oxygen demand
DAF	dissolved air flotation
DO	dissolved oxygen
DOC	dissolved organic carbon
ETAD	Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry.
HRT	hydraulic retention time
LC_{50}	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 -- equivalence/liter
NH_3-H	nitrogen present as ammonia
OrthoP	orhtophosphorus
POTW	publicly owned treatment works
SBR	sequencing batch reactor
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
Total P	total phosphorus
TSS	total suspended solids

APPENDIX B

TRE Flowchart
(EPA/600/3-88/034)

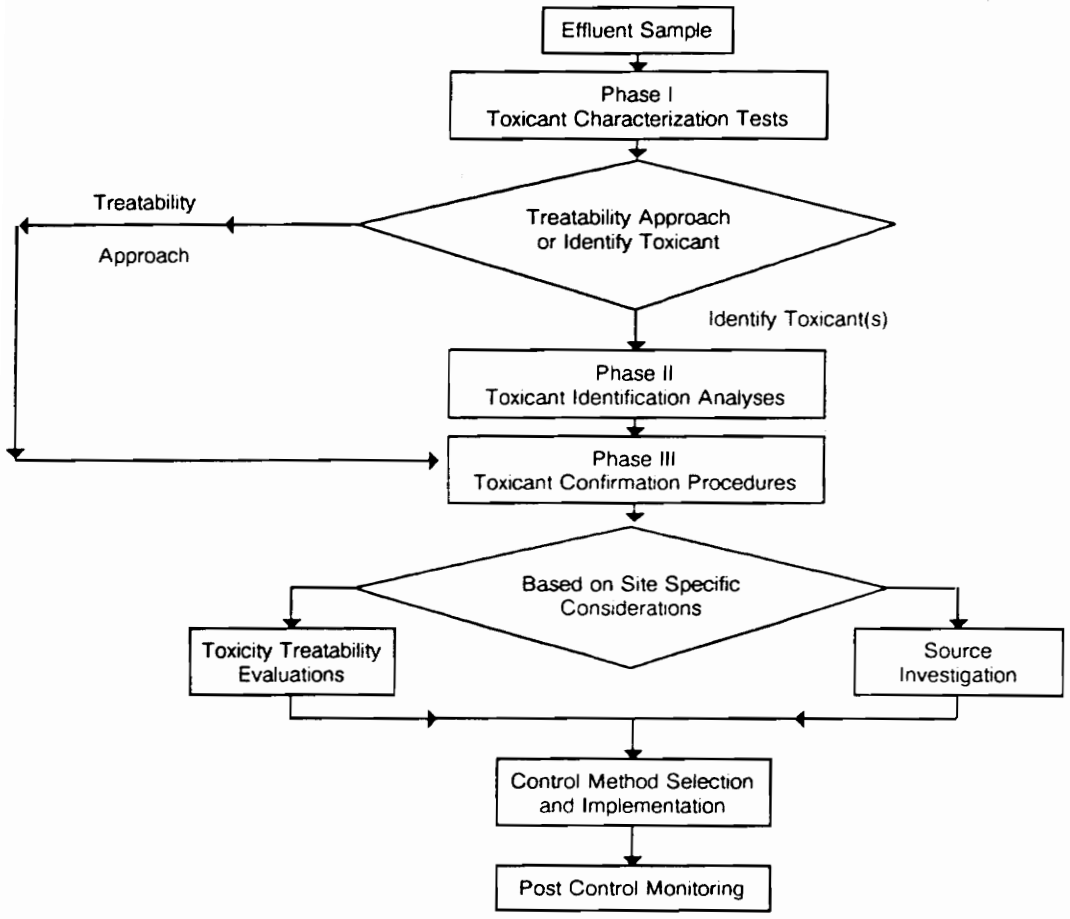

Figure B1. TRE Flowchart (EPA 600/3-88/034, 1988)

APPENDIX C

Pretreatment:

pH Adjustment
Anaerobic Degradation
Oxidation with H2O2
Preliminary Jar Tests
AL220 vs. C377
Additional Jar Tests

Table C1. pH Adjustment with Carbon Dioxide

Time (min)	pH		AL220 (mg/L)	Color (ADMI)	DOC (mg/L)
		CO2			
0	9.17		0	2290	96
0.5	8.75		400	904	88
1	8.34		500	1926	83
1.5	7.73		600	1404	83
2	7.13	ACID			
2.5	6.73		0	2663	109
3	6.45		400	372	97
3.5	6.22		500	314	83
4	6.07		600	215	74
4.5	5.96				
5	5.88				
5.5	5.8				
6	5.75				
6.5	5.7				
7	5.66				
7.5	5.62				
8	5.6				
8.5	5.57				
9	5.55				
9.5	5.53				
10	5.51				
10.5	5.49				
11	5.47				
11.5	5.46				
12	5.44				
12.5	5.43				
13	5.42				
13.5	5.42				
14	5.41				
14.5	5.4				
15	5.4				
15.5	5.39				
16	5.39				
16.5	5.38				
17	5.38				
17.5	5.38				
18	5.38				
18.5	5.37				
19	5.37				
19.5	5.37				
20	5.37				

Table C2. Color Removal by Anaerobic Degradation

Bleach & Finish: 100:0 Day	ADMI	75:25 Day	ADMI	50:50 Day	ADMI
0	619	0	482	0	397
2	733	2	589	2	477
4	676	4	628	4	513
6	763	6	597	6	482
10	740	10	635	10	519
14	768	14	600	14	461
21	808	21	604	21	520

Print: 100:0: Day	ADMI	75:25 Day	ADMI	50:50 Day	ADMI
0	911	0	745	0	457
2	1197	2	1044	2	699
4	1102	4	1026	4	618
6	1027	6	828	6	563
10	1160	10	859	10	588
14	1027	14	788	14	565
21	1064	21	892	21	584

Thermosol: 100:0: Day	ADMI	75:25 Day	ADMI	50:50 Day	ADMI
0	811	0	566	0	376
2	806	2	520	2	346
4	660	4	608	4	340
6	659	6	465	6	409
10	603	10	433	10	296
14	667	14	443	14	280
21	613	21	424	21	319

Table C3. Pretreatment of Bleach/Finish with Hydrogen Peroxide

Conc H2O2 (mg/L)	Color (ADMI)	DOC (mg/L)
0	3096	1604
50	2855	1550
100	3115	1539
150	3110	1532
200	3110	1510
250	3077	1589

Table C4. Preliminary Jar Testing

Print Waste: polymer	Conc. (mg/L)	Color (ADMI)	TSS (mg/L)	TOC (mg/L)
control	0	4516	720	87.07
C381	250	5502	300	126.5
	350	4174	340	190.2
	450	2836	160	95.68
control	0	3827	720	87.07
Magnifloc	250	4124	160	117.2
	350	4467		105
	450	1261	110	92.15
control	0	4516	620	90.91
Nalco	250	4514	260	214.2
	350	5025	130	105.6
	450	2117	90	105.6
control	0	3827	620	90.91
C372	250	3724	540	159.9
	350	4641	100	131.2
	450	3066	120	103.7
control	0	4516	620	90.91
C377	250	5231	380	183.3
	350	4391	50	107.6
	450	1791	100	103.6
control	0	4561	620	90.91
AL220	250	6069	360	124.5
	350	3811	400	110.4
	450	2800	220	87.82

Thermosol Waste: polymer	Conc. (mg/L)	Color (ADMI)	TSS (mg/L)	TOC (mg/L)
control	0	524	35	121
Nalco	30	92	40	93
	50	69	10	85
	75	66	10	75
control	0	524	35	121
Magnifloc	30	83	80	92
	50	70	10	82
	75	59	20	72
control	0	524	35	121
C381	30	122	40	88
	50	64	0	76
	75	70	0	71
control	0	524	35	121
C372	30	76	20	95
	50	171	10	88
	75	146	10	76
control	0	524	35	121
C377	30	87	35	90
	50	75	0	82
	75	64	5	68

Table C4 - continued

Bleach/Finish Waste: polymer	Conc. (mg/L)	Color (ADMI)	TSS (mg/L)	TOC (mg/L)
control	0	902	345	1700
Nalco	100	514	85	1638
	200	296	80	1563
	300	147	105	1518
control	0	902	345	1700
Magnifloc	100	505	145	1685
	200	411	115	1649
	300	137	50	1515
control	0	872	295	1831
C372	100	449	185	1695
	200	197	65	1625
	300	57	55	1636
control	0	844	185	1756
C381	50	611	130	1633
	150	415	20	1680
	250	145	110	1611
control	0	844	185	1756
C377	50	649	150	1702
	150	391	110	1654
	250	227	40	1611

Table C5. AL220 vs. C377 Polymer Testing

Print Waste: polymer	Conc. (mg/L)	Color (ADMI)	TSS (mg/L)	TOC (mg/L)
C377	0	1800	200	115
	75	1298	40	85
	100	593	215	64
	150	218	340	60
AL220	0	2107	270	129
	200	1238	60	70
	250	1025	40	60
	300	632	75	55
	350	678	45	56
Addition of A130:				
with	0	1021	40	85
100 mg/L	2.5	965	50	62
C377	5	1010	30	62
	10	867	70	62
	15	755	45	62
with	0	1238	60	70.4
200 mg/L	2.5	583	130	60
AL220	5	545	55	59
	10	526	45	60
	15	392	65	61

Table C5 - continued

Thermosol Waste: polymer	Conc. (mg/L)	Color (ADMI)	TSS (mg/L)	TOC (mg/L)
C377	0	1108	137	0
	75	292	92	0
	100	175	82	0
	150	159	58	0
	200	162	89	10
AL220	0	1499	131	35
	250	389	94	10
	300	207	85	30
	350	184	83	30
	400	350	83	25
Addition of A130:				
with	0	173	84	0
150 mg/L	2.5	171	84	0
C377	5	169	85	5
	10	171	87	0
	15	176	92	0
with	0	207	85	30
300 mg/L	2.5	207	86	20
AL220	5	205	88	5
	10	203	88	25
	15	200	88	35

Bleach/Finish Waste: polymer	Conc. (mg/L)	ADMI	TSS	TOC
control	0	1679	125	1240
C377	250	243	535	1218
	350	61	295	1201
	400	36	310	1194
	450	43	315	1185

Mix = 1:1:1 Print:Thermosol:Bleach: Polymer	Conc. (mg/L)	Color (ADMI)
control	0	929
AL220	100	1242
	200	1015
	300	629
	400	255
	500	217
	600	168
control	0	929
C377	100	342
	200	150
	300	109
	400	145
	500	159
	600	183

Table C5 - continued

Blend = 1:1 Print:Thermosol Polymer	Conc. (mg/L)	Color (ADMI)
control	0	1413
AL220	100	1333
	200	1401
	300	482
	400	186
	500	109
	600	94
control	0	1413
C377	100	237
	200	134
	300	83
	400	83
	500	181
	600	244

Table C6. Additional Jar Testing

Print Waste: Polymer	Conc. (mg/L)	Color (ADMI)	DOC (mg/L)
C377	0	2606	123
	75	3083	137
	100	3096	154
	200	1232	100
	300	440	77
AL220	0	2606	123
	400	513	72
	500	646	73
	600	297	69
	700	163	68

Thermosol Waste: Polymer	Conc. (mg/L)	Color (ADMI)	DOC (mg/L)
C377	0	898	127
	100	790	110
	150	806	105
	200	832	107
	300	822	100
AL220	0	898	127
	400	783	80
	500	791	94
	600	720	94
	700	723	93

Table C6 - continued

Combo: Polymer	Conc. (mg/L)	Color (ADMI)	DOC (mg/L)
C377	0	1135	129
	100	1177	131
	200	524	104
	300	475	95
	400	470	78
AL220	0	1458	139
	500	791	102
	600	520	82
	700	450	78
	800	438	81

Blend: Polymer	Conc. (mg/L)	Color (ADMI)	DOC (mg/L)
C377	0	2108	143
	100	1558	136
	200	650	101
	300	434	90
	400	393	89
AL220	0	2150	141
	500	936	95
	600	474	86
	700	386	67
	800	362	79

Future: Polymer	Conc. (mg/L)	Color (ADMI)	DOC (mg/L)
C377	0	2122	127
	50	1786	132
	100	1394	115
	200	486	84
AL220	0	2399	116
	500	716	95
	600	442	83
	700	346	82
	800	321	82

APPENDIX D

Bench-Scale Treatment:

Pretreatment - Color Removal
Sequencing Batch Reactor
Continuous Flow Reactors
Wastewater Characteristics

Table D1. Color removal achieved from various waste batches through pretreatment with AL220

Color (mg/L)	Batch 1 Color (ADMI)	Batch 2 Color (ADMI)	Batch 3 Color (ADMI)	Batch 4 Color (ADMI)	Batch 5 Color (ADMI)	Batch 6 Color (ADMI)	Average AL220 (ADMI)
0	1206	2247	2616	2072	1060	2367	1928.0
300	590	1204	1019	1818	95	1815	1090.2
400	688	509	988	595	147	275	533.7
500	335	124	200	751	172	452	339.0
600	145	296	167	430	31	104	195.5
700	408	255	149	162	51	89	185.7
	% Color Removal	% Color Removal	% Color Removal	% Color Removal	% Color Removal	% Color Removal	% Color Removal
300	51.1	46.4	61.0	12.3	91.0	23.3	47.5
400	43.0	77.3	62.2	71.3	86.1	88.4	71.4
500	72.2	94.5	92.4	63.8	83.8	80.9	81.2
600	88.0	86.8	93.6	79.2	97.1	95.6	90.1
700	66.2	88.7	94.3	92.2	95.2	96.2	88.8

Table D2. Sequencing Batch Reactor Steady State Data

Date	IN DOC (mg/L)	Out DOC (mg/L)	Sol COD In (mg/L)	Sol COD Out (mg/L)	MLSS (mg/L)	MLVSS (mg/L)	TSS (mg/L)	Color In (ADMI)	Color Out (ADMI)
9/6					1545				
9/7			1904					366	
9/8				230	1835	1010			82
9/9					2370				
9/10									
9/11					2260			1185	
9/12					2670				
9/13			2496	1036	3460			957	272
9/14									
9/15			2319	844	4160	3370		848	528
9/16				830	4460				
9/17			2284	920	4420				
9/18				730	4080	3370			
9/19	502		1904	820	3650	3010		421	325
9/20		278		913	3670		50		220
9/21	579		1495	744	3570		60	330	216
9/22	474	272	1574	783	3900		30		187
9/23	457	227	992	841	4170	3480	50	709	206
9/24		203		710	4160				195
9/25	265		885	624	4260		60	206	213
9/26		138	1067	482	4320		10	250	144
9/27			1242	326	3990				
9/28	336		928	240	3780	3240	30	330	159
9/29	315	132	800	220	3890	3340		239	
9/30		87	960	200	4220		10		
10/1	238		905	167	4050			178	158
10/2		92	1584	192	4900		20	172	
10/3	378		1904	456	4210		10	196	142
10/4		142	1498	312	5060	4320		246	87
10/5	412		1830	375	5000	4330	20	314	77
10/6		120	1583	226	4900			392	81
10/7	346		1600	303	4310		70	370	83
10/8		69		412	5260		100		77
Averages	391.1	160.0	1512.1	536.0	3884.3	3274.4	40.0	428.3	181.7

Table D3. Steady State Data for Continuous Flow Reactors

Day	Date	Influent COD	Influent Color
3	9/8	1485	389
6	9/11		1185
8	9/13	2496	957
10	9/15	2319	848
14	9/19	1904	421
16	9/21	1574	330
17	9/22	1495	
18	9/23	809	709
20	9/25	885	206
21	9/26	1067	250
22	9/27	1242	
23	9/28	928	330
24	9/29	900	278
26	10/1	905	178
28	10/3	1904	196
30	10/5	1830	314
32	10/7	1763	
34	10/9	864	640
36	10/11	1338	806
38	10/13	1040	809
40	10/15	1160	785
42	10/17	920	677
44	10/19	1384	154
46	10/21	1611	176
48	10/23	1433	244
50	10/25	1338	202
52	10/27	1310	229
54	10/29	1341	254
56	10/31	1850	599
58	11/2	1960	281
60	11/4	1810	258
62	11/6	1960	266
64	11/8	1687	341
66	11/10	1840	442
68	11/12	1600	513
69	11/13	1523	
71	11/15	1722	597
73	11/17	1619	407
75	11/19	1682	450
77	11/21	1387	416
79	11/23	1387	407
81	11/25	1616	330
83	11/27	1856	386
85	11/29	1648	421
87	12/1	1648	358
89	12/3	1912	396
91	12/5	1584	237
93	12/7	1536	381
94	12/8	1254	
96	12/10	1262	362
98	12/12	1240	170
100	12/14	1320	
102	12/16	1440	240
104	12/18	1360	

Table D3 - continued

8 day sludge age Day	Color (ADMI)	COD (mg/L)	MLSS (mg/L)	MLVSS (mg/L)	Date
1			2580		9/6
2					9/7
3	197	453	2815	2100	9/8
4			2670		9/9
5			2360		9/10
6			2130		9/11
7					9/12
8	472	1152	2250		9/13
9					9/14
10	467	1137	2110	1820	9/15
11					9/16
12	580	1257	2010		9/17
13					9/18
14		1215	1610	1400	9/19
15					9/20
16			1420		9/21
17	229	1015			9/22
18			1470	1300	9/23
19					9/24
20	209	885	1140		9/25
21					9/26
22		767	1000		9/27
23	175				9/28
24		488	810	760	9/29
26	176	674	760		10/1
28	159	760	740		10/3
30	181	832	940	870	10/5
32	194	709	1070		10/7
34	257	576	1230	1130	10/9
36	274	925	1240		10/11
38	373	500	1240		10/13
40	364	360	1115	975	10/15
42	341	388	1130		10/17
44	158	380	1095		10/19
46	129	885	1025		10/21
48	100	409	1010	861	10/23

Table D3 - continued

15 day sludge age

Day	Color (ADMI)	COD (mg/L)	MLSS (mg/L)	MLVSS (mg/L)	Date
1			3135		9/6
3	142	289	3455	2595	9/8
4			3240		9/9
5			3070		9/10
6			2960		9/11
8	318	1209	3100		9/13
10	377	938	3360	2740	9/15
12	494	1030	3120		9/17
14		996	3050	2510	9/19
16			2490		9/21
17	169	921			9/22
18			2480	2100	9/23
20	191	822	2280		9/25
22		633	2100		9/27
23	234				9/28
24		480	1900	1680	9/29
26	168	405	1810		10/1
28	161	560	1790		10/3
30	147	765	1900	1660	10/5
32	137	718	1860		10/7
34	156	704	1880	1670	10/9
36	215	487	1830		10/11
38	312	360	1840		10/13
40	333	420	1805	1565	10/15
42	297	220	1865		10/17
44	134	372	1730		10/19
46	137	655	1970		10/21
48	123	394	1735	1510	10/23
50	140	409	1765		10/25
52	116	789	1675		10/27
54	299	836	1610		10/29
56	104	838	1690	1505	10/31
58	162	838	1750		11/2
60	194	881	1590		11/4
79		1224			11/23
85	331	1192	1660		11/29
87	345	1332	1500		12/1
89	296	1210	1520		12/3
104		840			12/18

Table D3 - continued

20 day sludge age

Day	Color (ADMI)	COD (mg/L)	MLSS (mg/L)	MLVSS (mg/L)	Date
1			2555		9/6
3	154	343	3100	2400	9/8
4			2800		9/9
5			2670		9/10
6			2560		9/11
8	305	1044	2970		9/13
10	397	830	3110	2520	9/15
12	401	1052	3150		9/17
14	403	928	3130	2620	9/19
16			2810		9/21
17	182	819			9/22
18			2700	2300	9/23
20	191	743	2570		9/25
22		553	2500		9/27
23	146				9/28
24		360	2320	2020	9/29
26	176	365	2350		10/1
28	161	480	2250		10/3
30	132	540	2430	2120	10/5
32	156	426	2640		10/7
34	188	472	2620	2330	10/9
36	191	466	2580		10/11
38	206	300	2610		10/13
40	303	300	2485	2135	10/15
42	189	60	2350		10/17
44	106	260	2385		10/19
46	89	488	2420		10/21
48	211	283	2130	1910	10/23
50	99	315	2115		10/25
52	110	592	2240		10/27
54	94	611	2030		10/29
56	110	728	2265	2120	10/31
58	164	689	2300		11/2
60	211	630	2440		11/4
62	161	641	2620	2310	11/6
64	132	554	2570		11/8
66	132	488	2685		11/10
68	105	560	2660	2335	11/12
69		524	2290		11/13
71	208	325	2370		11/15
73	244	345	2530		11/17
75	186	325	2410	2150	11/19
77	228	490	2485		11/21
79	156	661	2605		11/23
81	156	808	2335		11/25
83	125	688	2440	2210	11/27
85	162	552	2270		11/29
87	208	664	2240		12/1
89	180	611	2140		12/3
91	118	440	2140	1960	12/5
93	299	312	2170		12/7
94		436	2100		12/8
96	297	516	1940		12/10
98	168	580	1935	1705	12/12

Table D3 -continued

100		700	2140		12/14
102	124	680	2135		12/16
104		608	2220		12/18

30 day sludge age

Day	Color (ADMI)	COD (mg/L)	MLSS (mg/L)	MLVSS (mg/L)	Date
1			2845		9/6
3	153	335	3240	2410	9/8
4			3210		9/9
5			3200		9/10
6			2800		9/11
8	284	952	3290		9/13
10	350	814	3570	2900	9/15
12	454	926	3700		9/17
14	516	936	3410	2840	9/19
16			3620		9/21
17	162	716			9/22
18			3460	2910	9/23
20	201	613	3350		9/25
22		404	3480		9/27
23	155				9/28
24		300	3080	2630	9/29
26	169	266	3770		10/1
28	157	360	3170		10/3
30	130	483	3680	3230	10/5
32	141	390	3340		10/7
34	165	480	3430	2980	10/9
36	225	325	3340		10/11
38	356	180	3430		10/13
40	277	260	3275	2810	10/15
42	213	40	3200		10/17
44	90	140	3470		10/19
46	75	377	3430		10/21
48	163	244	3280	2810	10/23
50	107	307	3405		10/25
52	107	473	3170		10/27
54	80	335	3045		10/29
56	200	492	3140	2755	10/31
58	169	642	3240		11/2
60	244	708	3360		11/4
62	152	724	3390	2910	11/6
64	132	649	3355		11/8
66	136	540	3250		11/10
68	134	600	3325	2970	11/12
69		635	3230		11/13
71	177	635	3520		11/15
73	215	635	3460		11/17
75	244	650	3430	2980	11/19
77	241	563	3485		11/21
79	199	775	3380		11/23
81	214	768	3590		11/25
83	159	765	3350	2940	11/27
85	165	672	3320		11/29
87	396	672	3450		12/1

Table D3 - continued

89	170	575	3450		12/3
91	173	328	3380	3035	12/5
93	176	288	3400		12/7
94		179	3360		12/8
96	166	198	3420		12/10
98	124	220	3295	2900	12/12
100		400	3350		12/14
102	62	320	3390		12/16
104		400	3295		12/18

Table D4. Characteristics of Wastewater Before and After Various Treatment

Total BOD (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/22					323.0					
9/27					300.0	107.0				
10/2					343.0	38.0				
10/7					488.0	58.0				
10/13		50.0		601.0						
10/14					333.0		129.0			
10/19					397.0		334.0	170.0		
10/26								158.0		
10/27					287.0			184.0		
11/1					547.0				207.0	228.0
11/6					695.0				254.0	288.0
11/29					418.0				247.0	250.0
12/10		128.0	64.0							
12/13					300.0				220.0	88.0
Average		89.0	64.0	601.0	402.8	67.7	231.5	170.7	232.0	213.5

Soluble BOD (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/22						153.0				
9/27						37.0				
10/2					147.0	16.0				
10/7					233.0	23.0				
10/13							87.0			
10/14							65.0			
10/19					221.0		127.0	158.0		
10/26								38.0		
10/27					203.0			30.0		
11/1									59.0	69.0
11/6									52.0	73.0
11/29					318.0			134.0	100.0	105.0
12/13					228.0				56.0	42.0
Average					225.0	57.3	93.0	90.0	66.8	72.3

Table D4 - continued

Total COD (mg/L) Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/20				7017.0		885.0				
9/22					1889.0	964.0				
9/23					992.0	872.0				
9/24						710.0				
9/25						612.0				
9/26					1343.0	466.0				
9/27						492.0				
10/4					2147.0	437.0				
10/5										
10/6					2255.0					
10/7						381.0				
10/8										
10/15							972.0			
10/19					1720.0		868.0			
10/22										
10/23					1858.0		590.0			
10/29					1894.0			1164.0		
11/2					2500.0			1472.0		
11/4					2488.0			1818.0		
11/6										
11/8					2341.0				641.0	765.0
11/12					2320.0				680.0	688.0
11/23		1176.0	320.0	6400.0	1877.0				669.0	816.0
12/1					2984.0			1572.0	688.0	752.0
12/3		1280.0	280.0	7241.0						
12/10		860.0	220.0	5754.0	1944.0				556.0	278.0
Average		1105.3	273.3	6603.0	2036.8	646.6	810.0	1506.5	646.8	659.8

Table D4 - continued

Soluble COD (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/20										
9/22				1495.0	783.0					
9/23				809.0	841.0					
9/24					710.0					
9/25					624.0					
9/26				1067.0	482.0					
9/27					326.0					
10/4				1498.0	375.0					
10/5										
10/6				1583.0						
10/7					303.0					
10/8	496.0	332.0								
10/15						360.0				
10/19				1384.0		380.0				
10/22	345.0	234.0								
10/23				1433.0		409.0				
10/29	295.0	250.0	2367.0	1341.0			836.0			
11/2				1960.0			838.0			
11/4			5707.0	1810.0			881.0			
11/6	252.0	252.0								
11/8				1687.0				554.0	649.0	
11/12	278.0	278.0	6000.0	1600.0				560.0	600.0	
11/23	344.0	280.0	5957.0	1387.0				661.0	775.0	
12/1				1648.0			1332.0	664.0	672.0	
12/3	216.0	280.0	4662.0							
12/10	140.0	100.0	4405.0	1262.0				516.0	198.0	
Average	295.8	250.8	4849.7	1464.3	555.5	383.0	971.8	591.0	578.8	

Table D4 - continued

TOC (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/20				893.0						
9/21					619.0					
9/22						301.0				
9/25										
9/26										
9/28					389.0					
9/29						120.0				
9/30										
10/1					375.0					
10/2						54.0				
10/3										
10/4										
10/5										
10/6										
10/7										
10/8										
10/15										
10/17										
10/19					579.0		297.0	216.0		
10/21										
10/22										
10/23					604.0		378.0	323.0		
10/29										
11/2					698.0				147.0	152.0
11/6										
11/8										
11/12										
11/20									160.0	166.0
11/23										
11/30										
12/1										
12/3			90.0	1451.0						
12/10			66.0							
Average			78.0	1451.0	544.0	158.3	337.5	269.5	153.5	159.0

Table D4 - continued

DOC (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/20					278.0					
9/22				474.0	272.0					
9/23				457.0	227.0					
9/24	121.0	85.0			203.0					
9/25				265.0						
9/26					138.0					
9/28				336.0						
9/29					132.0					
9/30	95.0	94.0			87.0					
10/1				238.0						
10/2					92.0					
10/3				378.0						
10/5				412.0						
10/6					120.0					
10/7				346.0						
10/8	96.0	95.0			69.0					
10/15	58.0	46.0		263.0		153.0	98.0			
10/17						120.0	97.0			
10/19				457.0		232.0	173.0			
10/21				441.0		282.0	230.0			
10/22	96.0	91.0								
10/23				477.0		303.0	272.0			
10/29	99.0	80.0		302.0				150.0	95.0	
11/2				382.0				221.0	125.0	
11/6	91.0	66.0								
11/8				371.0				188.0	143.0	
11/12	136.0	92.0								
11/20				461.0				117.0	159.0	
11/23	173.0	112.0								
11/30				779.0			445.0	234.0	197.0	
12/1										
12/3	91.0	72.0	951.0							
12/10	396.0	62.0	1014.0							
12/13				445.0				232.0	97.0	
Average	132.0	81.4	982.5	418.3	160.0	218.0	219.2	190.3	136.0	

Table D4 - continued

Total P (mg/L) Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21						0.7				
9/22					2.6					
9/23						0.5				
9/24					2.6					
9/25						0.5				
10/2					3.1					
10/3						0.0				
10/4						0.4				
10/7					3.7					
10/8						0.6				
10/10					2.0		0.7	0.3	0.3	0.7
10/15		0.2	0.0				0.8	1.2		
10/17		1.3	0.6				1.1	1.0		
10/19										
10/23					3.0		1.4	1.3		
11/5					3.1				0.1	0.4
11/6		1.3	0.8							
11/8					3.0				1.4	1.0
11/23		1.5	0.6							
11/27				6.4	3.4				0.5	0.7
12/3		2.2	0.4	12.7						
12/4					3.5				1.6	0.9
12/10		1.3	0.6	9.0						
12/11					2.4				0.4	1.0
Average		1.3	0.5	9.4	2.9	0.4	1.0	0.9	0.7	0.8

Table D4 - continued

OrthoP (mg/L) Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21						0.0				
9/22					0.8					
9/23						0.0				
9/24					0.7					
9/25						0.0				
10/2										
10/3										
10/4										
10/7					0.1					
10/8						0.1				
10/10					0.4		0.0	0.0	0.0	0.0
10/15		0.1	0.0							
10/17							0.0	0.0		
10/19					0.1		0.1	0.1		
10/23					0.2		0.0	0.0		
11/5										
11/6										
11/8										
11/23		0.4	0.1							
11/27				1.8	0.4				0.1	0.0
12/3		0.6	0.0	3.5						
12/4					1.1				0.0	0.0
12/10		0.5	0.3	1.3						
12/11					0.5				0.3	0.1
Average		0.4	0.1	2.2	0.5	0.0	0.1	0.0	0.1	0.0

Table D4 - continued

TKN (mg/L) Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21						20.2				
9/22					31.0					
9/23						21.8				
9/24					38.6					
9/25						22.1				
9/28					25.7	12.1				
9/29					27.4	10.9				
10/2					22.0					
10/3						8.7				
10/4						6.6				
10/7					33.0					
10/8						17.5				
10/10					25.0		13.0	9.4	15.0	11.3
10/15		13.7	12.0				11.1	10.2		
10/17							14.0	9.2		
10/19					30.5		15.3	12.6		
10/22		25.8	18.5							
11/5					65.0				20.7	21.6
11/6		20.7	13.4							
11/8					46.0			7.0	11.5	14.1
11/20					27.2				33.0	24.5
11/23		41.0	21.0							
11/30				54.0	56.6			48.7	31.0	23.5
12/3		24.0	14.6	37.5						
12/7					28.3				28.0	18.0
12/10		24.6	15.7	52.0						
12/11					45.0				17.4	14.6
Average		25.0	15.9	47.8	35.8	15.0	13.4	16.2	22.4	18.2

Table D4 - continued

NH3-N (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21						0.2				
9/22					6.0					
9/23						0.2				
9/24					5.8					
9/25						0.1				
9/28					6.0					
9/29					4.8	0.2				
10/2					18.0					
10/3						0.1				
10/4						0.1				
10/7					27.0					
10/8						10.0				
10/10					10.8		0.2	0.6	0.2	0.2
10/15		7.5	7.1				0.6	0.0		
10/17							0.3	0.0		
10/19					11.6		0.0	0.0		
10/22		10.3	9.6							
11/5					36.0				3.2	9.8
11/6		11.0	10.8							
11/8					21.4			0.2	0.1	1.8
11/20					26.2				1.4	
11/23										
11/30				13.2	22.1			18.0	8.7	12.5
12/3		11.8	11.4	4.3						
12/7					11.6				0.2	1.7
12/10		14.0	12.0	4.5						
12/11					7.3				0.1	0.1
Average		10.9	10.2	7.3	15.3	1.5	0.3	3.1	2.0	4.3

Table D4 - continued

Zinc (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21					0.2					
9/22						0.2				
9/23					0.1					
9/24						0.2				
9/25					0.1					
9/26						0.2				
10/15					0.2		0.4	0.3		
10/17		0.5		0.2			0.3	0.2		
10/19					0.1		0.2	0.2		
11/8					0.6			0.4	0.4	0.3
11/12		0.2	0.1							
11/20					0.3				0.2	0.2
11/23		0.2	0.1							
12/3		0.3	0.0	0.1	0.1			0.2	0.3	0.2
Average		0.3	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.3

Copper (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21					0.0					
9/22						0.0				
9/23					0.0					
9/24						0.0				
9/25					0.1					
9/26						0.0				
10/15					0.1		0.1	0.0		
10/17		0.2		0.1			0.0	0.1		
10/19					0.0		0.0	0.0		
11/8					0.0			0.0	0.0	0.0
11/12		0.0	0.0							
11/20					0.0				0.0	0.0
11/23		0.0	0.0							
12/3		0.0	0.0	0.0	0.0			0.0	0.0	0.0
Average		0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table D4 - continued

Cl- (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21				24.9						
9/22					22.4					
9/23				24.9						
9/24					25.2					
9/25				13.2						
9/26					98.2					
10/15				20.0			21.6	23.0		
10/17							19.6	22.6		
10/19				34.0			26.8	30.5		
11/8				18.5				22.2	19.1	21.0
11/12		10.2	13.4							
11/20				22.0					20.0	22.4
11/23		8.7	16.2							
12/3		14.3	26.3	33.1	27.4			28.0	26.4	26.3
Average		8.3	18.6	16.6	23.0	48.6	22.7	25.3	21.8	23.2

SO4-2 (mg/L)

Date	Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
9/21				145.0						
9/22					149.0					
9/23				136.0						
9/24					150.0					
9/25				561.0						
9/26					322.0					
10/15				354.0			396.0	413.0		
10/17							370.0	408.0		
10/19				392.0			327.0	410.0		
11/8				543.0				532.0	425.0	497.0
11/12		533.0	995.0							
11/20				866.0					721.0	817.0
11/23		365.0	797.0							
12/3		833.0	1228.0	90.3	497.0			674.0	671.0	666.0
Average		432.8	1006.7	45.2	436.8	207.0	364.3	487.4	605.7	660.0

Table D4 - continued

TSS (mg/L) Before Pretreat	After Pretreat	Bleach	Reactor Influent	SBR Effluent	8 day Sludge Age	15 day Sludge Age	20 day Sludge Age	30 day Sludge Age	
150	40	220	100	50	330	70	120	20	
70	0	150	170	60	210	50	90	70	
150	30	400	390	30	130	80	90	130	
		208	110	50	100	130	110	120	
123.33	23.33	244.50	100	60	100	120	70	90	
			70	10		140	140	150	
			160	30		150	170	80	
				10		130	90	70	
			157.14	20		80	230	30	
				10		50	50	80	
				80		10	40	60	
				20		40	60	50	
				70			80	70	
				100			50	90	
							140	30	
				42.86	174	87.5	80	100	
							160	50	
							110	70	
							80	20	
							100	30	
							30	20	
							140	40	
							170	0	
							70	70	
							40	70	
							60	60	
							140	110	
							100.4	65.9	

APPENDIX E

Kinetic Analysis

Table E1. Kinetic Analysis

1 - Influent COD = So = average over days 22-104
Effluent COD = Se = average % removal applied to influent COD

Oc (days)	1/Oc (1/day)	Se (mg/L)	So (mg/L)	t (days)	X (mg/L)	q (1/day)	1/q (day)	1/S (L/mg)
8.000	0.125	664.000	1475.000	3.000	1076.000	0.251	3.980	0.002
15.000	0.067	605.000	1475.000	3.000	1805.000	0.161	6.224	0.002
20.000	0.050	496.000	1475.000	3.000	2345.000	0.139	7.186	0.002
30.000	0.033	472.000	1475.000	3.000	3353.000	0.100	10.029	0.002

compute Ksk

Regression Output:		
Constant		-7.646
Std Err of Y Est		1.178
R Squared		0.853
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	7952.304	
Std Err of Coef.	2336.838	

y=mx+b=1/q

4.326
5.494
8.382
9.197

Compute Yld

Regression Output:		
Constant		-0.032
Std Err of Y Est		0.004
R Squared		0.993
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	0.619	
Std Err of Coef.	0.037	

y=mx+b=1/Oc

0.124
0.067
0.054
0.030

Talhle E1 continued

2 - Influent COD = average over days 22-104
Effluent COD = average over steady state range

Oc (days)	1/Oc (1/day)	Se (mg/L)	So (mg/L)	t (days)	X (mg/L)	q (1/day)	1/q (day)	1/S (L/mg)
8.000	0.125	611.000	1475.000	3.000	1076.000	0.268	3.736	0.002
15.000	0.067	588.000	1475.000	3.000	1805.000	0.164	6.105	0.002
20.000	0.050	504.000	1475.000	3.000	2345.000	0.138	7.245	0.002
30.000	0.033	509.000	1475.000	3.000	3353.000	0.096	10.413	0.002

Compute Ksk

Regression Output:		
Constant		-16.725
Std Err of Y Est		1.876
R Squared		0.695
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	12955.818	
Std Err of Coef.	6063.632	

y=mx+b=1/q

4.503
5.332
9.004
8.752

Compute Ykd

Regression Output:		
Constant		-0.022
Std Err of Y Est		0.003
R Squared		0.996
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	0.545	
Std Err of Coef.	0.026	

y=mx+b=1/Oc

0.124
0.067
0.053
0.030

Table E1 continued

3 - Influent COD = average over particular steady state range
Effluent COD = average over steady state range

Oc (days)	1/Oc (1/day)	Se (mg/L)	So (mg/L)	t (days)	X (mg/L)	q (1/day)	1/q (day)	1/S (L/mg)
8.000	0.125	611.000	1386.000	3.000	1076.000	0.240	4.165	0.002
15.000	0.067	588.000	1373.000	3.000	1805.000	0.145	6.898	0.002
20.000	0.050	504.000	1513.000	3.000	2345.000	0.143	6.972	0.002
30.000	0.033	509.000	1572.000	3.000	3353.000	0.106	9.463	0.002

Compute Ksk

Regression Output:

Constant		-9.958
Std Err of Y Est		1.714
R Squared		0.582
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	9240.738	
Std Err of Coef.	5541.914	

y=mx+b=1/q

5.164
5.756
8.375
8.195

Compute Ykd

Regression Output:

Constant		-0.040
Std Err of Y Est		0.008
R Squared		0.974
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	0.687	
Std Err of Coef.	0.079	

y=mx+b=1/Oc

0.125
0.060
0.059
0.033

Table E1 continued

4 - Influent COD = average over particular steady state range
Effluent COD = average % removal applied to influent COD

Oc (days)	1/Oc (1/day)	Se (mg/L)	So (mg/L)	t (days)	X (mg/L)	q (1/day)	1/q (day)	1/S (L/mg)
8.000	0.125	624.000	1386.000	3.000	1076.000	0.236	4.236	0.002
15.000	0.067	563.000	1373.000	3.000	1805.000	0.150	6.685	0.002
20.000	0.050	508.000	1513.000	3.000	2345.000	0.143	7.000	0.002
30.000	0.033	503.000	1572.000	3.000	3353.000	0.106	9.410	0.002

Compute Ksk

Regression Output:

Constant		-12.279
Std Err of Y Est		1.164
R Squared		0.798
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	10422.014	
Std Err of Coef.	3703.443	

y=mx+b=1/q

4.402
6.212
8.216
8.420

Compute Ykd

Regression Output:

Constant		-0.045
Std Err of Y Est		0.006
R Squared		0.983
No. of Observations		4.000
Degrees of Freedom		2.000
X Coefficient(s)	0.720	
Std Err of Coef.	0.066	

y=mx+b=1/Oc

0.125
0.062
0.057
0.031

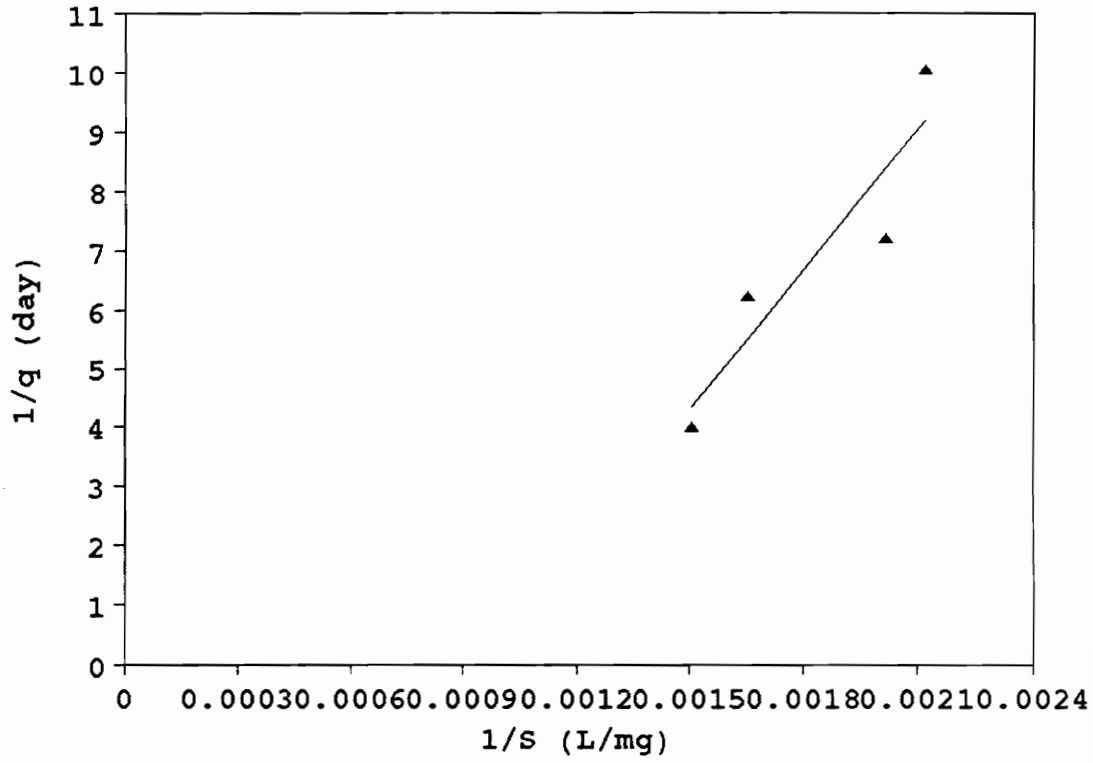

Figure E1. Kinetic analysis - Determine K_s and k

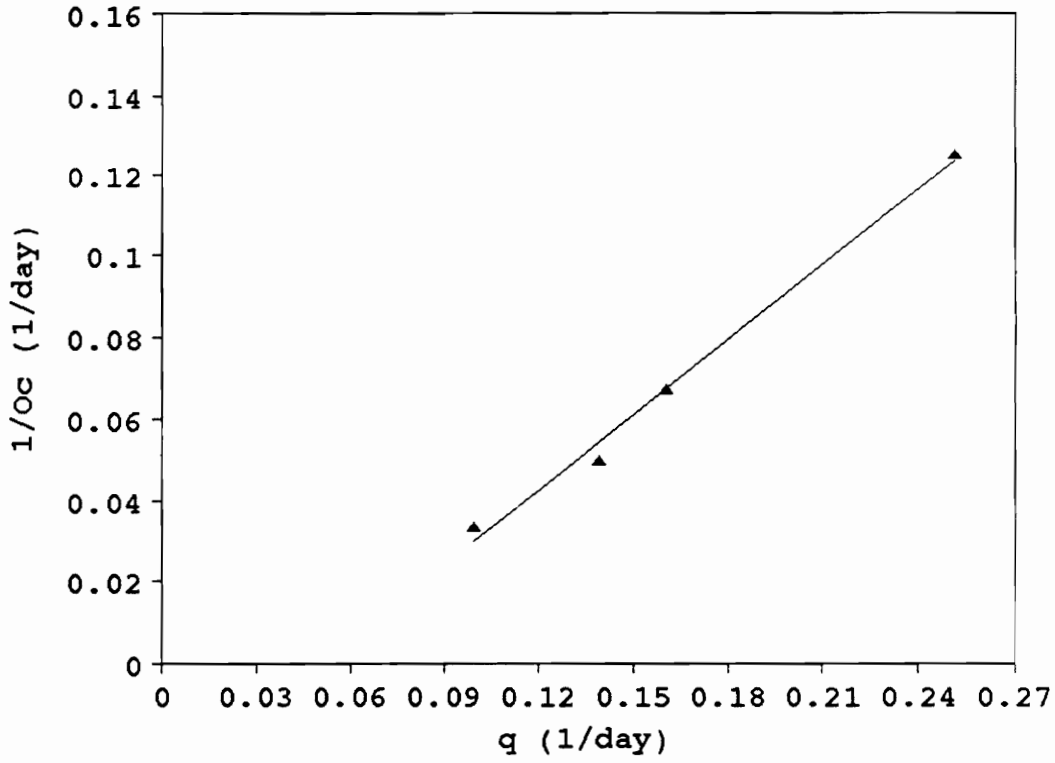

Figure E2. Kinetic analysis - Determine Y and k_d

VITA

Michelle L. Weber was born in Norwood, Massachusetts on January 12, 1969. She graduated from Walpole High School in Walpole, Massachusetts in 1987. That fall, she entered University of Massachusetts at Amherst and received a Bachelor of Science in Chemical Engineering in May 1991.

Following one year of employment in the environmental field, she entered Virginia Polytechnic Institute and State University in September 1992 to pursue a Master of Science degree in Environmental Engineering.