Investigation of Color Removal by Chemical Oxidation for Three Reactive Textile Dyes and Spent Textile Dye Wastewater

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ABSTRACT

This research investigated the efficacy of chlorine dioxide (ClO_2), ultraviolet (UV) irradiation, UV in combination with chlorine dioxide (UV/ClO_2), and UV in combination with hydrogen peroxide (UV/H_2O_2) for decolorizing three reactive azo dyes (sultan red, indigo blue and cypress green) and treated textile-manufacturing wastewater. The objective was to determine the best treatment for reducing color to the Virginia Pollutant Discharge Elimination System (VPDES) permit level of 300 American Dye Manufacturers Institute (ADMI) units. The effects of the three chemical oxidation treatments provided color reduction for all three dyes. The results suggested UV/H_2O_2 and UV/ClO_2 treatments provided maximum color reduction of the red and blue dyes, and UV/H_2O_2 was the most effective for maximum reduction of the green dye.

A research goal was to provide predictive models of the wastewater effluent for the treatment processes, including the UV exposure time required to reach the 300 ADMI permit value and the effective ClO_2 dose necessary to achieve the 300 units. The results of the investigations regarding the effluent indicated that UV/H_2O_2 and UV/ClO_2 (5 mg/L) provided reduction to 300 units in less than 10 minutes UV exposure when the initial effluent color was less than 500 ADMI units. Without the addition of oxidant, contact times longer than 10 minutes were required for UV to decolorize these effluents to 300 ADMI units. Chlorine dioxide dosages between 10 and 30 mg/L both with and without UV irradiation achieved the same results.

ACKNOWLEDGEMENTS

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CHAPTER 1: INTRODUCTION

The treatment of spent textile dyeing wastewater by traditional methods has proven to be ineffective for many wastewater treatment facilities. Conventional activated sludge treatment is the typical treatment method used today, though activated sludge was not originally intended for treatment of industrial waste, particularly textile wastes containing dyes and surfactants (Yang et al., 1998).   Additional textile treatment methods; such as combinations of biological, physical, and chemical methods including coagulation/flocculation, electrochemical oxidation and activated carbon adsorption, reverse osmosis, ozone and oxidative/reductive chemical processes; are all techniques that can be used for treating textile wastewater. Chemical oxidation technologies, however, seem to have the most potential for future use in the textile wastewater industry (Yang et al., 1998). Treatment of spent dye effluent by a process utilizing ultraviolet light (UV) and a strong oxidant is an effective alternative for color removal. Hydrogen peroxide (H_2O_2) is the most common oxidant used in combination with UV. Chlorine dioxide (ClO_2) also has oxidative capabilities for color removal. In addition, UV in combination with ClO_2 is a possible treatment for the reduction of colored effluent from textile dyeing facilities.

   The wastewater used in this study was final clarifier effluent from the Lower Smith Wastewater Treatment plant. Nearly 85 percent of the plant's influent originates from Bassett-Walker, a textile dyeing plant in Martinsville, Virginia. The plant treats approximately 4 million gallons per day and discharges into the Smith River. The plant's Virginia Pollutant Discharge Elimination System (VPDES) permit limits effluent color levels to 300 American Dye Manufacturers Institute (ADMI) color units. During this project, color levels in samples of the Lower Smith WWTP final clarifier effluent delivered to the Virginia Tech Environmental Laboratories where this study was conducted were consistently greater than 300 ADMI color units.

The objectives of this research project were: (1) to evaluate the effectiveness of three chemical oxidants [UV in combination with H_2O_2 (UV/H_2O_2), UV in combination with ClO_2 (UV/ClO_2) and ClO_2] for reducing ADMI color of three reactive azo dye solutions used in textile-dyeing operations and in final clarifier effluents from the Lower Smith Wastewater Treatment Plant (WWTP) and (2) to develop relationships and

predictive models for color reduction utilizing UV/H_2O_2, UV/ClO_2 and ClO_2. The desired outcome of this project was a recommendation to the WWTP regarding the most effective and efficient oxidation technology for use at the Lower Smith facility.

CHAPTER 2: LITERATURE REVIEW

Introduction

The treatment of spent dye wastewater effluent is a growing concern for the textile industry because of aesthetic conditions, as well as ecotoxicological issues regarding colored rinsing and process wastewater and the impact of that wastewater on the receiving streams. As regulations become more stringent, the effectiveness and cost of treatment processes becomes more significant. Conventional biological treatment can be ineffective for color removal, but chemical oxidative processes seem to provide an opportunity for future use in industrial wastewater. Examples of potentially effective chemical oxidants include hydrogen peroxide (H_2O_2), ozone (O_3), chlorine dioxide (ClO_2), ultraviolet irradiation following ClO_2 (UV/ClO_2), and H_2O_2/ultrasonication. Advanced oxidation processes (AOPs) include UV/H_2O_2, UV/O_3, O_3/H_2O_2, Fenton's reagent, and the wet-air oxidation process. The concept behind an AOP is that exposure of a strong oxidizing agent exposed to UV light generates hydroxyl free radicals (Ince and Gonenc, 1997), which are even stronger oxidants.

Color determination is based on the American Dye Manufacturers Institute (ADMI) tristimulus method for measuring "true" color, which is the color of a solution after turbidity has been removed (*Standard Methods*, 1995). While it is not usually specified as the required analytical method in National Pollutant Discharge Elimination Permits (NPDES), the ADMI method is considered to be the best available method for color analysis of wastewater (Barnhart, 1993).

Two other analyses commonly used for the analysis of wastewaters are total organic carbon (TOC) and chemical oxygen demand (COD), neither of which is specific for determining color reduction. A reduction in ADMI color level following the addition of an oxidant can occur either by degradation or alteration of the conjugated system of the dyes with the potential to create even more toxic chemicals in the effluent (Yang et al., 1998). The toxicity associated with color degradation will prove to be an important factor in the choice between oxidative treatments.

Previous research into the decolorization of dyes and spent textile dye effluent by chemical oxidation appeared to focus on specific dye decomposition (rates and kinetic

models), initial dye concentrations, hydrogen peroxide dosing concentrations, and UV intensity and contact times as important factors affecting color reduction.

Textile Dye Characteristics

Numerous structures of dyes exist. All are assigned a Color Index classification number. According to Shore (1990), most of the dyes and pigments in the Color Index are placed in one of the 25 structural classes according to their chemical type. Azo dyes, the largest class, are subdivided into four sections. Classification of the four sections depends on the number of azo groups within the dye molecule. The depth of color is related to the molecular structure of the dyes, which is related to the chromophores (-N=N- or >C=O) involved within the structure. In addition, visible and the UV irradiation electron transfer effects at varying wavelengths on the dye structures have been observed, supporting tautometic capabilities of the dye molecules (Shore 1990). An oscillation between the double and single bonds occurs along the conjugated molecular chain; therefore, as the chain becomes longer, the vibration rate becomes slower resulting in a slower kinetic degradation rate (Shore 1990).

Shore (1990) stated that the reactive dye structures are 95 percent azo dyes, except for some bright blues and greens. Reactive dyes react with a substrate to form a covalent dye-substrate bond, where a substance such as cellulose acts as the substrate (Shore 1990):

$$D\text{-}CH=CH_2 + OH\text{-}Cellulose \rightarrow D\text{-}CH_2CH_2O\text{-}Cellulose \qquad (1)$$
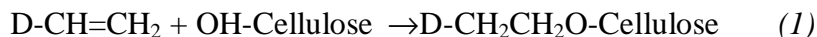
Where D = reactive dye structure

Dye fixation onto fibers depends on the dye property known as fastness, which describes its ability to bond to the material. Reactive dyes are very soluble in water and, therefore, are poorly adsorbed (Churchley and Upton, 1997). Any additional chemicals that are added during the dye application, such as salts or detergents, will affect the wastewater and subsequently the treatment process.

Ultraviolet Lamp and Reactor Characteristics

Ultraviolet light is an electromagnetic radiation spread between the wavelengths 100 nm and 400 nm. Most UV lamps used in wastewater treatments perform at a wavelength of 254 nm. A mercury vapor lamp is the most common UV light source (Hanzon and Vigilia, 1999). The lamp is filled with mercury vapor at different pressures,

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and excitation of the mercury atoms causes the emission of UV light. Typically, UV lamps are installed inside quartz sleeves and when implemented at a plant are usually placed in banks with the lamps evenly spaced either vertically or horizontally. The UV dosage applied to a wastewater is determined by the intensity of the UV radiation and the contact time involved and is commonly expressed in milliwatt-seconds per square centimeter (mW-sec/cm^2). Ultraviolet lamps are classified as either low, medium or high-pressure units. The intensity is a function of the lamp array's geometry as well as the UV transmittance of the wastewater. The literature investigated for this study dealt with low, medium and high-pressure lamps. The UV chambers vary in size and were configured by either vertical or horizontal lamp placement. Other factors that limit the effectiveness of the system are the wattage and output. The UV lamps described in the literature varied from 14 watts to 35 watts for a low pressure lamp (Shu et al., 1994; Namboodri and Walsh, 1996; Liao et al., 2000) and 200 and 300 watts for a medium pressure lamps (Glaze 1993; Yang et al., 1998).

UV/H$_2$O$_2$ and Factors that affect Efficiency

When a water or wastewater containing H$_2$O$_2$ is irradiated with UV, hydroxyl radicals are formed. The mechanism is represented by the following equation:

$$H_2O_2 + hv - 2OH\bullet \qquad\qquad (2)$$

The ultraviolet light, represented as *hv*, causes the dissociation of the H$_2$O$_2$ into two hydroxyl radicals (OH•). The hydroxyl radicals are strong oxidants that can readily oxidize organic compounds (Yang et al., 1998). The radicals degrade organic compounds by separating protons to yield organic radical compounds, which lead to either an abstraction of hydrogen atoms or addition to double bonds (Sundstrom et al., 1989).

Factors that affect the color removal by H$_2$O$_2$ and UV include: initial color intensity, H$_2$O$_2$ concentration, UV-irradiation time and intensity, pH and alkalinity. Studies have shown that the variation of initial azo dye concentration produces a variation in kinetics (Ince and Gonenc, 1997; Shu et al. 1994). In one study by Ince and Gonenc (1997), the decolorization rate constant for Reactive Black 5 increased with lower dye concentrations. Another study indicated that the more concentrated the Reactive Black 5 dye was, the slower the rate of degradation became. This was thought to be caused by the large five aromatic ring dye structure (Ince and Gonenc, 1997). Yang

et al. (1998) also investigated the Reactive Black 5 dye and discovered that as the dye concentration increased the time required to achieve identical color removal also increased, regardless of radiation intensities.

Hydrogen peroxide concentration has varying affects on dyes. It appears that an increase in peroxide will increase the overall efficiency of the oxidative system. However, it has also been shown that decolorization increases when the H_2O_2 concentration increases, but only to some point beyond which no further decolorization occurs (Ince and Gonenc, 1997). At increased concentrations H_2O_2peroxide concentrations, the excess can react with hydroxyl radicals already in solution to form water and oxygen (Ince and Gonenc, 1997; Yang et al., 1998).

Determination of the optimal H_2O_2 dosage for a particular treatment requires preliminary evaluation of each dye. If the dye structure is known, the theoretical H_2O_2 concentration necessary for color removal can be estimated. A balanced chemical equation involving the decomposition of the dye molecule into its theoretical decomposition by-products yields the required stoichiometric H_2O_2 concentration (Yang et al., 1998).

Like H_2O_2, UV radiation time and intensity must be determined separately for the various dyes. Yang et al. (1998) suggested that lamp pressures and radiation intensities for UV units used in treatment plant use should be based on a priority ranking of variables that are most important to the plant (cost, color removal, TOC or COD removal). He noted that color reduction is not significantly improved by use of the high-intensity lamp when dye concentrations are high (Yang et al., 1998). Lower dye concentrations, however, respond by increased decolorization when a high intensity lamp is used (Shu et al., 1994; Yang et al., 1998). Contact times required for each treatment are functions of the UV irradiation intensity, and the relationship between H_2O_2 and rate of decolorization will inevitably change the extent of color reduction. In addition, the time required for decolorization will also be a function of UV intensity. Contact times required to decolorize various wastewaters in several studies cited in the literature ranged from 30 seconds to 1 hour.

The pH and alkalinity of the dye effluent solutions can significantly affect the color reduction and the rate of reduction. According to Shu et al. (1994), dye

decomposition rates under UV/H_2O_2 decreased with increasing pH. In addition, it was discovered that H_2O_2 generally decomposed to water and oxygen rather than forming hydroxyl radicals under alkaline conditions, resulting in lower rates of decolorization of azo dyes at higher pH values.   Decolorization by UV/H_2O_2 was most effective at a neutral pH (Namboodri and Walsh, 1996; Ince and Gonenc, 1997; Shu et al., 1994;).

Hydrogen Peroxide Effects on Color Removal

Hydrogen peroxide alone produces hydroxyl radicals when it is added to water or wastewater; however, the rate of decolorization by H_2O_2 is extremely slow for many dyes (Ince and Gonenc, 1997). All of the literature investigated stated that color reduction was negligible (Ince and Gonenc, 1997; Liao et al., 2000; Namboodri and Walsh, 1996; Shu et al., 1994)

UV Effects on Color Removal

Ultraviolet light at 254 nm can degrade color. Limitations of UV as a treatment for color reduction appear to be lamp technology; the need is increased photon production to provide high enough energy to destroy organic material at a low cost. High-efficiency lamps that excite protons to high energy levels are required for effective degradation of organic compounds (Gregor 1992). The literature indicated both successes and failures of UV alone for decolorizing wastewaters. With the exception of Reactive Black 5, significant decolorization of reactive dyes (concentrations ranging from 100-300 mg/L) was achieved at various UV intensities and contact times (Gregor 1992; Namboodri and Walsh, 1996). One study reported a textile wastewater color (420 ADMI units) was reduced nearly 20 percent after 40 minutes exposure to UV generated with a 14 watt lamp (Liao et al. 2000). In two other studies, decolorization of Remazol Black 5 (40 mg/L) and Acid Red 1 and Yellow 23 (20 mg/L) solutions was negligible when they were exposed to UV. (Ince and Gonenc, 1997; Shu et al., 1994)

Chlorine Dioxide

Chlorine dioxide is commonly used as a disinfectant and oxidant during drinking water treatment and as a bleaching treatment in pulp and paper industries. As an oxidant, it readily attacks reducing substances, such as organic materials, primarily by a one-electron pathway (AWWA 1994).

$$ClO_2 + e^- \Leftrightarrow ClO_2^- \qquad\qquad (3)$$

No literature describing ClO_2 as a chemical oxidative process for decolorization of dye effluents could be found.

     Chlorine dioxide exists as a stable, nonmetallic, monomeric free radical (AWWA 1994) and is highly soluble in water. Because it does not hydrolyze in water, ClO_2 exists as a dissolved gas as long as the pH remains between 2 and 10. Once the ClO_2 has reacted with organic matter, chlorite (ClO_2^-) and chlorate (ClO_3^-) by-products are formed. Drinking water regulations specify a ClO_2 maximum residual disinfectant level of 0.8 mg/L and a ClO_2^- maximum contaminant level of 1.0 mg/L. Before these regulations were implemented, the recommended sum of ClO_2, ClO_2^- and ClO_3^- concentrations in drinking water was 1.0 mg/L (AWWA 1994). Reformation of ClO_2 is possible when ClO_2^- is in the presence of chorine; ClO_2^- is oxidized and regenerates ClO_2 (AWWA 1994, Gordon and Bubnis, 1999).

CHAPTER 3: MATERIALS AND METHODS

Introduction

Described in this chapter are the materials and methods used during this research, including the ADMI method of ClO_2 generation and analysis by amperometric titration, the UV unit and procedures used to dose the dye and effluent solutions with H_2O_2 and ClO_2. The compilation of the varying H_2O_2 and ClO_2 dosages and the varying UV contact times for the red, blue and green dyes and effluents make up the experimental matrix.

Chemicals

The following chemicals were used during the course of this project: 50 percent hydrogen peroxide (CAS# 7722-84-1; Fischer Scientific, Springfield, NJ), potassium iodide (CAS# 7681-11-0; Fischer Scientific), platinum cobalt chloride (CAS# 16921-30-5, CAS# 7646-79-9, CAS# 7647-01-01; Fischer Scientific), sodium chlorite cartridges (CAS # 7775-09-9; Composite Particles, Allentown, PA), Nitrogen gas (CAS# 7727-37-9; Holox, Norcross, GA), chlorine/nitrogen gas (CAS# 7728-50-5; Air Products, Tamaqua, PA), 0.00564 N phenylarsine oxide (CAS# 637-03-6; Fischer Scientific), 0.1 N sodium thiosulfate (CAS# 10102-17-7; Fischer Scientific), and potassium persulfate (CAS# 7727-21-1; Fischer Scientific).

Glassware

All glassware was washed with standard dishwashing detergent (Sparkleen, Fisher Scientific), rinsed with tap water and copious amounts of Nanopure water, Type I - Standard Methods, (Barnstead, Inc., Dubuque, IA) and then allowed to dry. After the pipettes were rinsed thoroughly with Nanopure water, they were checked regularly for proper draining. Amber-tinted volumetric flasks (Fischer Scientific # 55640) were cleaned as previously stated and used in the preparation of all chlorine dioxide (ClO_2) standards. Clean Pyrex gas washing bottles (# 31760-BO)) were used in ClO_2 generation.

Dye Solutions

The dye solutions were prepared by pipetting a known amount of dye into a 1-liter (L) Erlenmeyer flask and diluting it with a known amount of tap water. Three reactive concentrated azo dyes (Sultan Red, Indigo Blue, and Cypress Green) were obtained from Bassett Walker in Henry County, Virginia. The Classification number was not given for

any of the dyes. Bassett Walker uses a mix of several classifications. The flasks were covered with aluminum foil to avoid degradation by the laboratory fluorescent lights.

Before the oxidation experiments could be performed, it was necessary to choose the appropriate concentration of dye solutions. Since the effluent ADMI values ranged between 300 and 800 ADMI units, an initial 800 ADMI value seemed the most appropriate for experimentation. Dye solutions of 800 ADMI color units were prepared for all experiments and a 1600 ADMI unit solution was prepared for red dye experiments.

Wastewater Characteristics

The wastewater samples used in this study were effuents from the final clarifier at the Lower Smith WWTP in Axton, Virginia. At the time of this study, the effluent was dosed with polymer to aid in color reduction. Analytical data describing the daily clarifier-effluent quality was not available, but the following are representative values based either on analyses at the Lower Smith WWTP laboratory or in the Virginia Tech Environmental Laboratories: pH = 7.6, color = 450 ADMI units, TOC = 160 mg/L. The effluent was a murky, orange/maroon color and relatively free of particulate matter.

ADMI Spectrophotometric Color Analysis Method

The ADMI Tristimulus method (2120 D) described in *Standard Methods for the Examination of Water and Wastewater* (1995) was performed on a Genesis Spectrophotometer Model 5 (Spectronic Instruments (Rochester, NY)). The ADMI values were automatically calculated by a computer program written by Mr. Andrew Lash (Martinsville, Virginia). Standards of 100, 200, 300, 400 and 500 ADMI units were prepared from a commercial concentrated platinum cobalt color solution and analyzed to verify the instrument calibration and develop a calibration curve. The r^2 value associated with this curve was 0.9999. Periodically, a new standard curve was developed and verified. The Virginia Department of Environmental Quality accepts the ADMI color values and the computer calculations.

Chlorine Dioxide Generation

Chlorine dioxide stock solutions used during this study were generated from sodium chlorite ($NaClO_2$) by two methods, a wet-chemical method and the other a dry-chemical method with potassium persulfate according to the following reaction:

$$2NaClO_2 + K_2S_2O_8 \rightarrow 2ClO_{2(g)} + 2K_2SO_4 \qquad (4)$$
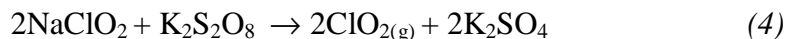
The reaction was carried out in clean Pyrex gas washing bottles equipped with fritted disks. The production set up was similar to that shown in *Standard Methods for the Examination of Water and Wastewater* (1995). Finally, gas exiting the ClO_2 trap was passed through a solution of KI to react with any untrapped oxidant. All gas- trapping vessels and cold water traps were covered in aluminum foil to prevent photodecomposition of the ClO_2.

Other ClO_2 stock solutions were prepared by a dry-chemical method with a laboratory-scale ClO_2 generator provided by CDG Technologies, Inc. in Allentown, Pennsylvania. The process involved passing a humidified stream of chlorine gas diluted in nitrogen gas through packed columns of Na_2ClO_2. The effluent ClO_2 stream was then passed through chilled distilled water traps and a final KI trap as previously described. Each pound of chlorine gas produces 1.9 pounds of ClO_2, and the stock solutions produced by this method were more concentrated than those generated by the wet-chemical method. Chlorine dioxide solution concentrations used during this study ranged from 700 to 1500 mg/L.

The stock solution concentrations were determined spectrophotometrically according to Beer's law. The absorbance of a diluted stock solution (usually 1:10 or 1:20 in distilled, deionized water) was determined at 360 nanometers (nm). The spectrophotometer was zeroed with deionized water and the concentration calculated from Beer's Law according to the following:

$$a = \varepsilon bc \qquad\qquad (5)$$

Where: a = absorbance, nm

              ε = ClO_2 extinction coefficient, 1225 $M^{-1}cm^{-1}$

              b = cuvette path length, centimeters

              c = ClO_2 concentration, moles/L

Chlorine Dioxide Analysis by Amperometric Titration

The titrator was a Fischer & Porter (Capital Controls, Inc., Colmar, PA) Series 17T2000, which uses a platinum measuring electrode and a platinum counter electrode to generate a current as a function of the oxidant concentration. The procedure performed in the amperometric titration was a modified version of Standard Method 4500-E-Chlorine Dioxide (Standard Methods, 1998).

Sample Preservation

Lower Smith wastewater effluent samples were 24-hour composite samples collected in plastic containers and delivered to Virginia Tech seven dates from March 29 through May 17, 1999. Samples taken after May 17, 1999 were grab samples. All samples were taken immediately before the point of chlorination at the treatment facility. Samples were refrigerated at 4°C. Prior to treatment, the samples were warmed to room temperature (24°C –27°C).

Prior to ClO$_2$ treatment, the samples were adjusted to pH 7 with HCl and filtered through 0.45 micrometer (μm) glass-fiber filters. The dosing vessel was treated as a continuously stirred tank reactor (CSTR), and samples were taken at intervals for evaluation of color reduction.

Ultraviolet Lamp Unit

The UV irradiation used in this study was a 31 cm (1.2 in) horizontal bench-scale reactor consisting of a 15 mm (0.6 in) diameter quartz tube and a low pressure mercury vapor lamp with a power of 14 watts emits ultraviolet irradiation at a wavelength of 254 nanometers (nm). The lamp has a base face length of 29 cm and an arc length of 21 cm and the output was approximately >35μwatts-sec/cm^2 at 1 meter. Solutions Consultants, Inc. (Jasper, Georgia) supplied the UV unit. The UV contact times were calculated on the basis of the pumping rates. Diagrams of the UV/H$_2$O$_2$ and UV/ClO$_2$ bench scale set up can be found in the Appendix (Figures A1 and A2).

Treatment by ClO$_2$

Dye solutions of 1-liter were dosed with 3 and 5 mg/L ClO$_2$ in foil-covered Erlenmeyer flasks. Effluent samples were adjusted to pH 7 with HCl and filtered through a 0.45 micrometer (μm) glass fiber filter. Varying concentrations (ranging from 5 mg/L to 30 mg/L) of ClO$_2$ were added to the effluent and ADMI color measurements were performed at varying exposure periods, extending to 60 minutes.

Treatment by UV/ClO$_2$

Chlorine dioxide will readily react with organic substances in the dye solutions and the effluent; therefore, it was imperative that a dosing method be developed that minimized the reaction time of ClO$_2$ prior to exposure of the solutions to UV. This was accomplished with two Cole Parmer (Chicago, IL) peristaltic pumps, one that pumped the

dye solutions through to the UV unit and the other that simultaneously pumped the ClO_2 solution to the unit. The tubing leading to both pumps was connected by a Y-connector, and the ClO_2 and dye/effluent solutions were mixed for only a few seconds before they were pumped into the UV irradiation unit. Contact times inside the UV unit were controlled by varying the pumping rates. The three dye solutions and the effluent were treated. The experimental matrix for UV/ClO_2 involved ClO_2 concentrations of 3 mg/L and 5 mg/L and UV contact times of 1 min, 3 min, 5 min, 7 min, and 10 minutes. Once the appropriate UV contact times had been achieved, samples were taken from the output and the ADMI evaluated.

Treatment by H_2O_2

Dye solutions and Lower Smith WWTP effluent samples in foil-covered and capped Erlenmeyer flasks were dosed with 25 mg/L H_2O_2 and continuously stirred during the prescribed reaction periods. Samples were withdrawn at five minute intervals for ADMI evaluation during the first hour and then once again after 24 hours.

Treatment by UV/H_2O_2

Effluent samples and dye solutions were dosed with several H_2O_2 concentrations and pumped through the UV unit at varying rates to provide various UV contact times. Individual 1-L samples were dosed with varying amounts of H_2O_2, stirred, pumped at varying rates through the UV unit and analyzed for remaining ADMI color.   The experimental matrix included concentrations of 5 mg/L, 12.5 mg/L, 25 mg/L H_2O_2 and UV contact times of 1 min, 3 min, 5 min, 7 min, and 10 minutes.

CHAPTER 4: RESULTS

The effectiveness of the various oxidative treatments for reducing color in dye solutions and wastewater was evaluated in bench-scale studies. A matrix of experimental variables was developed in which the UV exposure time, H_2O_2 concentration and ClO_2 concentration were varied and applied to each dye solution and the Lower Smith effluent. The goal was to develop predictive models that could be used in the design of dye-waste treatment systems.

Effects of UV and UV/H_2O_2 on Dyes and Wastewater Effluent Color

Before the UV/H_2O_2 studies began, color reduction by H_2O_2 alone and UV alone were investigated.   As shown in Table 1, H_2O_2 treatment alone did not substantially reduce the color intensity of either the pure dye solutions or the wastewater effluent (< 5 percent). The evaluations of UV as the sole decolorizing oxidant were conducted as control experiments for comparison with evaluations of UV/H_2O_2 and UV/ClO_2. The red and blue dyes were most rapidly decolorized, reaching the 300 ADMI value in 5 and 7 minutes, respectively (Figure 1). The green dye was more resistant to oxidation and the 300 ADMI goal would not be achieved unless the irradiation time had been extended to approximately 14 minutes (estimate based on a linear extrapolation).   The color of all the dye solutions decreased sharply during the first minute of UV exposure time and decreased in approximately a linear fashion during the remaining 9 minutes.

The addition of 5 mg/L, 12.5 mg/L and 25 mg/L H_2O_2 to each of the UV- dosed dye solutions noticeably increased both the rate and extent of color removal. Figures 2-4 show these effects compared to the effects of UV irradiation alone. Red dye solutions of two different initial color intensities were decolorized rapidly during the first minute and in approximately a linear fashion after the initial rapid decrease (Figure 2).   The color intensities of both the red and blue dye solutions (Figure 2b and 3, respectively) were reduced to the 300 ADMI permit limit in less than 3 minutes. Furthermore, the data in Figure 2b and Figure 3 clearly show that little benefit was gained by increasing the H_2O_2 dose beyond 5 mg/L H_2O_2 if the contact period were extended to 10 minutes. The benefits of the higher H_2O_2 dosages were evident, however, when the initial color of the red dye solution was 1600 ADMI units (Figure 2a). The color intensity of the green dye solution

Table 1. ADMI data of dyes and effluent for 25 mg/L H_2O_2 dosing

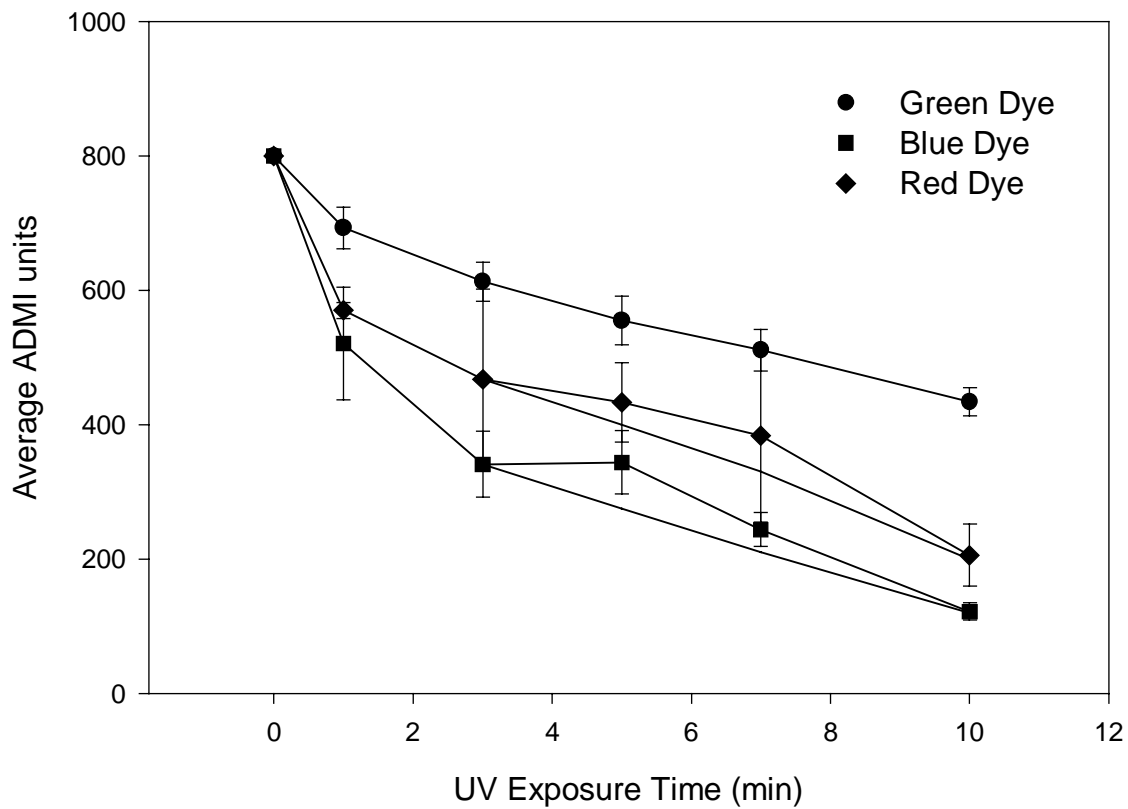|	Color Removal for Peroxide Only, ADMI units		
	Initial ADMI	Final ADMI	% Reduction
<u>Green</u>			
1 hour	800	777	2.9
24 hours	800	766	4.3
<u>Blue</u>			
1 hour	800	769	3.9
24 hours	800	766	4.2
<u>Red</u>			
1 hour	800	792	1.0
24 hours	800	786	1.8
<u>Effluent</u>			
1 hour	422	418	1.0
24 hours	422	411	2.6

Figure 1.   Color reduction in red, blue and green dye solutions by UV irradiation
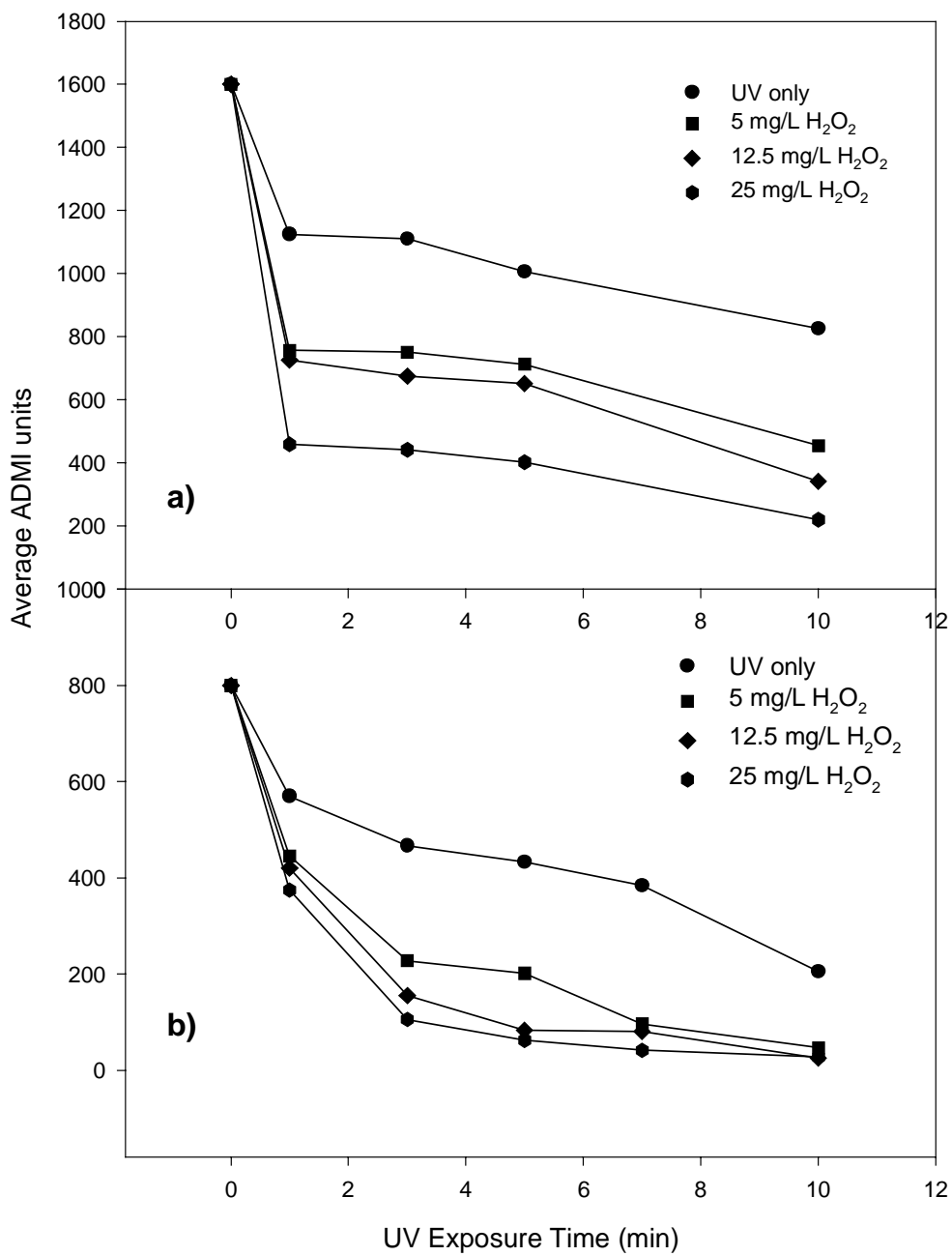during varying exposure times. (Standard deviation, n=3)

Figure 2. Decolorization of red dye solution by UV and UV/H_2O_2 for a) initial ADMI of 1600 units and b) initial ADMI of 800 units.
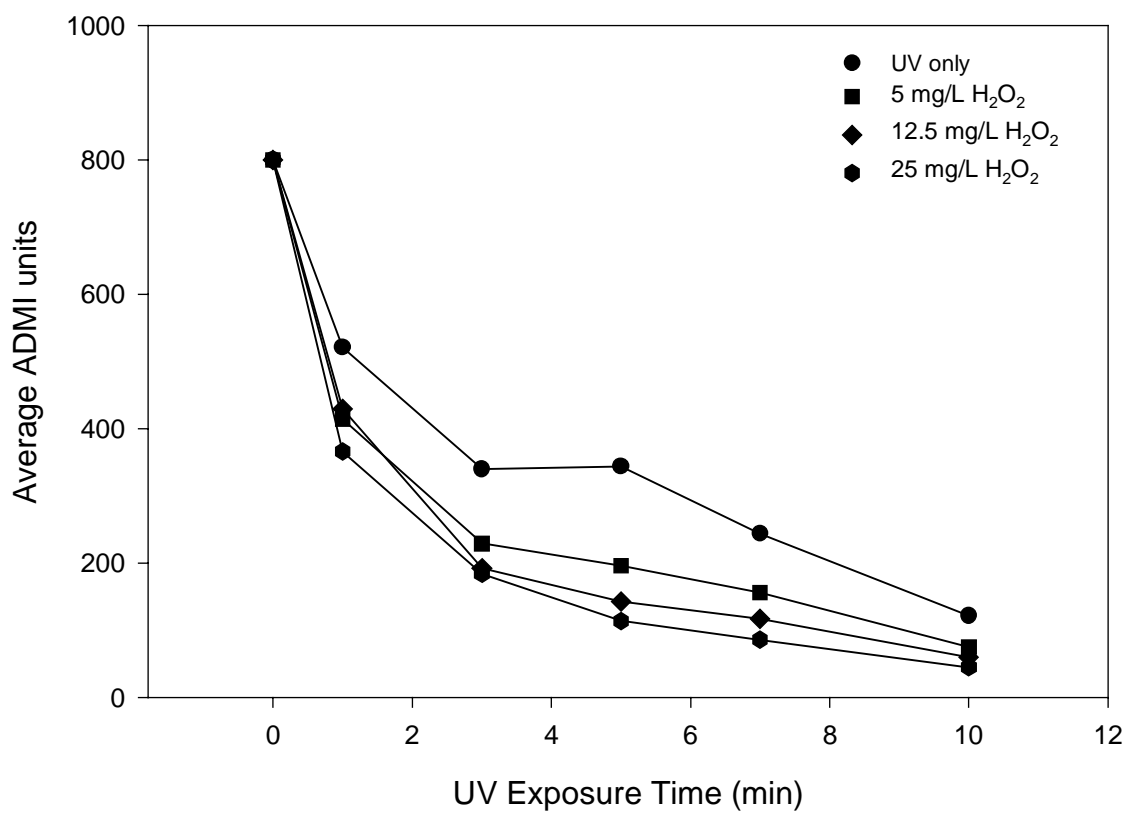
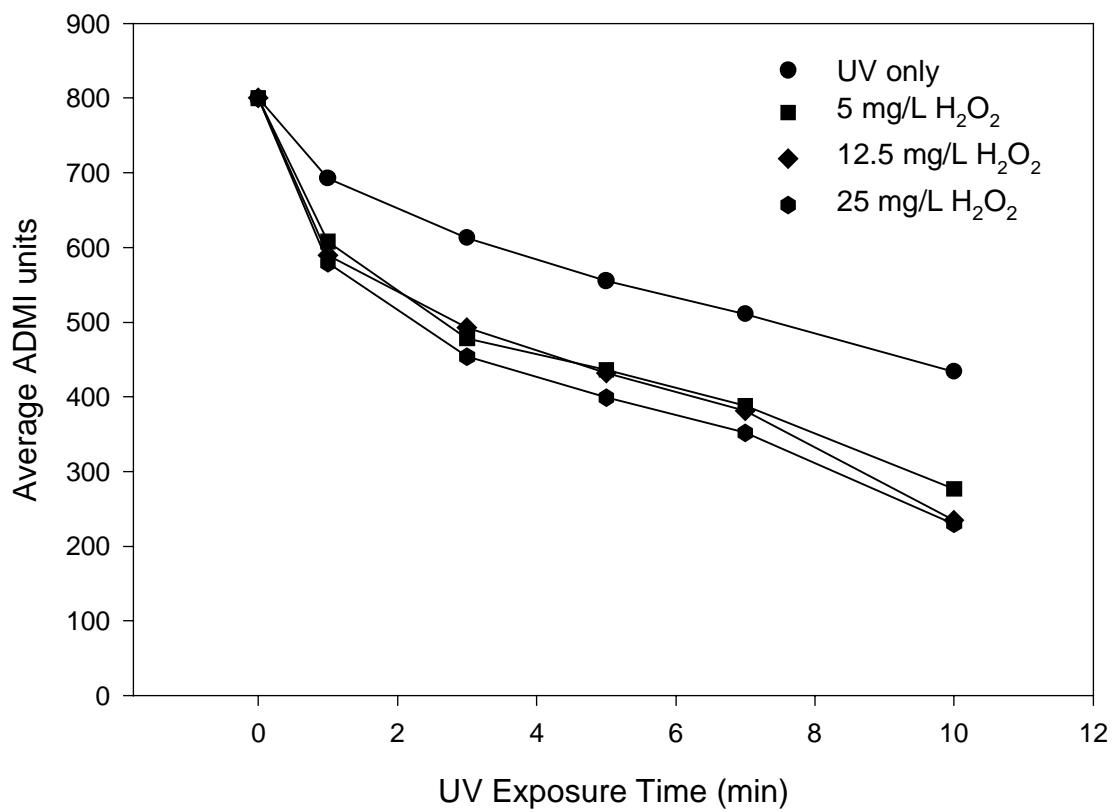Figure 3.   Decolorization of blue dye solutions by UV and UV/H_2O_2.

Figure 4.   Decolorization of green dye solutions by UV and UV/H_2O_2.

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dosed with UV/H_2O_2 decreased gradually to 300 ADMI units over the 10-minute UV exposure period, and increasing the H_2O_2 concentration beyond 5 mg/L provided little additional benefit (Figure 4).

The color-reduction patterns following treatment of Lower Smith effluents with UV were similar to those observed when the dye solutions were treated (Figure 5), but the data were less consistent and the color reduction was lower. Color reductions in the four UV-treated wastewater samples, which varied in initial color intensity from 320 to 505 ADMI units, were used to determine the rate of color loss, thereby providing a predictive model that indicated the time required for decolorization of each sample to 300 ADMI units. Figure 6 shows the effects of UV and UV/H_2O_2 on a single sample of wastewater. The time required to decolorize these samples to 300 ADMI units are plotted in Figure 7, and was based on regression analyses of the curves in Figures 5 and 6, and additional data not shown in these figures. Frequently, insufficient wastewater quantities were delivered which allowed no more than one or two oxidant combinations. Despite this limitation, each set of experimental data was used to determine the time required to reach 300 ADMI units seen in Figure 7. From these data a simpler predictive figure was created. Figure 8 shows the linear regression analysis that predicts the UV exposure time needed to reach 300 ADMI units for the initial ADMI minus 300 ADMI units. The equations generated by the linear regression show that UV alone could reduce an initial color intensity of 505 to 300 ADMI in 12.3 minutes. Another initial effluent color of 422 ADMI units could be decolorized to the same level in 7 minutes by UV and 5 mg/L H_2O_2 and in 5.5 minutes if the H_2O_2 dose were increased to 25 mg/L, based on linear regression. The rates of decolorization of the dye solutions and Lower Smith effluents as functions of the oxidant concentrations are shown in Figures 9a and b. As can be seen, the addition of as little as 5 mg/L H_2O_2 markedly increased the blue and red decolorization rates within the first minute of irradiation. The rates of decolorization of the green dye solution and wastewater effluent were much lower when compared to the
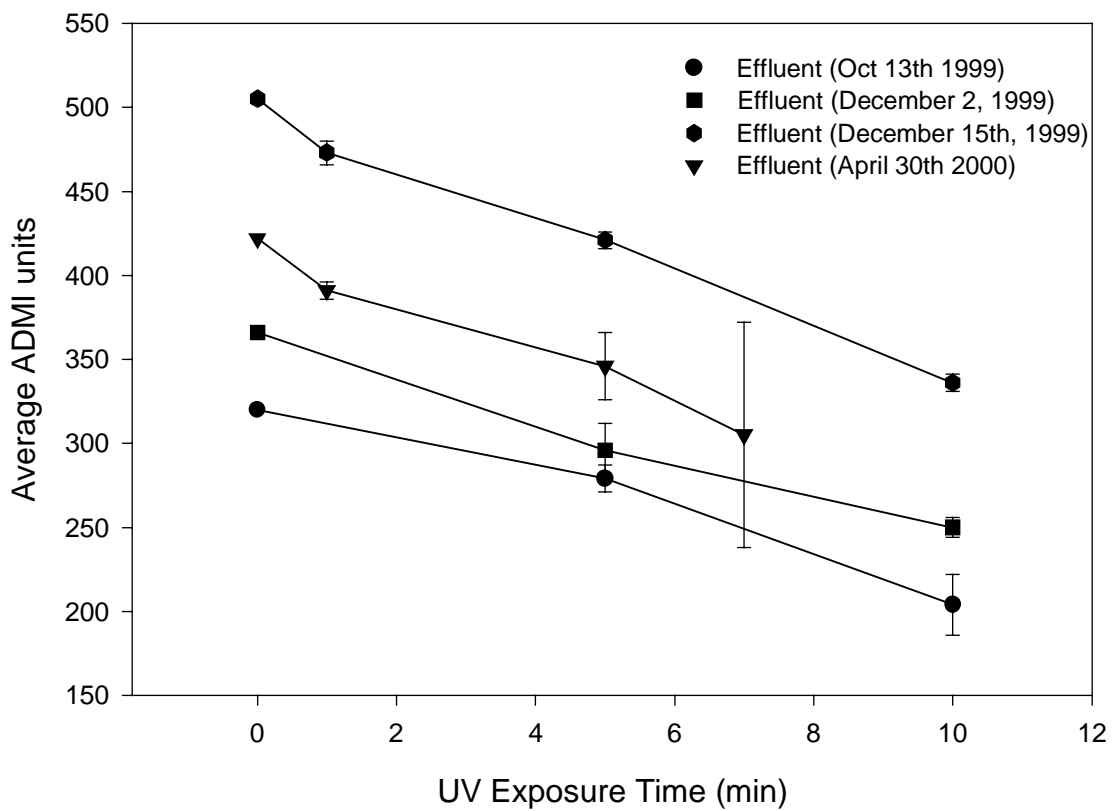
Figure 5. Color reduction of Lower Smith effluents for varying UV contact times. (Standard deviation, n=3)
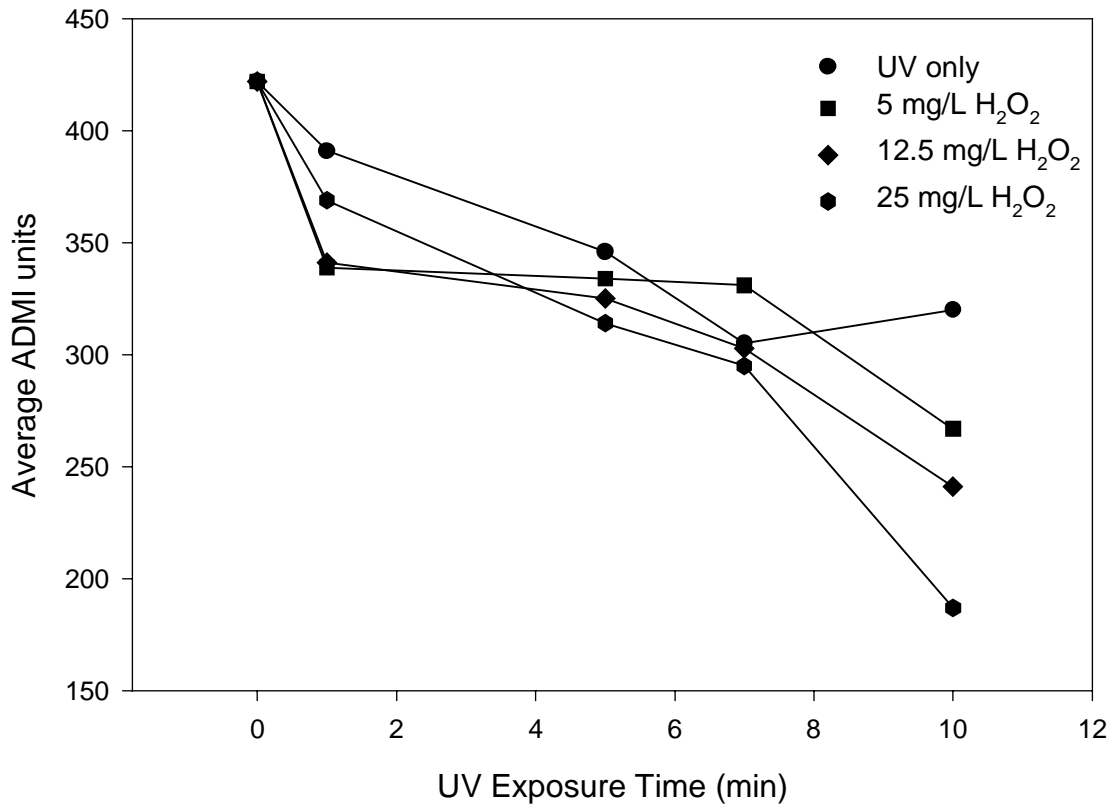
Figure 6.   Color reduction in Lower Smith effluent by treatment with UV irradiation
and UV/H_2O_2. (Lower Smith Effluent collected April 30, 2000)
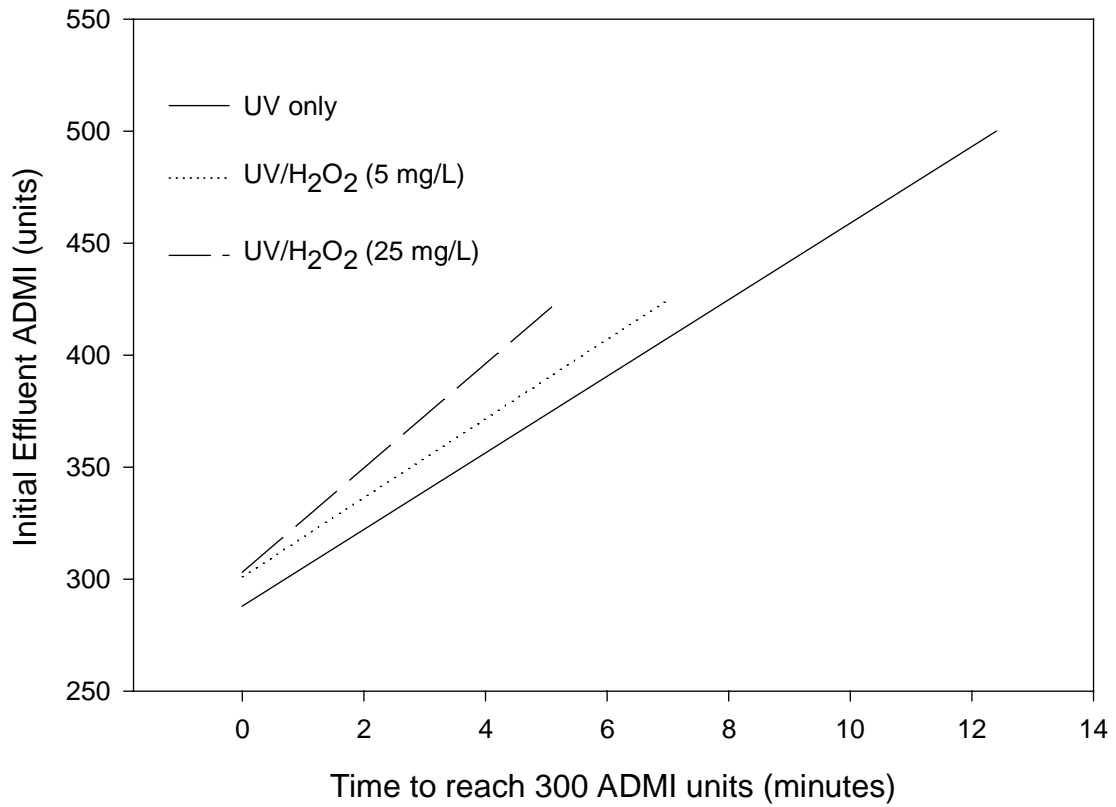
Figure 7   Linear regressions of UV exposure time needed to reach 300 ADMI unitsfor varying initial ADMI values of Lower Smith Effluent (UV and UV/H$_2$O$_2$ (5 and 25 mg/L)).
R^2 values: UV = 0.9859, UV/H$_2$O$_2$ (5 mg/L) = 0.9970, UV/H$_2$O$_2$ (25 mg/L) = 0.9896

Figure 8. Predictive models for Lower Smith Effluent treated with UV,UV/H$_2$O
(5 and 25 mg/L)R^2 values: UV = 0.9715, UV/H$_2$O$_2$ (5 mg/L) = 0.9973,
UV/H$_2$O$_2$ (25 mg/L) = 0.9937

a)

b)

Figure 9.   Average rate of decolorization in dye solutions and Lower Smith wastewater effluents a) one minute exposure b) remaining 9 minute exposure time.

red and blue dyes. The green dye rate of color reduction was positively affected by the increase of H_2O_2 during the first minute and remaining 9 minutes. 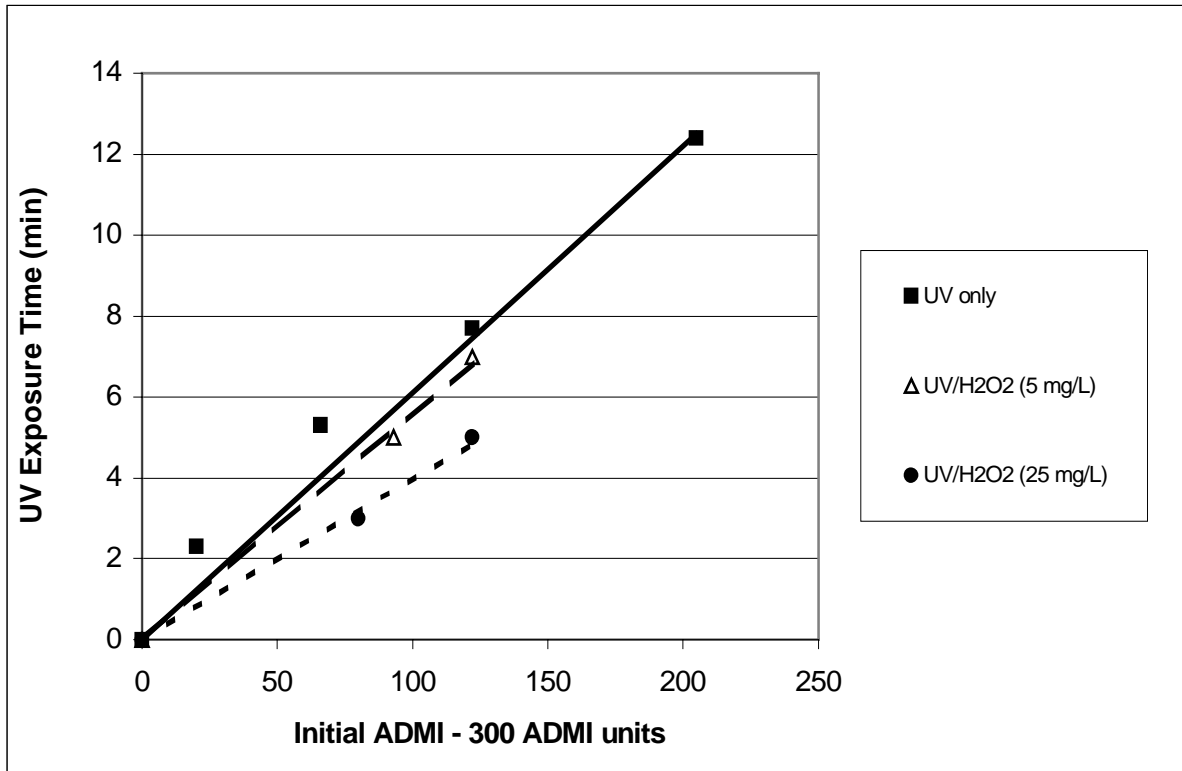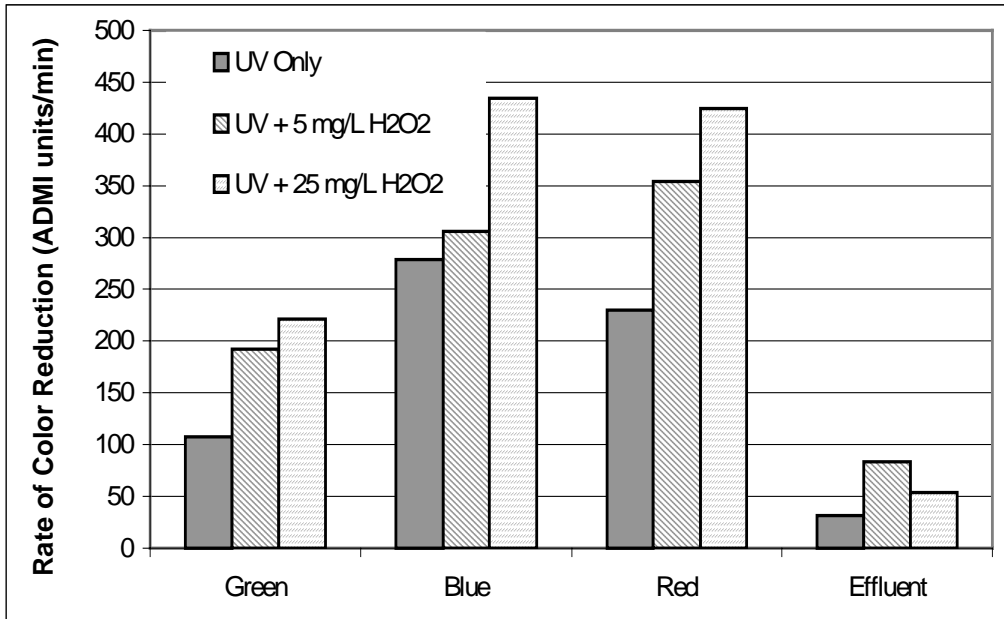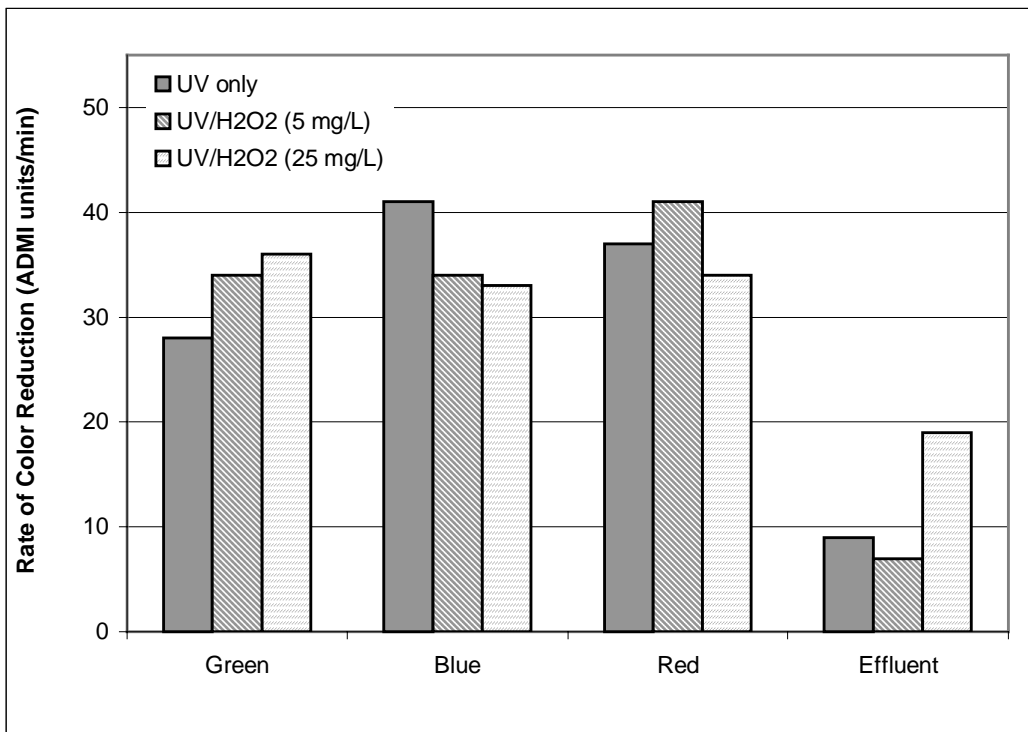The effluent rate increased with the addition of 5 mg/L H_2O_2 in the first minute. When 25 mg/L H_2O_2 was added, decolorization rates increased at a higher rate for the remaining 9 minutes.

Effect of ClO_2 and UV/ClO_2 on Dyes and Wastewater Effluent Color

Decolorization of the dye solutions and effluent by 5 mg/L ClO_2 proceeded in patterns similar to those observed when UV was the sole treatment agent. The effluent was decolorized only slightly (Figure 10). Table 2 contains the ClO_2 and chlorite ion (ClO_2^-) residuals at the end of five minutes. Additional residual data for Lower Smith effluent dosed at other ClO_2 concentrations are shown in Appendix Table A1.

As was expected, the dye-solution ClO_2 demands were much less than that of the effluent.   When treatment with 5 mg/L ClO_2 was followed by UV irradiation, decolorization of the dye solutions was improved, and a markedly increased decolorizing effect on the wastewater effluent color was noted (Figure 11). As shown in Figure 10, without ClO_2, the effluent ADMI did not reach 300 units over 10 minutes of exposure to 5 mg/L ClO_2, but with UV added the color level reached 300 ADMI units in 1 minute (Figure 11).

The Lower Smith effluent color was also considerably reduced by ClO_2 alone at higher dosages. ADMI color was monitored in effluents that were dosed with varying ClO_2 concentrations and curves were constructed to show the final color achieved after 45 minutes contact. These results are shown in Figure 12. Figure 12 shows the ClO_2 dosages required to reduce the effluent color to 300 ADMI in 45 minutes. The data indicate, as might be expected, that higher dosages would be required to reduce the highly colored effluents to the permit level. These data were used to generate a graph indicating the required ClO_2 dosage necessary to achieve reduction to 300 ADMI units for the Lower Smith effluent (Figure 13). Figure 13 is a linear regression defining the necessary ClO_2 dosage (mg/L) required for varying initial ADMI levels. When treatment with 5 mg/L ClO_2 was followed by UV irradiation on various initial ADMI effluents, that data were used to determine the rate of color loss. The time required to decolorize these samples to 300 ADMI units are plotted in Figure 14, providing a linear regression
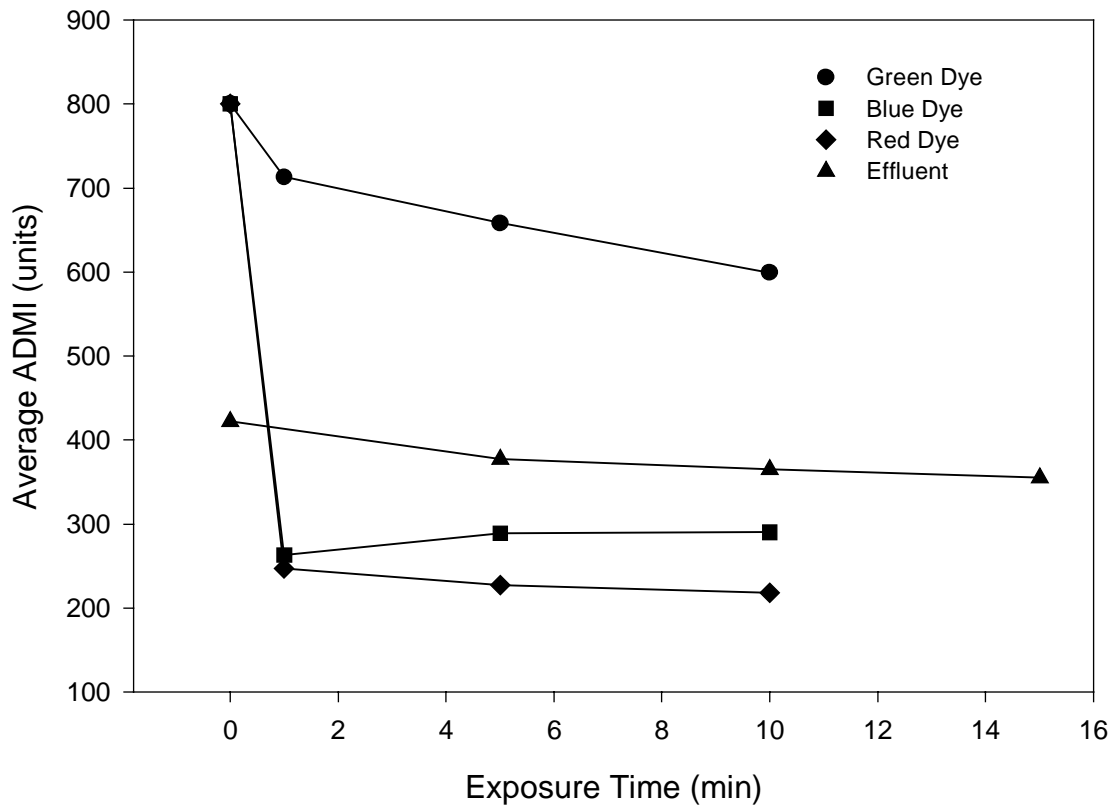
Figure 10.   Color reduction by 5 mg/L ClO_2 over varying exposure times.
(Lower Smith effluent collected on April 30, 2000)

Table 2. Chlorine Dioxide and Chlorite Residuals for 5 mg/L dosing of ClO_2 on all dyes and Effluent (n=3)

Sample analyzed after 5 minutes			
	Chlorine Dioxide and Chlorite Residuals for Dyes and Effluent		
Dye Solutions (ADMI color=800 units)	ClO_2 Conc. (mg/L)	ClO_2 Residuals (mg/L)	ClO_2- Residuals (mg/L)
Red Dye	5	1.43	1.97
Std. Devation		0.15	0.16
Blue Dye	5	1.43	2.2
Std. Deviation		0.21	0.12
Green Dye	5	0.85	1.56
Std. Deviation		0.06	0.11
Effluent April 30, 2000 (ADMI color = 422 units)	5	0.01	0.49
Std. Deviation		0.02	0.02
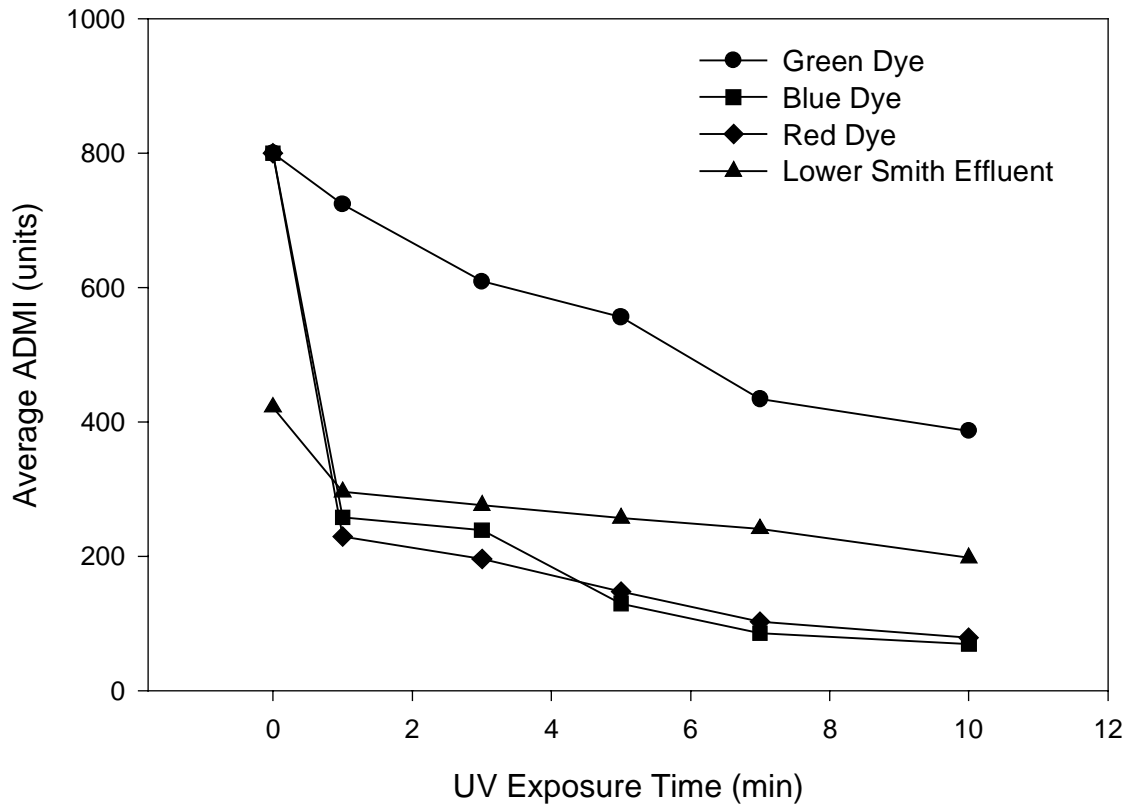
Figure 11.   Effects of UV/ClO$_2$ (5 mg/L) on color reduction of dyes and Lower Smith effluent at varying UV exposure times.
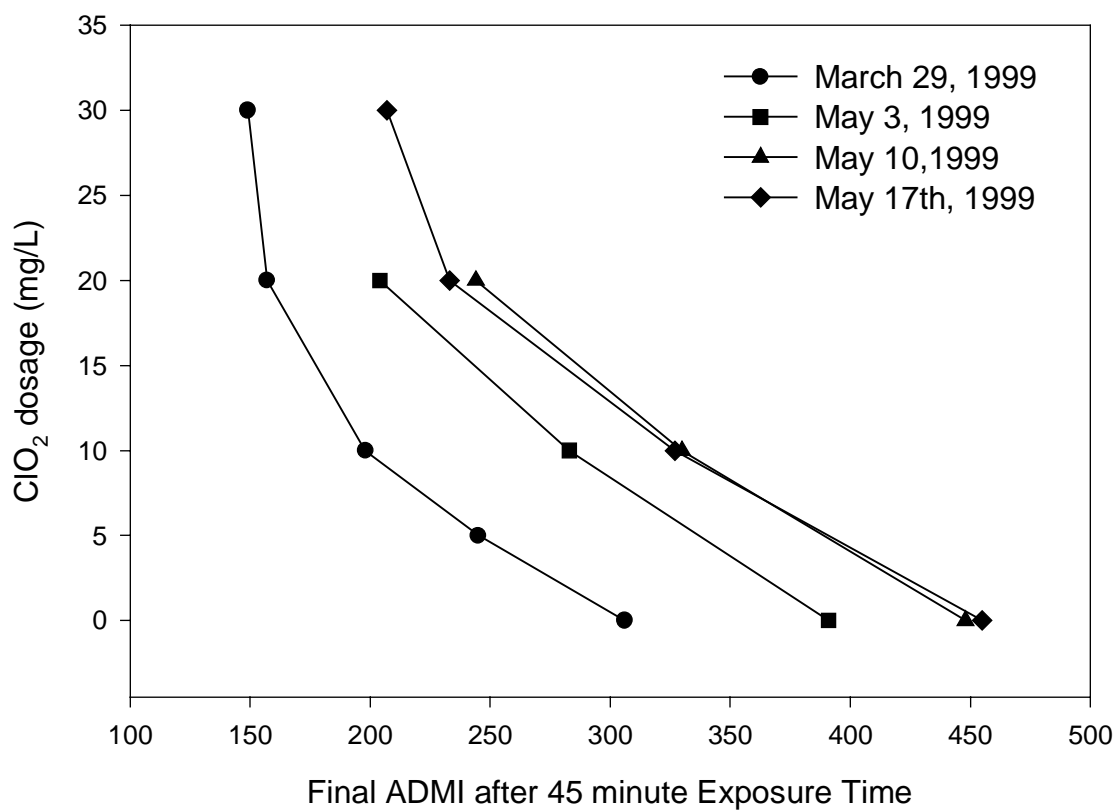
Figure 12.   Effects of increasing ClO$_2$ concentration on Lower Smith effluent ADMIs after 45 minute exposure time.
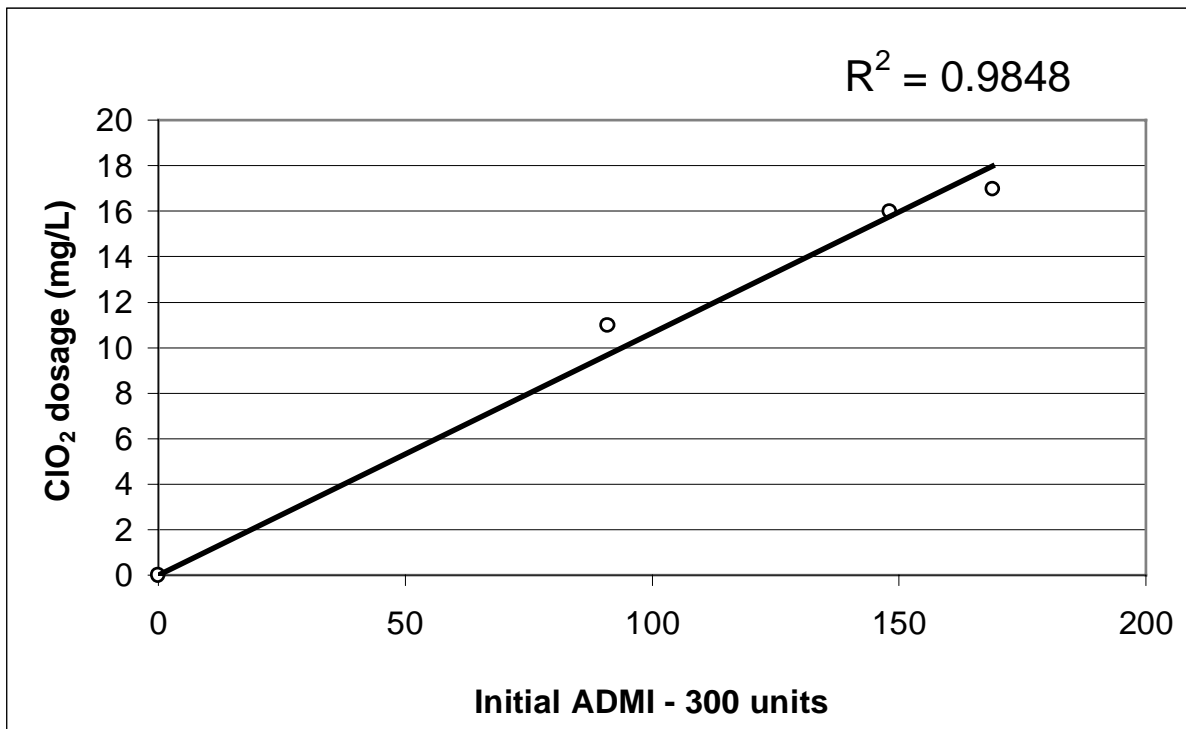
Figure 13.   Linear regression of ClO_2 dose (mg/L) needed to reach 300 ADMI units
for varying initial ADMI values of Lower Smith Effluent.
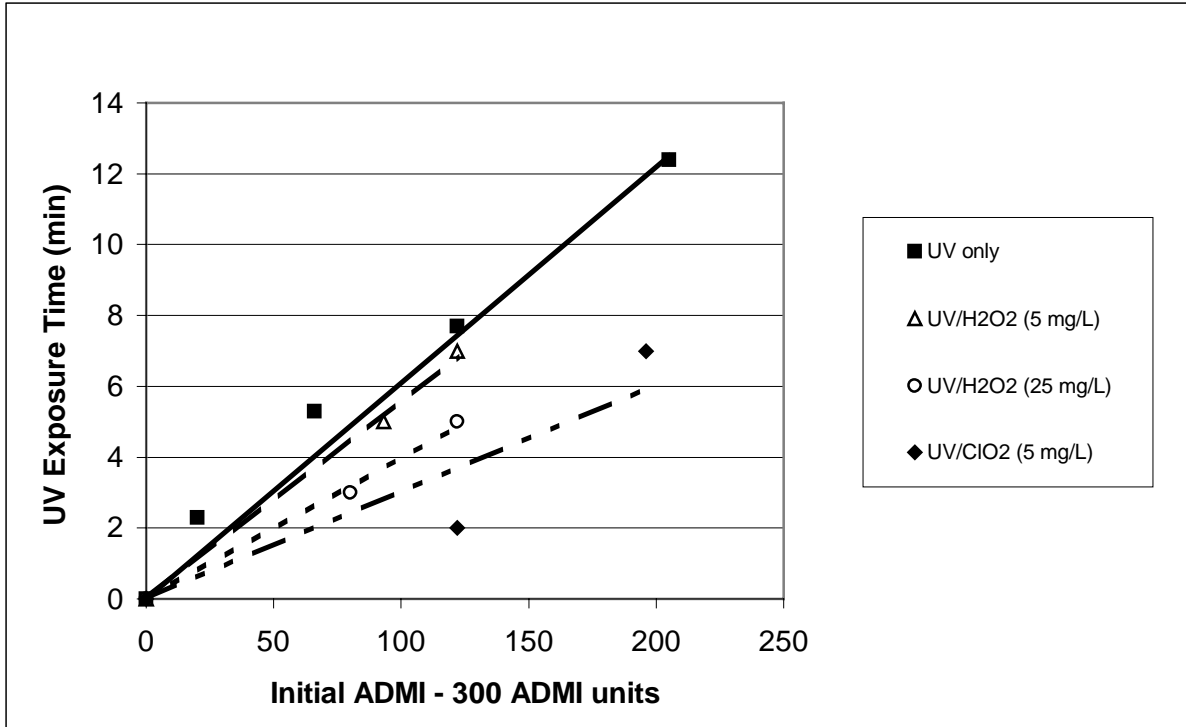
Figure 14.   Linear regressions of UV contact time needed to reach 300 ADMI units
for varying initial ADMI values of Lower Smith Effluent (UV and
UV/H$_2$O$_2$ (5 and 25 mg/L) and UV/ClO$_2$ (5 mg/L)).
R^2 values: UV = 0.9859, UV/H$_2$O$_2$ (5 mg/L) = 0.9970, UV/H$_2$O$_2$ (25
mg/L) = 0.9896, UV/ClO2 = 0.8600

analysis that indicates the UV providing a linear regression contact time required for decolorization of each effluent sample to 300 ADMI units. In Figure 14, the UV/ClO$_2$ treatment predictive model is compared to the predictive models of UV, UV/H$_2$O$_2$ (5 and 25 mg/L).

Comparison of Oxidant Treatments of Dyes and Wastewater Effluent Color

Data previously presented are compared in Figures 15 and 16 to show the effects of UV only, UV/H$_2$O$_2$ (5 mg/L), UV/ClO$_2$ (5 mg/L) and 5 mg/L ClO$_2$ on the red and blue dye solutions.   The largest reduction of color was achieved after 1-minute contact with 5 mg/L ClO$_2$, both with and without UV exposure. All the treatments decolorized the red and blue dyes to 300 units when given sufficient contact time. Figure 17 shows the responses of the green dye to the various oxidants and indicates that decolorization to 300 ADMI units occurred only after the addition of 5 mg/L H$_2$O$_2$ and a 9 minute UV exposure time.

The effects of the various treatments on the Lower Smith effluent seen in Figure 18 indicated superior color reduction below 300 units after a 1 minute UV exposure time by UV/ClO$_2$ (5 mg/L) and continual reduction to 200 units for the remaining 9 minutes. The other treatments, with the exception of UV/H$_2$O$_2$ (5 mg/L) given a 10 minute UV exposure time did not achieve 300 ADMI units. Linear regressions performed on the data after 1 minute of UV exposure time as seen in Figure 18 showed that the slopes of the treatments between 1 and 9 minutes exposure time were –8.78, -7.304 and –10.6 for UV, UV/H$_2$O$_2$ and UV/ClO$_2$, respectively.

Figure 15.   Effect of H_2O_2 and ClO_2 dosages on red dye solutions at varying UV exposure times or chemical exposure times. (Standard deviation, n=3)

Figure 16.   Effects of H_2O_2 and ClO_2 dosages on blue dye solutions at varying UV contact times or chemical exposure times. (Standard deviation, n=3)
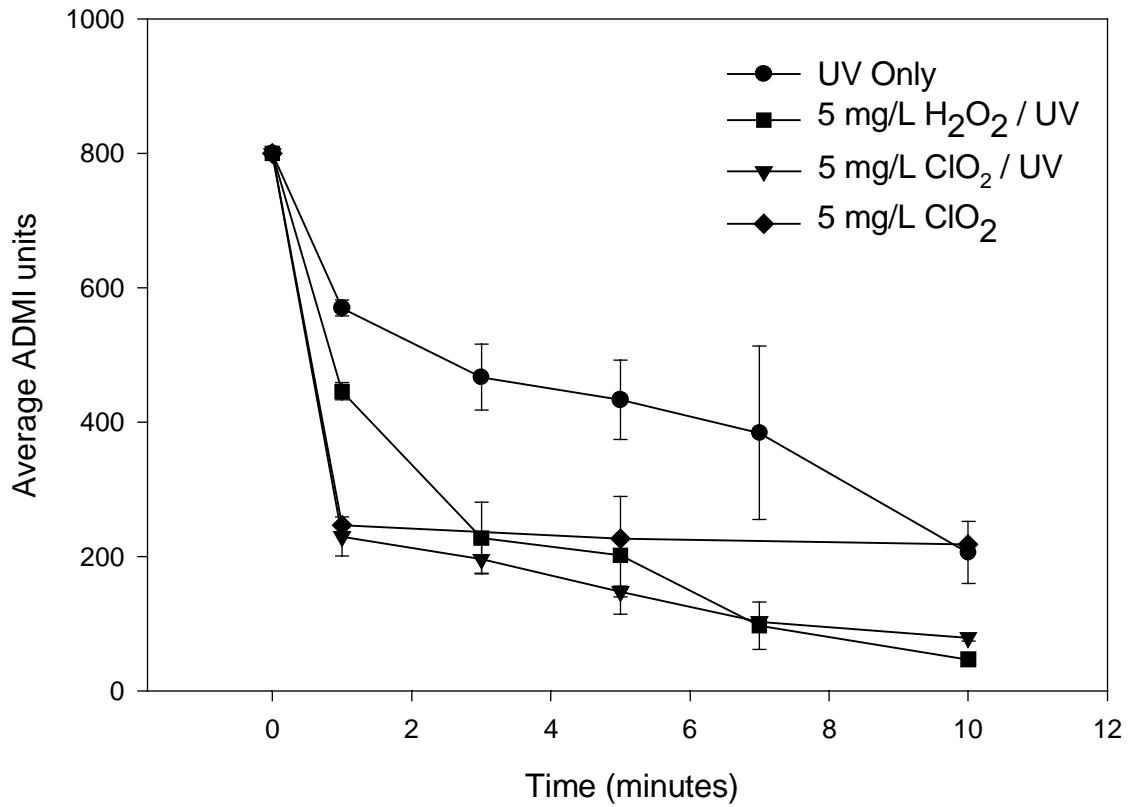
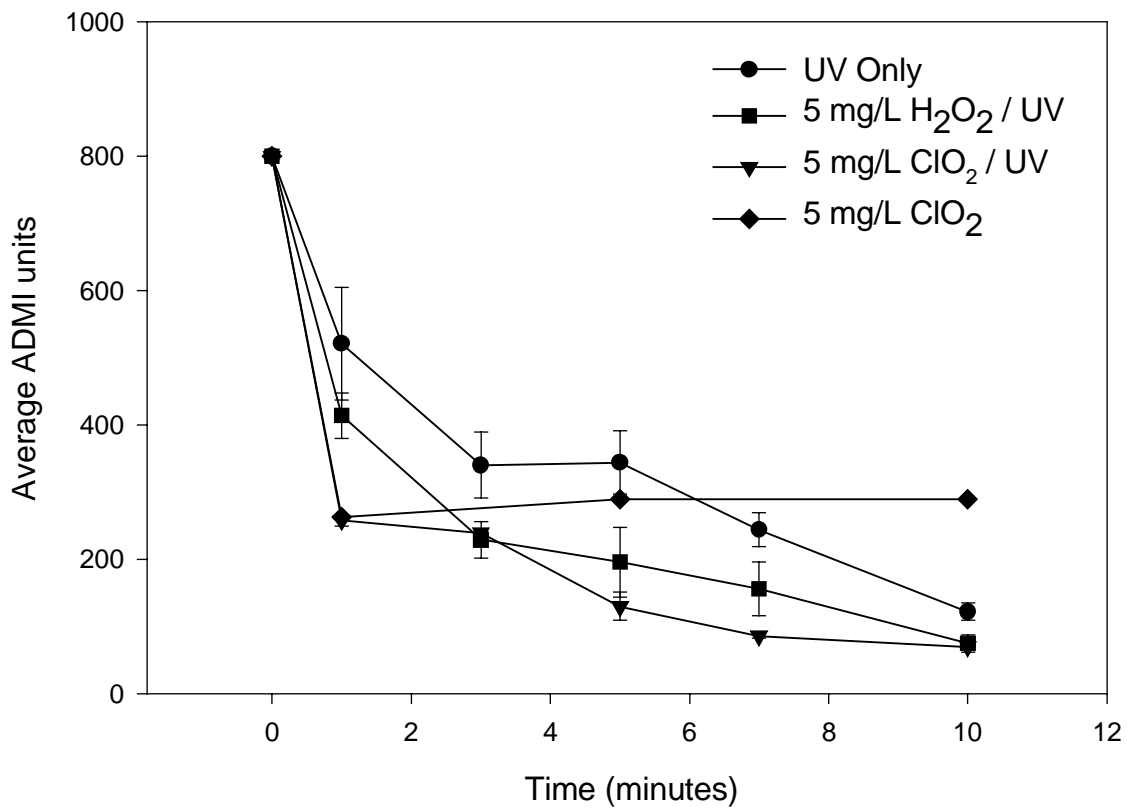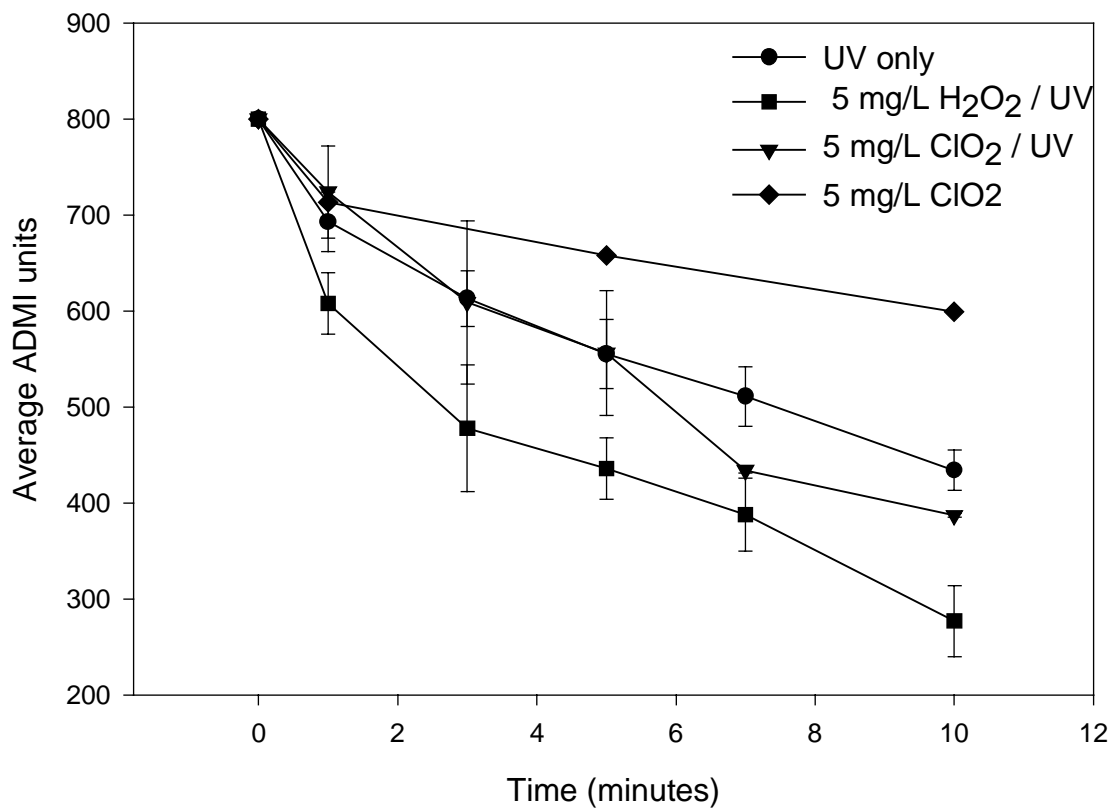Figure 17.   Effect of H_2O_2 and ClO_2 on green dye solutions at varying UV contact
times or chemical exposure times. (Standard deviation, n=3)
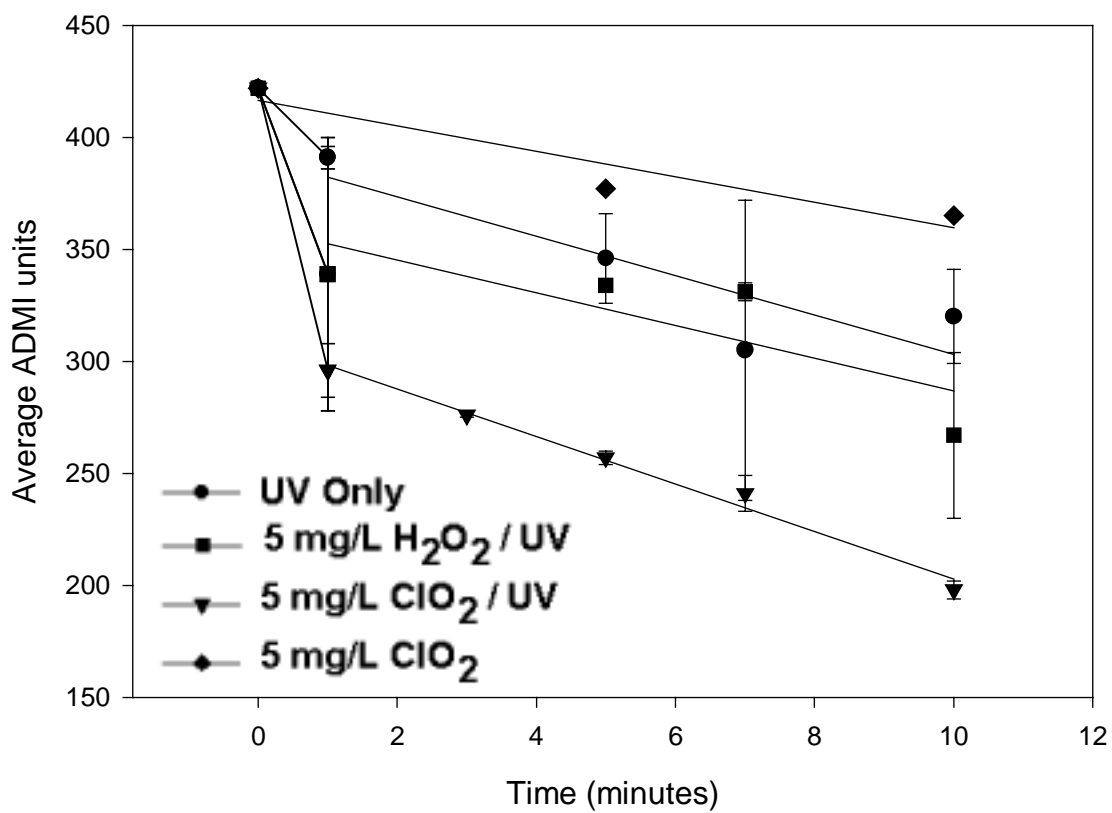
Figure 18. Effects of H_2O_2 and ClO_2 dosage on effluent at varying UV exposure times or chemical exposure times. Linear regressions applied after 1 minute (Standard deviation, n=3)

CHAPTER 5: DISCUSSION

Each of the treatments evaluated during this study decolorized the dyes and the Lower Smith Wastewater Treatment Plant effluent to varying degrees. The objective was not complete decolorization but, rather, to determine efficient means to comply with the Virginia Pollutant Discharge Elimination System (VPDES) permit level of 300 ADMI units. The efficacy of the oxidative treatments was dependent on the initial color intensity of the test solutions and, therefore, predictive models for each oxidative treatment process were created for the Lower Smith effluent. Additional attempts to model the combined oxidant/UV systems did not yield predictive results. The treatments involving UV irradiation, with or without the addition of a H_2O_2 or ClO_2, rely on the length of UV exposure time required to achieve the sufficient color reduction, which was thought to be a function of the initial ADMI value. The treatments involving ClO_2 relied on the ClO_2 demand required by the test solutions, which was also a response to the initial ADMI intensity.

Color removal by H_2O_2 alone and UV alone was evaluated. The literature states that H_2O_2 is not a viable oxidative treatment (Ince and Gonenc, 1997; Liao et al., 2000; Shu et al., 1994; Yang et al., 1998), and evidence from this study supports this finding. Ultraviolet light has the ability to degrade organic compounds, and exposure to UV irradiation resulted in decolorization of the three dyes and the Lower Smith effluent. A 10-minute UV exposure time was required to reduce color in the Lower Smith effluents to the 300 ADMI unit permit level when they were higher than 450 –500 units. Because a typical wastewater treatment plant is unlikely to allow a 10 minute contact time, and the effluent ADMI values will most likely be above 400 ADMI units, UV alone was not considered to be a feasible technology for the Lower Smith plant.

A trend seen throughout the experiments was that the red and blue dyes were more easily decolorized than either the green dye or the effluent. These findings regarding the dye solutions supported Gregor's (1992) findings that high color reduction required a 3-minute UV exposure time for red, orange and blue reactive azo dyes in a high-pressure UV system. Gregor (1992) also cited a low percent reduction (10%) for the green azo dye. One explanation was the structure of the red and blue dyes facilitated invasion by the reactive hydroxyl radicals, which attacked the dye molecule and provided

oxidation to various intermediates (Ince and Gonenc, 1997). It should be noted that the effluent was always more resistant to decolorization than the pure dye solutions, either because the addition of surfactants, salts of other process chemicals by the manufacturer interfered with treatment or because the more labile substances had already been removed by the addition of polymer added at the treatment plant.

During this study, color reduction in all three dyes and the effluent increased only marginally with the addition of H_2O_2 followed by UV irradiation. This finding was supported by Liao et al. (2000). An exception discovered during this study was the observed response of the red dye to H_2O_2 when the initial ADMI value was 1600 units. The addition of 25 mg/L H_2O_2 provided 20 percent more color reduction after one minute compared to the decolorization seen upon the addition of 5 and 12.5 mg/L H_2O_2. Ince and Gonenc (1997); Namboodri and Walsh (1996); Shu et al.(1994); Yang et al.(1998) stated that an increased UV exposure time was required to reach the identical percent reduction when the H_2O_2 concentration was kept constant for increased initial dye concentrations. These data suggest that stronger intensity dye solutions initially consumed the oxidant and the remaining color removal through 10 minutes was a product of UV oxidation.

The Lower Smith effluent response to increased H_2O_2 concentration and UV irradiation time shown from Figure 8 also demonstrated that higher ADMI values initially consume the oxidant and the extended UV irradiation time provides continuing decolorization. When the UV/ H_2O_2 (25 mg/L) and UV/ H_2O_2 (5 mg/L) treatment UV irradiation times were extrapolated to 500 ADMI unit initial effluent, an 8.0 minute and 11.3 minute irradiation periods were required. The length of UV contact time required by dye waste entering the treatment plant becomes a question of the facility's operation and cost plan. Linear relationships between the times required for decolorization of effluents to 300 ADMI and initial ADMI values are as follows:

- UV alone: UV exposure (min) = 0.061(Initial ADMI – 300 units)   *(6)*
- UV/H_2O_2 (5 mg/L): UV exposure (min) = 0.056 (Initial ADMI – 300 units) *(7)*
- UV/H_2O_2 (25 mg/L): UV exposure (min) = 0.040(Initial ADMI – 300 units)*(8)*

Chlorine dioxide (without UV) was consumed rapidly by the Lower Smith effluent, and the largest percent of color removal was obtained within the first 5-15 minutes following dosing with ClO_2. The data presented in Figure 13 indicate the effective dosage of ClO_2 in achieving the 300 ADMI level for various initial effluent ADMIs over 45 minutes of chemical exposure time. The ClO_2 concentrations used in this study ranged from 5 to 30 mg/L, and larger ClO_2 concentrations can be linearly extrapolated for higher initial effluent ADMIs based on Figure 13 up to nearly 500 units. The linear relationship between the effective ClO_2 dosage required for decolorization of effluent to 300 ADMI units and the initial ADMI effluent between 0 and 500 units is as follows:

Effective ClO_2 dosage (mg/L) = 0.1063 (Initial ADMI – 300 units)   *(9)*

The results from the study of ClO_2 effects on the dye solutions (Figure 10) suggested that a 5 mg/L ClO_2 dosage applied to the red and blue dyes reduced the color to below 300 ADMI units after 1 minute. Little additional reduction occurred over the next remaining 9 minutes. If an ADMI below 300 units was desired, an increased ClO_2 dose would be required, but the residual ClO_2 concentrations may become an obstacle because ClO_2 is toxic to stream organisms.

Only a few ClO_2 demand studies were performed during this investigation because the demand at the lower dosages appeared to be exerted rapidly. Higher ClO_2 dosages to the effluent produced larger color reductions within the first 15 minutes. Beyond 15 minutes, the effluent color stabilized indicating that the ClO_2 demand was at least as high as the highest applied ClO_2 dose. Chlorine dioxide residuals for three different effluents indicated little to no ClO_2 remained after 5 minutes (Appendix Table A1). Occasionally the ADMI color values (not necessarily the hue intensity of the effluent) would increase with higher dosages of ClO_2. This might have been caused by the delayed reformation of chromophores after the initial color reduction and consumption of ClO_2. Additional graphs of ADMI color versus ClO_2 exposure time of Lower Smith effluent for varying ClO_2 dosages can be found in the appendix (Figures A3-A7).

The results from the demand study of the dyes indicated that after a 5-minute exposure time, approximately 1.43 mg/L ClO_2 remained in the red and blue dye solutions (Table 2). It is possible that further decolorization might have taken place due to the remaining ClO_2 in solution. The color reduction over a 10-minute exposure time for the green dye indicated that a 5 mg/L dosage provided continual color removal, but during the 10-minute contact period did not reduce the color to 300 ADMI units. During the remaining chemical exposure time, the residual ClO_2 was most likely consumed, given the continual decolorization seen in the green dye solution.

The red and blue dye solutions were decolorized by the combination of UV and ClO_2 in a fashion similar to that seen by UV/H_2O_2. The green dye was resistant to the treatment and never reached 300 ADMI units in the 10-minute exposure time. During the first minute of contact, the intensity of the red and blue dyes decreased 200 ADMI units more than the decrease brought about by UV/H_2O_2 treatment. The UV exposure time required to reach the 300 ADMI units value for the Lower Smith effluent was slightly shorter for UV/ClO_2 (5 mg/L) than for UV/H_2O_2 (25 mg/L) according to Figure 14. The linear relationship of UV/ClO_2 (5 mg/L) between the UV exposure time required for decolorization of effluents to 300 ADMI units and initial ADMI values is:

UV exposure (min) = 0.030 (Initial ADMI – 300 units)   *(10)*

If color reduction below 300 ADMI units was required, the UV/ClO_2 treatment appeared to be the most effective. The oxidant concentration of 5 mg/L ClO_2 and 1 minute UV exposure time provided additional color reduction (Figures 15 -18) and continued decolorization for the remaining 9 minutes. This finding suggests that ClO_2 initially causes the sharp decrease in color and UV provides the remaining color reduction. These data also imply that ClO_2 oxidized the dyes better than H_2O_2 when irradiated with UV light. An explanation for this may be that the standard oxidation potential of the ClO_2 is larger than the oxidation potential of H_2O_2 (-1.15 volts and – 1.776 volts, respectively), thereby, providing more oxidative strength.

The effects of the different treatment processes on the dyes and the effluent provided varying results. The data indicated similar trends for the red and blue dyes regardless of the type of treatment. According to Figures 15 and 16, the most effective

treatments (i.e. the treatment providing the most color reduction within the shortest time period) were both ClO_2 alone and UV/ClO_2 (5 mg/L). The next best treatment process was UV/H_2O_2 (5 mg/L) after 3 minutes UV exposure time. It should be noted that the green dye was never decolorized to the 300 ADMI units during the first minute of either UV exposure time or chemical exposure time, and the only treatment process that achieved the 300 ADMI units was the UV/H_2O_2 (5 mg/L) after a 10-minute UV exposure time.

A comparison of the treatment processes on the Lower Smith effluent (Figure 18) showed that UV/ClO_2 (5 mg/L) treatment provided the best color removal after 1 minute of UV exposure time. The next most effective treatment process was UV/H_2O_2 (5 mg/L) given a 10 minute UV exposure time. However, the addition of ClO_2 without UV was able to reduce color to 300 ADMI units at concentrations greater than 5 mg/L, but required a chemical exposure period estimated at 30 minutes to 45 minutes. The response of the treatments using UV exposure showed a decrease in color within the first minute and then followed a linear pattern between 1 and 10 minute UV exposure time. The slopes of these linear patterns were determined based on linear regression of the data. The regression indicated that the greater slope of the UV/ClO_2 treatment between 1 and 10 minutes provided more color reduction and the smaller slopes of UV and UV/H_2O_2 treatments suggested similar reduction rates. One explanation for the increased rate of reduction is the oxidant is largely consumed within the first minute and the remaining decolorization is a result of UV exposure. The increased oxidizing strength of ClO_2 may have provided additional decolorization during the remaining 9 minutes of UV exposure.

CHAPTER 6: SUMMARY AND CONCLUSIONS

As evidenced in this study, certain reactive azo dyes and spent textile dye wastewater can be decolorized by chemical oxidation. The red, blue and green dyes were generally more easily decolorized than the Lower Smith effluent. These data will be more relevant to operations of the Lower Smith WWTP if the effluents from the textile manufacturers exhibit a dominant hue or color similar to the red, blue and green dyes.

The results of this investigation performed on the Lower Smith effluent indicated that ADMI color reduction to the VPDES permit of 300 units could be achieved by each of the treatments (UV, UV/H_2O_2, UV/ClO_2, and ClO_2). The most effective was UV exposure after the addition of 5 mg/L ClO_2. The use of UV becomes an obstacle for a wastewater treatment facility because UV equipment, operations, and maintenance are expensive. Difficulties inherent in the generation and dosing of ClO_2, in addition to the UV maintenance, may further complicate implementation of the process. The alternative treatment was ClO_2 as the sole oxidative agent. The results from the ClO_2 study indicated ClO_2 concentration as high as 30 mg/L might be required if the effluent ADMI was high.   The expense associated with generation of high concentrations of ClO_2 could potentially match or exceed costs of UV/ClO_2. The Lower Smith WWTP would need to perform a cost investigation and analysis of the ClO_2 and UV/ClO_2 treatments.

The by-products created after treatments by UV, UV/H_2O_2, ClO_2 and UV/ClO_2 are unknown. In addition, chlorite and chlorate by-products are known to be toxic. More research is necessary to analyze the by-products in the effluent and their potential toxicity to stream organisms.

The conclusions derived from this study are:

- The red and blue dye solutions (initial ADMI = 800 units) are readily decolorized by UV, UV/H_2O_2, ClO_2, and UV/ClO_2, but the green dye solution (initial ADMI = 800 units) is more resistant to the oxidants.
- Predictive linear models provide simple equations for UV exposure time or ClO_2 doses required to achieve 300 ADMI units for variable initial effluent. The data suggest UV/ClO_2 (5 mg/L) and UV/H_2O_2 (25 mg/L) will ensure adequate decolorization for typical effluent ADMI values.

- Chlorine dioxide treatment alone and with UV irradiation were the most effective treatments for reducing Lower Smith effluent color to 300 ADMI units and are recommended treatments for consideration at the WWTP.

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APPENDIX

Schematic of UV/H2O2
System

Spec

Peroxide
Dosing

DYE

UV unit
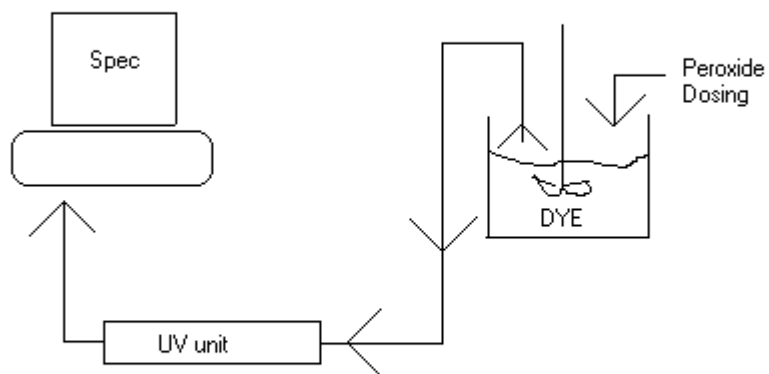
Figure 1A. UV/H$_2$O$_2$ bench study set up

Schematic of UV/ClO2 System

Spec

UV unit

DYE
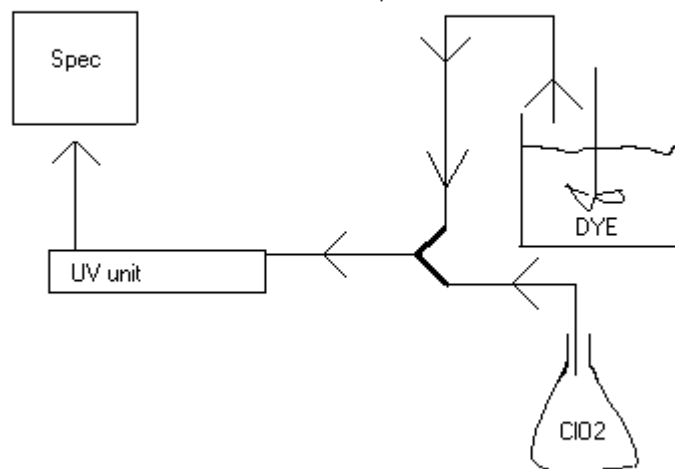
ClO2

Figure 2A. UV/ClO$_2$ bench study set-up

Table A1. Chlorine Dioxide and Chlorite Residuals for 5 mg/L dosing of ClO2 to

	Chlorine Dioxide and Chlorite Residuals for Dyes and Effluent		
	ClO_2 dosing Conc. (mg/L)	ClO_2 Residuals (mg/L)	ClO_2^- Residuals (mg/L)
Effluent March 5, 1999 (ADMI color = 737 units)	20	0	11.1
Effluent April 5, 1999 (ADMI color = 207 units)	10	0.08	5.8
Effluent April 13, 1999 (ADMI color = 335 units)	10	1.2	5.5
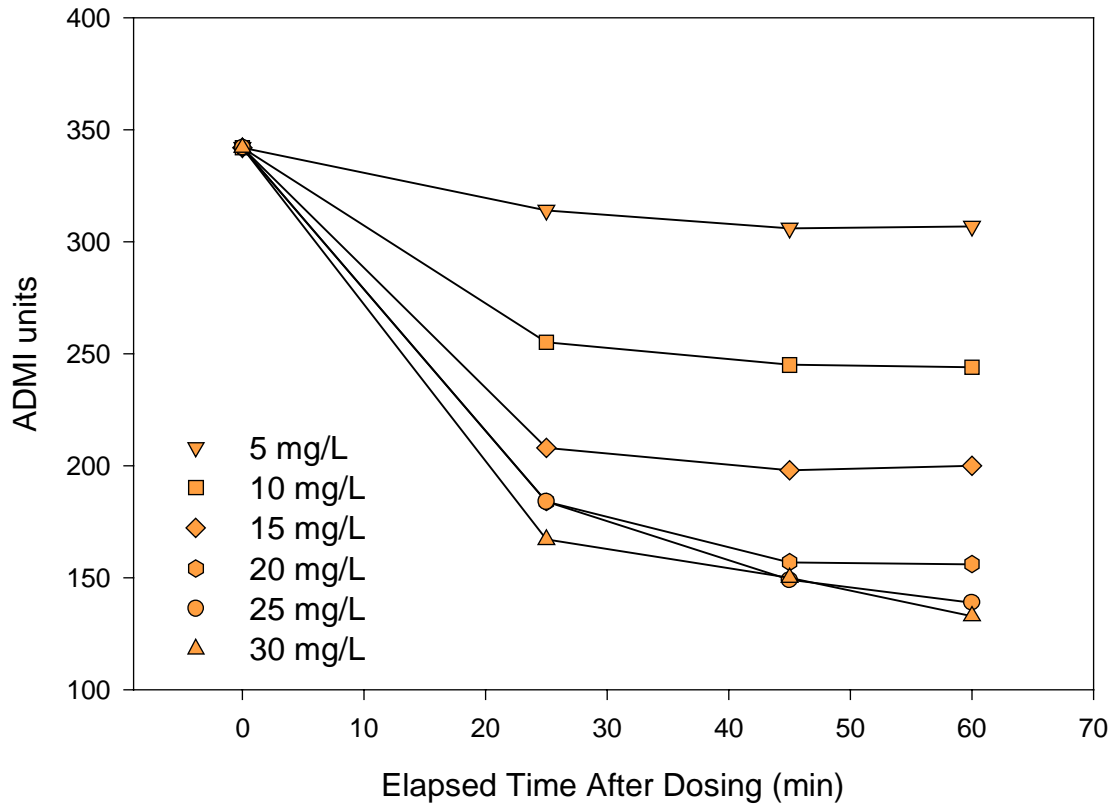
Figure A3. Color Reduction by chlorine dioxide treatment of effluent
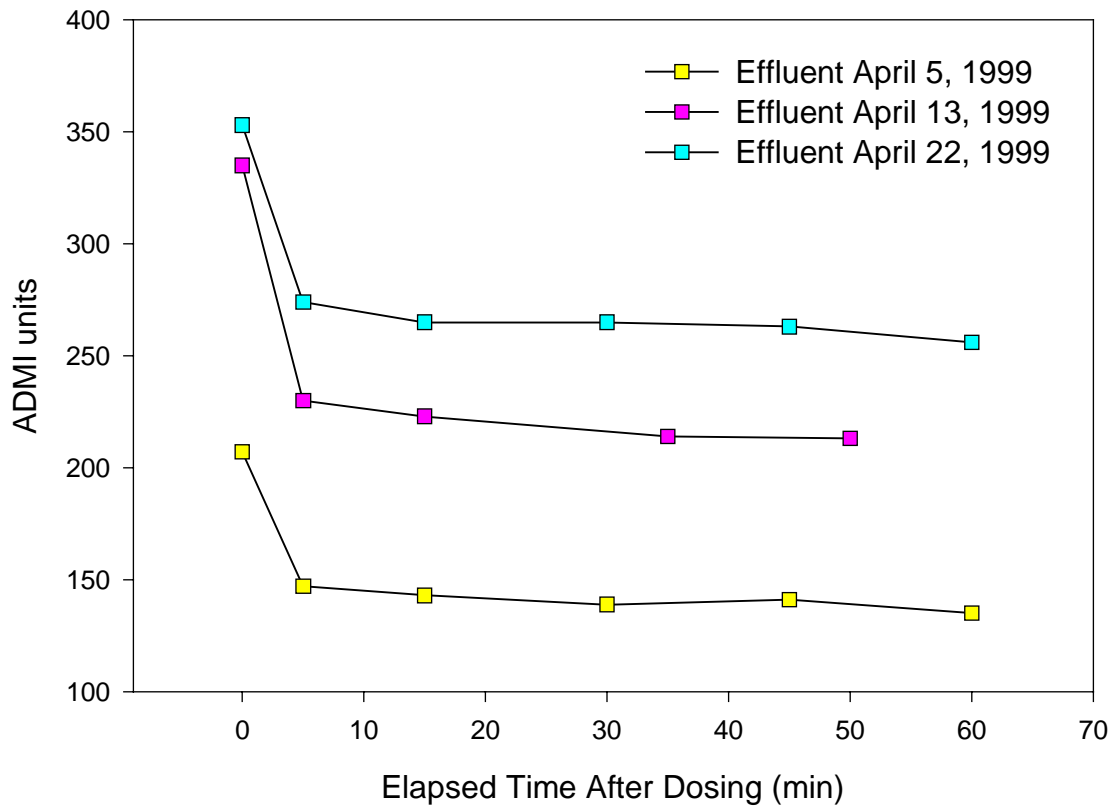(composite sample) collected March 29, 1999

Figure A4. Color Reduction by ClO_2 treatment of Effluent
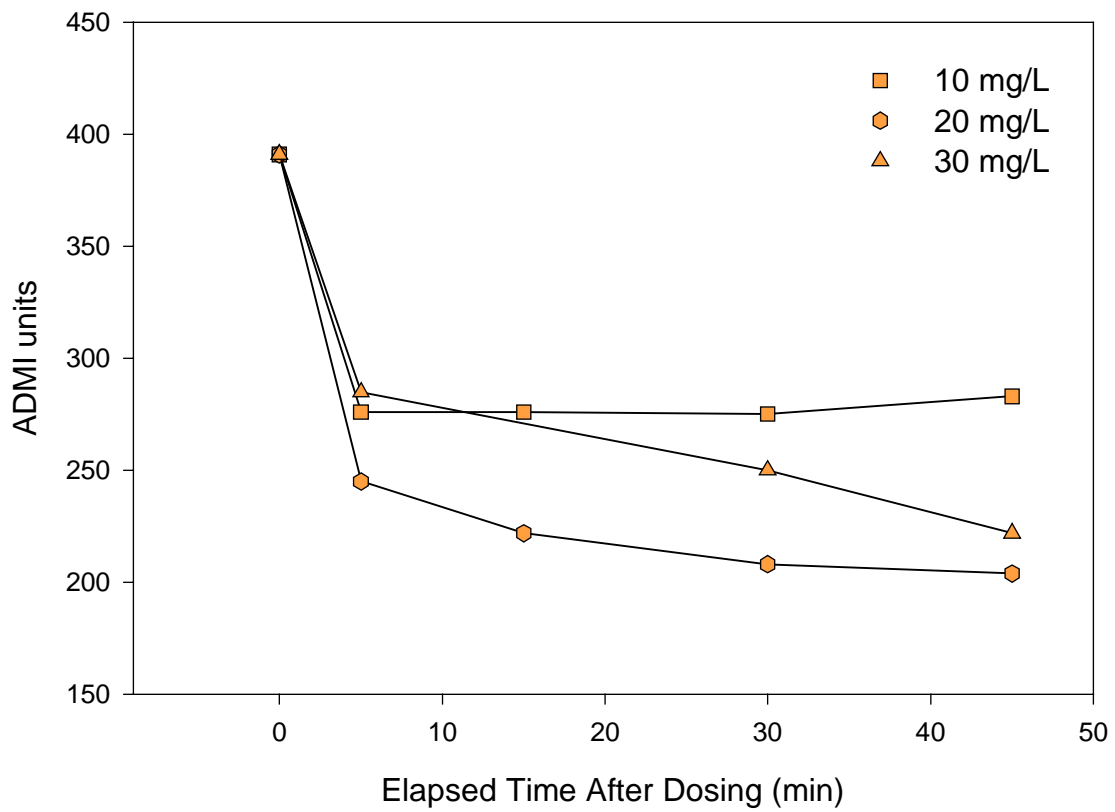(composite sample) for April 1999

Figure A5. Color Reduction by ClO$_2$ treatment of Effluent
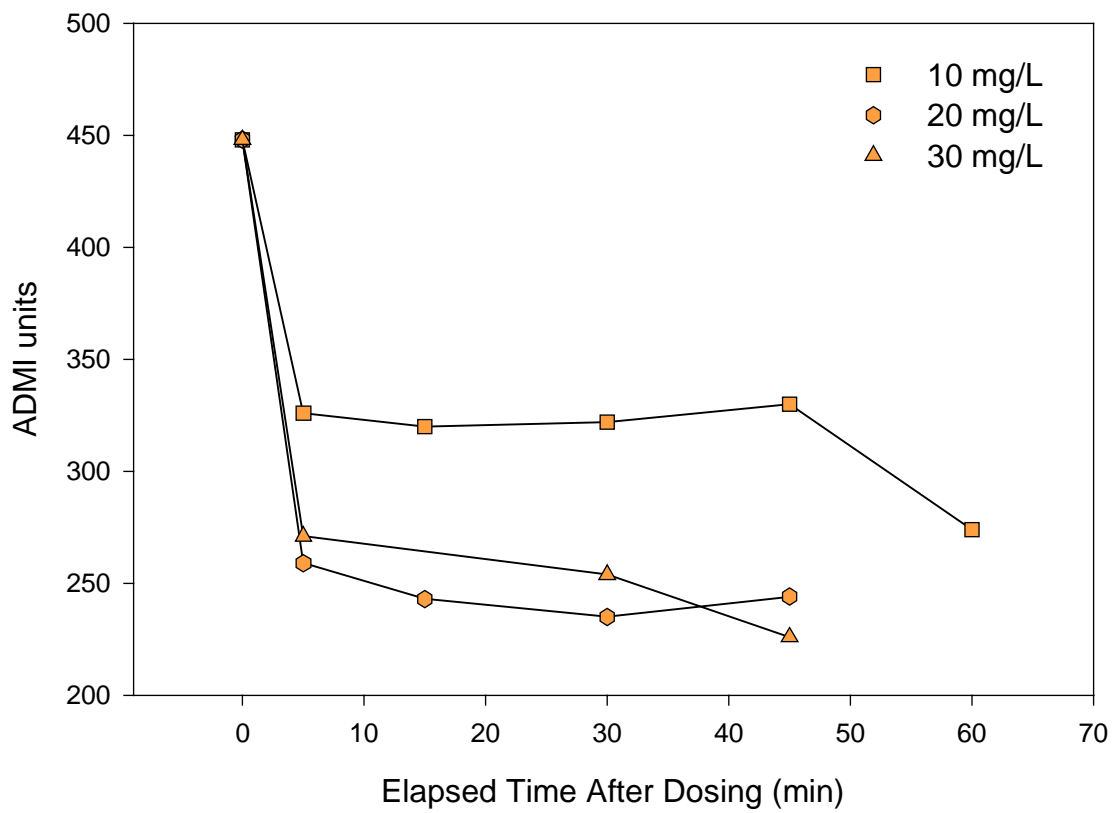(composite) collected May 3, 1999

Figure A6. Color Reduction for ClO$_2$ treatment of Effluent collected May 10, 1999
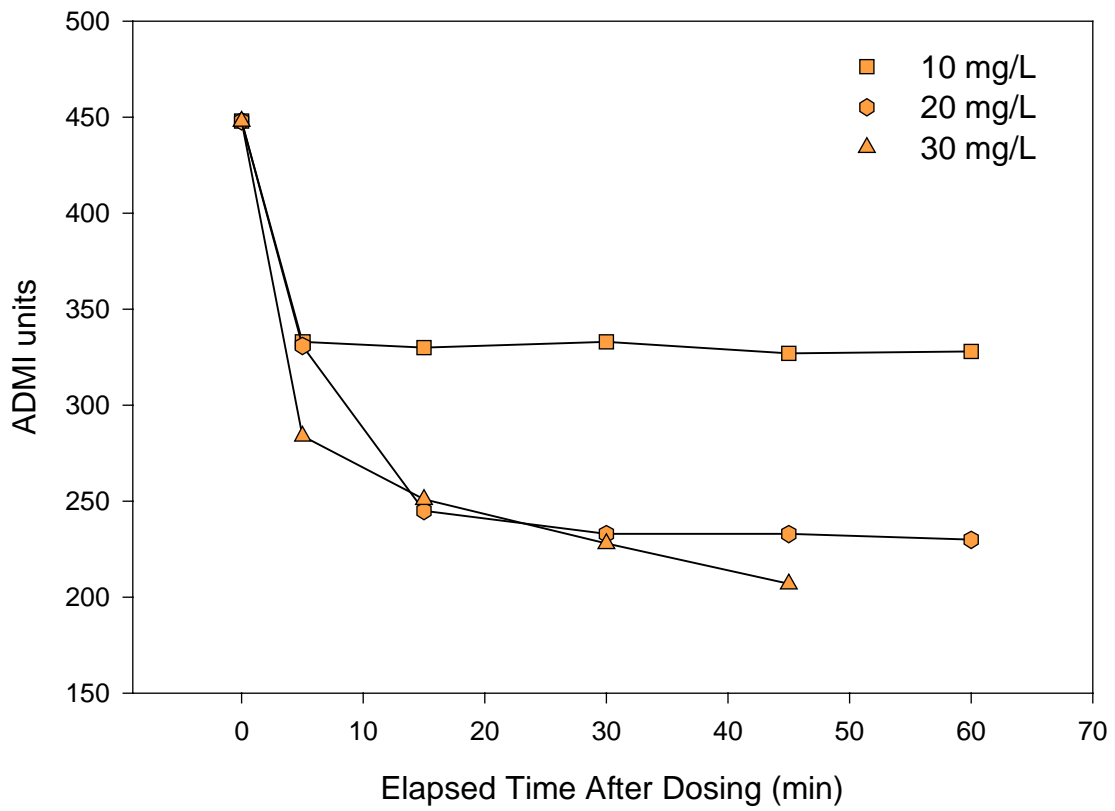
Figure A7. Color Reduction by ClO_2 Treatment of Effluent collected May, 17, 1999

VITA

Jessica Corinne Edwards was born on August 30, 1976 in Crookston, MN. She graduated from Skidmore College (Saratoga Springs, NY) in 1998 with a BA in Chemistry and a minor in English. In August of 1998, she entered the Department of Civil and Environmental Engineering - Master of Science program in Environmental Science and Engineering at Virginia Polytechnic Institute and State University (Blacksburg, VA). Following the completion of the degree requirements in July 2000, Jessica will begin employment with the Black and Veatch Corporation in Kansas City, MO as an environmental analyst in the Potable Water Division.