

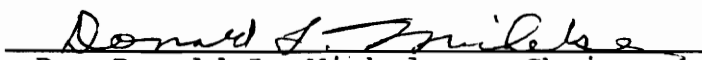
Continuous Color Removal From Concentrated Dye Waste
Discharges Using Reducing and Oxidizing Chemicals - A Pilot
Plant Study

by

Vaneaton Price, III

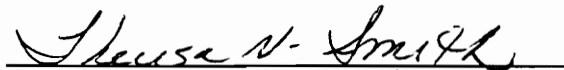
Thesis submitted to the Faculty of the Virginia Polytechnic
Institute and State University in partial fulfillment of the
requirements for the degree of
Master of Science
in
Chemical Engineering

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September, 1993
Blacksburg, Virginia

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Committee Chairman: Dr Donald L. Michelsen
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(Abstract)

The purpose of this research was to design, fabricate and test a 1 liter per minute pilot plant with a cascading sequence of continuously stirred tank reactors. The object of the research was to chemically decolorize selected reactive-dye bath concentrates resulting from exhaustive dyeing, and to remove metals and DOC using Fenton's Reagent or the reductive chemicals, thiourea dioxide and sodium hydrosulfite. For the Fenton's Reagent studies, ferrous sulfate was premixed with the dye waste concentrate before overflowing to the first reactor.

A feedback control system based on color remaining in the discharge was used to regulate reactants added. Transmittance was measured at several wavelengths (590, 540, and 438 nm) and the American Dye Manufacturers Institute (ADMI) value calculated. The results demonstrated that ADMI measurements could not be made on dark solutions (over 3000 ADMI) in the pilot plant and, typically, one wavelength was used for control. DOC removal was used as a means of

determining the biological activity in aerated reactors following color removal.

The initial pilot plant studies were conducted using Navy 106 jet-dye waste. Reductive pretreatment with thiourea dioxide resulted in 92.2% color removal with color returning upon aeration for an overall color removal of 76.6%. Oxidative pretreatment with Fenton's chemistry resulted in 98.8% color removal with overall color removal after aerobic treatment at 96.8%. Dissolved Organic Carbon (DOC) removal in aerobic treatment improved with oxidative pretreatment relative to reductive pretreatment on Navy 106 jet-dye concentrate.

On site operation of the pilot plant on other dye wastes showed color removals above 95% and DOC removals of 38% and 19% for an azo-based red dye waste concentrate and a copper-phthalocyanine-based dye, Ming Jade, respectively. The soluble copper concentration in the Ming Jade was decreased from 19.2 ppm to 4.5 ppm. This corresponded to a 3-fold increase in suspended solids from 0.575 g/L to 1.505 g/L.

The results showed that continuous oxidative pretreatment with a 15-minute residence time was controllable and more effective than reductive treatment for color removal. Oxidative pretreatment also decreased the soluble copper concentration in a copper containing waste water, and did not hinder biological activity.

Acknowledgements

I want to extend my appreciation to the many people who made this work possible. To Riley Chan, Jeff Balko, and Becky Woodby for their initial work on the idea and foundation of the pilot plant. To Lanette Fulk for her help with analytical work and Dale Blaylock for assistance with on site operation of the pilot plant. To the Blacksburg and Pepper's Ferry Waste Water Treatment Plants for providing primary effluent for biological studies and to Tultex in Martinsville, Virginia for providing dye waste and a test site location.

My appreciation is also extended to the EPA for funding which made this work possible and most importantly to my committee and Dr. Donald Michelsen for patience and guidance.

Table of Contents

Abstract.....	ii
Acknowledgements.....	iv
List of Figures.....	vii
1.0 Introduction.....	1
2.0 Literature Review.....	5
2.1 Reduction of Azo Dyes.....	5
2.2 Oxidation of Azo Dyes.....	6
2.3 Digital Control Systems.....	9
2.4 Discretizing the Differential Equations of Continuous PID-Controllers.....	12
2.5 Tuning of Feedback Controllers.....	15
3.0 Experimental Design.....	19
3.1 Waste Stream Characterization.....	19
3.2 Automatic Pilot Plant.....	23
3.2.1 Color Measurement.....	29
3.2.2 D/A and A/D Converters.....	30
3.2.3 PID Controls.....	31
3.2.4 Software.....	32
3.2.5 Pilot Plant Calibration.....	33
3.3 Biological Reactors.....	34
4.0 Materials and Methods.....	37
4.1 Laboratory Chemicals.....	37
4.2 Analytical Procedures.....	37
4.2.1 MLSS.....	37
4.2.2 Color Measurement.....	38
4.2.3 pH/Redox.....	39
4.2.4 DOC.....	39
4.3 Kinetics of Color Removal by Oxidation Using Fenton's Chemistry.....	40
4.4 Pilot Plant Test Procedures.....	41
4.4.1 Reduction.....	41
4.4.2 Oxidation.....	43
4.5 Bioreactor Test Procedures.....	44
4.6 On Site Pilot Plant Operations.....	45
5.0 Results and Discussion.....	47
5.1 Kinetics of Oxidation Using Fenton's Chemistry.....	47
5.2 Tuning of PID Parameters.....	48

5.3 Reduction.....52
5.3.1 Reduction of Slack Washer Waste.....52
5.3.2 Reduction of Concentrated Jet-dye
Waste.....53
5.3.3 Thiourea Dioxide Reduction of
Concentrated Jet-dye Waste.....55
5.3.4 Sodium Hydrosulfite Reduction
of Concentrated Jet-dye Waste.....58
5.4 Oxidation.....58
5.4.1 Lab Tests of Fenton's Oxidation.....58
5.5 Biological Testing Results.....61
5.6 On Site Pilot Plant Operation.....66
5.6.1 On Site Treatment of Navy 106.....66
5.6.2 On Site Treatment of Azo-based Red.....69
5.6.3 On Site Treatment of Ming Jade.....69
6.0 Conclusions.....74
Literature Cited.....76
Appendix I: Subroutine For PID Controls.....79
Appendix II: Subroutine For ADMI Calculation.....81

List of Figures

2.1.1	Effects of Various Reducing Chemicals on Color Removal of Navy 106 Jet-dye Waste.....	7
2.3.1	Signal Generated by Sampling and analog/digital conversion.....	10
2.3.2	The Process Computer as a Sampled-data Controller.....	11
2.3.3	Control Loop With a Computer as a Sampled-data Controller.....	13
2.5.1	Open Loop Response Curve for PID Parameter Tuning.....	18
3.1.1	Structure of Remazol Black B.....	20
3.1.2	Structure of Remazol Red RB.....	21
3.1.3	Structure of Remazol Yellow 3RA.....	22
3.2.1	Schematic Diagram of Pilot Plant Design For Reductiv Pretreatment.....	24
3.2.2	Schematic Diagram of Pilot Plant Dessign For Oxidative Pretreatment.....	26
3.2.3	Flow Diagram of Control Variable Conversion.....	28
3.3.1	Schematic of Continuous-Flow Biological Rector.....	36
5.1.1	ADMI vs Time for Fenton's Reaction Kinetics.....	49
5.2.1	Open Loop Response Curve for PID Parameter Tuning.....	50
5.3.1	Thiourea Dioxide Reduction of Navy 106 Slack Washer Waste.....	54
5.3.2	Thiourea Dioxide Reduction of Concentrated Jet-dye Waste.....	56

5.3.3	Sodium Hydrosulfite Reduction of Concentrated Jet-dye Waste.....	59
5.4.1	Fenton's Oxidation of Concentrated Jet-dye Waste.....	60
5.5.1	Effects of Oxidative and Reductive Pre-treatment on Color Removal From Concentrated Jet-dye Waste in Biological Reactors.....	63
5.5.2	Effects of Oxidative and Reductive Pre-treatment on DOC Reduction in Concentrated Jet-dye Waste in Biological React.ors.....	65
5.6.1	On Site Treatment of Navy 106 jet-dye waste.....	67
5.6.2	On Site Treatment of azo based red jet-dye waste.....	70
5.6.3	On Site Treatment of Ming Jade jet-dye waste....	72

1.0 INTRODUCTION

The fate of dyestuffs in waste streams resulting from textile dyeing has long been a concern for reasons of esthetics and toxicity in the environment. Today color removal is generally carried out by municipal wastewater treatment facilities. Fiber reactive dyes contribute greatly to the total color discharged to these Publicly Owned Treatment Works (POTWs) and, because of their high water-solubility, are not easily treated by typical activated-sludge treatment facilities (Pagga and Brown, 1986). Any color removal that is achieved in an aeration tank is more or less accidental and is the result of adsorption of color onto sludge which is removed by flocculation (Meyer, 1981).

Because of this ineffectiveness, color is typically removed using polymer sorbents at a very substantial cost to those companies discharging color to the POTWs, or by treatment with chlorine which must be followed by dechlorination, which can lead to a more toxic discharge. Furthermore, the dye-saturated polymers must be sent to landfills or incinerated for final disposal, creating an alternative demand on the environment. Also, increased pressure from regulatory agencies to reduce the final color value of discharges to waters of the United States has intensified the desire to find alternative methods for more

effectively treating color in dye waste streams.

Previous research has shown that both oxidative (Powell, et al., 1992), and reductive (McCurdy, et al., 1991) chemistry in the form of pre-treatment can be very effective for color removal in streams containing fiber-reactive azo and disazo dyes. Reductive pretreatment followed by biological treatment in sequenced batch reactors, while successfully removing color, was found by McCurdy to result in residuals that limited the total percent removal of color, COD, BOD, and TOC in aerobic treatment. Oxidative schemes, however, were shown to neither enhance nor hinder DOC removal in biological reactors and pose no threat to activated-sludge wastewater treatment plants (Powell, et al., 1992).

The idea for the continuous pre-treatment of textile dye waste was presented on April 5, 1991 (Mann and Woodby, 1991). The objective of the project was to "build, test, and use a portable, semi-automated, continuous flow pilot plant to chemically treat cotton dye wash streams..." The pilot plant was designed to use three source wavelengths of light to measure transmittance that could also be converted to an American Dye Manufacturers Institute (ADMI) color value (a value used to regulate local discharges). The ADMI value was then used for feedback control of the amount of pre-treatment chemical used in the reactor. The pilot plant

was operated with a dye waste input rate of 1 L/min.

The pilot plant was designed to use strong reducing agents such as sodium hydrosulfite or thiourea dioxide, or oxidative chemistry in the form of Fenton's Reagent (ferrous iron and hydrogen peroxide) to cleave the azo bonds of reactive dyes. The system has the capacity to continuously measure pH or redox potential from a probe in the recycle loop.

The dye wastes tested were the Navy 106 jet-dye concentrate and Navy 106 slack washer waste from Tultex (Martinsville, Virginia), which contained three Remazol dyes (Hoechst Celanese Corporation). The three dyes were Remazol Black B (reactive Black 5), Remazol Red RB (Reactive Red 198), and Remazol Golden Yellow 3RA (reactive Orange 16). This formulation was chosen because of the high frequency of its use and its high contribution to overall color discharged by the plant. The feed tank to the reactor was maintained at 55 to 65 °C, to mimic dye-bath and rinse-effluent conditions in the textile mill.

The object of this research was (a) to operate and optimize the pilot plant for the pre-treatment of the concentrated jet-dye waste stream, and (b) to find those conditions at which maximum color removal could be attained with ease of control. After long-term, steady-state runs in the lab with stored dye waste, the pilot plant was

transported to the Tultex mill and operated with fresh concentrated jet-dye waste, including Navy 106, an azo-based red dye, and a copper phthalocyanine based dye, Ming Jade.

Finally, the resulting waste streams from the chemical pre-treatment of Navy 106 jet-dye concentrate were aerobically digested in continuous flow, lab-scale biological reactors. This was done to ensure that no ill effects would occur to municipal treatment systems downstream from the site of pre-treatment.

2.0 Literature Review

2.1 Reduction of Azo Dyes

Chemical reduction has been proven to be very successful for color removal of the dyes used in the Navy 106 formulation (Michelsen, et al., 1991). In chemical reduction, the nitrogen-nitrogen (azo linkage) double bond is broken, destroying the chromophore of the system. When azo dye compounds are chemically reduced, the result is the regeneration of the aromatic amines from which the dyes were originally manufactured (Weber and Wolfe, 1987). The main dye constituent in the Navy 106 formula (Reactive Black 5), for example, reduces to a substituted aniline (p-(2-hydroxyethylsulfone)-aniline), and a substituted naphthalene (8-hydroxy-1,2,7-triamino-3,6-naphthalene disulfonic acid) (Bell, et al., 1992).

Because of their ease of handling, the reduction chemicals chosen for use in the pilot plant were thiourea dioxide (formamidine sulfinic acid, FAS) and sodium hydrosulfite (sodium dithionite). According to Michelsen, et al., "thiourea dioxide performed the best by requiring the least amount of reagent for the greatest color [removal]." Also, "more color removal per gram of each reducing chemical was observed for the more highly colored jet discharges." It is important to note that the above

results were obtained from bench-scale batch reactions and not on a continuous basis. The optimum color removal obtained using Navy 106 jet-dye concentrate was with 200 ppm and 500 ppm of thiourea dioxide and sodium hydrosulfite, respectively, as shown in figure 2.1.1.

2.2 Oxidation of Azo Dyes

There are many known oxidants that will decolorize azo dye wastes, including chlorine, ozone, and hydrogen peroxide. Chlorine is reported to produce potentially toxic organic by-products (Tincher, 1991). Ozone was found by Powell, *et al.*, to be very effective for wastewater streams that contain significant amounts of non-colored organic matter; however, he notes that streams in which most of the organics result from dyestuffs (e.g. Navy 106 jet-dye concentrate) effective decolorization could be achieved with hydrogen peroxide. Because of its availability and ease of handling, Fenton's reagent was chosen to oxidize dye waste in the pilot plant. Fenton's reagent uses ferrous iron in the form of iron salts to catalyze the reduction of hydrogen peroxide to an hydroxide ion and an hydroxyl radical, as shown in equation 2.2.1. The hydroxyl radicals become the oxidizing species of Fenton's reagent, and the ferrous iron



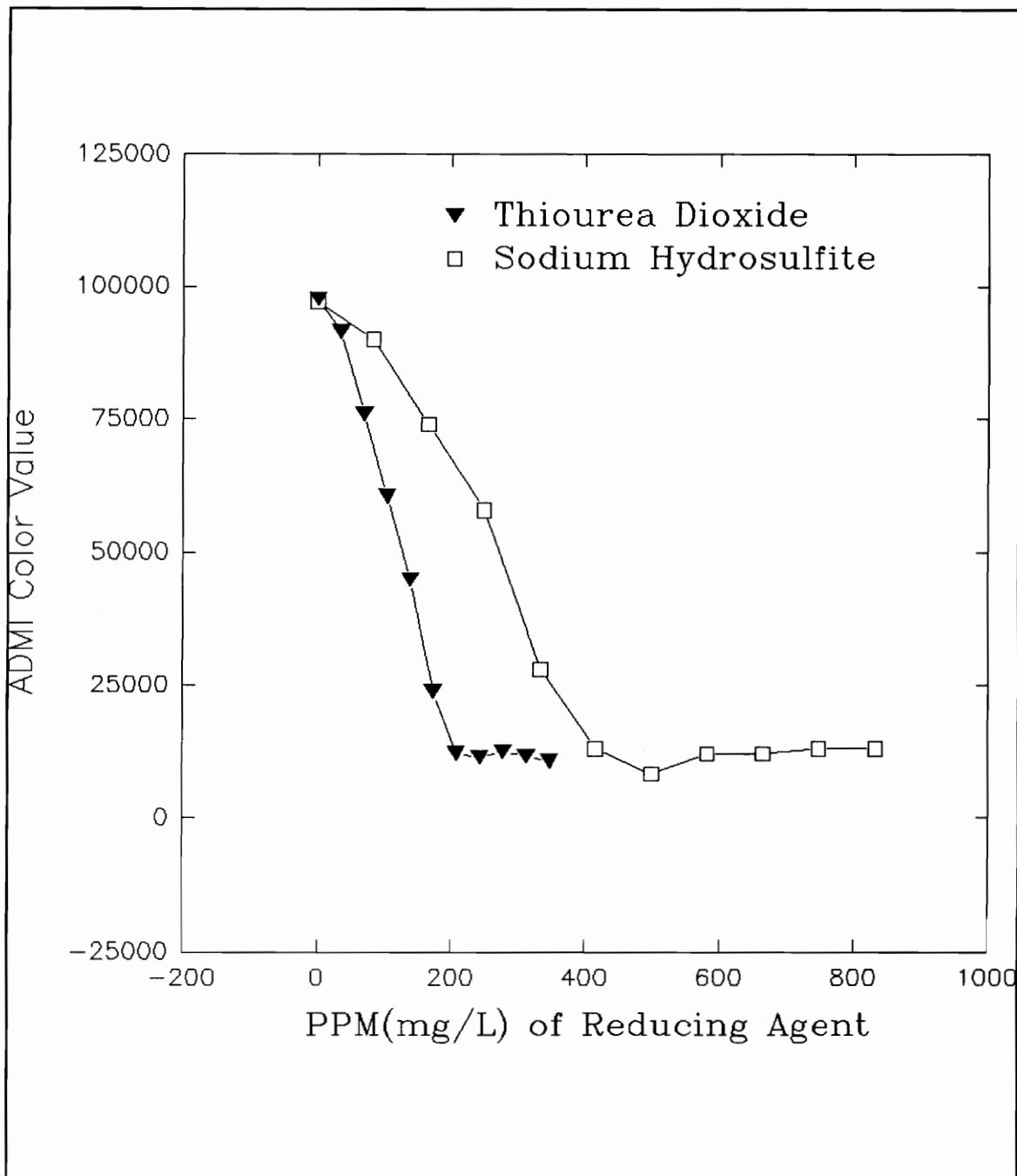


Figure 2.1.1 Reduction of Navy 106 jet-dye concentrate with varying concentrations of Thiourea Dioxide and Sodium Hydrosulfite (Michelsen, *et al.*, 1991). Results shown were from bench scale batch reactions at pH 11.8 and 70°C.

is reduced to ferric iron. The hydroxyl radical is an extremely powerful oxidant that reacts nonspecifically with organic compounds. This "broadcast" oxidative effect of Fenton's reagent makes it more effective on waste streams that contain concentrated dye waste with minimal auxiliary organics. The classical Fenton's reagent chemistry is performed in acidic media with relatively high hydrogen-peroxide-to-ferrous-iron ratios to prevent the precipitation of the iron salts into iron hydroxides. Another advantage of Fenton's reagent technology is that it has been shown to effectively reduce the toxicity in effluents prior to aerobic treatment (Linneman, et al., 1991).

In bench-scale batch reactions, Fenton's reagent decreased the ADMI color value to very low levels (from 50,000 to 60,000 ADMI to below 1000 ADMI for Navy 106 jet-dye concentrate effluent), (Powell, et al., 1992). According to Powell's research, the ratio of hydrogen peroxide to ferrous iron is important, with lower ratios (higher iron concentrations) having lower final color values. The optimum dose for color removal was found to be 1000 ppm hydrogen peroxide in a 13.6-to-1 ratio with ferrous iron. Powell also noted that lower iron concentrations (20:1 $\text{H}_2\text{O}_2:\text{Fe}^{3+}$ instead of 10:1 $\text{H}_2\text{O}_2:\text{Fe}^{3+}$) produced fewer solids. Solids are an issue in the feasibility of using transmittance for feedback control of the pilot plant

because of the turbidity they cause and thus the possible interference with optical transmittance.

2.3 Digital Controls Systems

In data processing with process computers, signals are sampled and digitized, resulting in discrete (discontinuous) signals that are quantized in amplitude and time, as shown in figure 2.3.1. Unlike continuous signals, these signals have discrete amplitude values at discrete points (times).

The sampling is usually performed periodically with sampling time, T , by a multiplexer that is constructed together with a measuring range selector and an analog/digital (A/D) converter. The digitized input data are sent to the central processor unit where the output data are calculated using programmed algorithms. If an analog signal is required for the actuator, the output data emerge through a digital/analog (D/A) converter followed by a hold device sometimes incorporated in the D/A device, (Astrom, 1984). A simplified block diagram is shown in figure 2.3.2. The samplers of the input and output signal do not actually operate in synchronism but are displaced by an interval T_r . This interval results from the A/D conversion and the data processing within the digital computer. This interval can be neglected if it can be considered to be small in comparison with the time constants of the actuators,

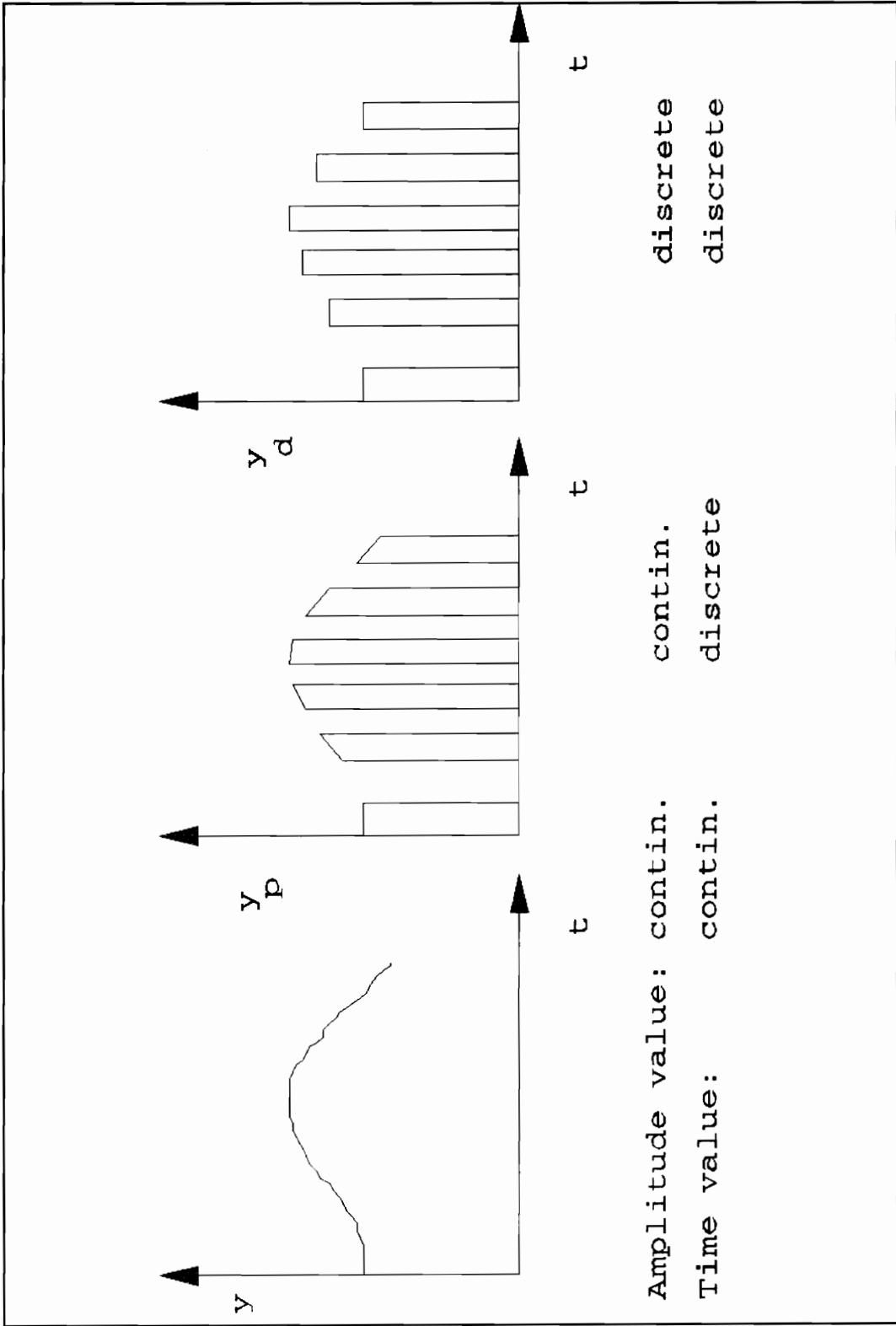
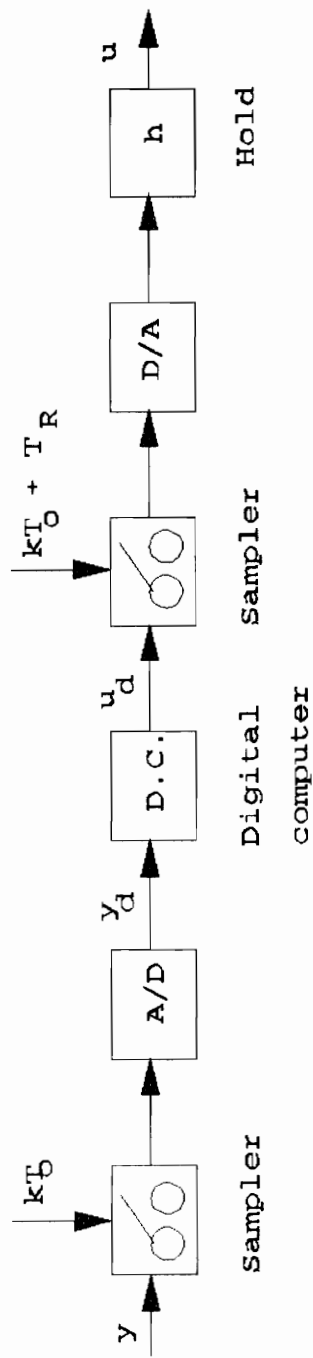


Figure 2.3.1 An amplitude modulated, discrete time and discrete amplitude signal generated by sampling and analog/digital conversion.



$k=t/T$ is a discrete time unit

y is the output signal of the process (controlled variable)

u is the input signal of the process (manipulated variable)

Figure 2.3.2 The process computer as sampled-data controller.

processes, and sensors. Then synchronous sampling of process computer inputs and outputs can be assumed. Also, the quantization error of the signal is small for computers with word lengths of 16 bits or more and A/D converters with at least 10 bits - so that the signal amplitudes can be considered continuous.

These simplifications allow the process computer to be considered as a sampled-data controller. The samplers now operate synchronously and generate discrete-time signals. The manipulated variable, u , is calculated by a control algorithm using the control variable, y , and the reference value, sp , as inputs as shown in figure 2.3.3.

2.4 Discretizing the Differential Equations of Continuous PID-Controllers.

As parameter optimized controllers have P, PI, or PID behavior, a number of attempts have been made to transfer their equations into sampled-data form by discretization. This would allow the established experience with continuous-time controllers to be used, and, in principle, their well known tuning rules could be applied.

The idealized equation of a PID-controller is

$$u(t) = K[e(t) + \frac{1}{T_I} \int e(t) dt + T_D \frac{de(t)}{dt}] \quad \text{Eq. 2.4.1}$$

where

K = gain

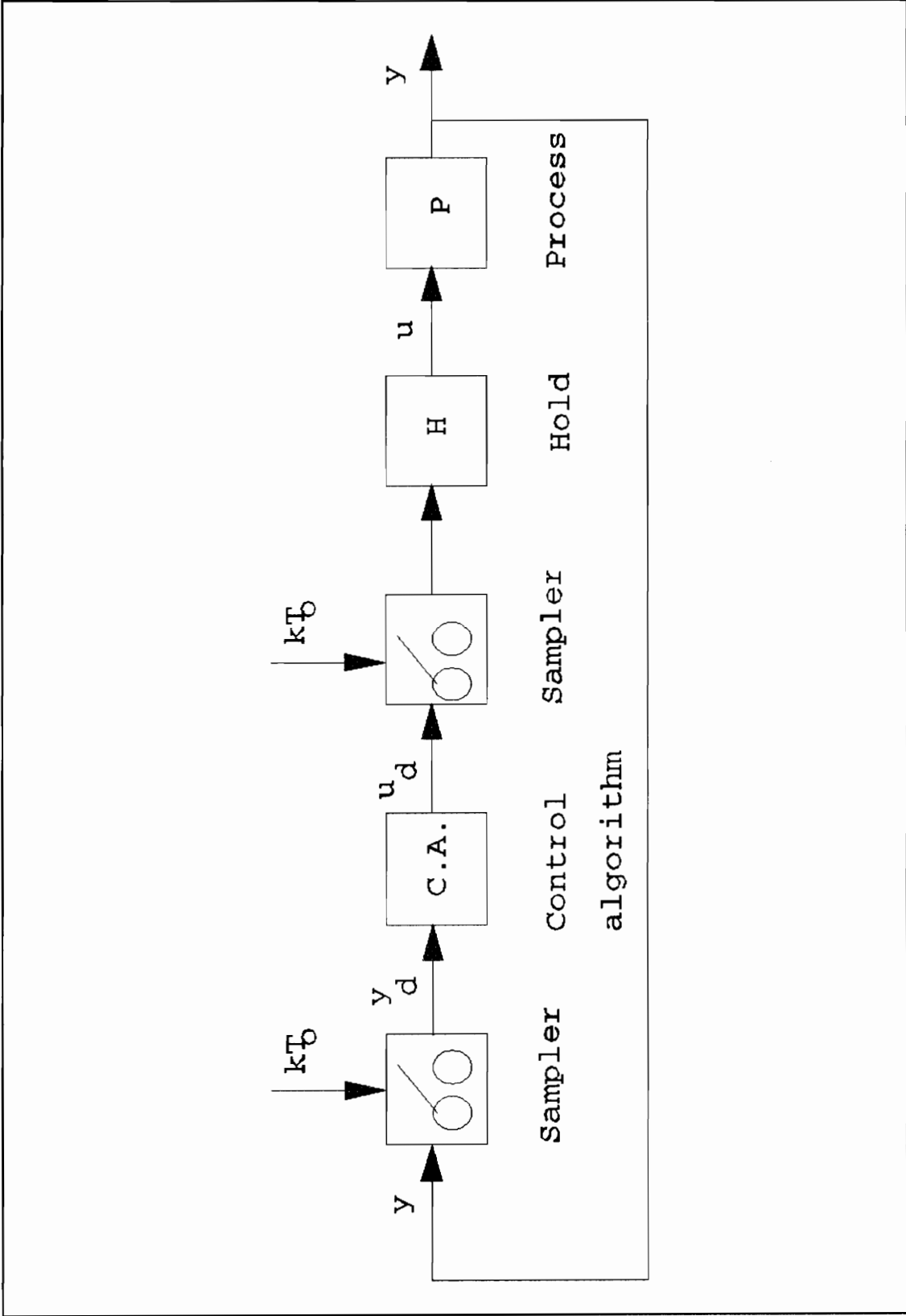


Figure 2.3.3 Control loop with a computer as a sampled-data controller.

$e(t)$ = error signal, difference between set point and controlled variable

T_I = integral or reset time (minutes/repeat), time that it takes the controller to repeat the proportional action

T_D = derivative time (lead time) (Smith and Corripio, 1985).

For small sample times, T_0 , this equation can be turned into a difference equation by discretization. The derivative term is simply replaced by a first order difference approximation and the integral term is replaced by a summation term. The continuous integration can be approximated by either rectangular or trapezoidal integration. Applying rectangular integration gives equation 2.4.2.

$$u(t) = K[e(t) + \frac{T}{T_I} \sum_{i=0}^{t-1} e(i) + \frac{T_D}{T} (e(t) - e(t-1))] + C \quad \text{Eq. 2.4.2}$$

The sum of all past errors has to be stored and thus this is a nonrecursive called a "position algorithm."

If the controlled variable contains relatively high frequency noise as is likely in transmittance data, large unwanted manipulated variable changes can occur if the first-order difference in the nonrecursive form is used as in equation 2.4.2. One possible solution is to smooth the derivative action by using 4 values (Cox, et al., 1966). First an average value of the form:

$$\bar{e}_k = \frac{1}{4} [e(t) + e(t-1) + e(t-2) + e(t-3)] \quad \text{Eq. 2.4.3}$$

is taken and then all approximations to the first derivative are averaged in relation to e_k . The derivative term for the nonrecursive form becomes

$$\frac{\overline{\Delta e}_t}{\Delta t} = \frac{1}{4} \left[\frac{e(t) - \bar{e}_t}{1.5\Delta t} + \frac{e(t-1) - \bar{e}_t}{0.5\Delta t} + \frac{\bar{e}_t - e(t-2)}{0.5\Delta t} + \frac{\bar{e}_t - e(t-3)}{1.5\Delta t} \right] \quad \text{Eq. 2.4.4}$$

which reduces to

$$\frac{\Delta e}{\Delta t} = \frac{1}{6\Delta t} [e(t) + 3e(t-1) - 3e(t-2) - e(t-3)] \quad \text{Eq. 2.4.5}$$

2.5 Tuning of Feedback Controllers

Tuning is the process of adjusting the feedback controller parameters to obtain a specified closed-loop response. The tuning of three-mode, or PID, controllers involves three parameters: the gain, the reset time, and the derivative time. The values of the tuning parameters depend on the desired closed-loop response and on the dynamic characteristics, or personality, of the other elements of the control loop, particularly the process. If the process is nonlinear, as is usually the case, its characteristics will change from one operating point to the next. This means that a particular set of tuning parameters can produce

the desired response at only one operating point, given that standard feedback controllers are basically linear devices. For operation in a range of operating conditions, a compromise must be reached in arriving at an acceptable set of tuning parameters, as the response will be sluggish at one end of the range and oscillatory at the other.

Most controller tuning formulas are based on the First-Order-Plus-Dead-Time, or FOPDT, model. This model characterizes the process by three parameters; the gain K , the dead time t_0 , and the time constant τ . These parameters can be determined for a given loop by performing some dynamic test on the actual system. The simplest test that can be performed is a step test.

The step test procedure is carried out as follows:

1. With the controller on "manual" (the loop opened), a step change in the controller output signal, $u(t)$ is applied to the process.
2. The response of the transmitter output signal $y(t)$ is recorded, making sure that the resolution is adequate in both the amplitude and the time scale. Typically, the length of the step depends upon the speed of response of the process.

By realizing that the model response must match the process reaction curve at steady state, the steady-state gain of the process, one of the model parameters is

described as:

$$K = \frac{\Delta y}{\Delta u} \qquad \text{Eq. 2.5.1}$$

There are several methods available for determining the dead time t_0 and the time constant τ . The one which gives the most reproducible results is described by the following equations (Smith and Corripio, 1985):

$$\tau = \frac{3}{2} (t_2 - t_1)$$

$$t_0 = t_2 - \tau$$

where

$$\begin{aligned} t_1 &= \text{time at which } \Delta y = 0.283 \Delta y_s \\ t_2 &= \text{time at which } \Delta y = 0.632 \Delta y_s. \end{aligned}$$

This becomes clear when shown graphically as in figure 2.5.1.

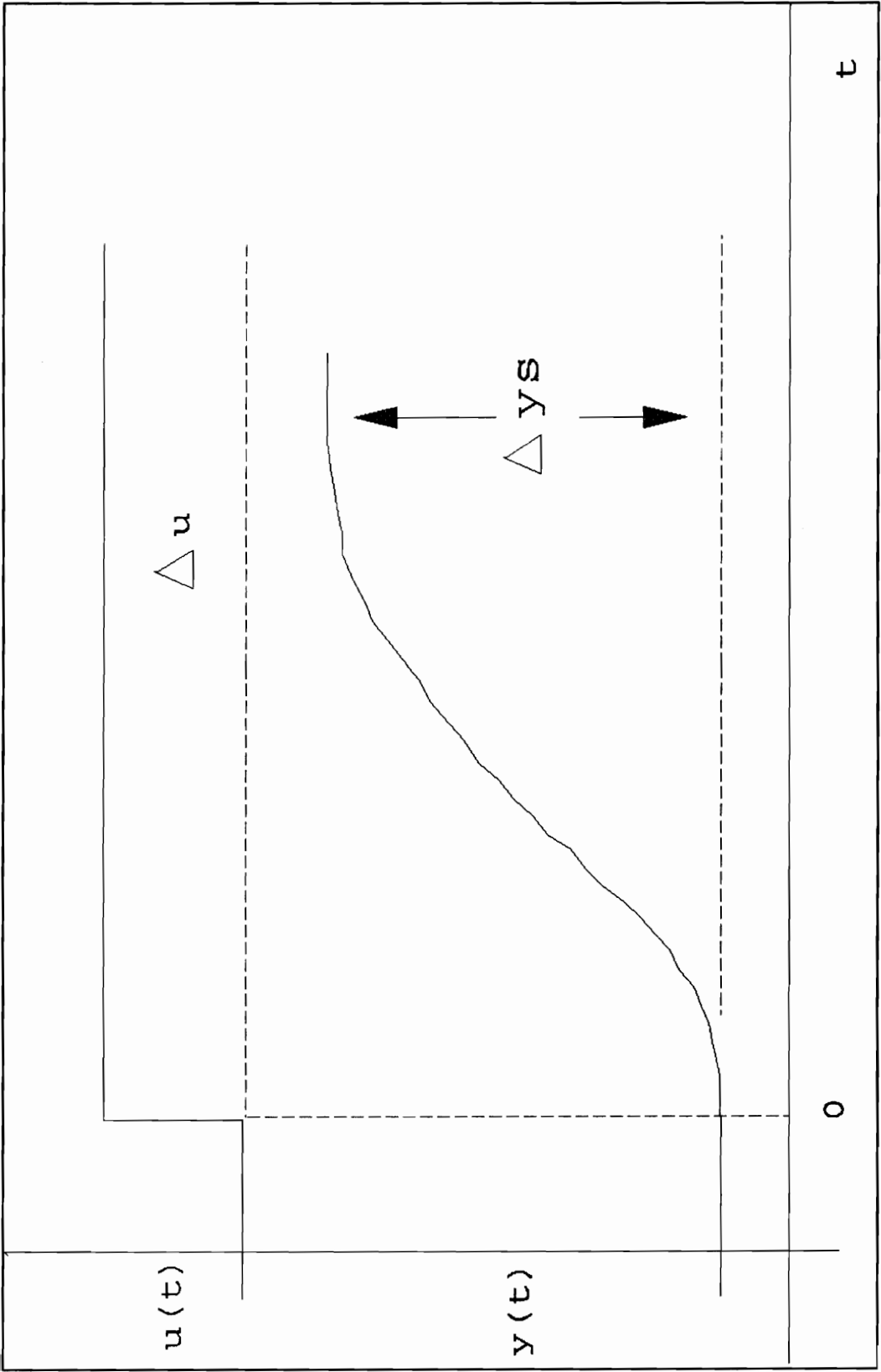


Figure 2.5.1 Process reaction curve or open-loop step response.

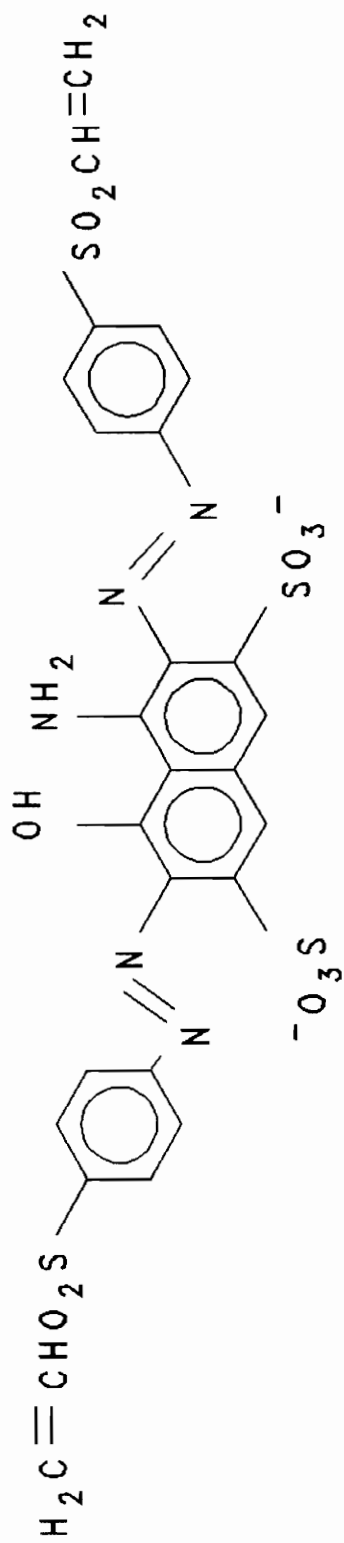
3.0 Experimental Design

3.1 Waste Stream Characterization

All experimentation for the pilot plant was carried out using dye waste resulting from the dyeing of the cotton portion of a 50/50 cotton/polyester blend. The dye formulation treated was the Navy 106 color used at Tultex in Martinsville, Virginia to dye cotton/polyester fleece. The cotton portion of the blend was dyed using Remazol dyes including Reactive Black 5, the single most used dye in the plant. The structure for the dyes used in the Navy 106 formulation; Reactive Black 5, Reactive Red 198, and Reactive Orange 16 are shown in figures 3.1.1, 3.1.2, and 3.1.3, respectively. The cotton can be dyed either by cold pad batch method or directly in the jet-dye machine used for polyester dyeing.

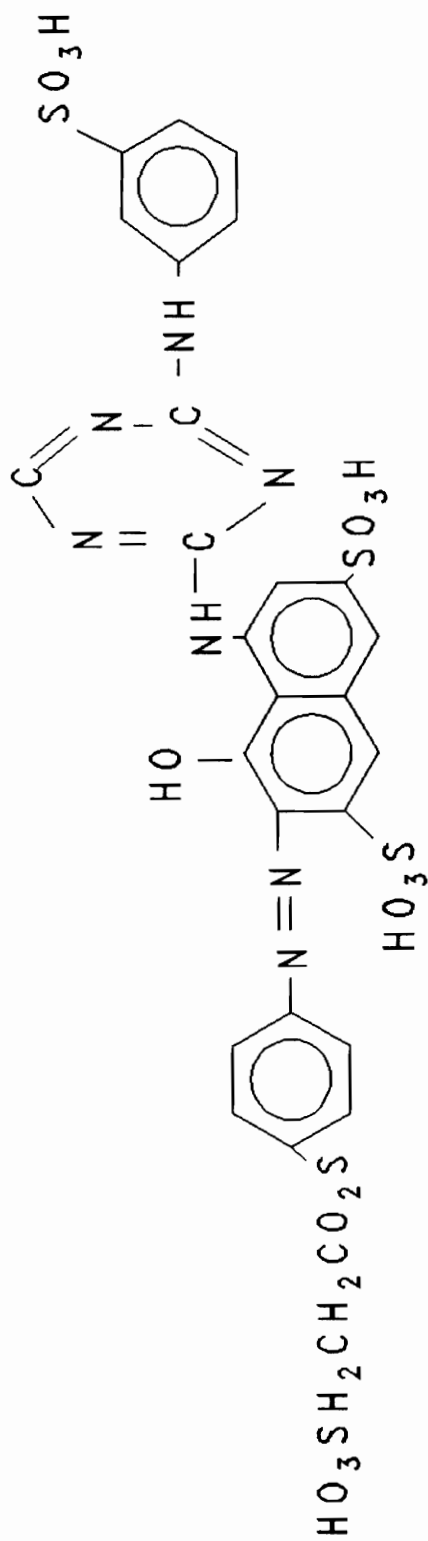
Fabric dyed by cold pad batch method is subsequently washed to remove excess dyes and chemicals. This results in the slack washer waste stream - the initial dye waste stream tested in the pilot plant. This stream is relatively dilute and typically has a color value between 2000 and 5000 ADMI. This stream has a high pH (>12) because of high caustic concentrations. It also contains surfactants, defoamers, and other dyeing assist chemicals.

The other waste stream tested results from jet-dyeing



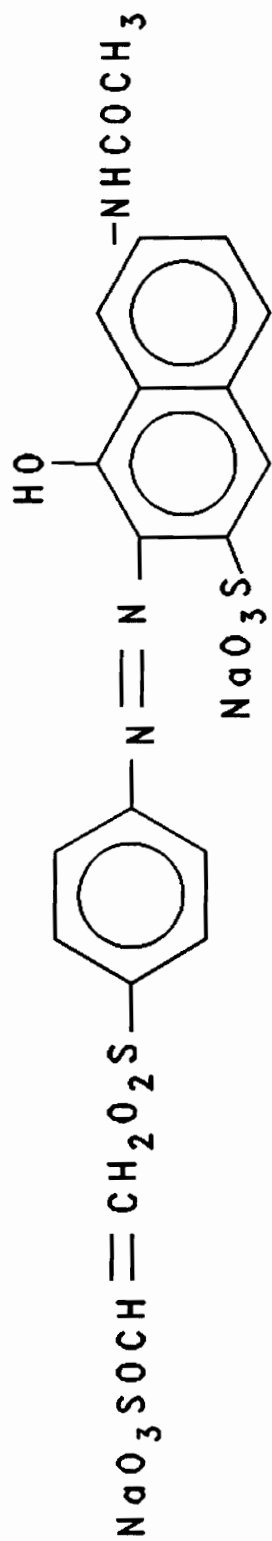
REMAZOL BLACK B

Figure 3.1.1.1 Chemical structure for Reactive Black 5.



REMAZOL RED RB (POSTULATED)

Figure 3.1.2 Chemical structure for Reactive Red 198.



C. I. REACTIVE ORANGE 16

Figure 3.1.3 Chemical structure for Reactive Orange 16.

the cotton portion of the blend. This stream is simply the leftover dye after dyeing is complete. Jet-dye waste typically has a pH of approximately 11 and has a very high chloride concentration. The color of the jet-dye waste stream is typically between 55,000 and 75,000 ADMI.

For initial trials in the pilot plant to test the control scheme, slack washer waste was used. However, because jet-dye waste is a much greater contributor to the total color in the plant's effluent, all subsequent work was done on the jet-dye waste stream. Jet-dye waste also has high dye concentration with minimum auxiliary organics which makes it more attractive for treatment with Fenton's chemistry.

3.2 Automatic Pilot Plant

The pilot plant was operated using two different designs. The first design was used for reductive pretreatment and the second was used with oxidative (Fenton's) chemistry. Transformation between the two schemes was easily managed.

The design for reductive pretreatment (shown in figure 3.2.1) consisted of a 5 gallon bucket equipped with hydrostatic overflow that maintained a constant volume of 16 L. The recycle and feed were pumped using a masterflex peristaltic pump at 1.1 L/min which gave a residence time of

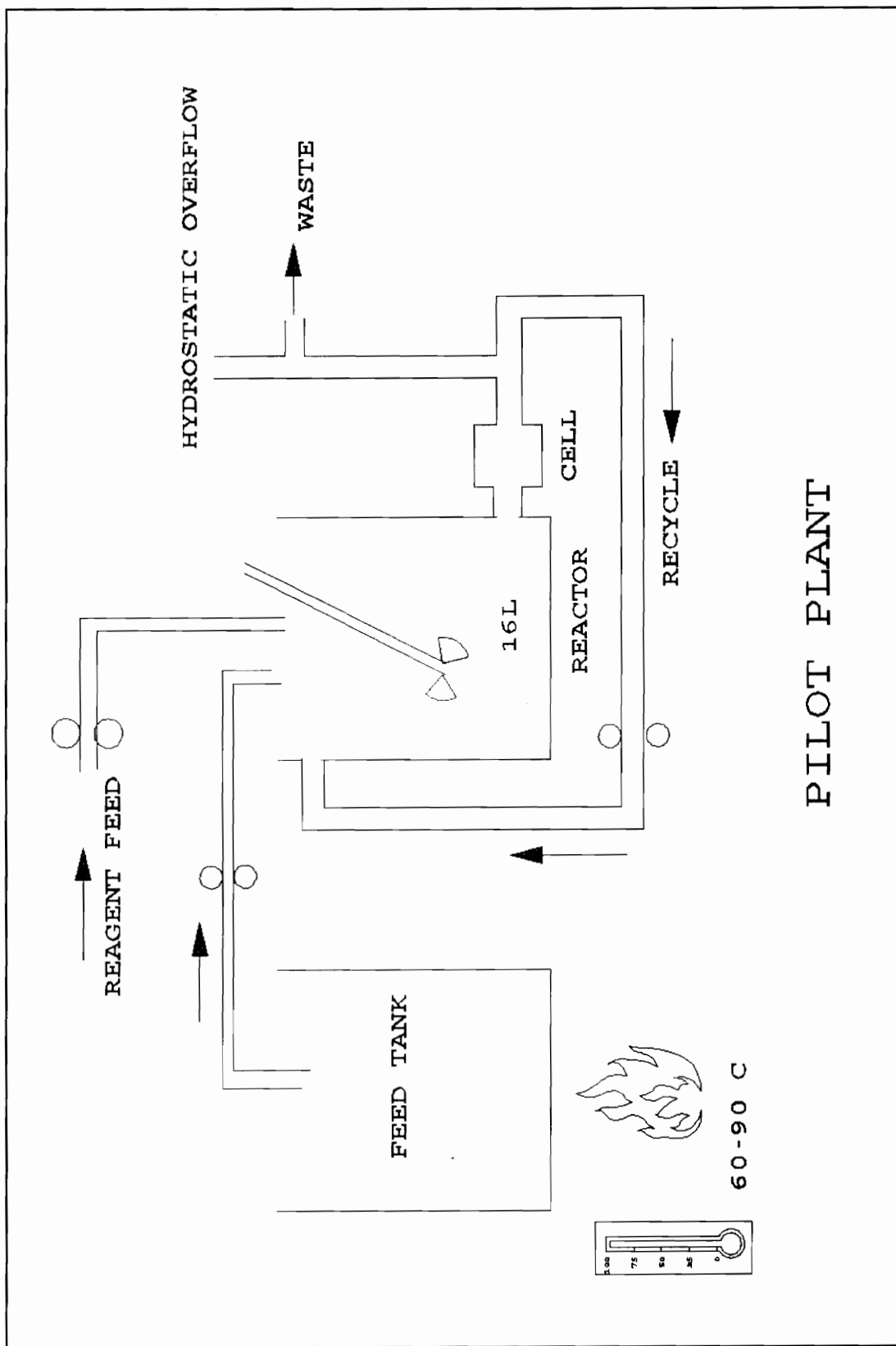


Figure 3.2.1 Schematic of pilot plant design for reductive pretreatment.

14.5 minutes. The feed was maintained at 60 °C by an electric heater and the reactor was continuously stirred by a three inch diameter prop driven by an electric motor.

The design used for oxidative pretreatment had three cascading reactors. The first reactor was used as the mixing vessel for the ferrous iron solution and the dye waste feed and had a volume of 2 L. The second reactor was the main reacting vessel. It was used for the addition of the hydrogen peroxide solution, it had a volume of 10 L. The third reactor was maintained at 6 L and was used as a source and return for the recycle loop. Again, a masterflex peristaltic pump was used to feed dye waste to the pilot plant at 1.1 L/min, giving a residence time of 16.4 minutes. A schematic is shown in figure 3.2.2.

Both pilot plant schemes had a silicon glass cell located in the recycle loop (Figures 3.2.1 and 3.2.2). The cell was fabricated in the glass shop using 1cm by 0.3cm rectangular glass tubing ordered from Wilmad Glass. Light from a 12 volt(V) 50 watt(W) halogen bulb, (purchased at WAL-MART), was shone through the cell, which provided a 0.3 cm pathlength, and received on the other side by three photodiode receptors. The photodiode receptors were covered with interference filters of nominal values of 589, 540, and 436 nm. A fourth photodiode, which was connected directly to the light source by a glass light pipe, was used for

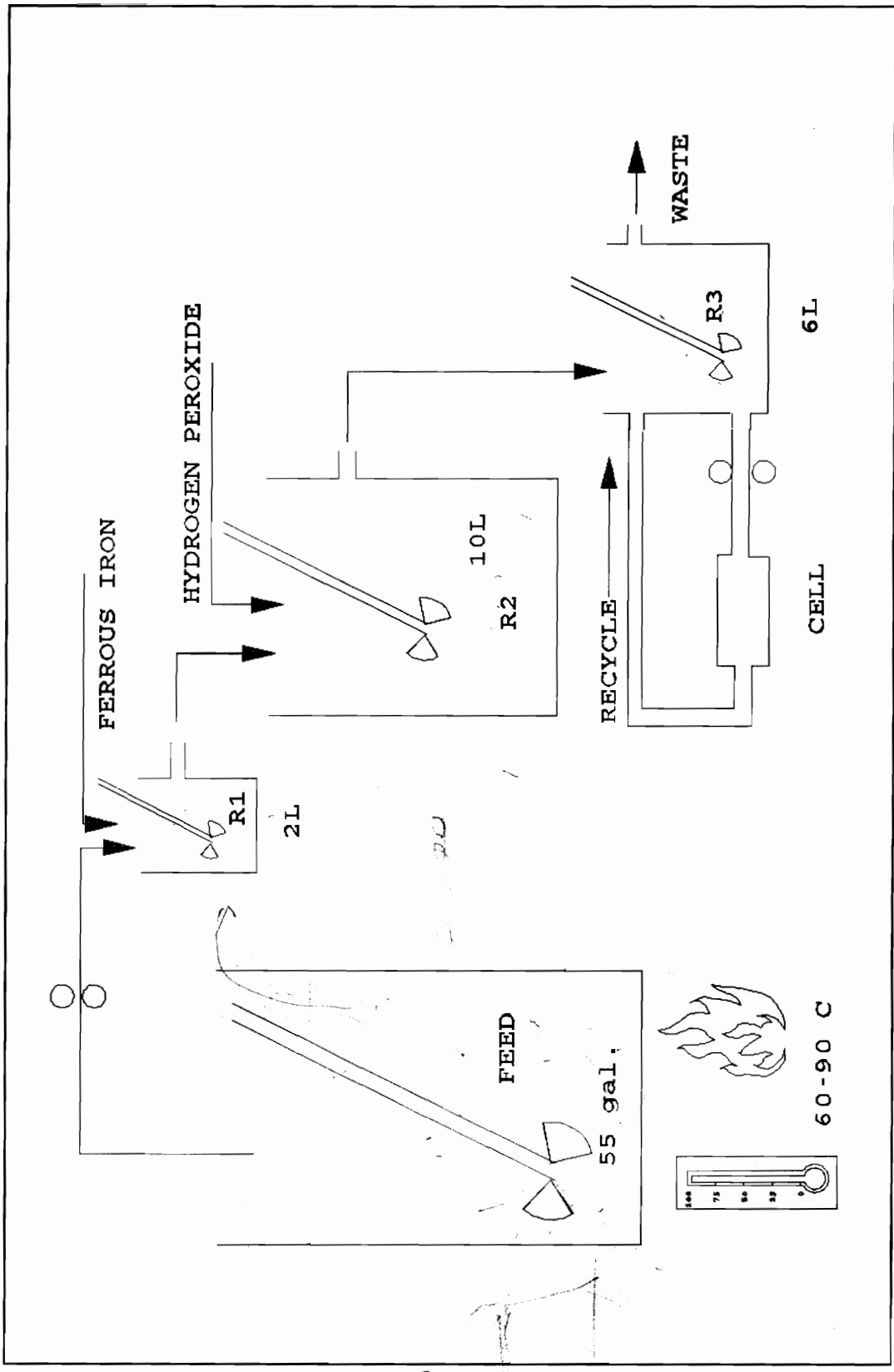


Figure 3.2.2 Schematic of pilot plant for oxidative pretreatment using Fenton's chemistry.

proportional feedback control of the light intensity.

Each of the three filtered photodiode detectors produces a current which is sent to separate current to voltage converters. The voltage is filtered and amplified to a of 0 to 5 V. An analog to digital converter is then used to convert the voltages to three 12-bit binary codes which are converted to ASCII by an IBM PC/XT which is running a compiled Quick BASIC program. The program converts the three signals to percent transmittance using a model taken from data for solutions measured both by the photodiodes and a Bausch & Lomb Spectronic 20 spectrophotometer (Balko, 1991). The transmittance values are used to calculate Munsell values which are used in the Adams-Nickerson difference equation (APHA, 1989) to determine the control variable (ADMI).

The program uses PID (proportional, integral, derivative) control to compare the calculated ADMI value to the set point and determine the response which is sent to the reagent pump. A digital to analog converter is used to convert the response to a 0 to 5 V signal. The voltage is converted in a voltage to current converter which gives a 4 to 20 mA signal used to regulate the speed of a Masterflex pump. A flow diagram of the above sequence is shown in figure 3.2.3.

The entire system is mounted on a steel frame. The

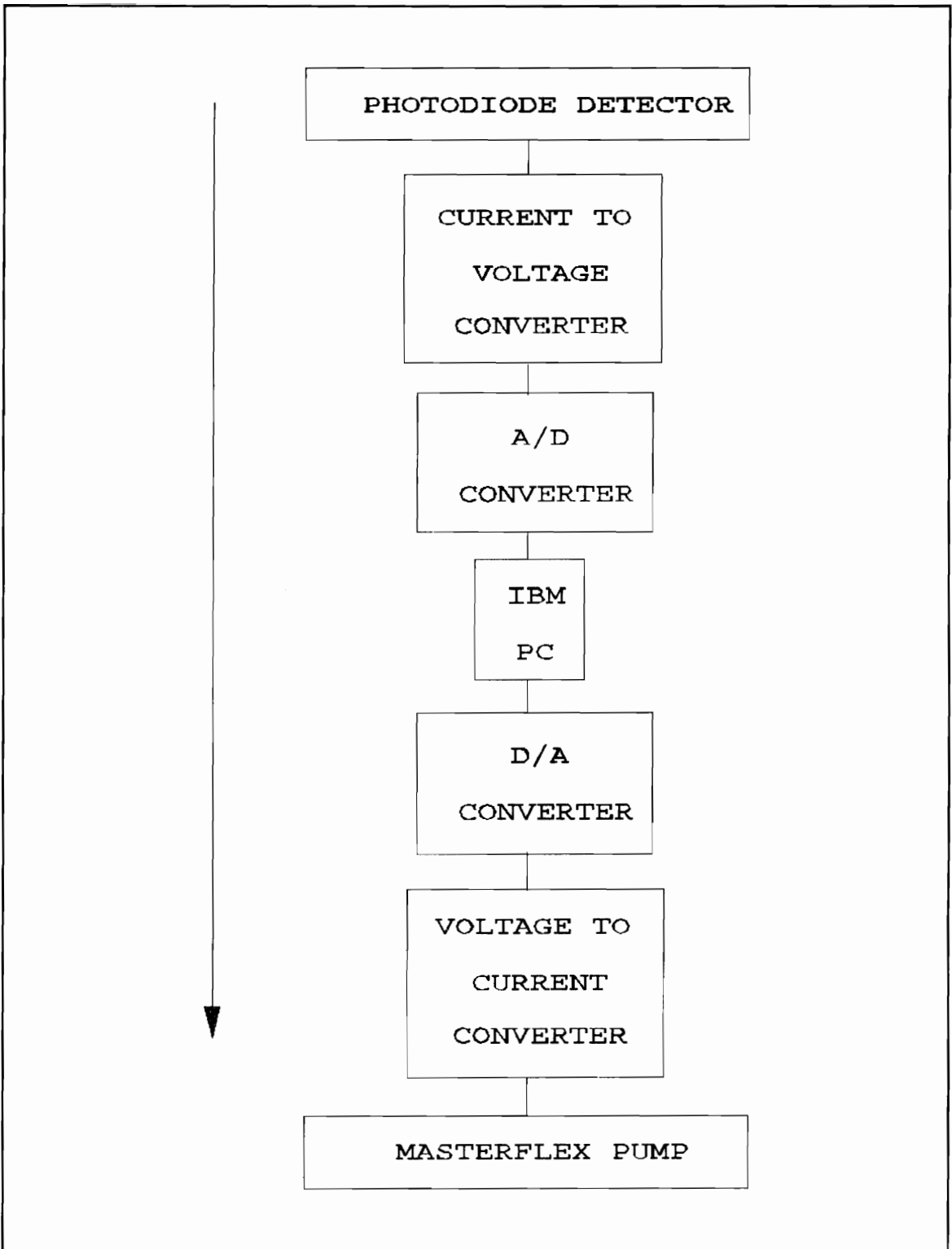


Figure 3.2.3 Flow diagram for transmittance signal.

frame is fitted with casters and is completely portable. The circuitry was designed and built and the software was written by Riley Chan (Electrical Engineer for the Department).

3.2.1 Color Measurement

The color measurement calculation used in the pilot plant is based on the ADMI Tristimulus Filter Method (Proposed) 2120E in APHA (1989). This method was chosen because of the restrictions placed on POTW'S by the EPA which stipulate ADMI units.

The ADMI method requires that light transmittance be measured at 3 different wavelengths, namely 590, 540, and 438 nm. The relation between the number generated by the pilot plant (0-4095) at each of the wavelengths was assumed to be linear when related to transmittance (100% - 0%) so the simple conversion

$$TX = 100 - 0.024 * X$$

was used where

X = Transmittance for wavelength X from Pilot Plant (0 - 4095)

TX = % transmittance (100% - 0%).

The transmittances are used to calculate tristimulus values which relate the measured color to a position in

color-space. Color-space uses a reference point; usually (0,0,0) in a three dimensional field in which the dimensions are darkness, red-green, and yellow-blue, respectively. Munsell values based on the tristimulus values are calculated using a curve-fit equation and the color value is calculated as the relative distance from the reference point in color space. The subroutine used to calculate the ADMI values including the equations for the Munsell values is shown in APPENDIX I.

3.2.2 D/A and A/D Converters

A Qua Tech PXB-721 parallel expansion adapter is used to support the analog to digital(A/D) and digital to analog(D/A) converters. The ADM12-11 is the 12-bit analog to digital converter Qua Tech daughter board used to convert the voltages to binary codes. The 12-bits convert the range of 0 to 5 V from the photodiode signal into 4096 intervals (0 to 4095). The value received by the computer in the 0 to 4095 range is then converted to percent transmittance by the computer. The three transmittance values are used to calculate the ADMI value which controls the reactor.

The PID output is converted by a DM8-10 Qua Tech daughter board. The DM8-10 is an 8-bit digital to analog converter. The output from the D/A converter is converted to a current and used to regulate the reagent pump.

3.2.3 PID Control

The PID control is handled in a "DO" loop in the Quick BASIC program. The loop retrieves the most recent values of the three transmittances stored. The calculation subroutine is called and a new ADMI value is calculated. The most recent value of ADMI calculated is retrieved and filtered using the following weighing equation.

$$ADMIfiltered = ADMI * 0.7 + lastADMIfiltered * 0.3 \quad \text{Eq. 3.2.1}$$

An error is determined by subtracting the filtered ADMI value from the setpoint.

The proportional term is determined by multiplying the error by the proportional gain, K_c . The integral term is calculated by multiplying the integral gain, K_i , by a summation of the error term and the sample interval. Finally, the derivative term is calculated using a filtered error determined as follows;

$$E_{filtered} = [E(i) + 3 * E(i-1) - 3 * E(i-2) - E(i-3)] / 6 \quad \text{Eq. 3.2.2}$$

where $E(i)$ is the current error, $E(i-1)$ is the previous error, $E(i-2)$ is the second previous error, and $E(i-3)$ is the third previous error. The derivative term is calculated by dividing the derivative gain, K_d , by the sample interval and multiplying by the filtered error. The three terms are combined to give the controller output, "PID", in equation

3.2.3.

$$PID = K_c * [E(i) + INTEGRALterm + DERIVATIVEterm] \quad \text{Eq. 3.2.3}$$

The PID subroutine is shown in Appendix 1.

3.2.4 SOFTWARE

The pilot plant is driven by an IBM PC/XT which has a 16-bit 8088 microprocessor, an 8-bit memory bus, 256 Kbyte of RAM, and a clock rate of 4.77 MHz (Eggebrech, 1983). The PC runs a compiled Quick BASIC program written by Riley Chan. This program contains five subprograms that carry out specific tasks for the user. The options are as follows:

1. Collect Data
2. PID Control
3. Adjustments (Hardware, Software, Motor)
4. Replot
5. Filing (Save, Retrieve)

The first option, "Collect Data," allows the system to collect transmittance data without any controller action. Signals from the photodiode detectors are retrieved through the A/D converter and stored in arrays. The arrays are dimensioned for 3600 entries and are limited to that size because of the disk buffer associated with the floppy diskette. If the arrays become filled, the program stops and the data can be stored on floppy disk. The ADMI value is calculated and plotted on a real time basis.

The "PID" option collects data just as the "Collect

Data" option does. It also calculates the ADMI, determines the error between the ADMI and the set point, and calculates the response sent to the reagent pump. (The subroutine for the ADMI calculation is shown in Appendix 2). The ADMI is plotted on the screen and is updated with every new point. Also included on the plot screen is the percent error, the controller output signal, and the setpoint.

The "Adjustment" program allows for changes in the Hardware, Software, and Motor control. "Hardware" adjustments include changes in the A/D and D/A converter parameters. The null and gain of the light receiving circuitry can be adjusted in the "Software" calibration section. Finally, "Motor" adjustments allows control of the range of the controller output for different size pump heads.

The "Replot" option allows old data files to be reviewed on screen or plotted on a printer.

Finally, the "Filing" option is used to save or retrieve data files. Other things such as dye lot information, time, date, and anything else the user wishes to save is entered during the "save" procedure.

3.2.5 Pilot Plant Calibration

Prior to operation of the pilot plant the circuitry is allowed to warm up for approximately 30 minutes. During the

warm up period, fresh tap water is circulated through the system. After the system has warmed up it is calibrated.

This is done by first covering the light source with a reflective material. This is assumed to be total darkness or zero transmission. For each of the three wavelengths measured the null is adjusted to read 4095 (described in section 3.2.1). This part of the calibration tends to "nullify" the effects of the ambient lighting. The reflective material is then removed and the light source is allowed to shine through the tap water which is being circulated through the system. This is assumed to be 100% transmittance and the gain for each of the three wavelengths is adjusted.

Calibration is repeated every time the system is started or if there are significant changes in the ambient lighting.

3.3 Biological Reactors

Biological reactors were used to insure that the oxidative and reductive chemistry used in the pilot plant would not adversely affect any POTW (Publicly Owned Treatment Works) operating down-stream. Three continuous-flow biological reactors (CFBRs) were operated simultaneously at room temperature to perform aerobic biological treatment. A diagram showing the reactor set up is shown in figure

3.3.1. The biological reactors were made from 5 gallon buckets. A baffle was placed inside the reactors which resulted in a smaller section that contained approximately 15% of the total reactor volume. This smaller section simulated a secondary clarifier and provided biomass recycle. The secondary clarify section was not aerated or agitated. The larger compartment in the reactors simulated the activated sludge process in a wastewater treatment plant. A drain was placed on the clarified side of the reactors to give an overflow volume of 12 L. A masterflex pump with three pump heads supplied feed to each of the three reactors at a constant rate of 2.1 mL/min. The feed to the reactors was maintained at 3 L per day which gave a 4 day hydraulic retention time. DOC measurements were used to monitor the reduction of organic carbon levels in the reactors.

The biological reactors were initially seeded with waste activated sludge that originated from the Martinsville, Virginia POTW. The microorganisms making up this sludge were assumed to be accustomed to exposure to the textile dyes used. To provide the necessary nutrients for the biomass, the dye waste was mixed with primary clarified waste from a local wastewater treatment plant. All three reactors were continuously aerated and agitated using lab air maintained at 20 psi.

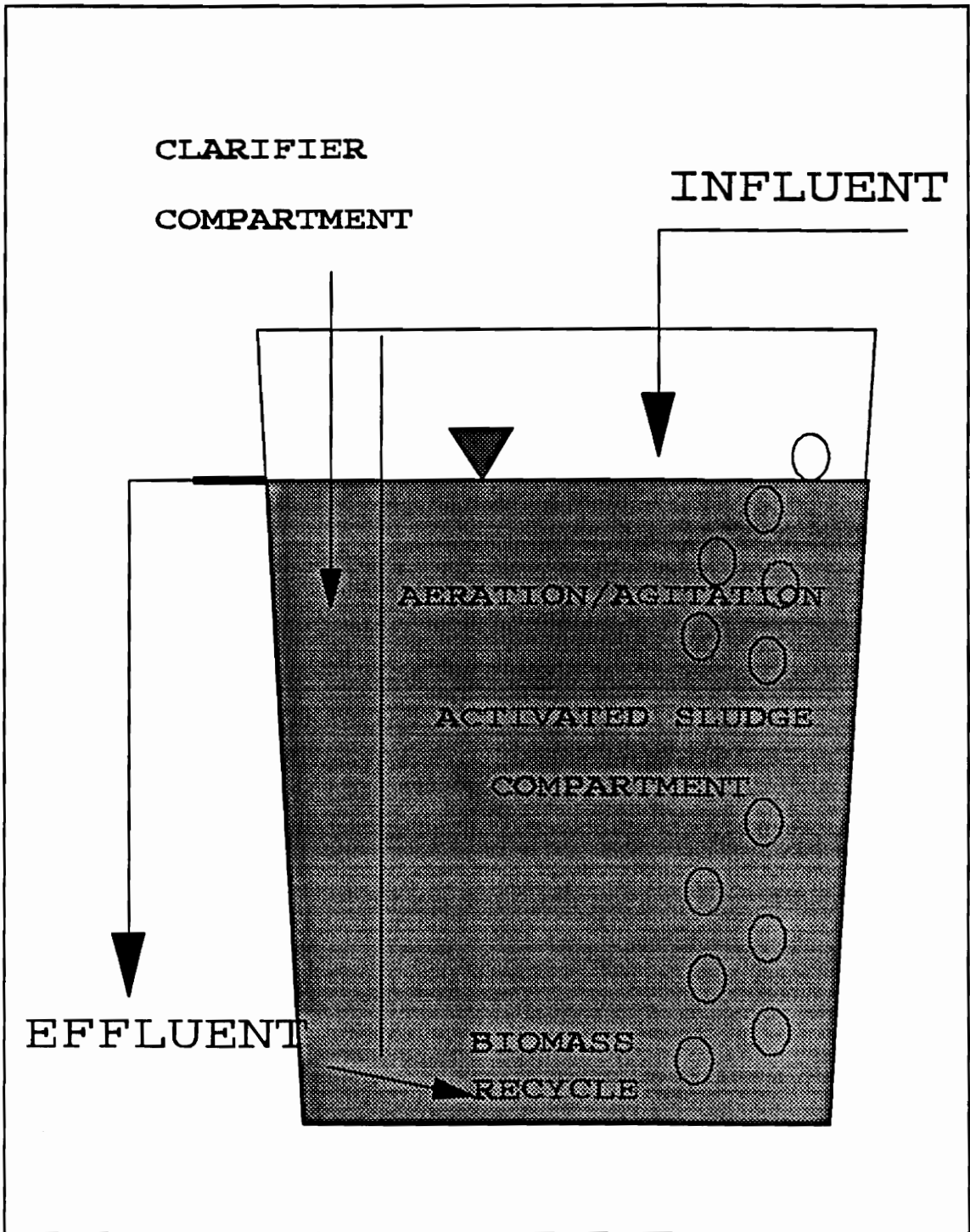


Figure 3.3.1: Schematic of Continuous-Flow Biological Reactor (CFBR) used for Aerobic Treatment

4.0 Materials and Methods

4.1 Laboratory Chemicals

Reagents used for experimentation were diluted in distilled deionized water. A Corning "Mega-pure" automatic still was used to convert available tap water into a source of reagent water.

For oxidation work a stock solution of H_2O_2 (3%) was prepared by dilution of commercially available 30% H_2O_2 solution (J.T. Baker Inc.). Ferrous iron was prepared fresh in deionized water by dissolving 7.5 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ powder (J.T. Baker Inc.) and acidifying it to a pH 3.

For reduction work a Thiourea dioxide concentration of 6 g/L was prepared fresh in deionized water by dissolving $\text{NH}_2\text{CNHSO}_2\text{H}$ powder (Eastman Kodak Company). Sodium Hydrosulfite was prepared fresh in deionized water by dissolving 12 g/L $\text{Na}_2\text{S}_2\text{O}_4$ powder (Mallinckrodt).

4.2 Analytical Procedures

4.2.1 Mixed Liquid Suspended Solids

Mixed Liquid suspended solids was determined for samples taken from the activated sludge compartment of, and the feed to the biological reactors. Mixed Liquid suspended solids were measured in accordance with section 209 °C of

Standard Methods (APHA, et al., 1989). A 7 cm glass-fiber filter was washed with distilled water, dried at 105 °C, placed in a desiccator and allowed to cool to room temperature, and weighed. A measured amount of sample was pipetted onto the filter and dried at 105 °C for 1 hour. The filter was again placed in a desiccator and allowed to cool to room temperature and then reweighed.

4.2.2 Color Measurement

Section 204 D 4 of Standard Methods (APHA, et al., 1989), ADMI Tristimulus Filter (Tentative) Method (alternate), was used for color measurement. A Bausch and Lomb Spectronic 20 spectrophotometer with a 1 cm path length was used to measure transmittance of the samples at three wavelengths. The selected wavelengths used for color measurement were 590 nm, 540 nm, and 438 nm. Distilled water blanks were used for 100 percent transmittance. For the spectrophotometer used, a calibration curve was developed using a range of known platinum-cobalt color standards, yielding a calibration factor incorporated in the ADMI calculation.

Samples were prepared by first adjusting the pH to 7.6 using sulfuric acid or sodium hydroxide. The samples were then filtered three times through a washed glass fiber filter. If necessary samples were diluted 1:10 or 1:20 to

put the sample color within the range calibrated for.

The transmittances were then measured and recorded. These values were then entered into a spreadsheet which automatically calculated the ADMI values incorporating the equations found in APPENDIX 2.

4.2.3 pH/Redox

A digital pH meter (Corning 250) was used for all pH measurements. The meter was calibrated daily using buffer solutions obtained from Fisher Scientific.

Redox measurements were made using a Corning 220 pH meter and a Corning redox combination electrode. The meter was connected to an Omega RD-2000 strip chart recorder for a continuous analog display of REDOX potential data.

4.2.4 Dissolved Organic Carbon

Total carbon analysis was used to examine the performance of the biological reactors. The analyses were performed using a Shimadzu TOC-5000 Total Carbon Analyzer. The TOC-5000 uses a CO₂-free air stream as a carrier gas to transport a sample (approximately 13 microliters) into a furnace. The sample is then combusted at 680 °C over a platinum catalyst and an infrared detector is used to determine the amount of carbon dioxide formed and thus the total carbon (TC) in the sample.

The TOC-5000 also determines the inorganic carbon (IC) level in the sample. This is done by injecting the sample into a 25% phosphoric acid solution. The IC bubbles out of the sample as CO₂ and is picked up by the carrier gas and measured by the infrared detector. The organic carbon is then determined by simply subtracting the inorganic carbon from the total carbon.

4.3 Kinetics of Color Removal by Oxidation Using Fenton's Chemistry

Bench-scale, batch oxidation reactions were run to determine the order and rate constant for color removal using Fenton's chemistry. 150 ml samples of concentrated jet-dye waste were adjusted to pH 3 using sulfuric acid. The samples were then heated to 60 °C and the reagents were added, first Ferrous Iron to give a concentration of 200 ppm, then hydrogen peroxide was added to give a concentration of 2000 ppm. The reaction was allowed to proceed a fixed amount of time between 10 seconds and 10 minutes, at which point the reaction mixture was quenched with excess sodium sulfite to halt color removal. The samples were then prepared for color measurement in the spectrophotometer.

4.4 Pilot Plant Test Procedures

4.4.1 Tuning Parameters for PID Controls

The control parameters which include the gain, the integral time constant, and the derivative time constant were determined for the oxidative test runs only. The control parameters used for the reductive runs were chosen at random and seemed to work well.

The tuning parameters for the oxidative tests were determined using the process step testing method described in section 2.5. The pilot plant was operated in the "Collect Data" mode so that no reagent was being added to the jet-dye waste. The system was assumed to be at steady state after two residence times or approximately 30 minutes of operation. When steady state was achieved, a step change was made in the manipulated variable (reagent feed). The reagent feed pump was turned on at full speed (30 mL/min) and the resulting response in the controlled variable, color, was recorded. The control parameters were determined from the resulting data and used in the PID equations.

4.4.1 Reduction

Both slack washer and jet-dye waste were treated with reductive chemistry in the pilot plant. The dye waste was heated to 60°C, using an electric heater, to return it to

the actual conditions found in the textile plant. A 6000 ppm solution of thiourea dioxide or a 12,000 ppm solution of sodium hydrosulfite was prepared for use as the pre-treatment reagent. The control circuitry was allowed to warm-up for 30 minutes and then the null and gain of the "spectrophotometer" were calibrated as described in section 3.2.4 - Pilot Plant Calibration.

After calibration was completed and the dye waste had reached the prescribed temperature the feed/circulation pump was started. This began the dye waste flow into the reactor and the recycle stream through the light cell, both at 1 L/min. In the main menu of the control program, "P" was selected for PID control of the reactor. The set point was set to the desired value of ADMI units and the system was allowed to run continuously until it came to steady state.

After approximately 15 minutes the reactor volume reached its maximum and treated dye waste began to leave the system through the hydrostatic overflow at the same rate that fresh dye waste was being fed to the reactor (1 L/min). Some of this waste was collected and refrigerated for future use in the biological reactors to insure no ill effects during aerobic treatment

The exact concentration of pre-treatment reagent in the reactor was not known at any given time, however, it was known that the maximum feed rate for the reagent pump, which

the PID software controlled, was 31 mL/min so that the maximum possible concentration of thiourea dioxide in the reactor was 200 ppm and that for sodium hydrosulfite was 400 ppm.

4.4.2 Oxidation

Oxidation in the pilot plant was run virtually the same as reduction as far as initial start up including heating the dye waste, calibrating the light sensing circuitry, using the PID control option, and starting the feed/recycle pump. For oxidative treatment, however, a second pump head was added to the reagent feed pump being utilized by the control software. This allowed for Fenton's reagent, (hydrogen peroxide and ferrous iron), to be added. A 3 percent hydrogen peroxide solution (30,000 ppm) was used for feed into the main reactor. As in the reduction procedure, a 31 mL/min maximum reagent feed rate gave a maximum peroxide concentration of 930 ppm in the reactor. The second head on the reagent pump was used to supply the ferrous iron solution made in a 20 to 1 ratio ($\text{H}_2\text{O}_2:\text{Fe}^{3+}$) or 1500 ppm. The ferrous iron solution was fed into the first reactor of the cascading system along with the jet-dye waste. Only jet-dye waste was oxidized in the pilot plant.

4.5 Bioreactor Test Procedures

Three aerobic biological reactors were maintained to observe the effects of the oxidized or reduced dye waste on biomass. The reactors were made from 5 gallon buckets with a divider placed inside each reactor which resulted in a clarified compartment and an activated sludge compartment. A drain was placed on the clarified side of the reactors to give an overflow volume of 12 L. A masterflex pump with three pump heads supplied feed to each of the three reactors at a constant rate of 2.1 mL/min. This rate gave each reactor a 4 day hydraulic retention time. All three reactors were continuously aerated at 20 psi using lab air.

The reactors were seeded with biomass which originated from the Martinsville, Va POTW. This biomass was chosen because of its "familiarity" with the type of dye waste being used in this experimentation.

The feed for the reactors was made in the ratio of 1:9:3 jet-dye waste to tap water to primary clarified sewage. This ratio provided for the feed mix to be 75%-10% jet-dye waste in water and 25% municipal waste. This feed mix was determined to best match actual conditions at the Martinsville, VA POTW (Lloyd, 1992). The primary clarified sewage was obtained from Pepper's Ferry, a local POTW. The Pepper's Ferry waste maintained an average BOD of 144 ppm and a suspended solids level of 100 ppm.

While waiting for the reactors to come to steady-state, all three reactors were fed from the same tank. When steady state was achieved, additional feed tanks were added and the feed formula was changed so that one reactor continued to treat the original feed formula and the other reactors had oxidized or reduced dye waste substituted for the jet-dye waste portion of the formula.

Samples were taken for analysis twice weekly. 50 ml was removed from each clarified compartment, each activated sludge compartment and each feed tank. Each sample was analyzed for pH and color (ADMI). DOC was measured on feed samples and samples from the clarified compartment, and TSS solids was measured on feed samples and samples from the activated sludge compartment.

4.6 On Site Pilot Plant Operations

The pilot plant was set up and operated on site at Tultex in Martinsville, Virginia. Three different fresh jet-dye waste concentrates were used in the pilot plant to demonstrate its effectiveness and to observe operation with several different color formulas. The dye formulas treated included Navy 106, an azo based Red formulation, and a phthalocyanine based formulation, Ming Jade.

The jet-dye waste was pumped into the pilot plant feed tank. There its pH was adjusted to 3 using 70 percent

sulfuric acid, it was stirred and heated to 65°C. After calibration of the light sensing circuitry, operation of the pilot plant began. The feed and recycle flow rate were both set to 1.1 L/min. A 6000 ppm hydrogen peroxide solution was made using bulk 50 percent peroxide from Tultex. A corresponding Ferrous iron solution (300 ppm) was made by dissolving 29 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The pilot plant was operated for several hours with each dye waste and data was collected for analysis of color and DOC removal and for cost of operation.

5.0 Results and Discussion

5.1 Kinetics of Oxidation Using Fenton's Chemistry

Table 5.1.1 shows the results of data obtained from bench scale batch oxidation reactions using Fenton's chemistry. The ADMI values were obtained using the lab

Table 5.1.1 Kinetic data for oxidation of concentrated Navy 106 jet-dye waste from exhaust dyeing of 50/50 polyester cotton using Fenton's chemistry. * represents samples diluted 20:1 for color measurement. ** represents samples diluted 10:1 for color measurement.

Reaction Time (s)	Percent Transmittance 590 nm	Percent Transmittance 540 nm	Percent Transmittance 438 nm	ADMI
0	24	28	51	34,355*
10	74	65.5	48.5	7,525**
15	74	66	49	7,348**
25	81	75	53	7,114**
45	86	81	58	6,646**
60	85	81	58	6,687**
90	92	89	71	4,488**
120	95	94	82	2,778**
180	95	94	84.5	2,177**
240	73	64	29	1,467
300	81	70	36	1,273
360	88.5	84	36	762
600	99	98.84	77.5	483

spectrophotometer. Assuming first order kinetics, the rate

expression can be expressed as

$$\frac{d(ADMI)}{dt} = k*(ADMI) \quad \text{Eq. 5.1.1}$$

Separating and integrating leads to

$$\ln (ADMI) = -kt \quad \text{Eq. 5.1.2}$$

Therefore if the color removal is first order, a graph of the \ln ADMI vs time should approximate a straight line with a slope of $-k$, the rate constant. A graph of \ln ADMI vs time is shown in figure 5.1.1. The data does approximate a line so the reaction is first order with respect to color removal and the rate constant is 0.00597.

5.2 Tuning of PID parameters

The tuning parameters for the PID controller were determined for the pilot plant for the oxidation mode of operation for Navy 106 jet-dye concentrate. The green wavelength was used as the control variable and its response to the process step testing method was used to compute the Process gain K , time constant τ , and the dead time t_0 . These values were in turn used to determine the controller gain K_c , the integral time constant T_I , and the derivative time constant T_D . Figure 5.2.1 shows the graph of the control variable, the green wavelength, vs time. Δy_s was

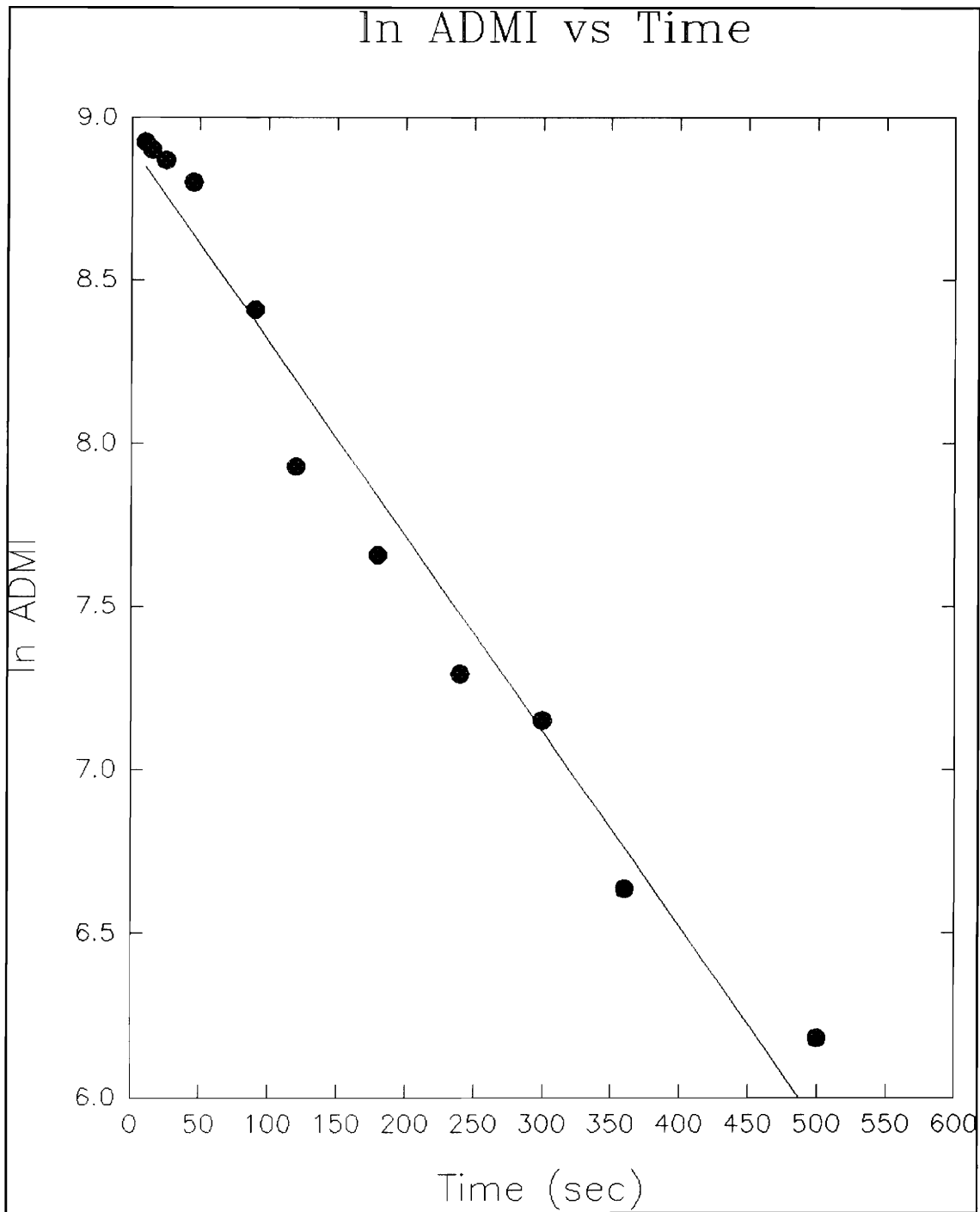


Figure 5.1.1 A graph showing ln ADMI vs time for data from bench scale batch reactions using Fenton's chemistry on Navy 106 jet-dye concentrate waste. The reaction matches first order kinetics with rate constant 0.00597

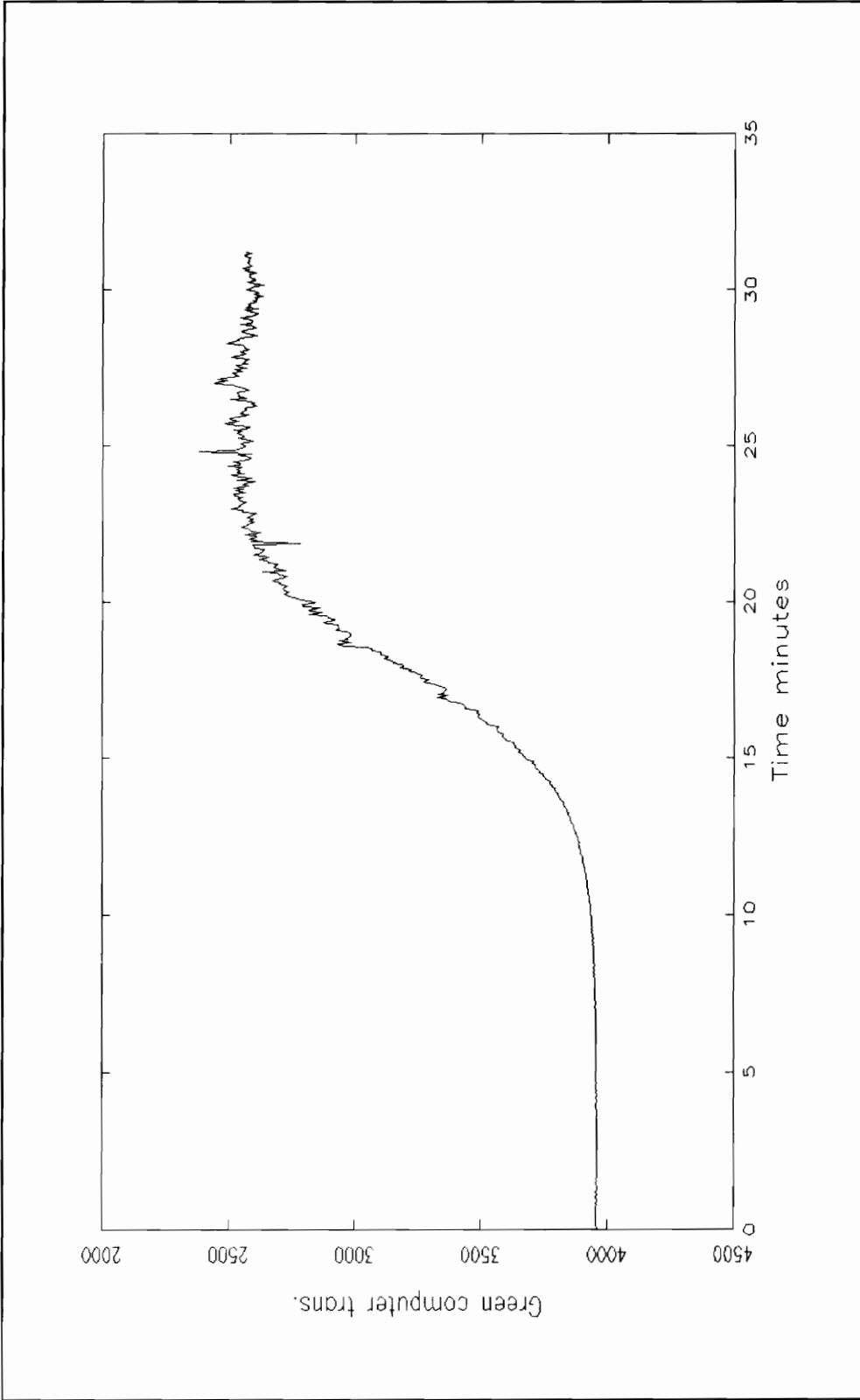


Figure 5.2.1 A graph showing the response of the controlled variable, green transmittance, to a step change in the manipulated variable, reagent feed for Fenton's oxidation in the Pilot Plant. This graph was used to determine the values necessary to tune the PID equation parameters.

determined to be 1394 wavelength units and Δu , the change in the manipulated variable, was 16 mA. The process gain K or the ratio of Δy_s to Δu was determined as follows;

$$K = \text{Process Gain} = \frac{1394}{16} = 87.13$$

The two points t_1 and t_2 were determined to be 394.5 sec and 881.0 sec, respectively. The process time constant and dead time were calculated to be

$$T = \frac{3}{2} (t_2 - t_1) = 486.5 \text{ sec}$$

and

$$t_0 = (t_2 - T) = 395 \text{ sec}$$

These three value were then used to calculate the control parameters using the ITAE (Integral of the Time-Weighted Absolute Value of the Error) equations. The results are as follows:

$$K_c = \frac{a_1}{K} \left(\frac{t_0}{\tau} \right)^{b_1} = 0.1679$$

$$T_I = \frac{\tau}{a_2} \left(\frac{t_0}{\tau} \right)^{b_2} = 495.44 \text{ s} = 8.26 \text{ min}$$

$$T_D = a_3 \tau \left(\frac{t_0}{\tau} \right)^{b_3} = 150.65 \text{ s} = 2.51 \text{ min}$$

where

a_1	=	1.357
b_1	=	-0.947
a_2	=	0.842

$$\begin{aligned}b_2 &= 0.738 \\a_3 &= 0.381 \\b_3 &= 0.995.\end{aligned}$$

5.3 Reduction

5.3.1 Reduction of Slack Washer Waste

The first trials with the pilot plant were run on Navy 106 slack washer waste (described in section 3.1 - Waste Stream Characterization). These trials were designed to test the ability of the control system to operate as designed and to get some initial reduction data.

The slack washer waste was heated to 60°C, using an electric emersion heater, to return it to the actual conditions found in the textile plant. A 6000 ppm solution of thiourea dioxide was prepared for use as the pretreatment reagent. The control circuitry was allowed to warm-up for 30 minutes and then the null and gain of the "spectrophotometer" were calibrated as described in section 3.2.5 - Pilot Plant Calibration.

After calibration was completed and the dye waste had reached the prescribed temperature the feed/circulation pump was started. This began the dye waste flow into the reactor and the recycle stream through the light cell, both at 1 L/min. At the main menu of the control program, "P" was selected for PID control of the reactor. The set point was

set to 400 ADMI units and the system was allowed to run continuously. After approximately 15 minutes the reactor volume reached its maximum and treated dye waste began to leave the system through the hydrostatic overflow at the same rate that fresh dye waste was being fed to the reactor (1 L/min).

The results of this trial are shown in figure 5.3.1. This graph shows the control variable (ADMI) vs run time. The initial ADMI value of the dye waste according to the pilot plant was 2980. The setpoint was reached 20 minutes after the reactor was started. This is just longer than 1 residence time in the reactor. The control variable oscillated about the setpoint with a decreasing amplitude, showing that the controller was working and that the control was underdamped. No biological data was collected for reduced slack washer waste and all pilot plant work following this run was done with concentrated jet-dye waste.

5.3.2 Reduction of Concentrated Jet-dye Waste

It was determined during the course of this research that it would be advantageous to study the pretreatment of jet-dye waste discharges because of the extremely high contribution to overall color of the mill effluent relative to volume added. This presented some problems in color measurement that had to be addressed. The ADMI calculation

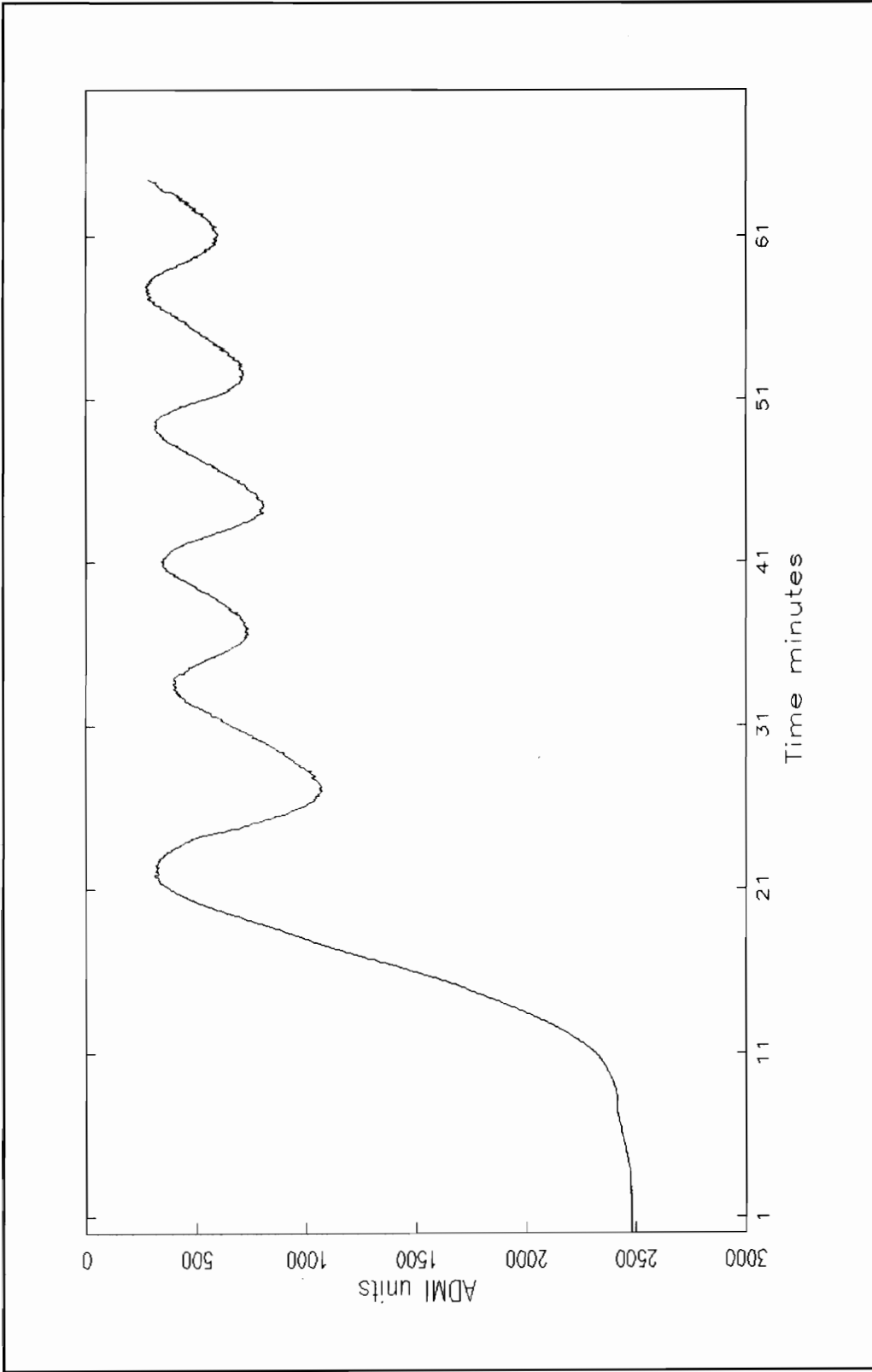


Figure 5.3.1 Results of reductive pretreatment of slack washer waste with thiourea dioxide in the Pilot Plant used to verify operation of control system. Setpoint at 400 ADMU.

was designed to be effective in the range of 0 to 2000 ADMI. Because the jet-dye waste being treated has an initial color of from 55,000 to 75,000 ADMI and dilution was not practical, alternative solutions had to be looked at.

One obvious solution was to decrease the path length for the spectrophotometer. The smallest thickness glass tubing available that was broad enough to accommodate the photodiode receptors was 3 mm. This was a 70% decrease in the path length and was easily adapted for in the control software in the last line of the subroutine for the ADMI calculation shown in Appendix 2. The second solution was to abandon the ADMI calculation and simply choose one of the three wavelengths being measured and use it as the feed back control variable. In the end, it was determined that a combination of the narrower cell and the use of a single wavelength was best for control of the Pilot Plant.

5.3.3 Thiourea Dioxide Reduction of Concentrated Jet-dye Waste

Figure 5.3.2 shows data collected for two residence times of reductive pretreatment using thiourea dioxide at an approximate concentration of 300 ppm. The graph shows the three individual wavelengths represented in computer units (not percent transmittance) plotted versus time. The concentrated jet-dye waste was too dark for use of the ADMI

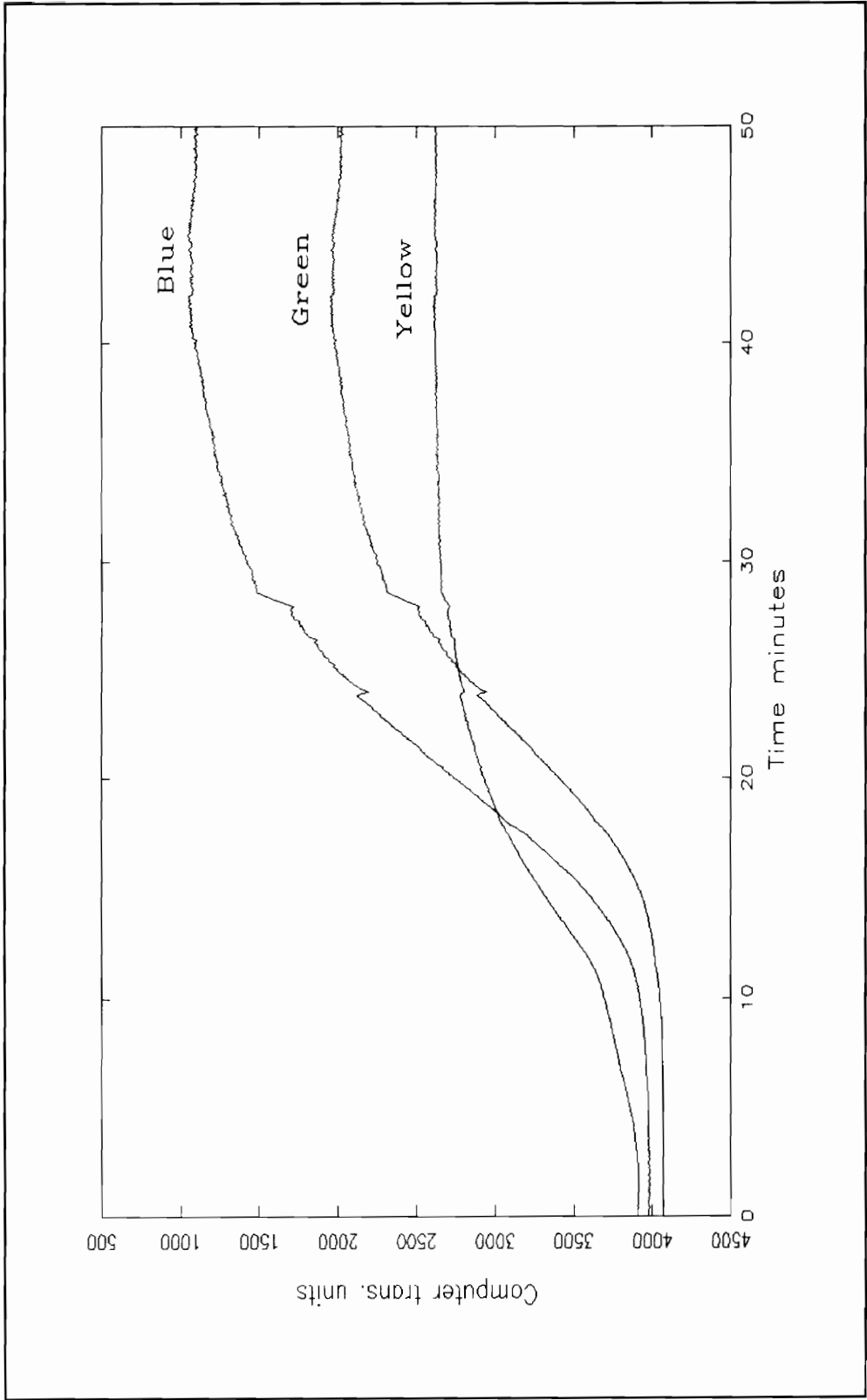


Figure 5.3.2 Graph showing the response of each wavelength vs time for reductive pretreatment of concentrated jet-dye waste using thiourea dioxide. From this graph it was determined that the blue wavelength would suit best for the control variable for this type of pretreatment.

calculation, so this data was used to determine which wavelength gave the best response for control purposes and what value should be used for the setpoint for PID control. From this data it was determined that the blue wavelength would be best for reactor control of reductive pretreatment because of the wide range of its response. This was probably due to the blue color of the particular dye formula used in this research; one of the other wavelengths may be advantageous for red or yellow shades. A blue transmittance of 1200 was determined from figure 5.3.2 to be the optimum set point setting for the controller.

The color of the waste resulting from the thiourea dioxide pretreatment was measured immediately without pH adjustment or filtration in the laboratory spectrophotometer and found to be 3900 ADMI. This value corresponds to the lowest level attainable in bench scale batch trials. The resulting stream was a rich yellow color (which contributed to the 3900 ADMI value) that resulted from the reduction products (amines) of the concentrated jet-dye waste. The sample was aerated (oxygenated) for 3 minutes and the result was a change in color from yellow to deep purple. The sample was then diluted with distilled water, filtered, and the ADMI value was read on the laboratory spectrophotometer. The ADMI value went up to 8987 which clearly demonstrates color return. The waste resulting from the reduction trial

was stored in a refrigerator and used for feed material to the biological reactors.

5.3.4 Sodium Hydrosulfite Reduction of Concentrated Jet-dye Waste

Figure 5.3.3 shows data collected for two residence times of reductive pretreatment using sodium hydrosulfite at an approximate concentration of 600 ppm. The graph shows the three individual wavelengths plotted verses time. Sodium hydrosulfite was not effective for color removal in the pilot plant and was not used further.

5.4 Oxidation

5.4.1 Lab Tests of Fenton's Oxidation

Figure 5.4.1 shows the response of the individual wavelengths verses time for oxidative pretreatment. The data shows that the green or yellow wavelength is best for reactor control.

The color of the waste resulting from the Fenton's reagent pretreatment was measured in the laboratory spectrophotometer and found to be 577 ADMI. This is a reduction of 98.8% relative to the concentrated jet-dye waste. There was no return of color observed in any oxidized samples. The resulting waste stream from the oxidative pretreatment was stored in a refrigerator and used

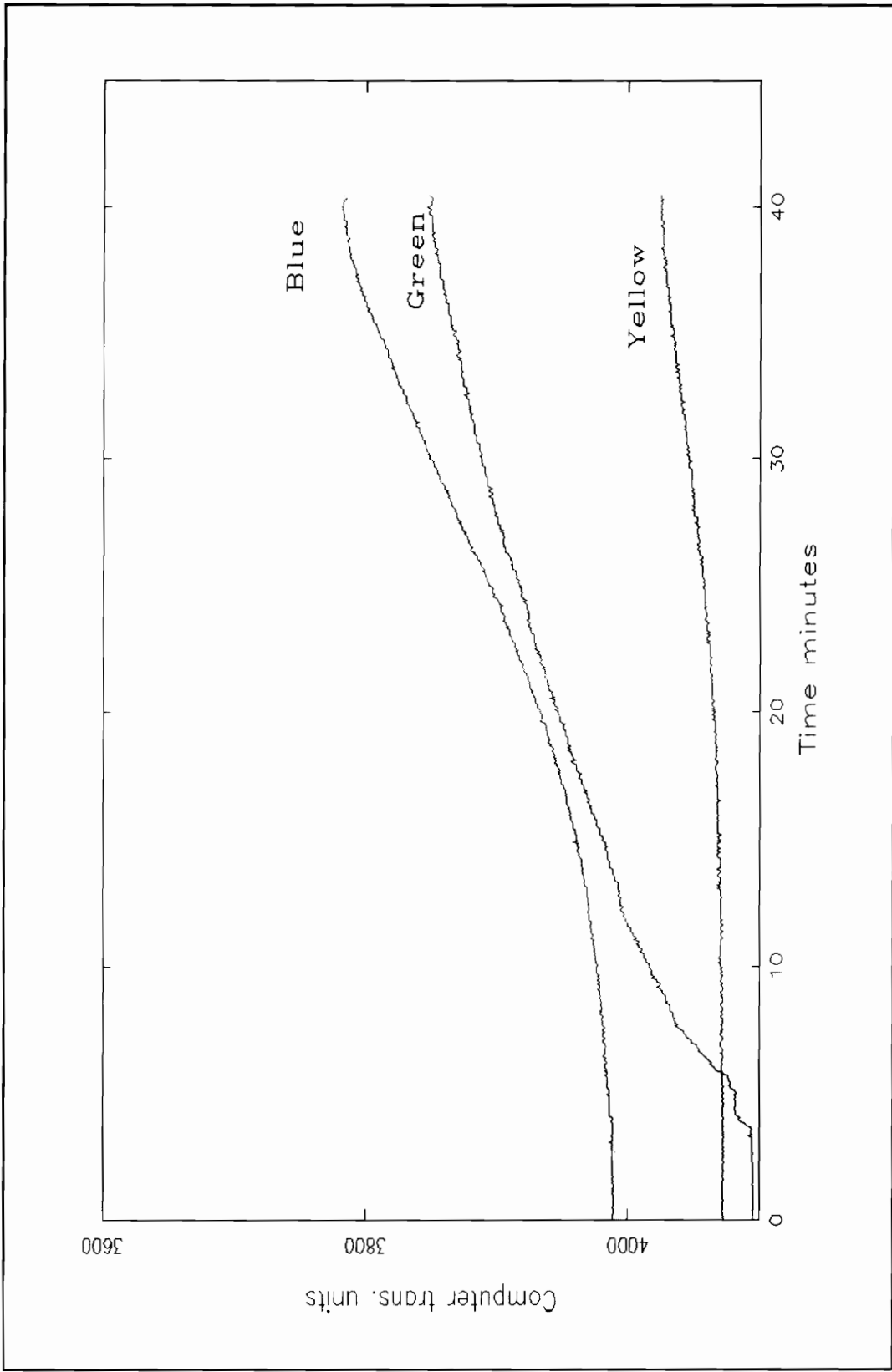


Figure 5.3.3 Graph showing the response of each wavelength vs time for reductive pretreatment using sodium hydrosulfite.

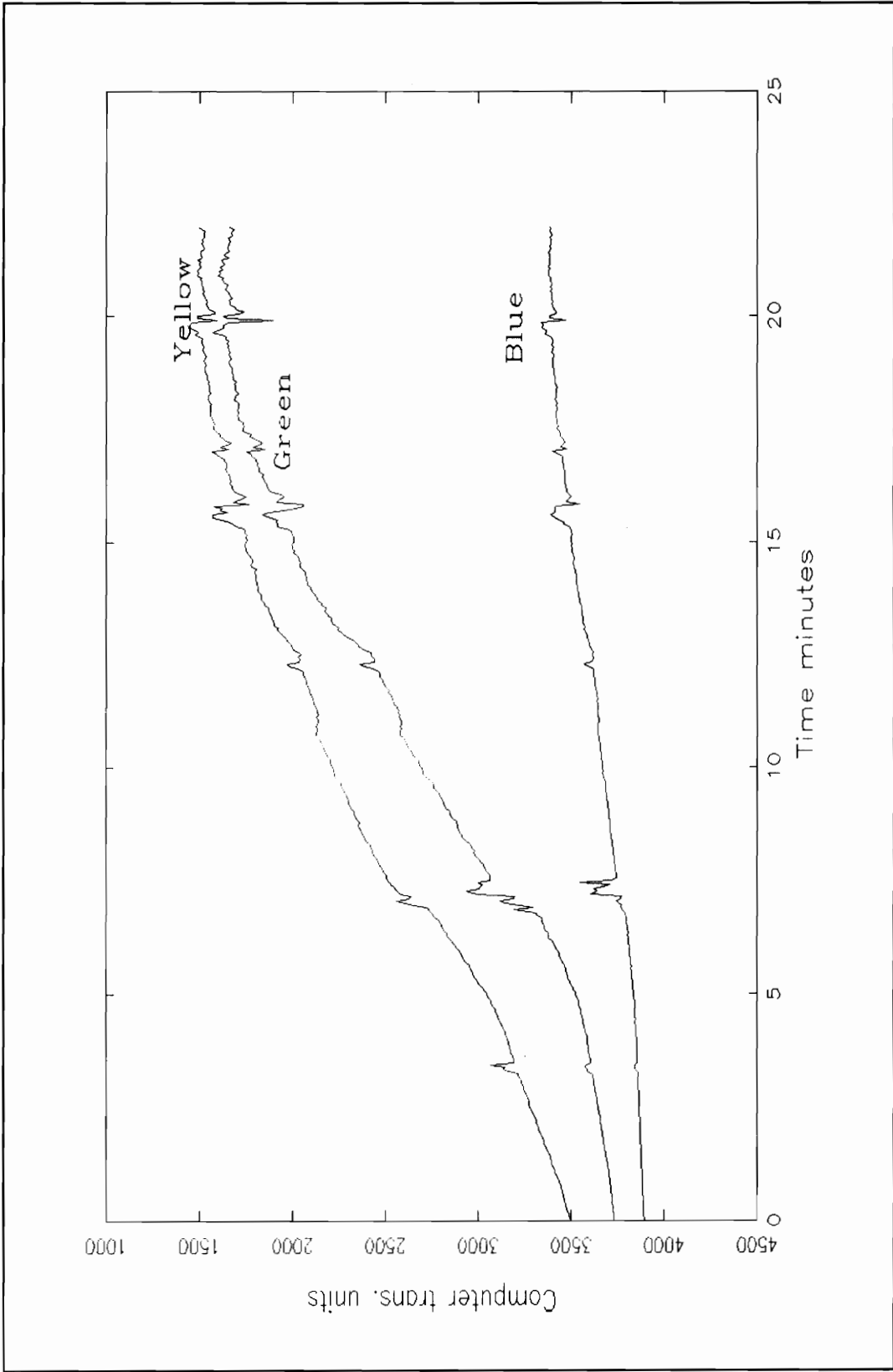


Figure 5.4.1 Graph showing response to oxidative treatment.

as feed material for biological treatment.

5.5 Biological Testing Results

Table 5.5.1 shows the steady state conditions of the biological reactors prior to the introduction of pretreated waste. The reactor feed contained 75 percent concentrated jet-dye waste diluted 1:10 with tap water and 25 percent primary clarified waste from a local POTW. The data represent a 12 day average which includes 4 hydraulic retention times. The data indicate that all three reactors were successfully degrading waste as is evidenced by the roughly 55 percent decrease in organic carbon levels. Color removal, as shown in previous research (Powell, *et al.*, 1992), was not significant in the aerobic reactors. The reactors were allowed to operate for 2 months before steady state conditions were reached.

Figure 5.5.1 represents the results of biological action on the jet-dye waste after pretreatment in the pilot plant. All three biological reactors are represented with reactor 1 being the control, reactor 2 treating oxidized dye waste treated with Fenton's reagent, and reactor 3 treating reduced dye waste treated with thiourea dioxide. All reactor conditions were kept constant except that the feed to reactor 2 contained 75 percent oxidized dye waste diluted 1:10 with tap water, and the feed to reactor 3 contained 75

Table 5.5.1. Steady State Conditions of Biological Reactors. Data Represent 12 Day (4 Hydraulic Retention Times) Average. Feed Contains 75% Untreated Jet-dye Waste at 10% Concentration and 25% Municipal Waste and Was Fed in Equal Amounts Simultaneously to all Reactors.

	ADMI	pH	TC	IC	DOC	TSS
PURE JET-DYE WASTE	50,133	12.16	777.3	461.4	315.9	188
FEED	3650	7.5	113	69.97	43.03	50.2
BIO-REACTOR 1	3592	8.1	50.47	31.27	19.2	276.3
BIO-REACTOR 2	3628	8.1	52.69	33.03	19.66	288.7
BIO-REACTOR 3	3613	8.3	51.88	32.5	19.3	290.4

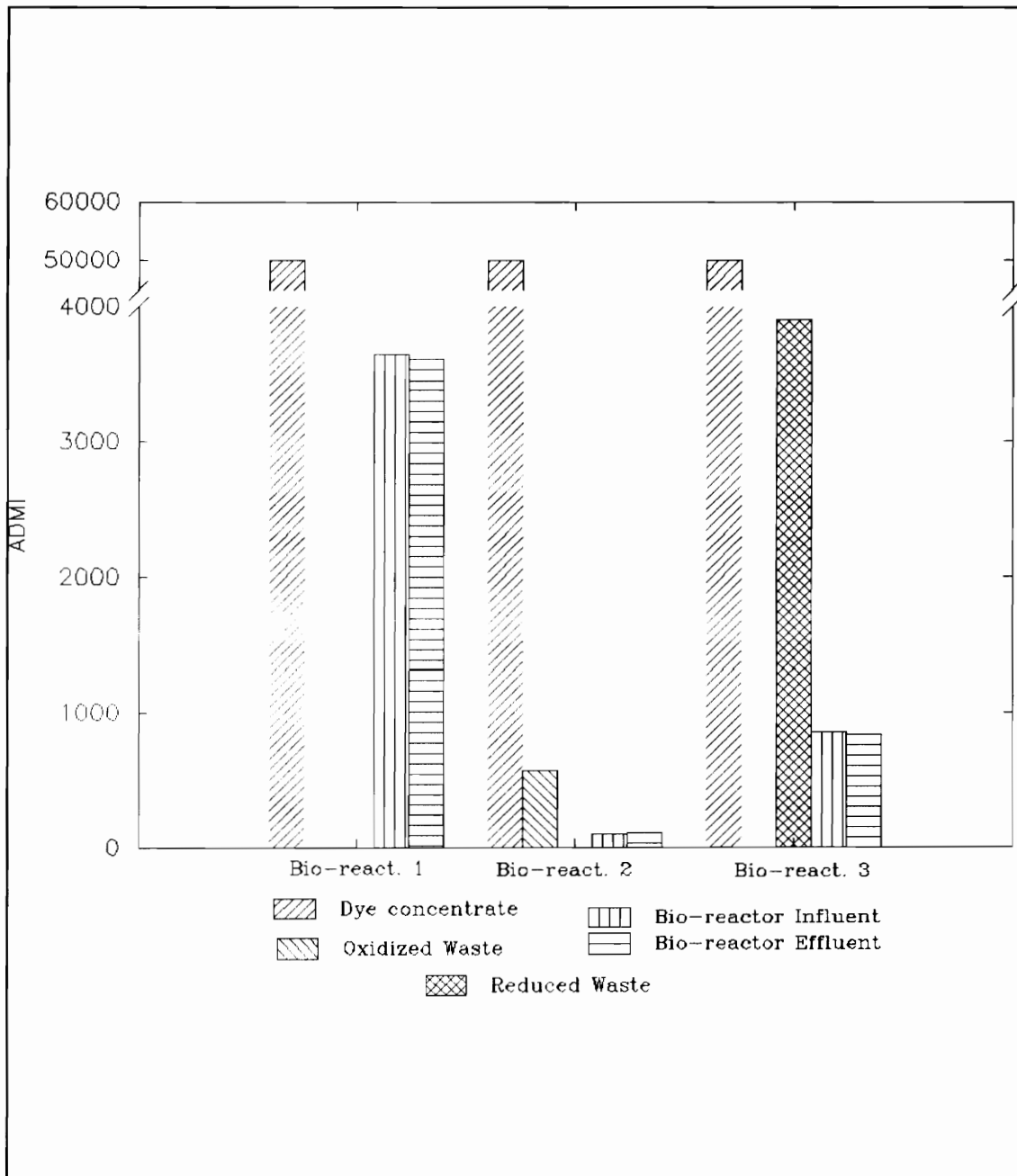


Figure 5.5.1: Effects of Oxidative and Reductive Pre-treatment on the Removal of Color From Concentrated Jet-dye Waste in Biological Reactors. Reactor 1 is the Control Reactor, Reactor 2 Represents the Aerobic Treatment of Oxidized Jet-dye Waste, and Reactor 3 Represents the Aerobic Treatment of Reduced Jet-dye Waste.

percent reduced jet-dye waste diluted 1:10 with tap water. The results show that oxidative pre-treatment removed 98.8% of the color in the pilot plant and had an over-all color removal after aerobic digestion in bio-reactor 2 of 96.8%.

The concentrated jet-dye waste that was reductively pre-treated had a minimal color value of 3900 ADMI which was a 92.2% reduction in color from the concentrated dye waste. The over-all color removal after aerobic digestion in bio-reactor 3 was 76.6%. The pilot plant effluent stream from reductive pre-treatment was a deep yellow color and upon dilution, prior to biological treatment, a significant amount of blue color returned and was not removed significantly in biological treatment resulting in the decrease in the percent color removal. Figure 5.3.2 shows the results of DOC removal after oxidative and reductive pretreatment and is intended as an indication of biological activity.

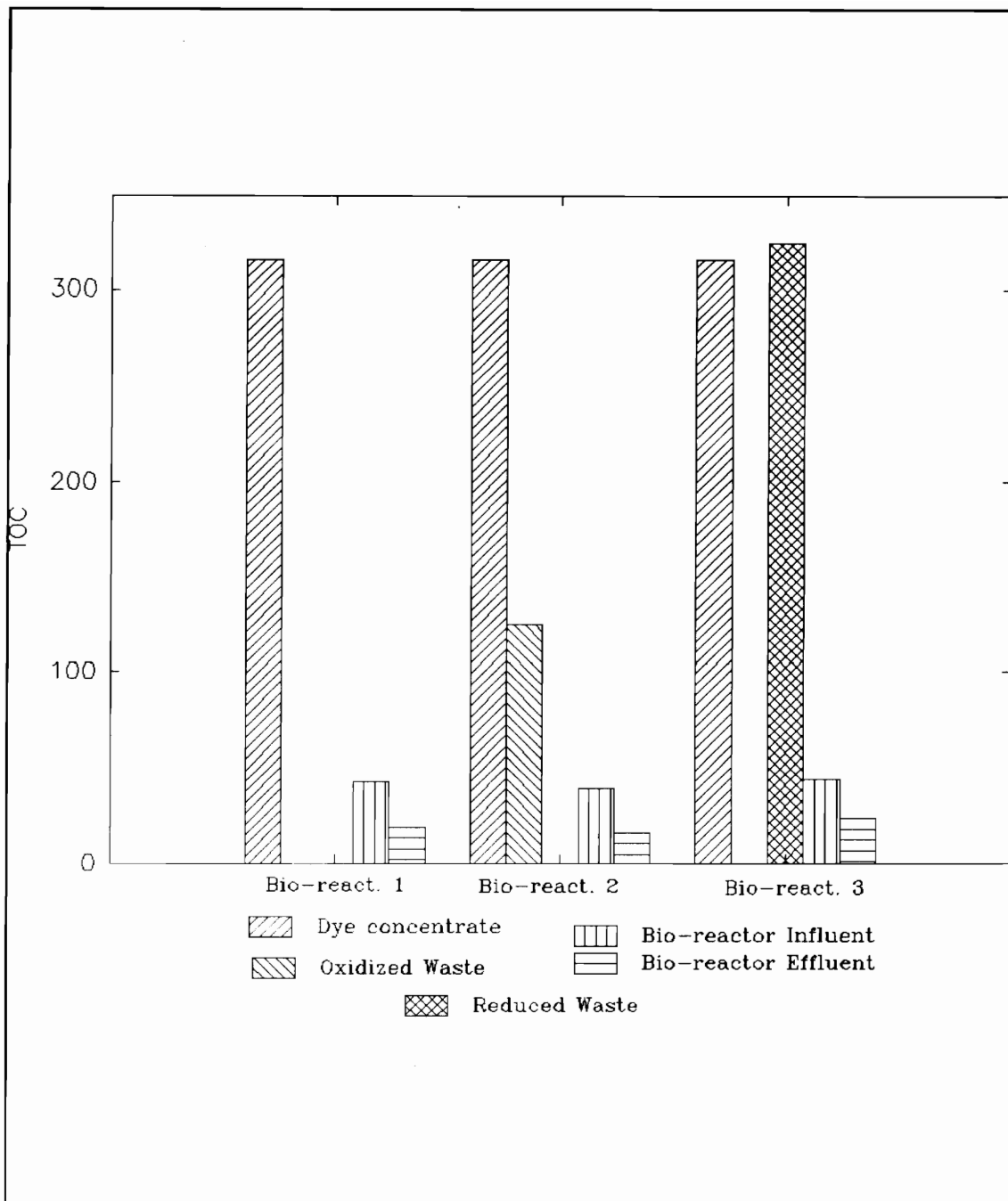


Figure 5.5.2: Effects of Oxidative and Reductive Pre-treatment on the Removal of DOC From Concentrated Jet-dye Waste in Biological Reactors. Reactor 1 is the Control Reactor, Reactor 2 Represents the Aerobic Treatment of Oxidized Jet-dye Waste, and Reactor 3 Represents the Aerobic Treatment of Reduced Jet-dye Waste.

5.6 On Site Pilot Plant Operation

The following results were obtained from on site Pilot Plant operations at Tultex in Martinsville, Va. Three different jet-dye concentrate formulas were tested in the pilot plant for color removal. They included Navy 106 jet-dye concentrate, an azo-based Red jet-dye concentrate, and a copper phthalocyanine based Ming Jade.

The Pilot Plant was transported to the textile mill and set up on site for continuous treatment of fresh jet-dye waste. The waste was pumped from the jet into a 55 gallon tank after the dye cycle was complete. Low pressure steam was used to keep the dye at the exit temperature of 60 °C. The pH of the dye waste was adjusted to 3.0 using 70 percent sulfuric acid and pilot plant operation was begun.

The initial ADMI values as read on the laboratory spectrophotometer were 48,432, 59,757, and 114,990 for the navy, red, and jade, respectively.

5.6.1 On Site Treatment of Navy 106

Figure 5.6.1 shows the three wavelengths vs time resulting from the treatment of Navy 106 jet-dye concentrate. The green wavelength was used as the controlled variable and the setpoint was set at 2800. Although this was not the lowest level attainable, it was

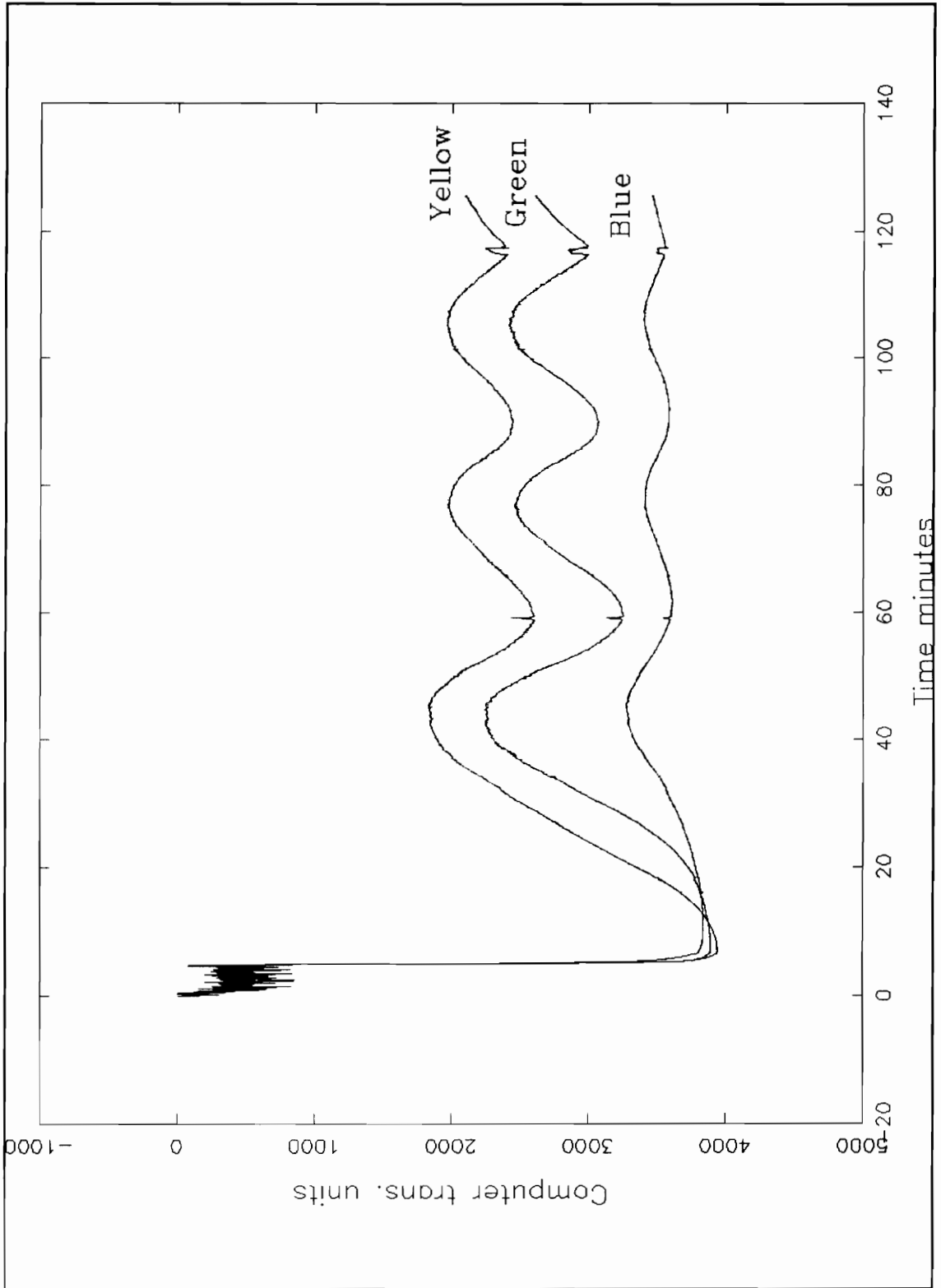


Figure 5.6.1 On site treatment of Navy 106 jet-dye

chosen to allow the pilot plant to reach a steady state sooner so that data for reagent consumption could be obtained. Although the waste stream from the Pilot Plant maintained a darkish gray-brown color, a sample taken from that stream which was quenched with sodium hydrosulfite and filtered using a syringe and a .22 μm showed that the color was effectively removed. The ADMI of the filtered sample was measured on the laboratory spectrophotometer and found to be 822 ADMI units which represents a 98% reduction in color.

Table 5.6.1 summarizes the cost involved in treating the Navy 106 jet-dye concentrate. Data for reagent consumption was obtained by recording the volume of reagent used during a fixed time period. Data on sulfuric acid consumption was

Table 5.6.1 Cost summary for treatment of Navy 106 jet-dye waste concentrate at Tultex. Prices are from Chemical Management Review June 7, 1993. The cost for H_2O_2 is from Tultex, Martinsville, Virginia.

Reagent	Consumption	Cost	Total
H_2SO_4 (70%)	39.5g/gal	\$0.0375/lb	\$3.25/1000gal
H_2O_2 (50%)	0.0084 lbs/gal	\$0.4/lb	\$3.37/1000gal
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.447g/gal	\$0.005/lb	\$0.0045/1000gal
			\$6.63/1000gal

based on the amount of 70% sulfuric acid required to reduce

the pH of the jet-dye concentrate to 3 in the 55 gallon feed tank. No data on the cost of heating and maintaining the feed tank at 60°C using the mill's steam was obtained.

5.6.2 On Site Treatment of Red

Figure 5.6.2 shows the results of the on site treatment of the red jet-dye concentrate. Once again the green wavelength was used as the control variable and the setpoint was set at 3000. A sample of the pilot plant waste stream was recovered and quenched with sodium hydrosulfite. The sample was then syringed through a 0.22 μm filter and the color was measured on the laboratory spectrophotometer. The color was found to be 5690 ADMI units which represents a 90% reduction in color. Table 5.6.2 shows the cost data involved in treating the Red jet-dye concentrate waste.

Table 5.6.2 Cost summary for treatment of an azo based Red jet-dye waste concentrate at Tultex. Prices are from Chemical Management Review June 7, 1993. The cost for H_2O_2 is from Tultex, Martinsville, Virginia.

Reagent	Consumption	Cost	Total
H_2SO_4 (70%)	21.27g/gal	\$0.0375/lb	\$1.76/1000gal
H_2O_2 (50%)	0.0132 lb/gal	\$0.4/lb	\$5.28/1000gal
FeSO_4	0.698 g/gal	\$0.005/g	\$0.007/1000gal
			\$7.05/1000gal

5.6.3 On Site Treatment of Ming Jade

Figure 5.6.3 shows the results of the treatment of the

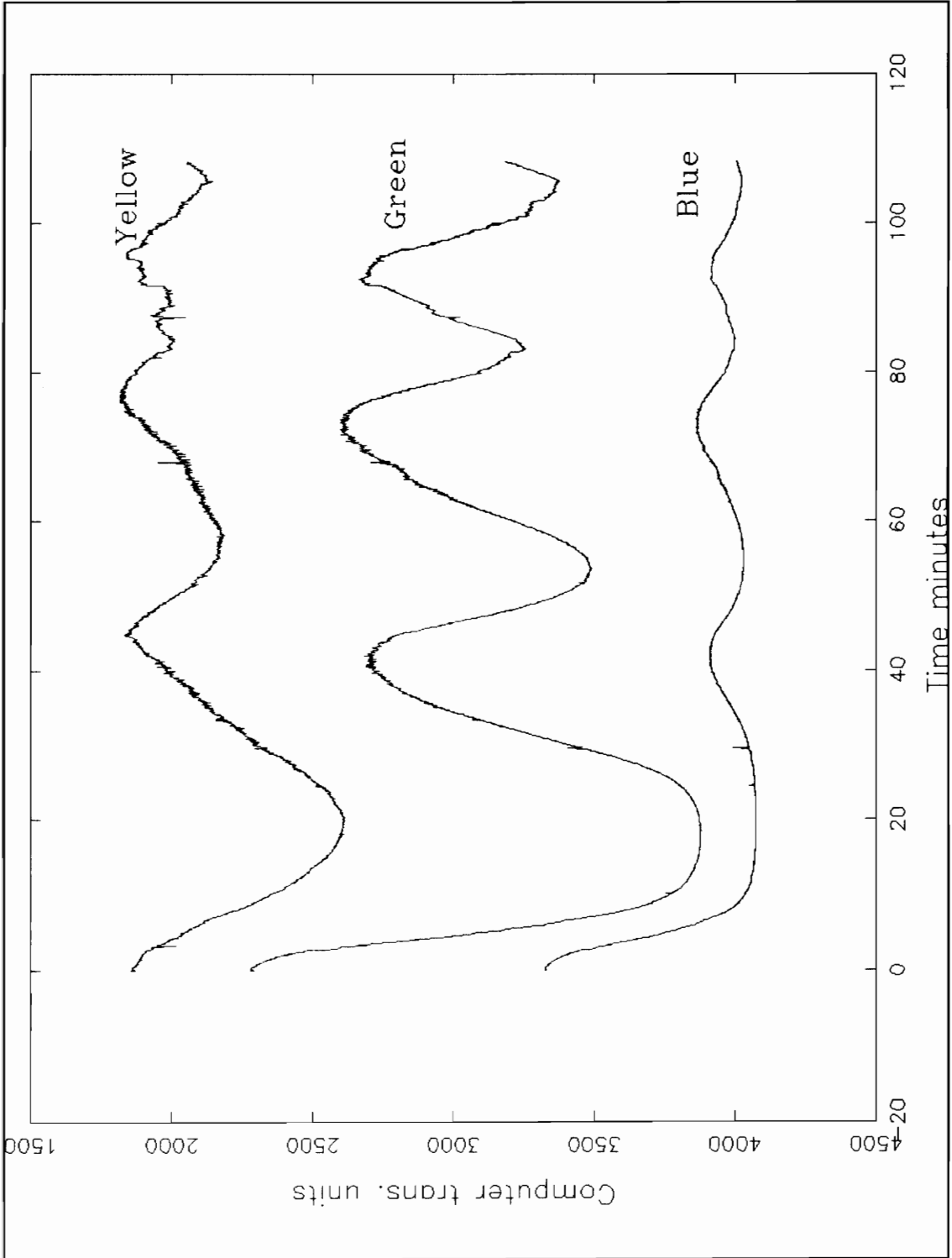


Figure 5.5.2 On site treatment of Red jet-dye waste

Ming Jade jet-dye concentrate waste. The run is shorter because not as much jet-dye waste was obtained for treatment.

It appeared at first that the pilot plant was not effectively treating the Ming Jade waste because there was very little color change between the feed line to the pilot was quenched and filtered it was obvious that most of the apparent color change between the pilot plant and the overflow waste stream. However, when a sample of the waste stream was quenched and filtered it was obvious that most of the apparent color could be attributed to solids. The color of the filtered sample was measured on the laboratory spectrophotometer and found to be 1320 ADMI units which represents a 99% reduction in color. Also, the copper concentration was measured for the treated filtered sample and for the untreated sample in a flame atomic absorption spectrophotometer. The untreated sample had a value of 19.22 ppm Cu while the treated and filtered sample had a concentration of 4.5 ppm, a 75% reduction in copper concentration.

Because the solids concentration was so high upon treatment in the pilot plant, the value for cost of operation shown in table 5.6.3 is not representative of the actual cost as the values for reagent consumed are meaningless.

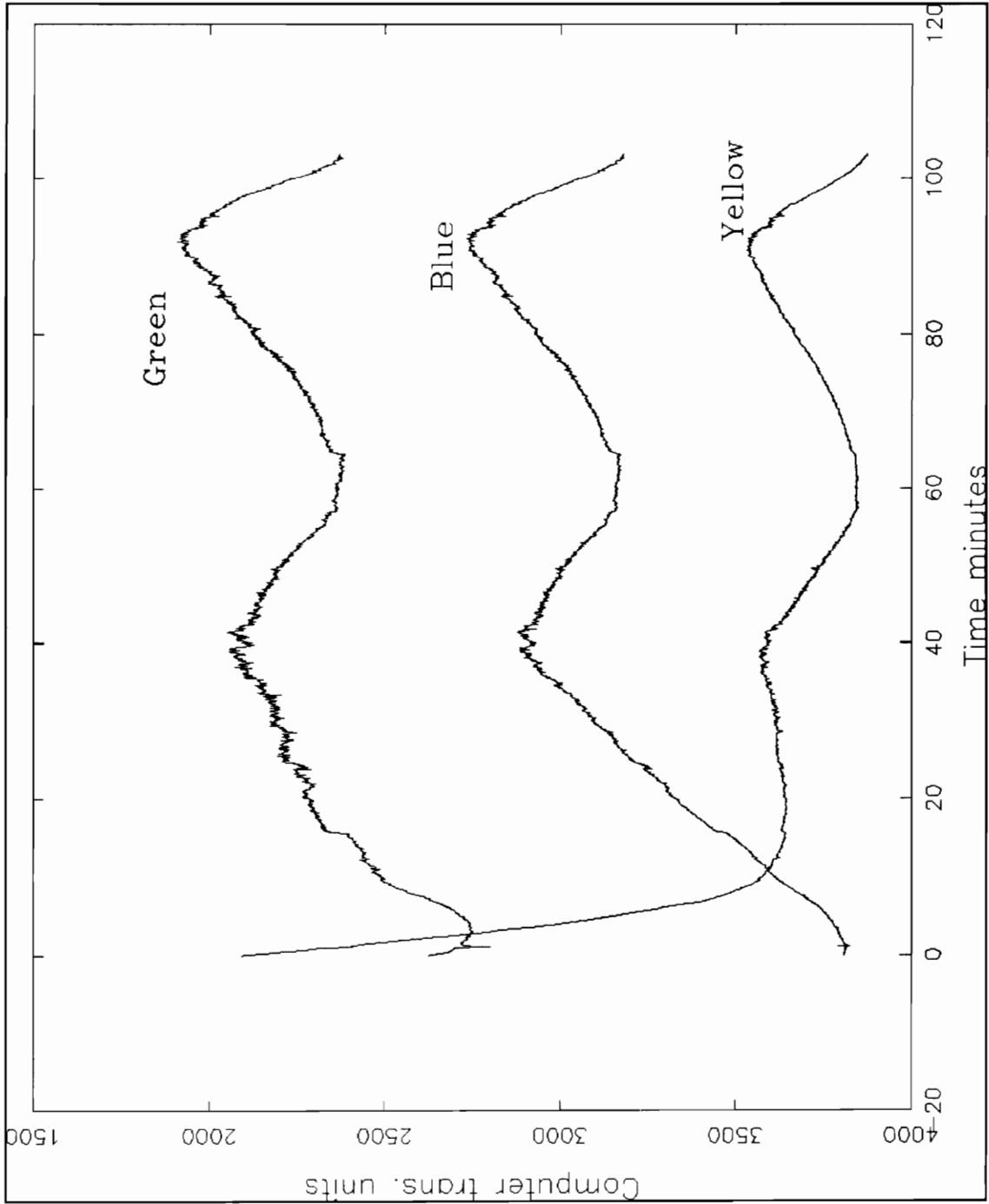


Figure 5.6.3 On site treatment of Ming Jade jet-dye waste

Table 5.6.3 Cost summary for treatment of a copper phthalocyanine containing Ming Jade jet-dye waste concentrate at Tultex. Prices are from Chemical Management Review June 7, 1993. The cost for H₂O₂ is from Tultex, Martinsville, Virginia.

Reagent	Consumption	Cost	Total
H ₂ SO ₄ (70%)	26.96g/gal	\$0.0375/lb	\$2.23/1000gal
H ₂ O ₂ (50%)	0.0102lb/gal	\$0.4/lb	\$5.28/1000gal
FeSO ₄	0.54g/gal	\$.005/lb	\$0.006/1000gal
			\$7.52/1000gal

Table 5.6.4 shows data on DOC and TSS for the three jet dye concentrates before and after treatment.

Table 5.6.4 Total Organic Carbon and Total Suspended Solids data for dyes treated on site at Tultex, Martinsville, Virginia.

Sample	DOC ppm	TSS g/l
Navy before treatment	515.2	0.988
Navy after treatment	500.0	1.5
Red before treatment	452.2	0.732
Red after treatment	368	1.766
Jade before treatment	432.2	0.575
Jade after treatment	350.4	1.505 g/L

6.0 CONCLUSIONS

1. Oxidation in the form of Fenton's chemistry is more effective at color removal on a continuous basis than reducing chemicals (thiourea dioxide or sodium hydrosulfite) in the pilot plant. Fenton's reagent achieved color removals of 98 and 90 percent for continuous treatment of jet-dye waste concentrates including Navy 106 and an azo based Red color, respectively, and 99 percent color removal for a phthalocyanine, Ming Jade. Also, color return upon aeration was noted in samples treated with reduction chemistry so that color removal after aeration for reduction chemistry was 76.6%.

2. DOC reduction of 50 to 55 percent in continuously operated biological reactors indicated that the reaction products of oxidative and reductive chemistry of Navy 106 jet-dye concentrate did not increase toxicity to biological activity.

3. Color control of oxidative and reductive pretreatment of reactive dye waste water streams is practical. ADMI color value control is possible on those waste water streams with an initial color value below 3000 ADMI. Above 3000

ADMI, transmittance at a single wave length is a viable method of control with the best wavelength being dependent on the color of the waste being treated.

4. Oxidative treatment decreased soluble copper concentration in a copper containing waste stream by 76 percent from 19.2 ppm to 4.5 ppm, thereby increasing the total suspended solids in that waste by 62 percent.

5. Color removal of 98 percent was attained for Navy 106 jet-dye waste concentrate using Fenton's chemistry at an approximate chemical cost of \$6.60 per 1000 gallons.

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APPENDIX 1

SUBROUTINE FOR PID CONTROLS

PIDcontrols:

```
ON KEY(2) GOSUB newSETPOINT: KEY(2) ON
ON KEY(4) GOSUB PARAMETERSinput: KEY(4) ON
ON KEY(11) GOSUB changeSETPOINT1: KEY(11) ON
ON KEY(14) GOSUB changeSETPOINT2: KEY(14) ON
```

DO

```
clearKEY$ = INKEY$
CHANNEL0% = 0: CALL INADC12S(CHANNEL0%, Bvalue%)
CHANNEL1% = 1: CALL INADC12S(CHANNEL1%, Gvalue%)
CHANNEL2% = 2: CALL INADC12S(CHANNEL2%, Yvalue%)
CHANNEL3% = 3: CALL INADC12S(CHANNEL3%, Lvalue%)
Bintensity = Bvalue%
Gintensity = Gvalue%
Yintensity = Yvalue%
GOSUB calculation
ADMIfilterV = .7 * ADMIvalue + .3 * lastADMIfilterV
lastADMIfilterV = ADMIfilterV
ERRORterm = SETPOINT - ADMIfilterV
IF VALUE% > 1 AND VALUE% < 255 THEN
  ERRORt = ERRORt + ERRORterm
END IF
INTEGRALterm = KI * ERRORt * sampleINTERVAL
DIFFERENCEterm = (ERRORterm + 3 * ET1 - 3 * ET2 - ET3)
```

/ 6

```
ET3 = ET2: ET2 = ET1: ET1 = ERRORterm
DIFFERENTIALterm = KD / sampleINTERVAL *
DIFFERENCEterm
PID = KC * (ERRORterm + INTEGRALterm +
DIFFERENTIALterm)
IF PID < 0 THEN PID = 0
IF PID > 255 THEN PID = 255
VALUE% = (1 - PIDfilterC) * PID + PIDfilterC *
lastPIDfilterV
lastPIDfilterV = VALUE%
VALUE0% = 255 - VALUE%
CHANNEL% = 0: CALL OUTDAC8S(CHANNEL%, VALUE0%)
LOOP
```

APPENDIX 2

SUBROUTINE FOR ADMI CALCULATION

calculation:

```

constA = 30.6459571#
constB = -97.17236680000001#
constC = 292.9487603#
constD = -608.8463882999999#
constE = 870.8293729#
constF = -840.7901111#
constG = 521.727698#
constH = -187.6371487#
constI = 29.7284594#

```

```

TX = 100 - .0244 * Bintensity%      'blue channel   =
Barray%(I)

```

```

TY = 100 - .0244 * Gintensity%      'green channel  =
Garray%(I)

```

```

TZ = 100 - .0244 * Yintensity%      'yellow channel =
Yarray%(I)

```

```

IF TX < 0 THEN TX = 0
IF TX > 100 THEN TX = 100
IF TY < 0 THEN TY = 0
IF TY > 100 THEN TY = 100
IF TZ < 0 THEN TZ = 0
IF TZ > 100 THEN TZ = 100

```

```

XS = TX * .1899 + TZ * .791

```

```

XSS = SQR(XS / 98.06)

```

```

VXS = ABS(constA * XSS + constB * XSS ^ 2 + constC * XSS
^ 3 + constD * XSS ^ 4 + constE * XSS ^ 5 + constF * XSS ^ 6
+ constG * XSS ^ 7 + constH * XSS ^ 8 + constI * XSS ^ 9 -
1.5323707#)

```

```

YS = TY

```

```

YSS = SQR(YS / 100)

```

```

VYS = ABS(constA * YSS + constB * YSS ^ 2 + constC * YSS
^ 3 + constD * YSS ^ 4 + constE * YSS ^ 5 + constF * YSS ^ 6
+ constG * YSS ^ 7 + constH * YSS ^ 8 + constI * YSS ^ 9 -
1.5323707#)

```

```

ZS = TX * 1.1835

```

```

ZSS = SQR(ZS / 118.11)

```

```

VZS = ABS(constA * ZSS + constB * ZSS ^ 2 + constC * ZSS
^ 3 + constD * ZSS ^ 4 + constE * ZSS ^ 5 + constF * ZSS ^ 6
+ constG * ZSS ^ 7 + constH * ZSS ^ 8 + constI * ZSS ^ 9 -
1.5323707#)

```

```

DE = SQR((.23 * (9.902 - VYS)) ^ 2 + (.002 - VXS + VYS) ^

```

```
2 + (.4 * (-.08 - VYS + VZS)) ^ 2)
  FF = 1203.26 + (233.886 * DE)
  ADMIvalue = DE * FF/1.0
```

```
RETURN
```

VITA

Vaneaton Price, III, the son of Vaneaton and Janet Wyse Price, Jr. was born on May 10, 1967, in Greenville, South Carolina. He has two sisters: Lisa Price Doggett, and Sarah Adella Wyse Price.

Vandy attended high school in Aiken, South Carolina and graduated in 1985. He was awarded a Bachelor of Science degree in Chemical Engineering from the University of South Carolina, Columbia, South Carolina in May, 1991. He entered Virginia Polytechnic Institute and State University in the fall of 1991 to pursue a Master's degree in Chemical Engineering. That degree was completed in September of 1993.

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Vandy Price