Abstract

PISCZEK, JAIME CHRISTINE. An Evaluation of Anoxic/Aerobic Treatment for the Removal of Chemical Oxygen Demand and Fiber Reactive Azo Dye Color. (Under the direction of Dr. Brent Smith)

Textile dye effluent is mainly characterized by salts, organic matter, and color and the color of water discharged by manufacturing locations may be regulated. Industry is constantly searching for more effective and economical methods for meeting these regulations. The standard method of treating textile wastes uses aerobic microorganisms to cost effectively decompose organic waste. This process is ineffective in removing color related to azo dyes. Fiber reactive azo dyes, which represent a significant market portion, were chosen for investigation in this study and four hydrolyzed dyestuffs were utilized, containing C. I. Reactive Red 198, Yellow 86, Black 5, and Violet 5. This research investigated the effectiveness of a sequential anoxic/aerobic treatment process for the removal of chemical oxygen demand (COD) and fiber reactive azo dye color from wastewater using a bench-scale treatment system. The performance of the anoxic/aerobic process was compared to a bench-scale aerobic system, which represented a conventional treatment system. A viable anoxic/aerobic biomass was developed and acclimated to a synthetic influent. Using fully acclimated biomass, kinetic rate studies were performed to determine the percent and rates of COD and color removal by the anoxic/aerobic process and the aerobic control. The rate of COD removal under aerobic conditions was twice the rate under anoxic conditions. The percent COD removal by the anoxic/aerobic process was 95% vs. 97% removal by the aerobic control. The rate of color removal was highest for Reactive Violet 5, followed by Reactive Black 5, Reactive Red 198, and

Reactive Yellow 86. For each dye, the degradation rate during the anoxic phase was over ten times the rate during the aerobic phase. The percent color removal by the anoxic phase was five times the removal by the aerobic phase and by the aerobic control. Reactive Yellow 86 exhibited lower color removal and certain structural differences, as compared to the other three dyes studied. This information indicates that certain structural features prevent degradation of a dye under both anoxic and aerobic conditions. In terms of process design, the kinetic rate studies for COD and color removal indicate that the majority of the time in an anoxic/aerobic cycle should be devoted to the anoxic phase, in order to maximize color removal. Since certain products of dye degradation have been identified as toxic, the toxicity removal of the anoxic/aerobic system must be investigated before specific design recommendations can be made.

AN EVALUATION OF ANOXIC/AEROBIC TREATMENT FOR THE REMOVAL OF CHEMICAL OXYGEN DEMAND AND FIBER REACTIVE AZO DYE COLOR

By

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This thesis is dedicated to my grandfathers, Phil Myers and Ernie Hayden,
who taught me how to win at checkers, ride a bike, read the comics, root for the Fighting Illini, drive a pontoon boat, flirt with the wait-staff, and dilute my tea with lemonade, and who passed away this year.

Biography

The author was born in Columbus, Indiana on April 4, 1979, the first and only child of parents Candace and Michael Hayden. She grew up in Bloomington, Illinois and Warren, Michigan and her upbringing was influenced by her grandparents Dora Lea and G. Philip Myers and Mary Ann and Ernest Hayden. She attended high school at Oakland Christian School in Auburn Hills, Michigan and then graduated from Southeast Guilford High School in Greensboro, North Carolina. In May 2001, she graduated from North Carolina State University with a Bachelor of Science in Textile Engineering with a concentration in Product Design and a minor in Graphics Communication. Upon graduation, she accepted a position as a Product and Process Improvement Engineer at Milliken & Company's Cedar Hill Plant. On November 24, 2001, she married Michael Pisczek. In 2003, she entered the Institute of Textile Technology's Fellowship Program at North Carolina State University as a Milliken Industrial Fellow. In 2005, she is a candidate for the Master of Science in Textile Chemistry with a minor in Textile Technology. Upon graduation, she will return to work at Milliken & Company's Magnolia Finishing Plant.

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List of Symbols and Abbreviations

ADMI	American Dye Manufacturers Institute color determination method
APHA	American Public Health Association color determination method
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
HRT	Hydraulic Retention Time
MLSS	Mixed Liquor Suspended Solids
OECD	Organization for Economic Cooperation and Development
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
λmax	Wavelength of maximum absorbance in visible region

1. Introduction

Environmental regulations exist to ensure the quality of the environment and these regulations include the characteristics of the water discharged by manufacturing locations. Industry is constantly searching for more effective and economical methods for meeting these regulations. Textile dye effluent is mainly characterized by salts, organic matter, and color. The standard method of treating textile wastes is the activated sludge process, in which aerobic microorganisms are used to decompose organic waste. This process is effective and cost efficient for the reduction of organic matter and toxicity. A biological, chemical, or physical process can be used to remove the color in the wastewater with varying effectiveness depending on the types of dyes present. However, there is no effective and universal method for the removal of color resulting from the presence of all dye types. Chemical and physical decolorization processes are often expensive and, therefore, biological processes are preferred (5). Many reactive dyes are of the azo chemical class and contain nitrogen – nitrogen double bonds which can be broken to achieve decolorization. Aerobic processes utilize oxygen, which can inhibit azo bond cleavage. Anoxic and anaerobic processes are capable of azo bond cleavage because they require an environment with a low level of dissolved oxygen (35). As a result, anoxic and anaerobic processes are capable of more efficient decolorization than the conventional aerobic system. Despite the drawbacks of the conventional aerobic system in regard to color removal, aerobic processes are very effective for the removal of chemical oxygen demand and toxicity. While anaerobic processes require special equipment, aerobic treatment lagoons can be easily modified to incorporate an anoxic pre-treatment (3). This research investigated the applicability of a sequential

anoxic/aerobic treatment process for the removal of chemical oxygen demand and fiber reactive azo dye color from wastewater. This type of treatment process has the potential to be more effective and less expensive than a conventional aerobic system with tertiary chemical or other advanced post-treatment for color removal.

The specific objectives for this study were to:

1. Develop a viable biomass that could be effective in both an anoxic and aerobic environment.
2. Compare the degradation of COD by this biomass under anoxic vs. aerobic conditions.
3. Determine the kinetic parameters for COD removal for each phase of the anoxic/aerobic process and an aerobic control process, using fully acclimated biomass.
4. Compare the degradation of fiber reactive azo dyes by this biomass under anoxic vs. aerobic conditions.
5. Determine the kinetic parameters for color removal (as measured by dye concentration and ADMI color value) for each phase of the anoxic/aerobic.
6. Compare the color removal for the dyes studied in terms of dye structure.
7. Make recommendations for the design of an anoxic/aerobic sequential wastewater treatment facility.

2. Literature Review

This research involves the treatment of wastewater containing fiber reactive azo dye color and chemical oxygen demand (COD) by anoxic and aerobic biological respiration. Anoxic and aerobic respiration are differentiated by the oxygen level of the environment in which they occur. Topics related to this study include the environmental and regulatory impact of color in wastewater (2.1), the characteristics of fiber reactive dyes (2.2), the currently available methods of color removal (2.3), specifics on the available biological methods for color removal (2.4), and the applicability of these biological processes for the degradation of azo dyes (2.5).

2.1. Environmental and Regulatory Impact of Color in Wastewater

Textile manufacturing locations use a significant amount of water and chemicals for wet processing activities such as preparation, dyeing, and finishing of fabrics. Compared to other industries, textile manufacturing is one of the largest producers of wastewater (8). Synthetic dyes are widely used in the textile industry, and unused dye remains in the water after processing because a certain percentage remains unfixed to the fiber (4). As a result, water discharged from textile wet processing facilities is often brownish in color (8). In extreme cases, this attribute can disrupt photosynthesis, which is harmful to the natural ecosystem. Even though the dye molecules themselves are not typically toxic at the levels found in most effluent, colored lakes and rivers are generally viewed as polluted. Even very low concentrations of dye are extremely visible in receiving waters and the human eye can detect the presence of dye at a concentration of one part per million (2, 22). Consequently, the presence of dye in wastewater can

represent an aesthetic environmental problem, even if the effluent stream is diluted when joining the receiving stream. The color of effluent from textile manufacturing facilities can be regulated and in some cases, treatment is necessary to prevent a compliance issue (8). Since many textile plants are located in rural areas and operate on-site wastewater treatment facilities due to the increasing cost of municipal treatment centers, the development of cost effective methods for color removal is of importance to the industry (2).

2.2. Fiber Reactive Dyes

Fiber reactive dyes are fixated to cellulose by the formation of covalent bonds and they are characterized both by the type of chromophore and the type(s) of reactive group(s) present in the structure (25). The chromophore subclasses of fiber reactive dyes include azo (mono-, dis- or tri-), anthraquinone, and phthalocyanine (31), while the possible reactive groups include monochlorotriazines, dichlorotriazines, and vinyl sulfones (7). Bifunctional dyes are also available and these structures have more than one reactive group, which may be the same, in the case of homobifunctional dyes, or different, in the case of heterobifunctional dyes (25).

Fiber reactive dyes for use with cellulose represent approximately thirty percent of the total dye market (22). Among fiber reactive dyes, eighty percent contain one or more azo bonds (16). Fiber reactive dyes are preferred for their relatively low cost, excellent shade range, the availability of several application methods, and their good wet fastness. However, during dyeing with fiber reactive dyes, a hydrolysis reaction competes with the fixation of the dye onto the fiber. This results in dye molecules reacting with the water rather than the hydroxyl groups on the cellulose. Consequently,

up to fifty percent of the dye remains unfixed after processing and exits the manufacturing location in the wastewater. The hydrolyzed form of the fiber reactive dye is very water soluble and the bright shades, which are characteristic of these dyes, are very visible in wastewater (22). Due to these factors and structural characteristics which allow these dyes to resist conventional treatment, fiber reactive azo dyes are among the most problematic for wastewater management facilities (26).

2.2.2. Fiber Reactive Azo Dyes Used in this Experiment

Due to the large market use of fiber reactive azo dyes and their resistance to conventional wastewater treatment, four fiber reactive azo dyes were identified for investigation in this study. The dyes were selected to represent a range of colors and structural features, with a focus on dyes of major use by the industry.

2.2.2.1. Monoazo (C. I. Reactive Yellow 86)

Reactive Yellow 86, as shown below in Figure 1.1, is a monoazo with a dichlorotriazine reactive group.

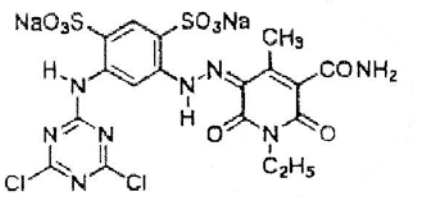

Figure 1.1 C. I. Reactive Yellow 86 Structure

2.2.2.2. Disazo (C. I. Reactive Black 5)

Reactive Black 5, shown below in Figure 1.2, is a disazo with two vinyl sulfone reactive groups.

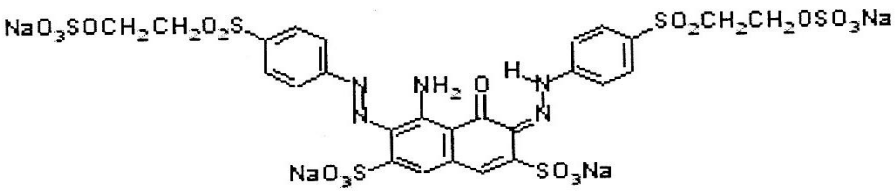

Figure 1.2 C. I. Reactive Black 5 Structure

2.2.2.3. Bifunctional (C. I. Reactive Red 198)

Reactive Red 198, shown below in Figure 1.3, is a heterobifunctional monoazo with both a monochlorotriazine and a vinyl sulfone reactive group.

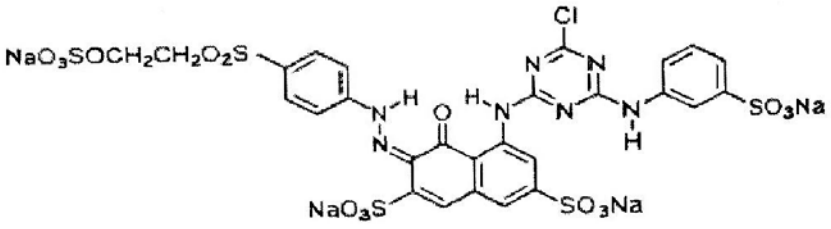

Figure 1.3 C. I. Reactive Red 198 Structure

2.2.2.4. Metal Complex (C. I. Reactive Violet 5)

Reactive Violet 5, shown below in Figure 1.4, is a 1:2 metal complex dye with a vinyl sulfone reactive group.

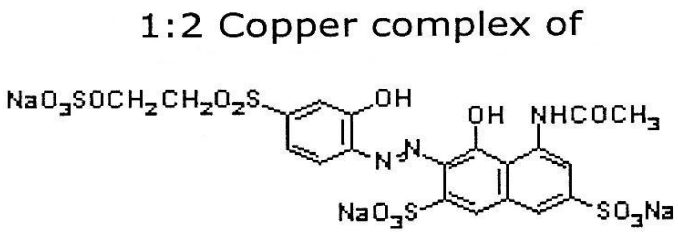

Figure 1.4 C. I. Reactive Violet 5 Structure

2.3. Methods of Color Removal from Textile Wastewater

Treatment processes for decolorization can be categorized as adsorptive, precipitative, or reactive to indicate the method of color removal. Adsorptive and precipitative methods physically remove the dye molecule from the wastewater, while reactive methods degrade a portion of the chromophore (the characteristic of the dye molecule which gives it color) (14). As illustrated in Figure 1.5, each method contains several treatment options.

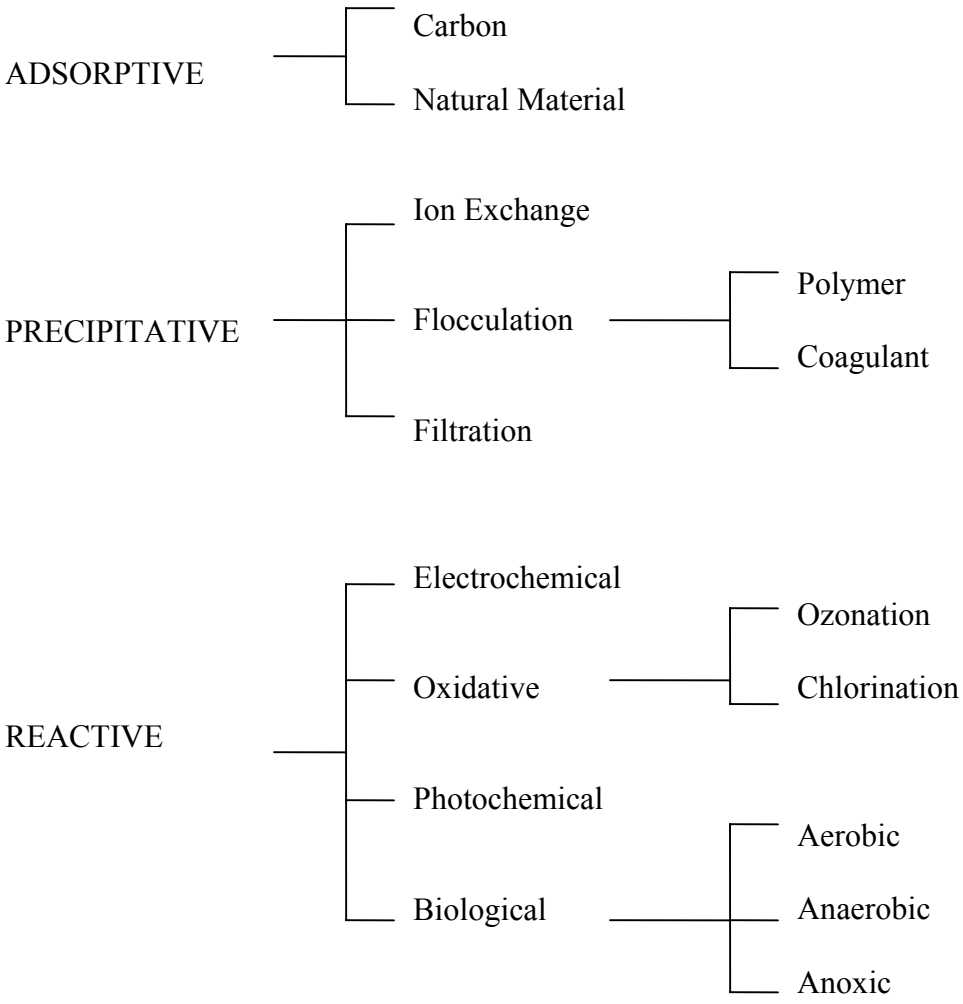

Figure 1.5 Decolorization Methods

Note: Adapted from Color Reduction in Textile Wastewater via Chitin Adsorbent (pg. 7), by A. S. Koonce, 1993, Unpublished master's thesis, North Carolina State University, Raleigh, NC.

2.3.1. Adsorptive Methods

Adsorption is a physical-chemical process for decolorizing textile wastewater by sorption of the dye molecule into a sorbent medium such as activated carbon or some other natural material (14, 26). This method is successful with a wide range of dyes and can be rapidly tailored to new requirements by changing the sorbent medium (14, 22). However, adsorption requires the disposal of contaminated waste (22) and its efficiency

can be affected by dye properties and factors such as temperature, pH, and contact time (26). Large amounts of absorbing material are often required to achieve efficient decolorization (5) and the cost of the sorbent medium can be prohibitive (14).

2.3.2. Precipitative Methods

Precipitative methods such as ion exchange, flocculation, and filtration decolorize by settling the dye molecules out of solution and adsorbing the molecules into a precipitate material. The ion exchange method uses a resin to form ionic bonds with dye molecules in solution. This process is capable of removing even the most soluble dyes and the resin can be regenerated after all of the ionic sites are filled. However, this method does not decolorize disperse dyes and can involve expensive components (26). Another common technique uses a polymer flocculent to bond with the dye molecules and reduce their solubility. The combined molecules are then settled out of the wastewater (14). Instead of a polymer, a coagulation compound can be used as a flocculent (5). Methods involving coagulation-flocculation are generally cost effective (22), but some coagulants are expensive (5). Success requires careful selection of the appropriate coagulant and good pH control (5). Membrane filtration can also be used to physically remove dye molecules from wastewater. This method is successful with all dye types (22), but is costly to apply to large volume wastewater streams (5). Flocculation and filtration generally produce a large quantity of sludge and disposal of this contaminated material can become an issue (14, 22).

2.3.3. Reactive Methods

Reactive methods decolorize by degrading the dye molecule and include electrochemical, oxidative, photochemical, and biological degradation. Electrochemical destruction uses electrical current to destroy the dye molecules rapidly, efficiently, and without the use of chemicals. However, this method requires a significant amount of electricity and its efficiency can decrease as flow rate increases (26). Oxidative methods are widely used because of their simplicity (26) and speed of decolorization (22). Hydrogen peroxide, ozone, or chlorine compounds may be used as the oxidizing agent, which cleaves the aromatic rings in the dye molecule. Of the three, ozone is the best oxidizing agent because it is the most unstable, can be applied in the gaseous form, and does not change the volume of water or sludge. However, ozone has a very short half life and must be applied continuously, which has significant cost disadvantages (26). Many reactive dyes are designed to be ozone-resistant and are not degraded by this method (5). Ozone treatment is also dependent on pH, can produce harmful byproducts, and requires safety precautions (14). Chlorination systems are less expensive and simpler than ozonation (5, 14), but may require large amounts of the oxidizing agent to achieve full decolorization, resulting in the release of large amounts of chlorine into the environment (26). In addition, chlorine may react with natural organics to form potential carcinogens, which are regulated in many countries (5). Photochemical treatment can be used to degrade dye molecules using ultra-violet light. This method produces no sludge or odor, but can produce unwanted byproducts (26) and can involve high capital costs (22).

2.4. Biological Reactive Methods for Color Removal

In biological wastewater treatment, microorganisms (known as biomass or sludge) break down organic wastes through a series of oxidation-reduction reactions, called respiration. Conventional biological methods involve aerobic respiration (2.4.1), while alternative methods utilize anaerobic or anoxic respiration (2.4.2).

2.4.1. Conventional Biological Methods (Aerobic)

Aerobic treatment is the most commonly used biological process for large scale industrial waste treatment due to its success in reducing the biochemical oxygen demand of wastewater (5, 11). In aerobic respiration, oxygen is the terminal electron acceptor and is used to convert organic wastes into carbon dioxide, water, and energy. The energy released following this reaction is used by the organisms for cell synthesis (1, 5, 11).

The most common aerobic system is the activated sludge process, which is composed of an aeration tank and clarifier, as shown in Figure 1.6.

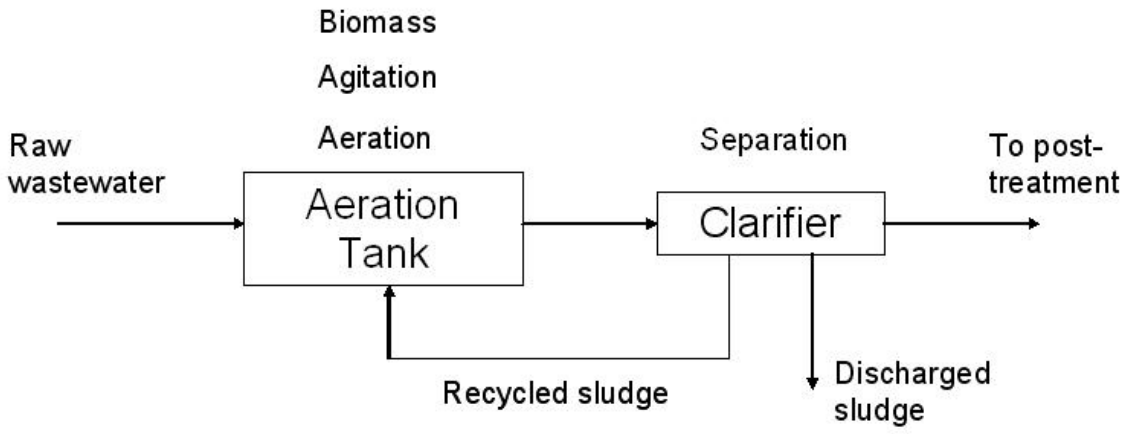

Figure 1.6 Activated Sludge Process

The raw wastewater enters the aeration tank, where it is mixed with the bacteria-laden sludge, agitated, and aerated so that organic wastes can be oxidized rapidly. Next, the

wastewater is sent to the clarifier, where sludge and other particles are separated from the effluent. The sludge is either recycled back to the aeration tank to continue the oxidation process or discharged for treatment and disposal. The effluent may be discharged to the receiving waters or sent to a further treatment step (5, 11). The sludge age, concentration of organic material, and nutrient (N, P) to microorganism ratio must be maintained at a constant level for the activated sludge system to be effective (11).

2.4.2. Alternative Biological Methods (Anaerobic and Anoxic)

As stated above, biological reactive methods use bacteria to break down organic wastes by a series of oxidation-reduction reactions, called respiration. In aerobic respiration, the terminal electron acceptor is oxygen. Oxygen is the strongest oxidizing agent available to the microorganism and provides the most energy for cell synthesis. As a result, the biomass will utilize any dissolved oxygen (DO) in the wastewater and only turn to alternative electron acceptors when the DO level lowers beyond a certain point. When alternative electron acceptors such as nitrate, sulfate, or carbon dioxide are utilized, degradation occurs via anaerobic or anoxic respiration (1). Since anaerobic and anoxic biological processes utilize weaker oxidizing agents as electron acceptors, the biomass is adapted to lower energy requirements and has a lower rate of cell synthesis. As a result of these characteristics, alternative biological processes do not require aeration, produce less biomass, and require less maintenance, inorganic nutrients, and sludge disposal (18).

Anaerobic respiration requires environments that are oxygen-free and, therefore, must be carried out in a closed system to eliminate the presence of DO. The products of anaerobic respiration are carbon dioxide, methane, and cell synthesis and the methane gas

which is produced can be used as an energy source. Since anaerobic respiration involves a fermentation reaction and utilizes weaker oxidizing agents, as compared with anoxic and aerobic respiration, the temperature in an anaerobic treatment reactor must be maintained at approximately 35°C in order to achieve optimum microbial growth and organic waste degradation (5).

Despite their similarities, anaerobic and anoxic respiration require very different operating conditions. Anoxic environments allow very low levels of DO, as opposed to the oxygen-free requirement for anaerobic processes. As a result, anoxic treatment does not require a closed system. An additional difference between the two alternative biological processes involves the terminal electron acceptor for the oxidation-reduction mechanism of degradation. Anaerobic processes utilize sulfate or carbon dioxide as the terminal electron acceptor, while anoxic processes use nitrate (3, 18, 28). While nitrate is not as strong an oxidizing agent as oxygen, it is stronger than sulfate and carbon dioxide. As a result, anoxic processes do not require an elevated temperature in order to achieve an acceptable degradation rate and efficiency (18). Due to the use of nitrate as the electron acceptor, anoxic conditions are typically utilized for denitrification (3, 21, 33).

Anaerobic treatment facilities have certain disadvantages in that they require a closed, oxygen-free vessel which operates at an elevated temperature. In contrast, anoxic respiration can be carried out under operating conditions that are similar to those required by aerobic respiration (5, 18). As a result of these characteristics, a conventional aerobic wastewater treatment lagoon can be converted to an anoxic/aerobic sequential process with little capital investment, as long as the lagoon is of adequate volume. This is accomplished by placing aerators and mechanical stirrers to create zones of low and high

DO (3). The lab-scale wastewater treatment system utilized in this experiment was designed to model such a facility in a batch process.

Since anoxic processes utilize a weaker oxidizing agent than aerobic respiration, anoxic treatments are generally considered to have a lower substrate removal rate than conventional aerobic processes (6). However, alternative biological processes are capable of degrading certain components that are resistant to aerobic treatment, such as azo dyes (10, 16, 26). In addition, experimental results have indicated that anoxic respiration is capable of sufficient substrate removal. For example, an experiment involving an anoxic sequencing batch reactor for the removal of phenol and chemical oxygen demand (COD) achieved better than 95% phenol and COD removal under the conditions tested (27). Many studies of the rates of substrate removal in a treatment process involving multiple modes of respiration separate the two bacterial populations and little experimental data exists concerning substrate removal rates of biomass that is grown in alternating anoxic/aerobic systems (6). One goal of this study is to determine the substrate removal rates for such a dual-population biomass.

2.5. Treatment of Fiber Reactive Azo Dye Color

Synthetic dye molecules have a very stable aromatic molecular structure and are designed to resist degradation by light, water, soap, perspiration, and oxidizing agents (2, 10). Among azo dyes, reactive dyes represent the greatest challenge for wastewater treatment facilities due to several factors including their high solubility and low fixation efficiency (26). Conventional biological methods are not capable of degrading azo dyes to achieve satisfactory color removal levels, but success in color removal by anaerobic and anoxic respiration has been demonstrated (2.5.1). These alternative biological

processes have been combined with conventional aerobic respiration to create multi-phase treatment systems for effective removal of both color and COD (2.5.2). In order to obtain a better understanding of the dye degradation process, researchers have identified the optimal operating parameters (2.5.3), investigated toxicity issues related to the production of aromatic amines (2.5.4), and attempted to define a relationship between dye structure and the rate of degradation (2.5.5).

2.5.1. Mechanism of Decolorization

Azo dye molecules have color due to their azo bond, auxochromes, and system of conjugated double bonds (35). The azo bond, while resistant to aerobic degradation, can be cleaved under anaerobic or anoxic conditions, resulting in decolorization and the production of aromatic amines (10, 20, 22, 26, 32, 34). Biological dye degradation occurs when an auxiliary substrate is oxidized by the bacteria and reduction equivalents are transferred to the dye molecule, resulting in cleavage of the azo bond (17). If reaction partners with a higher redox potential than the dyes are locally present, the electrons and protons that were obtained by the oxidation of the auxiliary substrate will react with these alternative partners instead of the dye and decolorization will not occur (34). Due to this phenomenon, the success of alternative biological methods in decolorizing azo dyes is related to the level of DO in these systems as opposed to aerobic systems. Researchers have quantified the relationship between DO and decolorization by measuring the color removal of controlled bacterial cultures when put in contact with several varieties of acid, direct, and reactive dyes, including azo, anthraquinone, and indigo chromophores. The results indicated that the azo dyes studied could not be decolorized in an environment where the DO concentration was greater than 0.45 mg/L (4).

In the past, researchers questioned whether biological decolorization was mainly effected by adsorption to the biomass or by biological degradation. Adsorption is not an effective mechanism for decolorization since a saturation point is quickly reached and replacement of the biomass is necessary for continued color removal. In an investigation of decolorization under anoxic conditions, it was determined that color removal was primarily carried out by biological degradation, since the examined biomass remained largely colorless (4).

2.5.2. Multi-Phase Treatment Processes

In order to take advantage of the merits of conventional biological treatment methods in the area of effluent decolorization, pre-treatments involving oxygen-limiting processes such as anaerobic and anoxic respiration are being investigated. These alternative biological methods could be combined with conventional biological treatment to create sequential processes that effectively remove both color and COD from textile wastewater (2). A sequential anaerobic/aerobic treatment system has been extensively investigated in a laboratory setting and has exhibited significant azo dye degradation during the anaerobic phase. Anaerobic/aerobic processes have been demonstrated to decolorize azo dyes including C. I. Reactive Black 5, C. I. Direct Black 38, C. I. Reactive Violet 5, and C. I. Mordant Yellow 10 (5, 10, 12, 17, 30).

Anaerobic processes are advantageous because they can decolorize azo dyes and require less energy and produce less sludge than aerobic and anoxic systems, but disadvantages associated with such a system include the requirement for a closed, oxygen-free vessel at an elevated temperature (5). These requirements for anaerobic treatment require very different equipment for each phase of the process in an

anaerobic/aerobic system. As an alternative to anaerobic/aerobic treatment, anoxic/aerobic sequential processes are being investigated since both phases can be operated in a similar treatment facility.

The degradation of several different types of azo dyes has been confirmed under anoxic conditions. The dyes investigated included a disperse azo dye and several different categories of fiber reactive azo dyes, including monoazo (C. I. Reactive Red 198), diazo (C. I. Reactive Black 5), formazan, and a copper complexed azo dye (5, 16, 35). The degradation of C. I. Reactive Black 5 has been observed in a sequential anoxic/aerobic process with varying phase times and dye concentrations. The experiment involved 16-liter reaction vessels with a mixed liquor suspended solids (MLSS) of 1500-2500 mg/L, a 24-hour hydraulic retention time (HRT), and an eight-day sludge age. In the anoxic phase, significant color change and shifts in the λ_{max} of the effluent were observed. The aerobic phase resulted in little color change and no λ_{max} shift. A relationship was identified between the length of time allotted to the anoxic phase and the percent decolorization, with increasing time resulting in increasing color removal, up to a maximum level of decolorization. No impact of varying dye concentration was observed. A COD removal of greater than 95% was achieved by all experimental conditions, with most of the COD removal occurring during the first two hours of the cycle (19).

This experiment has been designed to continue the evaluation of an anoxic/aerobic wastewater treatment process and build on the research discussed above. In addition to Reactive Black 5, three additional fiber reactive azo dyes have been chosen for evaluation, in order to compare the degradation in terms of dye structure. Different reactor parameters have also been chosen to more accurately model operating conditions

that are commonly used in the textile industry, including an MLSS of 3500 – 4500 mg/L, a 48-hour HRT, and a thirty-day sludge age. In this experiment, a 24-hour cycle was divided into an eight-hour anoxic phase, followed by a 16-hour aerobic phase. It was theorized that these lengthy phases would allow the color and COD to reach a constant level in the reactor and facilitate the collection of kinetic data.

2.5.3. Optimal Conditions for Anoxic Color Removal

In addition to the level of DO in the system, additional factors can affect the rate of color removal of a treatment process. Researchers investigated the impact of operating parameters, including pH, temperature, dye concentration, and substrate, on the degradation of fiber reactive azo dyes under anoxic conditions using controlled bacterial cultures. The dyes utilized in the study were C. I. Reactive Red 198 and C. I. Reactive Black 5. It was determined that color removal was optimized at a neutral pH and a temperature of 30°C. Under these ideal conditions, it was found that decolorization efficiency decreased at dye concentrations above 0.3 g/L, but acceptable color removal was still achieved at concentrations up to 0.8 g/L. Peptone, a commonly used bacteriological culture media composed of protein derivatives, was determined to be the ideal substrate, since it is an excellent source of nitrogen for anoxic respiration. In addition, high concentrations of glucose were shown to decrease the decolorization efficiency of the system. The optimal operating parameters identified by the experiment were verified using a mixture of dyes (composed of acid, direct, and fiber reactive structures) (4).

2.5.4. Toxicity Related to Aromatic Amines

Decolorization of azo dyes by the cleavage of the azo bond produces aromatic amines and several of these species have been identified as toxic or carcinogenic. In several experiments involving anaerobic/aerobic processes, an increase in the toxicity of effluent from the anaerobic phase and a subsequent reduction in toxicity after the aerobic phase have been demonstrated (10, 12). However, not all experiments involving anaerobic/aerobic processes have achieved these straightforward results. In an experiment involving the decolorization of azo Mordant Yellow 10, the anaerobic degradation process resulted in the formation of two different aromatic amines. One of these by-products was successfully degraded by a subsequent conventional aerobic process, but the other species had to be mineralized using a specifically engineered bacterial strain (30). In an experiment involving the anaerobic/aerobic degradation of C. I. Reactive Black 5, the colorless aromatic amines created by dye degradation in the anaerobic phase were oxidized by the subsequent aerobic stage and formed a by-product which absorbed in the visual range at a similar λ_{max} as the dye. This by-product was not removed during the aerobic phase (17). This phenomenon is supported by additional experimental results (32). Difficulties in the degradation of aromatic amines have also been noted in experiments involving anoxic/aerobic treatment. In an experiment involving the decolorization of six fiber reactive dyes under anoxic conditions, a subsequent aerobic phase utilizing the same biomass only partially degraded the resulting aromatic amines, so a partial ozonation post-treatment was added to further degrade the by-products (15).

The isolated aerobic treatment of aromatic amines has been studied in activated sludge systems. Depending on the experimental parameters, the estimated half-life of the aromatic amines ranged from 10 to 140 hours, which indicates that long retention times may be necessary for complete mineralization of these by-products. Studies have indicated that specially adapted microbial strains may be necessary for the degradation of resistant aromatic amines (24, 30).

2.5.5. Dye Structure vs. Rate of Degradation

Attempts have been made by several researchers to define a relationship between dye structure and the rate of dye degradation and some general observations have been made. Experimental results have indicated that monoazo dyes are more effectively decolorized than diazo, triazo, and anthraquinone structures (4, 22). Similarly, it has been shown that simple, low molecular weight dyes have more rapid degradation rates than higher molecular weight dyes that are highly substituted. It has also been observed that the type and location of groups on the chromophore affect the degradation rate. Dyes containing hydroxyl or amino groups were observed to degrade more rapidly than dyes containing methyl, methoxy, sulfo, or nitro groups. In addition, the substitution of groups in the para position to the azo bond, which affects the electron density in the region of the azo bond, has been shown to affect the degradation rate if the groups are of the electron-withdrawing variety, such as SO_3H or SO_2NH_2 (22).

3. Experimental Methods and Procedures

The purpose of this study was to operate a bench-scale wastewater treatment process involving sequential anoxic and aerobic respiration phases and to determine the applicability of the process for removing chemical oxygen demand (COD) and color from a synthetic wastewater containing fiber reactive dyestuffs.

3.1. Materials

The study utilized reaction vessels (3.1.1), biomass (3.1.2), synthetic wastewater (3.1.3), and hydrolyzed dye solutions (3.1.4).

3.1.1. Reaction Vessels

Reaction vessels were constructed to propagate the biomass and to create anoxic and aerobic phases of wastewater treatment. The reaction vessels were composed of plastic cylinders, aerators, stirring mechanisms, and feed/decant pumps. Four versions of the reactor design were utilized during the study: large anoxic/aerobic (3.1.1.1), small anoxic/aerobic (3.1.1.3), aerobic control (3.1.1.4), and modified aerobic control (3.1.1.5) reaction vessels. Additional reactors were used to store acclimated biomass from Reactors 1 and 2 until needed by the smaller vessels (3.1.1.2).

3.1.1.1. Large Anoxic/Aerobic Reaction Vessels (Reactors 1 and 2)

The large anoxic/aerobic reaction vessels were constructed using fifteen-liter plastic cylinders to hold the biomass and wastewater. The total volume of mixed liquor in these vessels was maintained at seven liters. The aerobic phase of the wastewater treatment process required a dissolved oxygen (DO) content of greater than 2 mg/L in the

mixed liquor. For this purpose, aeration was supplied to reaction vessels via aerators whose outlet air supply was fixed at a specific area of the vessel using a glass rod. These reactors had two aerators directed to the bottom of the vessel and a third aerator directed to the middle of the mixed liquor (at the 3.5 L level). The anoxic phase of the treatment process required a DO content of less than 0.5 mg/L in the mixed liquor and mixing was achieved through mechanical stirring, provided by magnetic bars placed at the bottom of the cylinder. The stirring bars were activated by magnetic stirring plates placed under the cylinder. Pumps were used to control the rates of decanting and feeding of the large reaction vessels at approximately 230 mL/min. The setup for these reaction vessels is shown below in Figure 3.1.

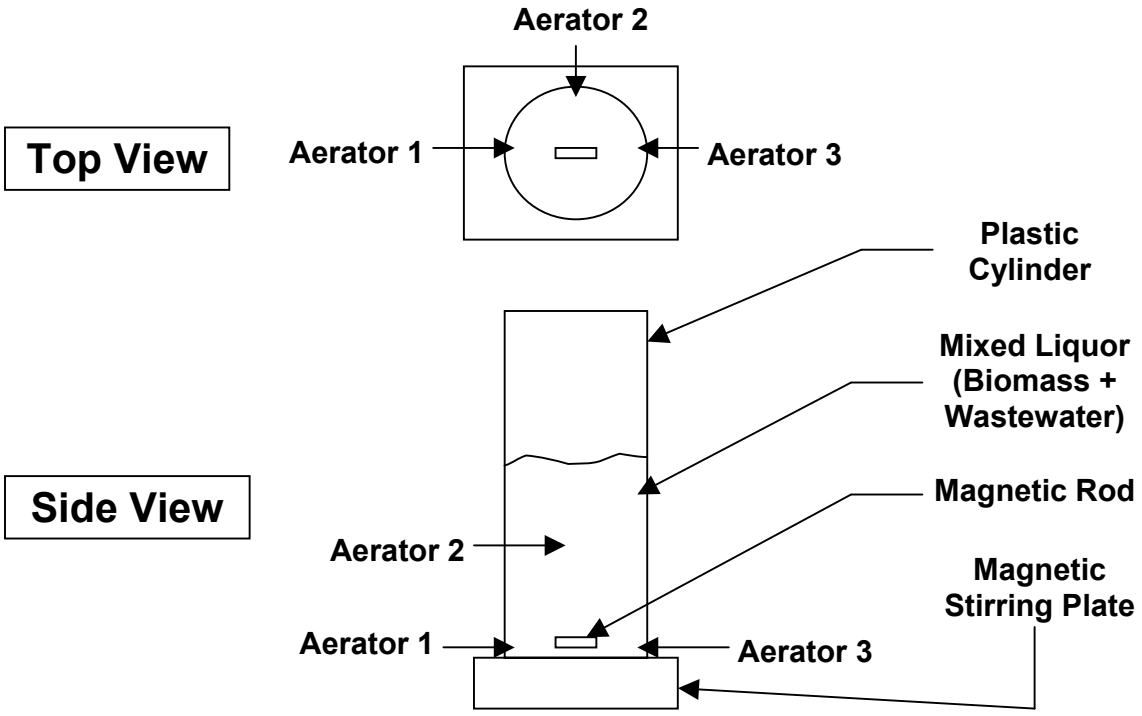

Figure 3.1 Large Anoxic/Aerobic Reaction Vessel

Reactors 1 and 2 were constructed using the previously described setup. These vessels were used first for determining the rates of COD removal for the anoxic and

aerobic respiration processes using synthetic wastewater only. Subsequently, these two vessels were used in the color removal studies. The influent for Reactor 1 included Remazol Red RB and Procion Yellow PX-8G dyestuffs, which contained the hydrolyzed forms of C. I. Reactive Red 198 and C. I. Reactive Yellow 86, respectively. The influent for Reactor 2 included Remazol Black B dyestuff, which contained the hydrolyzed form of C. I. Reactive Black 5. The dyestuffs were hydrolyzed using the procedure described in 3.1.4.

3.1.1.2. Reactors for Storage of Acclimated Biomass (Reactors 3 and 4)

A modified version of the aerobic control vessel described in section 3.1.1.4 was used to store acclimated biomass until needed for the aerobic control studies. Mixed liquor that was removed from Reactors 1 and 2 to maintain the sludge age was placed in Reactors 3 and 4 and fed the same synthetic wastewater influent. These reaction vessels had the same setup as described in section 3.1.1.4, with the exception of a four-liter plastic cylinder and a 3500 mL total volume of mixed liquor. Reactors 3 and 4 were used only for biomass storage and were not involved in any experimental studies. As a result, no testing was completed for these vessels.

3.1.1.3. Small Anoxic/Aerobic Reaction Vessel (Reactor 5)

A small anoxic/aerobic reaction vessel was constructed using a two-liter graduated cylinder with a 1500 mL total volume of mixed liquor. This vessel had one aerator, which was fixed to the bottom of the reaction vessel using a glass rod, to provide aeration for the aerobic phase. The vessel was placed on a magnetic stirring plate to

provide mechanical stirring via a magnetic Teflon-coated stirring bar for the anoxic phase, as shown below in Figure 3.2. Decanting and feeding were performed manually.

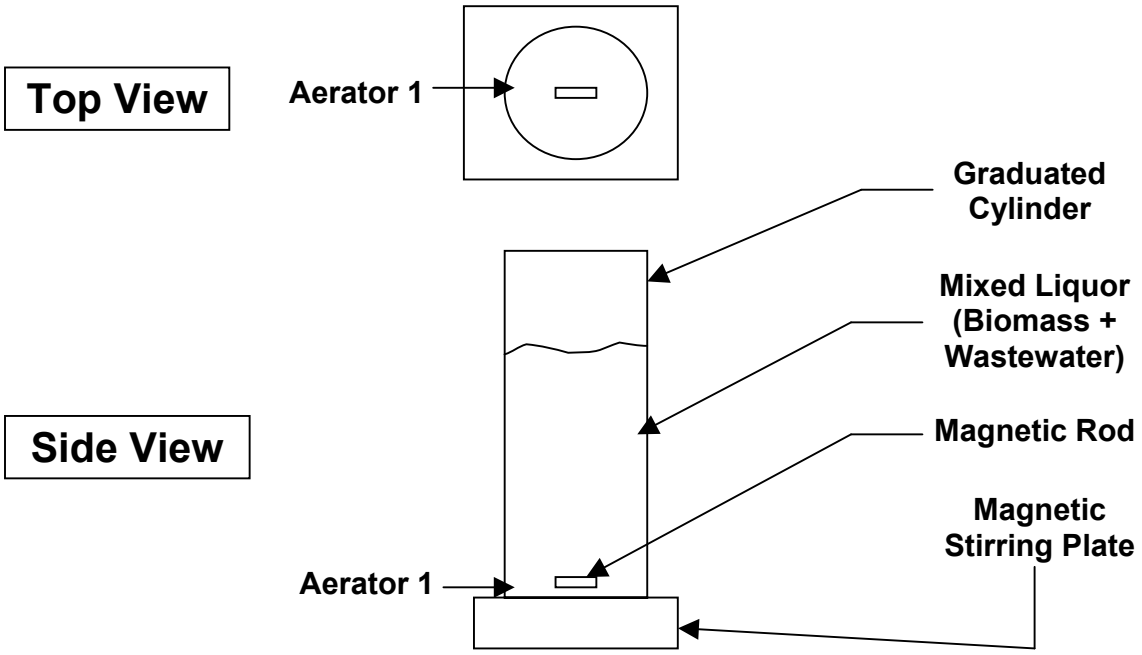

Figure 3.2 Small Anoxic/Aerobic Reaction Vessel

Reactor 5 was constructed using the setup described above and the acclimated biomass seed for this reactor was transferred directly from Reactors 1 and 2. This vessel was utilized in the kinetic study for determining the rates of color removal for the anoxic and aerobic respiration processes. The influent for Reactor 5 included Remazol Brilliant Violet 5R dyestuff, which included the hydrolyzed form of C. I. Reactive Violet 5.

3.1.1.4. Aerobic Control Vessel (Reactor 6)

A small aerobic reaction vessel was constructed using a two-liter graduated cylinder with a 1500 mL total volume of mixed liquor. This vessel had one aerator, which was fixed to the bottom of the reaction vessel by a glass rod, to provide aeration, as shown in Figure 3.3. Decanting and feeding were performed manually.

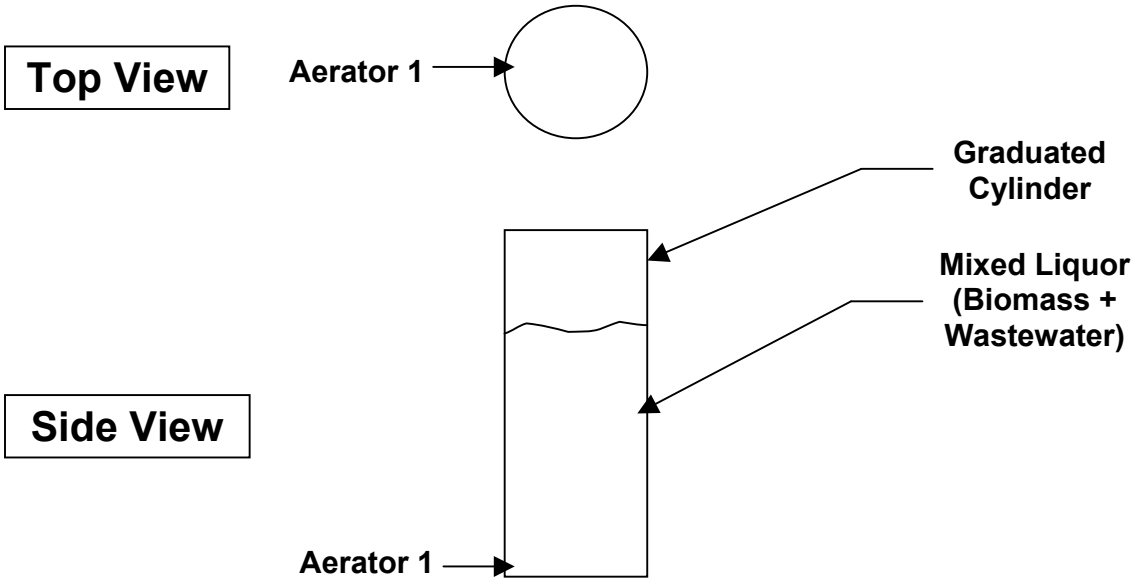

Figure 3.3 Aerobic Control Vessel

Reactor 6 was constructed using the prior setup. This vessel was used in the kinetic study to determine the rate of COD removal of the aerobic respiration process when separate from the anoxic respiration phase. This reactor was fed synthetic wastewater influent containing no dye.

3.1.1.5. Modified Aerobic Control Vessels (Reactors 7, 8, 9)

A modified version of the aerobic control vessel described in section 3.1.1.4 was used to test color removal through aerobic respiration when separate from the anoxic respiration phase. These reaction vessels had the same setup as described in section 3.1.1.4, except for a 1000 mL total volume of mixed liquor.

Reactors 7, 8, and 9 were constructed according to the setup above. In order to compare the color removal of the two treatment processes, Reactor 7 was fed the same influent as Reactor 1, Reactor 8 was fed the same influent as Reactor 2, and Reactor 9 was fed the same influent as Reactor 5.

3.1.2. Biomass

The biomass seed used in the study was obtained from the Alexander City Sugar Creek Wastewater Treatment Plant in Alexander City, Alabama. Approximately five gallons of concentrated mixed liquor were obtained, approximately ten liters of the mixed liquor were poured into the reaction vessel, and the solids were allowed to settle. After settling was complete, the supernatant was removed and the vessel was filled with deionized water to a total volume of seven liters. The resulting mixed liquor was aerated for thirty minutes and the solids were allowed to settle. The supernatant was removed and replaced with fresh deionized water to a volume of seven liters. This process was repeated until the solids had been subjected to six total washings.

3.1.3. Synthetic Wastewater

In order to maintain consistent influent characteristics throughout the study, synthetic wastewater was prepared according to a set recipe. A dilution of the synthetic sewage recipe described in Organization for Economic Cooperation and Development (OECD) Procedure 302 C was utilized to achieve an influent with a COD of approximately 1000 mg/L, in order to simulate the characteristics of wastewater from a typical textile dyeing and finishing location. The recipe that was used in the study also included four mineral nutrient solutions from OECD Procedure 302 B, as shown below:

Table 3.1 Recipes for Nutrient Solutions

Solution	Ingredient	Concentration
A	Potassium dihydrogen orthophosphate, KH_2PO_4	8.5 g/L
	Dipotassium hydrogen orthophosphate, K_2HPO_4	21.75 g/L
	Disodium hydrogen orthophosphate dihydrate, $Na_2HPO_4 . 7H_2O$	50.3 g/L
	Ammonium chloride, NH_4Cl	0.5 g/L
B	Calcium chloride, anhydrous, $CaCl_2$	27.5 g/L
C	Magnesium sulfate heptahydrate, $MgSO_4 . 7H_2O$	22.5 g/L
D	Iron (III) chloride hexahydrate, $FeCl_3 . 6H_2O$	0.25 g/L
	Concentrated hydrochloric acid, HCl	0.1 mL/L

The mineral solutions were prepared by dissolving the ingredients in deionized water supplied by the NCSU College of Textiles stockroom. One liter each of solutions B, C, and D were used throughout the entire study. Solution A was prepared every two weeks.

The synthetic wastewater was composed of synthetic feed components, salt (NaCl), sodium hydroxide solution for pH adjustment, and mineral solutions, according to the following recipe:

Table 3.2 Synthetic Wastewater Recipe

Ingredient	Concentration
Solution A	10 mL/L
Solution B	1 mL/L
Solution C	1 mL/L
Solution D	1 mL/L
60 g/L NaOH	2 mL/L
Salt (NaCl)	1.5 g/L
Peptone	0.5 g/L
Glucose	0.5 g/L
Monopotassium phosphate (KH_2PO_4)	0.5 g/L

Note: salt was added to synthetic wastewater at the start of the anoxic/aerobic cycles.

During the initial acclimation phase of Reactors 1 and 2, twenty-liter batches of synthetic wastewater were prepared and stored until needed. To ensure that there was no contamination of the storage vessel, which would reduce the COD of the synthetic wastewater, a modified procedure was used for the removal studies that followed the

acclimation phase. A concentrate of all synthetic wastewater components except peptone was prepared and refrigerated. A concentrated solution of peptone was also prepared and refrigerated. Feed was prepared daily by combining appropriate volumes of each concentrate with deionized water. During the color removal study, appropriate volumes of concentrated dye solutions were also added. The concentration of each dye was chosen in order to simulate the American Dye Manufacturers Institute (ADMI) color value of typical effluent from a textile dyeing and finishing location, as described in section 3.3.3.3.

3.1.4. Hydrolyzed Dye Solutions

Dyestuffs containing fiber reactive azo dyes were used in this study:

- Remazol Red RB, which contains C. I. Reactive Red 198 (powder)
- Procion Yellow PX-8G, which contains C. I. Reactive Yellow 86 (400 g/L paste)
- Remazol Black B, which contains C. I. Reactive Black 5 (powder)
- Remazol Brilliant Violet 5R, which contains C. I. Reactive Violet 5 (powder)

Commercial dyestuff samples were provided by Russell Corporation and DyStar and a 5 g/L solution of each unpurified dyestuff was prepared. To simulate the color in textile dyeing wastewater, the dyestuff solutions were subjected to a mock dyeing process to obtain the hydrolyzed form of the dyes. One g/L sodium hydroxide was added to bring the solutions to approximately 12 pH and the solutions were heated to approximately 90°C for over 24 hours. The solutions were then neutralized with hydrochloric acid. The same one-liter batch of each dye was used throughout the entire study to maintain consistency.

3.2. General Reactor Procedures

In order to maintain characteristics of the lab-scale wastewater processes used in the study, certain general procedures were followed daily.

3.2.1. Reactor Conditions

Certain reactor conditions, including sludge age (3.2.1.1), hydraulic retention time (3.2.1.2), pH (3.2.1.3), temperature (3.2.1.4), and DO content (3.2.1.5) were maintained throughout the study.

3.2.1.1. Sludge Age

The nutrients and feed that the biomass takes from the influent are primarily used for cell synthesis. This necessitates continuous removal of biomass to maintain the desired constant concentration of mixed liquor suspended solids (MLSS). The residence time of solids in the system (sludge age) was maintained in order to prevent poor efficiency due to inadequately acclimated sludge or clumping and septic conditions from sludge that had remained in the reactor too long. The sludge age is defined as the total volume of solids divided by the volume of solids removed per day. In this study, a 30-day sludge age was maintained by removing $1/30^{th}$ of the mixed liquor each day.

3.2.1.2. Hydraulic Retention Time

The hydraulic retention time (HRT) is defined as the average residence time of the wastewater in the system (23). A 48-hour average HRT was maintained by removing half of the supernatant from each reactor every 24 hours.

3.2.1.3. pH

The pH of the synthetic wastewater was adjusted using sodium hydroxide in order to maintain a reactor pH of 6.5 to 8.0. The reactor pH was measured using an Oaklon pH 10 Series instrument.

3.2.1.4. Temperature

The temperature of the reactor was recorded and the conditions remained between 18 and 23°C. The temperature of the reactor was recorded using an Oaklon pH 10 Series instrument.

3.2.1.5. Dissolved Oxygen

The study involved anoxic and aerobic respiration, which required different levels of dissolved oxygen (DO) to be present in the reactor. The anoxic phase required less than 0.5 mg/L of DO, while the aerobic phase required greater than 2 mg/L DO. The DO content of the reactor was measured using YSI 52 and YSI 54 DO meters.

3.2.2. General Procedure for Operation of Anoxic/Aerobic Reaction Vessels

The general procedure for the daily operation of the anoxic/aerobic reaction vessels (Reactors 1, 2, and 5) is outlined below and given in Figure 3.4:

1. Decanting: After one hour of settling time, supernatant equal to half of the total volume of the reactor contents was decanted over a fifteen-minute period using pumps to control the rate of flow. For Reactor 5, the decant was removed by pouring. A sample of decant was taken from each reactor in order to test for the effluent conditions at the end of the aerobic respiration phase.

2. Feeding: The magnetic stirring plate was turned on to activate the stirring rod and synthetic wastewater was pumped into the reactor to the previous volume over a fifteen-minute period. (In the case of Reactor 5, feed was added manually.)
3. Reactor Conditions at Beginning of Anoxic Phase: Immediately after feeding was completed, a ten mL sample of mixed liquor was taken from the reactor and filtered through a 0.45 μ glass fiber filter. The filtered sample was used to test for the reactor conditions at the beginning of the anoxic respiration phase. The pH, DO, and volume of the reactor were measured and recorded.
4. Anoxic Phase: The reactors were allowed to stir for eight hours to complete the anoxic respiration phase.
5. Reactor Conditions at End of Anoxic Phase: At the end of the eight-hour period of stirring, a ten mL sample of mixed liquor was taken from the reactor and filtered through a 0.45 μ glass fiber filter. The filtered sample was used to test for the reactor conditions at the end of the anoxic respiration phase. The pH, DO, and volume of the reactor were measured and recorded. (Note: samples and measurements were not taken at the end of the anoxic phase during the reactor acclimation period of the study.)
6. Aerobic Phase: When the eight-hour anoxic respiration phase was completed, the aerators were activated to mark the beginning of the aerobic respiration phase. The aerators operated for 14.5 hours.
7. Reactor Conditions at End of Aerobic Phase: At the end of the aerobic respiration phase, the pH, DO, volume, and temperature of the reactor were measured and recorded. A sample of mixed liquor was removed to test for the MLSS of the

reactor. The volume of the mixed liquor sample was equal to 1/30th of the total reactor volume minus the volume of any other mixed liquor samples taken during the cycle.

8. Settling: The aerators were turned off and the reactor was allowed to settle for one hour.

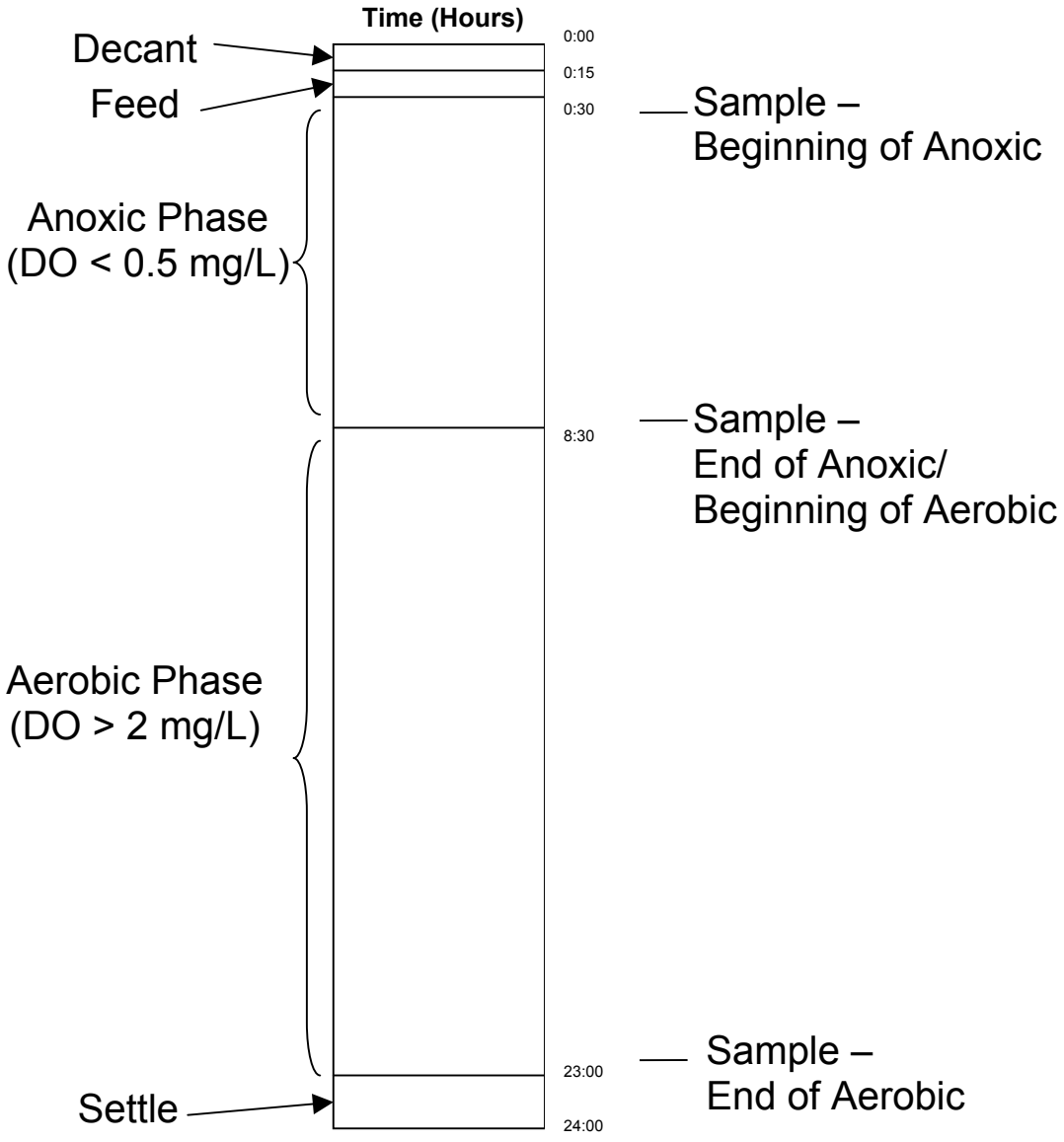

Figure 3.4 Anoxic/Aerobic Reactor Procedure (One Cycle)

3.2.3. General Procedure for Operation of Aerobic Reaction Vessels

The general daily procedure for running the aerobic reaction vessels (Reactors 6, 7, 8, and 9) is outlined below:

1. Decanting: After one hour of settling time, half of the total volume was decanted by pouring. A sample of decant was taken from each reactor in order to test for the effluent conditions at the end of the aerobic respiration phase.
2. Feeding: The aerators were activated and synthetic wastewater was added manually to the previous volume level.
3. Reactor Conditions at Beginning of Aerobic Phase: Immediately after feeding was completed, a ten mL sample of mixed liquor was taken from the reactor and filtered through a 0.45 μ glass fiber filter. The filtered sample was used to test for the reactor conditions at the beginning of the aerobic respiration phase. The pH, DO, and volume of the reactor were measured and recorded.
4. Aerobic Phase: The aerators operated for 23 hours.
5. Reactor Conditions at End of Aerobic Phase: At the end of the aerobic respiration phase, the pH, DO, volume, and temperature of the reactor were measured and recorded. A sample of mixed liquor was removed to test for the MLSS of the reactor. The volume of the mixed liquor sample was equal to $1/30^{th}$ of the total reactor volume minus the volume of any other mixed liquor samples taken during the cycle.
6. Settling: The aerators were turned off and the reactor was allowed to settle for one hour.

3.2.4. Procedure for Acclimation of Biomass

The anoxic/aerobic biomass (Reactors 1 and 2) was subjected to an acclimation phase in order to ensure that the biomass was fully acclimated to the synthetic wastewater and the anoxic/aerobic phases. Fourteen aerobic cycles were completed, followed by thirty-four anoxic/aerobic cycles. At the start of the anoxic/aerobic cycles, the synthetic wastewater recipe (3.1.3) was modified to include 1.5 g/L of salt (NaCl). During the acclimation phase, the sludge age and HRT were maintained and the COD, MLSS, and reactor conditions were measured. The reactors were deemed to be acclimated when the soluble COD of the effluent reached a stable level.

Reactors 5, 6, 7, 8, and 9 did not undergo a separate acclimation phase because they were seeded with biomass that had been removed from Reactors 1 and 2, which had already been acclimated and consistently fed the same synthetic wastewater, while stored in Reactors 3 and 4.

3.3. Computational Procedures

Reactor samples were tested for solids (3.3.1), soluble COD (3.3.2), and color (3.3.3) using standard test methods in order to assess the activity of the lab-scale wastewater treatment process.

3.3.1. Determination of Solids

The MLSS in the reactor (3.3.1.1), total suspended solids (TSS) in the decant and feed (3.3.1.2), and the total dissolved solids (TDS) in the decant and feed (3.3.1.3) were determined by testing according to Standard Methods for the Examination of Water and Wastewater 2540.

3.3.1.1. Mixed Liquor Suspended Solids

The MLSS indicate the level of solids (biomass) present in the reactor and this measurement was used to assess the growth of the biomass in the reactor. The MLSS was determined according to Standard Methods for the Examination of Water and Wastewater 2450 D using a four-mL sample of the mixed liquor. The MLSS was calculated using the average of the two sample weights and the weight of the filter (in grams) according to the following formula:

$$MLSS = \frac{AverageSampleWeights - FilterWeight}{4} \times 100{,}000 mg / L$$

3.3.1.2. Total Suspended Solids

The TSS of the decant and feed were tested. The TSS of the decant indicates the level of biomass being removing during the decanting process and the TSS of the feed indicates the level of solid material present in the influent. The TSS was determined according to Standard Methods for the Examination of Water and Wastewater 2450 D using a 16-mL sample of decant and a four-mL sample of feed. The TSS was calculated using the average of the two sample weights (which agreed within ±0.0002 g) and the weight of the filter (in grams) according to the following formulas:

$$TSS_{Feed} = \frac{AverageSampleWeights - FilterWeight}{4} \times 100{,}000 mg / L$$

$$TSS_{Decant} = \frac{AverageSampleWeights - FilterWeight}{16} \times 100{,}000 mg / L$$

3.3.1.3. Total Dissolved Solids

The TDS of the decant and feed were tested. The TDS indicates the portion of solids present in the wastewater that pass through the filter. The TDS was determined

according to Standard Methods for the Examination of Water and Wastewater 2450 C using the washings from the TSS tests for decant and feed. The TDS was calculated using the average of the two sample weights and the weight of the dish (in grams) according to the following formulas:

$$TDS_{Feed} = \frac{AverageSampleWeights - DishWeight}{4} \times 100{,}000 mg/L$$

$$TDS_{Decant} = \frac{AverageSampleWeights - DishWeight}{16} \times 100{,}000 mg/L$$

3.3.2. Determination of Soluble Chemical Oxygen Demand

The soluble COD of the reactor and feed samples were determined according to Standard Methods for the Examination of Water and Wastewater 5220 D using a HACH Model 45600 COD reactor. The testing procedure is outlined below:

1. The COD reactor was preheated to 150°C until the heating unit began to cycle on and off.
2. The sample was filtered through a 0.45 µ glass fiber filter that had been washed three times with deionized water while under suction.
3. Two mL of the filtered sample was added to a COD digestion reagent vial of the appropriate range (low range = 0-150 ppm, high range = 0-1500 ppm).
4. The vial cap was tightened and the vial was shaken and placed in the COD reactor for two hours.
5. The vial was cooled to room temperature.
6. A blank vial was prepared according to steps 1 through 4 using deionized water instead of a sample.

7. The HACH spectrophotometer was set to the appropriate wavelength for the range of vial to be read (420 nm for low range and 620 nm for high range vials) and zeroed using the blank vial.
8. The sample vial was read on the spectrophotometer in mg/L.

3.3.3. Determination of Color

The color of reactor and feed samples was determined both by the dye concentration in solution (3.3.3.1) and the American Dye Manufacturers Institute (ADMI) color value (3.3.3.2.). During the initial calibration stage, the correlation between dye concentration and ADMI color value was determined in order to choose appropriate dye concentrations for the synthetic wastewater influent (3.3.3.3.).

3.3.3.1. Dye Concentration in Solution

The dye concentration in solution was determined spectrophotometrically using calibration curves that were created according to the Beer-Lambert Law. The procedure for the creation of calibration curves for each dye is outlined below:

1. Dilutions of the 5 g/L hydrolyzed dyestuff solution (3.1.4) were prepared in volumetric flasks with deionized water at concentrations of 0.0025, 0.005, 0.0075, 0.0125, 0.025, and 0.05 g/L (C. I. Reactive Black 5 also had an additional dilution at 0.01 g/L).
2. The dilutions were placed in polystyrene cuvets with a one-cm path length.
3. Two one-cm polystyrene cuvets filled with deionized water were prepared as blanks and a baseline was run on the spectrophotometer.

4. The blank in the front position was replaced with the cuvet containing the sample and the blank in the back position was left in place.
5. The absorbance of the sample was scanned from 350 to 700 nm using a double beam and baseline correction.
6. The wavelength of maximum absorbance (λ_{max}) was determined for each standard solution and the average λ_{max} was determined for the dye (see Appendix A).
7. The absorbance of each standard solution at λ_{max} was determined.

8. The concentration of each standard solution was graphed vs. the absorbance and linear regression was used to determine a relationship between the two according to the Beer-Lambert Law, as indicated below (29):

$$A = \varepsilon c l$$

Where: A = absorbance

ε = absorptivity

c = concentration

l = path length = 1 cm

The calibration equations for each dye are shown below (see regression analysis in Appendix A):

C. I. Reactive Red 198 (λ_{max} = 510 nm, R^2 = 1.00000):

$$c = \frac{A - 0.00282}{21.42582}$$

C. I. Reactive Yellow 86 (λ_{max} = 424 nm, R^2 = 0.99651):

$$c = \frac{A - 0.01786}{13.69412}$$

C. I. Reactive Black 5 (λ_{max} = 594 nm, R^2 = 0.99995):

$$c = \frac{A + 0.00194}{27.52295}$$

C. I. Reactive Violet 5 (λ_{max} = 565 nm, R^2 = 0.99999):

$$c = \frac{A - 0.00294}{12.23324}$$

The dye concentration present in reactor and feed samples was determined using the following procedure:

1. The sample was filtered through a 0.45 μ glass fiber filter that had been washed three times with deionized water while under suction.
2. One mL of sample was added to a one-cm polystyrene cuvet and diluted with three mL of deionized water.
3. Two one-cm polystyrene cuvets filled with deionized water were prepared as blanks and a baseline was run on the spectrophotometer.
4. The blank in the front position was replaced with the cuvet containing the sample and the blank in the back position was left in place.
5. The absorbance of the sample was scanned from 350 to 700 nm using a double beam and baseline correction.
6. The absorbance at λ_{max} was entered into the appropriate equation shown above to determine the dye concentration in solution.

3.3.3.2. American Dye Manufacturers Institute Color Value

The American Dye Manufacturers Institute (ADMI) color value was determined spectrophotometrically according to Standard Methods for the Examination of Water and Wastewater 2120 E and Environmental Protection Agency Method 110.1. Platinum-

Cobalt standards were prepared with color values of 31.25, 62.5, 125, 166.7, 250, and 500. Using these standards, a calibration curve was created on a Cary 3E UV-Visible Spectrophotometer in polystyrene cuvets with a one-cm path length (see Appendix B). The procedure for testing samples for ADMI color value is listed below:

1. The sample was filtered through a 0.45 μ glass fiber filter that had been washed three times with deionized water while under suction.
2. One mL of sample was added to a one-cm polystyrene cuvet and diluted with three mL of deionized water.
3. Two one-cm polystyrene cuvets filled with deionized water were prepared as blanks and a baseline was run on the spectrophotometer.
4. The blank in the front position was replaced with the cuvet containing the sample and the blank in the back position was left in place.
5. The absorbance of the sample was scanned from 350 to 700 nm using a double beam and baseline correction.
6. The absorbance (*a*) at 590, 540, and 438 nm was converted to percent transmittance (%*T*) using the following formula:

$$\%T = \frac{1}{10^{a}} \times 100$$

   These percent transmittance values were designated T_1, T_2, and T_3, respectively.
7. The tristimulus values were calculated for each sample (X_S, Y_S, Z_S) and standard using the following equations:

$$X = (T_3 \times 0.1899) + (T_1 \times 0.791)$$
$$Y = T_2$$
$$Z = T_3 \times 1.1835$$

The tristimulus values for the blank were always set at the following values, which corresponded to standard illuminant C:

$$X_C = 98.09$$
$$Y_C = 100.0$$
$$Z_C = 118.35$$

8. The tristimulus values were converted to Munsell values using published tables (13), and these values were represesented by V_x, V_y, and V_z.

9. The DE value was calculated using the following formulas (where the subscript *s* refers to the sample and subscript *c* refers to the blank):

$$\Delta V_y = V_{ys} - V_{yc}$$
$$\Delta(V_x - V_y) = (V_{xs} - V_{ys}) - (V_{xc} - V_{yc})$$
$$\Delta(V_y - V_z) = (V_{ys} - V_{zs}) - (V_{yc} - V_{zc})$$
$$DE = \{(0.23\Delta V_y)^2 + [\Delta(V_x - V_y)]^2 + [0.4\Delta(V_y - V_z)]^2\}^{1/2}$$

10. Using the *DE* values for the standards, a calibration factor, F_n, was created for each standard according to the equation below:

$$F_n = \frac{(APHA)_n (b)}{(DE)_n}$$

Where: $(APHA)_n$ = APHA color value for Platinum-Cobalt standard *n*

$(DE)_n$ = DE value for standard *n*

b = cell light path (cm)

The calibration curve was created by plotting $(DE)_n$ vs. F_n.

11. The *F* value for each sample was determined using the calibration curve and the *DE* value of the sample. The ADMI color values were calculated for the samples using the following formula:

$$ADMI = \frac{(F)(DE)}{b}$$

12. The calculated ADMI color value was multiplied by the dilution factor of 4 to achieve the final ADMI value.

3.3.3.3. Relationship between Dye Concentration and ADMI Color Value

In order to achieve a synthetic wastewater influent with an ADMI value that modeled typical industry values, a relationship between dye concentration and ADMI color value was determined for each of the individual dyes. For each dye, the ADMI values of the calibration standards used in section 3.3.3.1. were calculated according to procedures in 3.3.3.2. A plot of dye concentration vs. ADMI value was made for each dye. Since the Platinum-Cobalt standards used to create the ADMI calibration curve ranged from zero to 500 ADMI, additional dilutions were prepared for each dye to expand the number of calibration standards in this range (see Appendix C). Based on these data, the following dyestuff concentrations were chosen, in order to achieve a color level of approximately 1000 ADMI due to each dyestuff in the influent of each reactor:

- Remazol Red RB (C. I. Reactive Red 198) = 0.01 g/L
- Procion Yellow PX-8G (C. I. Reactive Yellow 86) = 0.01 g/L
- Remazol Black B (C. I. Reactive Black 5) = 0.01 g/L
- Remazol Brilliant Violet 5R (C. I. Reactive Violet 5) = 0.02 g/L

3.4. Kinetic Studies

Kinetic studies were performed in order to determine the rates of removal of COD (3.4.1.1) and color (3.4.1.2) from the wastewater by the sequential anoxic and aerobic respiration processes. An additional study of the rate of COD removal in a separate

aerobic respiration process was performed as a control (3.4.2). The results were analyzed in order to determine the kinetic characteristics of the processes (3.4.3).

3.4.1. Experimental Design for Anoxic/Aerobic Sequential Process

Two separate kinetic studies of the anoxic/aerobic sequential process were performed. The first involved the rates of removal of soluble COD (3.4.1.1) and the second involved the rates of color removal (3.4.1.2).

3.4.1.1. Chemical Oxygen Demand

The large anoxic/aerobic reaction vessels (Reactors 1 and 2) were sampled according to a set testing scheme for six subsequent cycles in order to determine the rates of removal of COD in the sequential anoxic and aerobic phases. In the initial sampling scheme, samples were taken during the anoxic phase at 0, 5, 10, 15, 30, 45, 60, 120, 240, and 480 minutes after feeding and during the aerobic phase at 0, 5, 10, 15, 30, 45, 60, 120, 240, 480, and 870 minutes after the beginning of aeration. Data were collected for two complete anoxic/aerobic cycles using this scheme. After an initial analysis of the data, the sampling scheme for the remaining four cycles of the study was adapted. In the modified plan, samples were taken during the anoxic phase at 0, 30, 60, 90, 120, 240, and 480 minutes after feeding and during the aerobic phase at 0, 5, 10, 15, 20, 25, 30, 60, 180, 360, 720, and 870 minutes after the beginning of aeration.

At each sampling time, 10 mL of mixed liquor was removed from the reactor by pipette and immediately filtered under suction through a 0.45 μ glass filter that had been washed with deionized water. The samples were tested for soluble COD (3.3.2).

3.4.1.2. Color

The large and small anoxic/aerobic reaction vessels (Reactors 1, 2, and 5) were sampled according to a set testing scheme for six subsequent cycles in order to determine the rates of color removal in the sequential anoxic and aerobic phases. Samples were taken during the anoxic phase at 0, 5, 10, 15, 20, 25, 30, 60, 120, 240, and 480 minutes after feeding and during the aerobic phase at 0, 30, 60, 120, 240, 480, and 870 minutes after the beginning of aeration. The influent of Reactor 1 contained 0.01 g/L of both C. I. Reactive Red 198 and C. I. Reactive Yellow 86. The influent of Reactor 2 contained 0.01 g/L of C. I. Reactive Black 5. The influent of Reactor 5 contained 0.02 g/L of C. I. Reactive Violet 5.

At each sampling time, 10 mL of mixed liquor was removed from the reactor by pipette and immediately filtered under suction through a 0.45 μ glass filter that had been washed with deionized water. The samples were analyzed to determine the dye concentration in solution (3.3.3.1) and ADMI color value (3.3.3.2). The samples taken during the anoxic phase at time 0, 30, 60, and 480 and during the aerobic phase at 0, 30, 60, and 870 were also tested for soluble chemical oxygen demand (3.3.2).

3.4.2. Experimental Design for Aerobic Control

An aerobic control reaction vessel (Reactor 6) was sampled according to a set testing scheme for five subsequent cycles in order to determine the rate of COD removal in a separate aerobic respiration process. Samples were taken at 0, 5, 10, 15, 20, 25, 30, 60, 120, 240, 480, 960, and 1380 minutes after feeding and the beginning of aeration. The samples were tested for soluble COD (3.3.2).

4. Results and Discussion

Certain reactor conditions (4.1 and 4.2) were maintained throughout the study in order to remove interference in detecting changes in the main variables under consideration (COD and color). After an initial acclimation phase to synthetic wastewater influent which contained no dye (4.3), a kinetic study of the rates of removal of COD was performed for both the separate aerobic process and the anoxic/aerobic sequential process (4.4). In another set of experiments, dyestuffs were added to the influent and, after an initial acclimation phase (4.5), a kinetic study of the rates of removal of color from the wastewater (4.6) was completed. In addition to the rate of color removal, the amount of color removal was evaluated (4.7). These results make it possible to understand the underlying physical and chemical principles of the degradation of certain representative fiber reactive azo dye molecules by anoxic and aerobic degradation (4.8). The studies and the reactors that were utilized for each study are summarized below in Table 4.1.

Table 4.1 Experimental Summary

Study	Process	Reactor
COD Removal (Non-Colored Influent)	Anoxic/Aerobic	1, 2
	Aerobic Control	6
COD Removal (Colored Influent)	Anoxic/Aerobic	1, 2, 5
Color Removal - C. I. Reactive Red 198	Anoxic/Aerobic	1
	Aerobic Control	7
Color Removal - C. I. Reactive Yellow 86	Anoxic/Aerobic	1
	Aerobic Control	7
Color Removal - C. I. Reactive Black 5	Anoxic/Aerobic	2
	Aerobic Control	8
Color Removal - C. I. Reactive Violet 5	Anoxic/Aerobic	5
	Aerobic Control	9

4.1. Reactor Conditions

Certain reactor conditions, including dissolved oxygen content and pH were measured throughout the study. The following table shows the range of values for these characteristics for both the anoxic/aerobic reactors and the aerobic control reaction vessels.

Table 4.2 Conditions for Anoxic/Aerobic Reactors

Reactor	Dissolved Oxygen (mg/L)						pH (SU)		
	Anoxic Phase			Aerobic Phase					
	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.
1	0.01	0.13	0.40	6.2	8.7	10.0	6.5	6.9	7.4
2	0.02	0.12	0.30	5.8	8.4	10.0	6.4	6.9	7.3
5	0.01	0.06	0.30	7.4	8.0	9.4	6.9	7.1	7.5

Table 4.3 Conditions for Aerobic Reactors

Reactor	Dissolved Oxygen (mg/L)			pH (SU)		
	Aerobic Phase					
	Min.	Avg.	Max.	Min.	Avg.	Max.
6	7.3	8.0	9.6	6.7	6.8	6.9
7	7.1	7.5	7.8	6.7	6.8	7.0
8	7.2	7.6	8.0	6.6	6.7	6.8
9	8.1	8.4	8.7	6.6	6.7	6.7

See Appendix D for all data related to reactor conditions.

4.2. Solids

The MLSS of the reaction vessels was measured to determine the growth of the biomass during the study. Near the end of the acclimation phase and before the kinetic experiments were begun, any biomass build-up on the walls of the large reaction vessels was returned to the mixed liquor in order to stabilize the MLSS level. This increased the

MLSS present in the reactors and the biomass remained at this increased level throughout the experimental stages. The MLSS over time for the two large anoxic/aerobic reaction vessels is shown below in Figures 4.1 and 4.2.

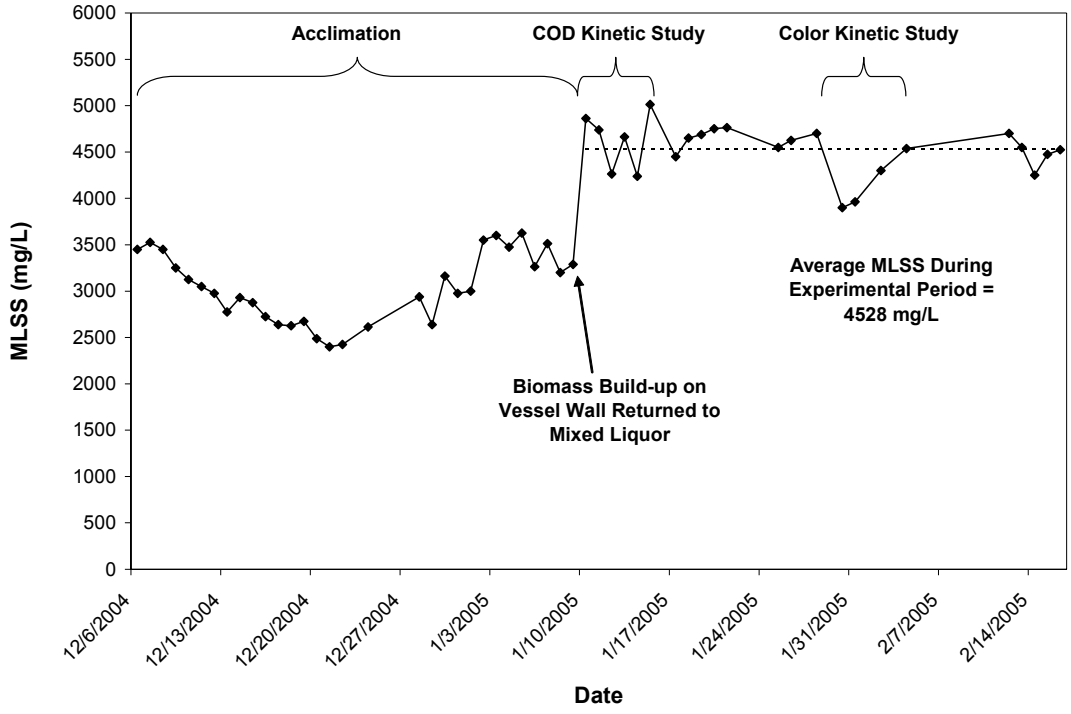

Figure 4.1 MLSS vs. Time for Large Anoxic/Aerobic Reaction Vessel (Reactor 1)

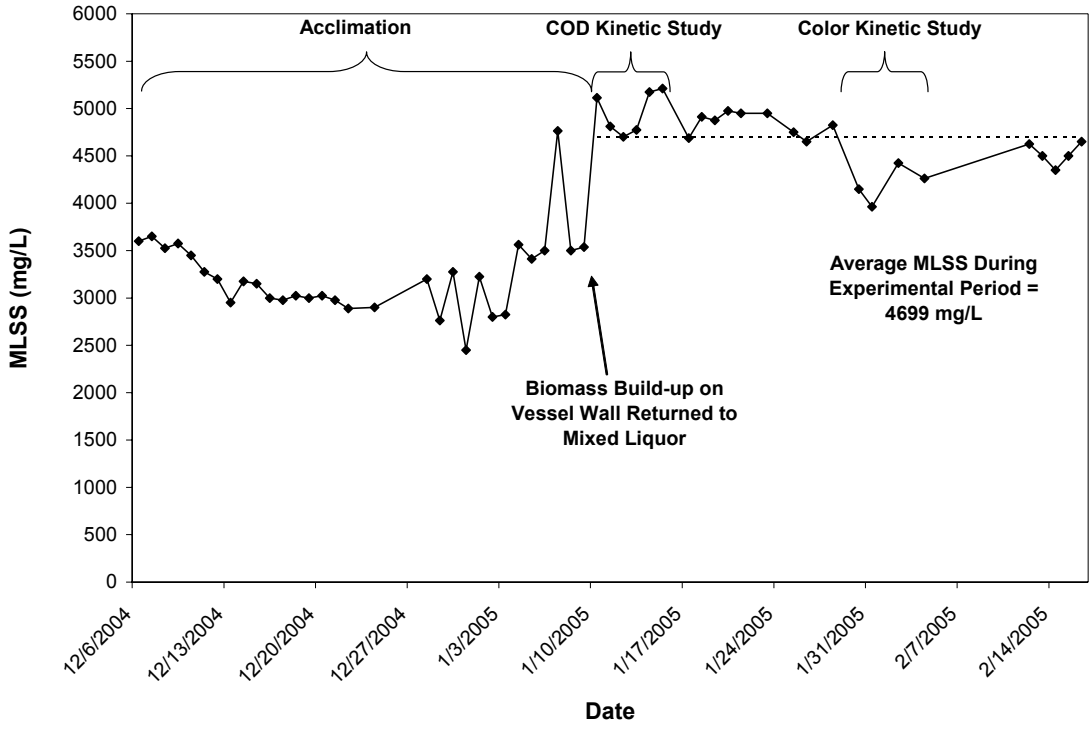

Figure 4.2 MLSS vs. Time for Large Anoxic/Aerobic Reaction Vessel (Reactor 2)

The average MLSS for the small, short-term reactors is summarized in Table 4.4 below.

Table 4.4 Average MLSS for Small Reactors

Reactor	Average MLSS (mg/L)
Small Anoxic/Aerobic (Reactor 5)	4243
Aerobic Control (Reactor 6)	3721
Modified Aerobic Control (Reactor 7)	3370
Modified Aerobic Control (Reactor 8)	3445
Modified Aerobic Control (Reactor 9)	3893

The TSS and TDS of the treated effluent from the two large anoxic/aerobic reaction vessels (Reactors 1 and 2) was also measured. A summary of the results is shown below in Table 4.5, for the time period between the start of the anoxic/aerobic cycles and the addition of color to the influent.

Table 4.5 TSS and TDS for Treated Effluent

Reactor	Average TSS (mg/L)	Average TDS (mg/L)
Large Anoxic/Aerobic (Reactor 1)	11	2537
Large Anoxic/Aerobic (Reactor 2)	15	2514
Small Anoxic/Aerobic (Reactor 5)*	25	2762

*Note: Reactor 5 data includes only one measurement.

See Appendix E for all solids measurements.

4.3. Acclimation to Non-Colored Influent

In order to ensure that the biomass was fully acclimated to the synthetic wastewater, the large anoxic/aerobic reaction vessels (Reactors 1 and 2) were subjected to an acclimation phase which began with fourteen aerobic cycles, followed by thirty-four anoxic/aerobic cycles. During this phase, the characteristics of the synthetic wastewater (4.3.1) and the COD in the effluent from the reaction vessels were monitored (4.3.2). The reactors were deemed to be acclimated when the COD of the effluent reached a stable level.

4.3.1. Characteristics of Non-Colored Influent

During the acclimation phase, COD, pH, TSS, and TDS of the influent were measured. Figure 4.3 shows the COD of the influent from the time the anoxic/aerobic cycles were begun until color was introduced. The graph notes the beginning of the modified feed preparation process (3.1.3) to prevent microbial contamination and the time period when the COD kinetic study was performed. The average influent COD using the modified feed preparation process was 1101 mg/L with a standard deviation of 96 mg/L.

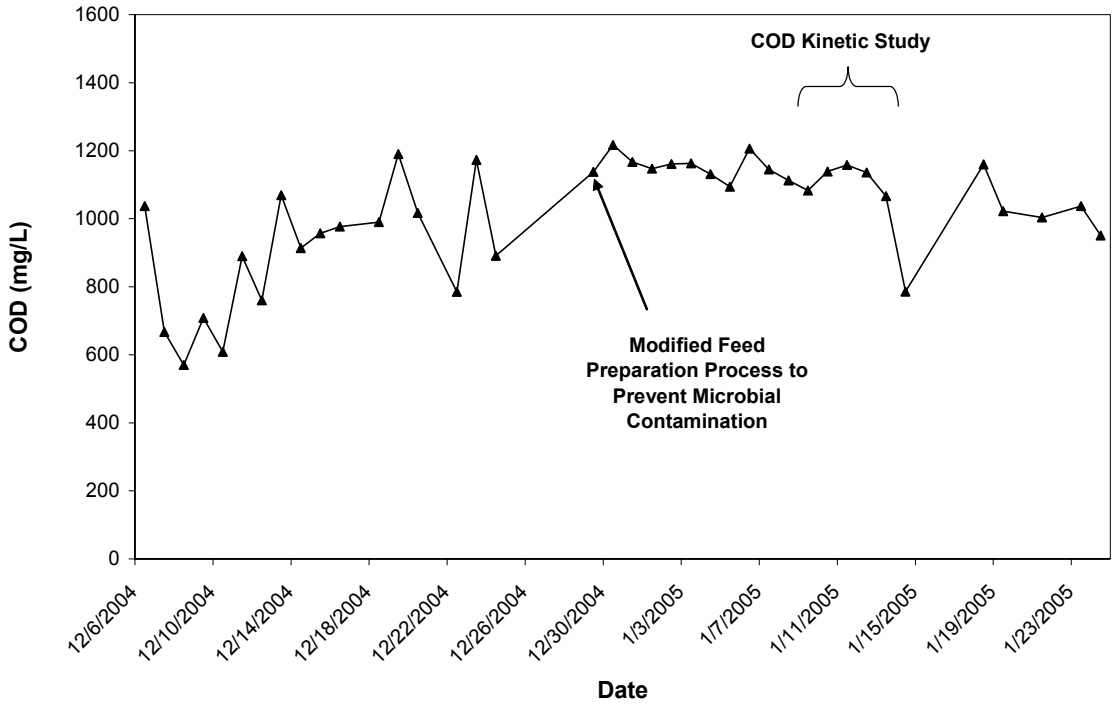

Figure 4.3 COD of Non-Colored Influent

The TSS, TDS, and pH of the influent were also measured and these data are summarized in Table 4.6 below, for the time period between the start of the anoxic/aerobic cycles and the addition of color to the influent.

Table 4.6 Characteristics of Non-Colored Influent

Characteristic	Minimum	Average	Maximum
Total Suspended Solids (mg/L)	0	20	125
Total Dissolved Solids (mg/L)	2088	2708	3050
pH (SU)	6.3	7.1	8.6

See Appendix F for all data related to non-colored influent.

4.3.2. COD of Effluent

During the acclimation phase, the COD of the effluent from the large anoxic/aerobic reaction vessels (Reactors 1 and 2) was monitored in order to affirm that the biomass was acclimated to the synthetic wastewater. The COD kinetic study was not performed until the effluent COD had reached a stable level and remained there for over ten cycles. The COD of the effluent vs. time for Reactors 1 and 2 is shown below in Figures 4.4 and 4.5.

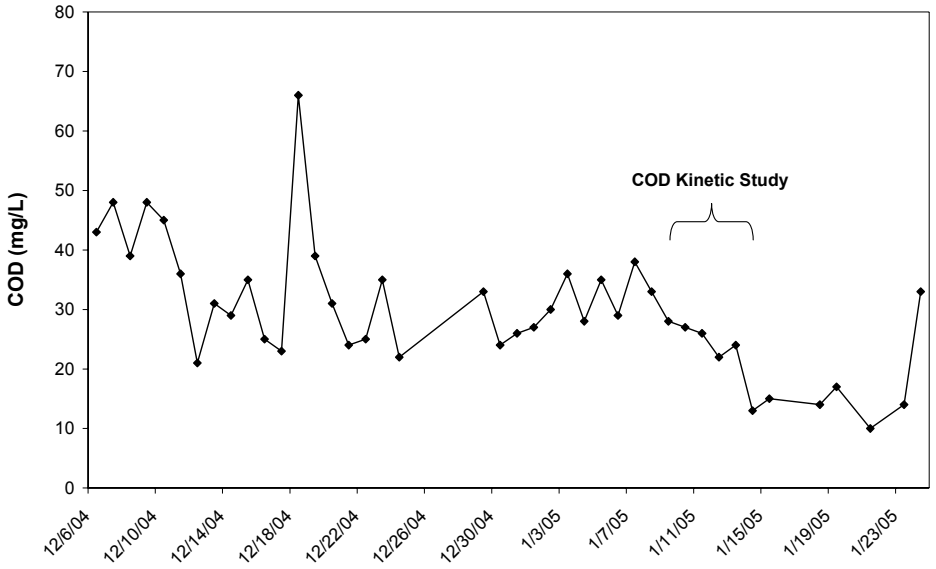

Figure 4.4 Reactor 1, Effluent COD

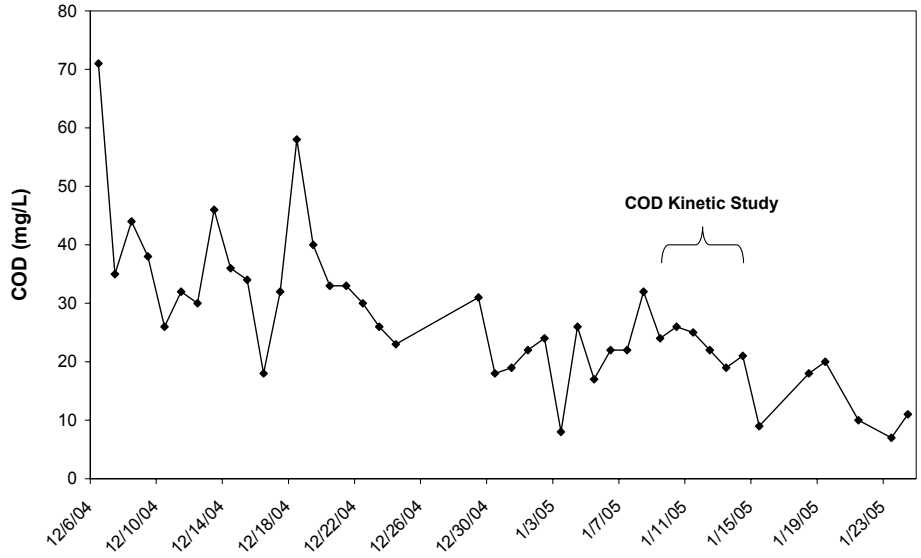

Figure 4.5 Reactor 2, Effluent COD

See Appendix G for effluent COD measurements.

4.4. Kinetics of Removal of Chemical Oxygen Demand

Kinetic studies were performed according to a set method (4.4.1) to estimate the rates of removal of COD by a separate aerobic process (4.4.2) and an anoxic/aerobic sequential process (4.4.3). The results of the kinetic analysis were compared in order to assess the applicability of an anoxic/aerobic sequential process for COD removal as contrasted with the conventional aerobic method (4.4.4).

4.4.1. General Method for Analysis

For studies involving measurements of COD, the raw data were normalized by dividing each data point, C, by the initial concentration for that cycle, C_0. The fraction of concentration remaining (C/C_0) was plotted vs. time with the cycles superimposed to visually assess the correlation between cycles. The average of the cycle data (C/C_0) was calculated and added to the graph. A first-order kinetic model was used in which a plot

of ln(C/C_0) vs. time was made for the superimposed cycle data for the first five points of each phase of the anoxic/aerobic process (zero to 120 minutes for the anoxic phase and zero to 20 minutes for the aerobic phase). The first-order rate law is as follows:

$$\frac{dC}{dt} = -kC$$

$$\frac{dC}{C} = -kdt$$

$$\int \frac{dC}{C} = -k\int dt$$

$$\int_{C_0}^{C_t} \frac{dC}{C} = -k\int_0^t dt$$

$$\ln C_t - \ln C_0 = -kt$$

$$\ln \frac{C_t}{C_0} = -kt$$

$$\frac{C_t}{C_0} = e^{-kt}$$

where, t = time (minutes)
C_t = concentration at time t
C_0 = initial concentration
k = rate constant (min^{-1})

The data were fitted using linear regression and the slope of the line was determined to be the negative of the rate constant (k). The data from each cycle were adjusted in order to minimize the cumulative error and improve the fit. The half-life ($t_{1/2}$) of each phase of the process was calculated according to the following equation:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

Using the estimated rate constant for each phase of the process, a model for the removal of COD was developed and plotted vs. the average measured cycle data. Each model had the following format (with C_0 set to unity):

Anoxic phase:

$$C_{anoxic} = (C_0 - C_1)e^{-k_1 t} + C_1$$

Aerobic phase:

$$C_{aerobic} = (C_1 - C_2)e^{-k_2 t} + C_2$$

Where: C = concentration at any time
C_0 = average concentration at start of anoxic phase
C_1 = average concentration at end of anoxic phase
C_2 = average concentration at end of aerobic phase
k_1 = estimated rate constant for anoxic phase
k_2 = estimated rate constant for aerobic phase
t = time (minutes)

The average difference between the model and the average measured data was calculated in order to assess the robustness of the model.

4.4.2. Aerobic Control (Reactor 6)

An aerobic control reaction vessel (Reactor 6) was sampled according to a set testing scheme for five subsequent cycles in order to determine the rate of COD removal in a separate aerobic respiration process. Mixed liquor samples from Reactor 6 were taken at set times after feeding and tested for soluble COD. The data from the first cycle is shown below in Table 4.7 as an example.

Table 4.7 Example COD Data for Aerobic Control

Time (minutes)	COD (mg/L)
0	435
5	300
10	219
15	262
20	142
25	132
30	169
60	108
120	35
240	37
480	11
960	20
1380	8

Each cycle was normalized using the initial concentration at time zero and the average cycle data were calculated, as shown in Figure 4.6 below.

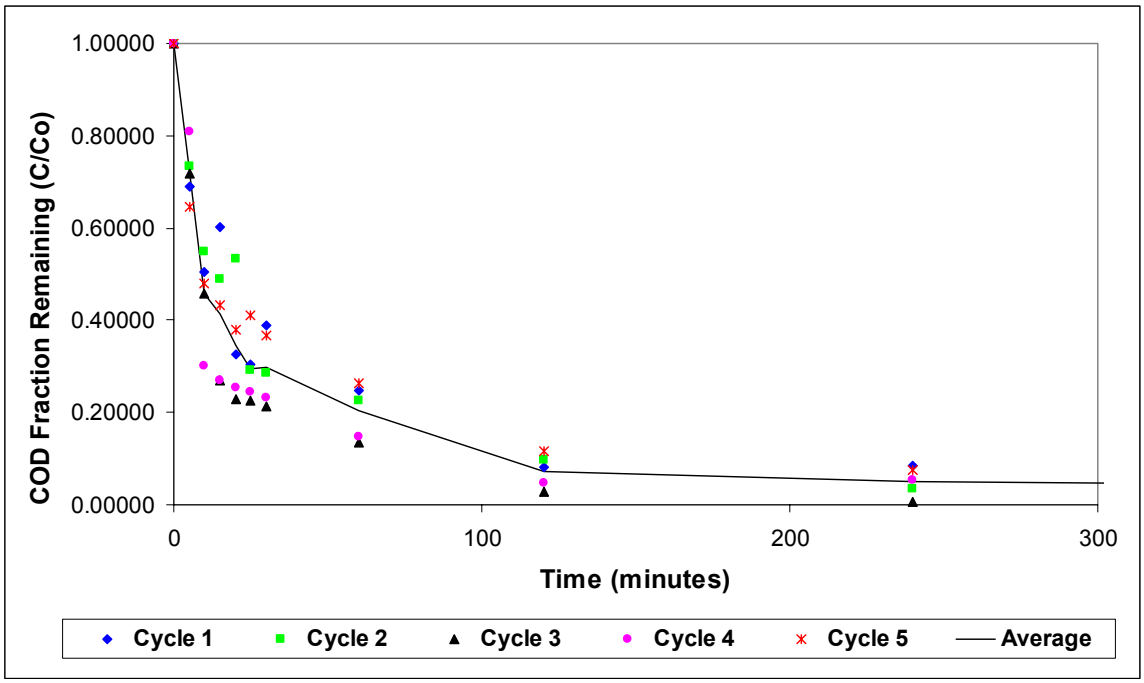

Figure 4.6 Aerobic Control, COD Fraction Remaining vs. Time

An inspection of the previous figure shows good correlation between the data for the five cycles and this is confirmed statistically by the fact that each cycle has an R^2 value above 0.86 and an F-ratio above 67.3 with the other four cycles.

Using the analysis method described in 4.4, a model was developed for the removal of COD by a separate aerobic respiration process. The rate constant under the experimental conditions was estimated to be 0.05658 minute^{-1}. From k, the half-life ($t_{1/2}$) of the process was calculated to be 12.3 minutes. The model for COD removal is shown below:

$$C = 0.02918 + e^{-(0.05658)t}$$

As shown in Figure 4.7, the model shows good agreement with the average of the measured data, with an average error of 21.9 mg/L of COD.

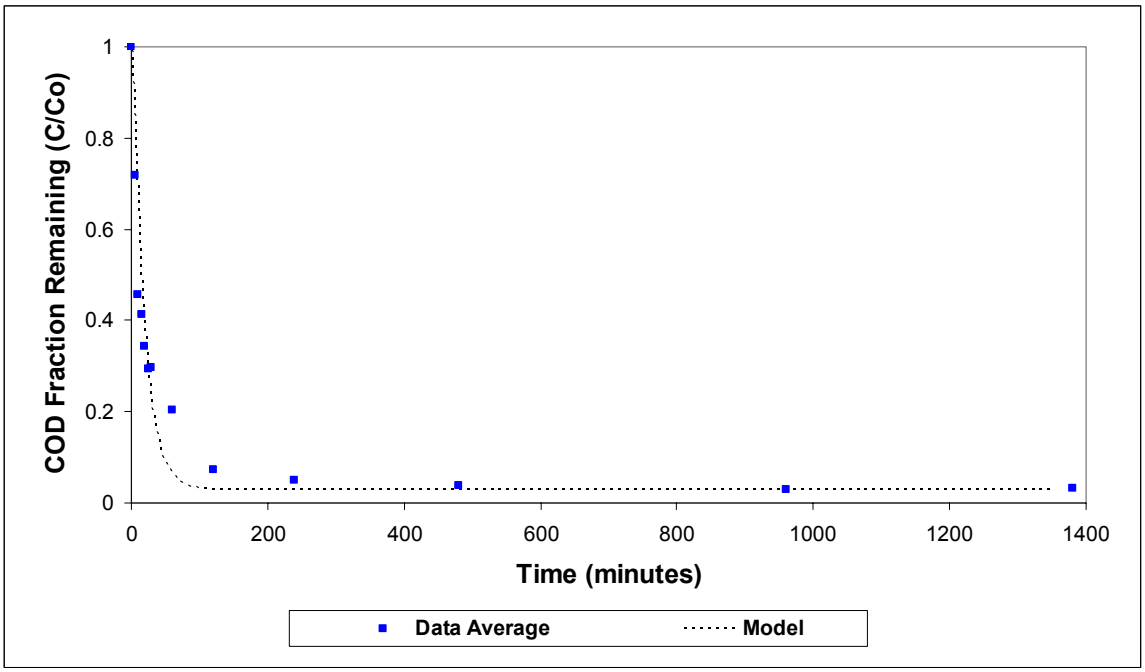

Figure 4.7 Model vs. Average Measured Data for Aerobic Control

See Appendix H for all data and analysis related to this study.

4.4.3. Anoxic/Aerobic (Reactors 1 and 2)

The large anoxic/aerobic reaction vessels (Reactors 1 and 2) were sampled according to a set testing scheme for six subsequent cycles in order to determine the rates of removal of COD in a sequential anoxic/aerobic process. The raw COD data collected from Reactor 1 in the third cycle is shown below in Table 4.8 as an example.

Table 4.8 Example COD Data for Anoxic/Aerobic Reactor

Phase	Time (Minutes)	COD (mg/L)
Anoxic	0	350
	30	301
	60	296
	90	244
	120	249
	240	213
	480	206
Aerobic	5	100
	10	60
	15	51
	20	35
	25	39
	30	38
	60	15
	180	32
	360	20
	720	21
	870	12

The normalized cycle data for Reactors 1 and 2 are shown below in Figures 4.8 and 4.9. A comparison of the two figures shows good visual correlation between the two reactors and between individual cycles within each reactor. Matched pair t-tests performed on the normalized cycle data indicated that the fraction of COD remaining for Reactors 1 and 2 was statistically different (at a 95% confidence level) only during the first 25 minutes of the aerobic phase. During the entire anoxic phase and the latter portion of the aerobic phase, the fraction of COD remaining was not statistically different (see Appendix I).

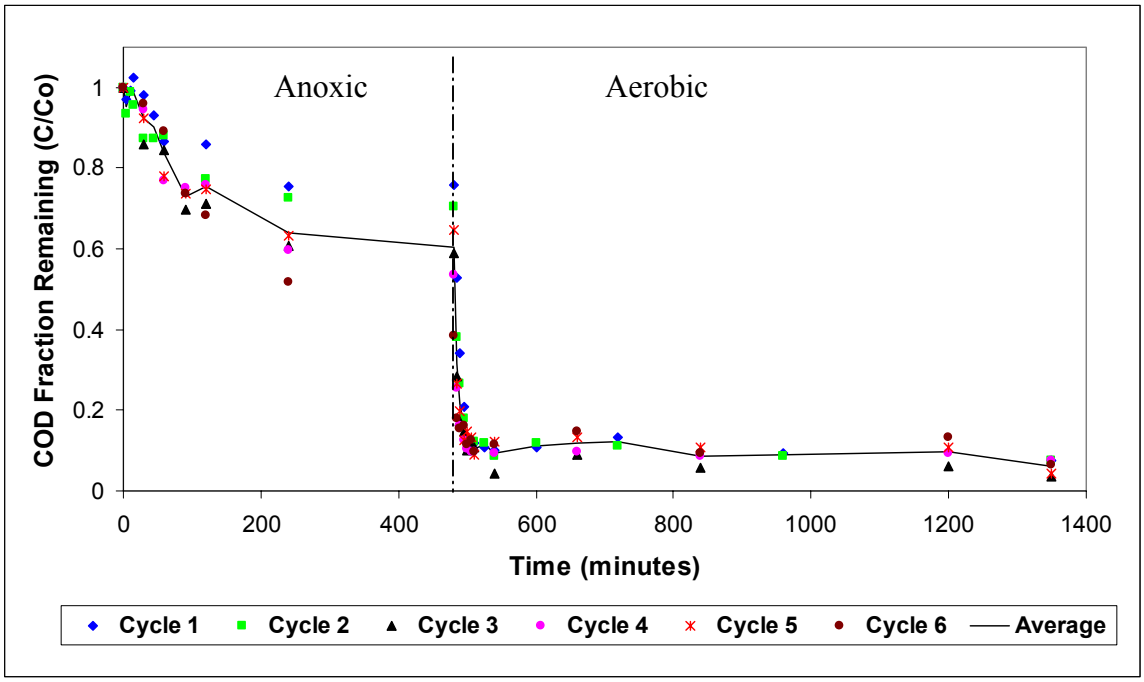

Figure 4.8 Anoxic/Aerobic Reactor 1, COD Fraction Remaining vs. Time

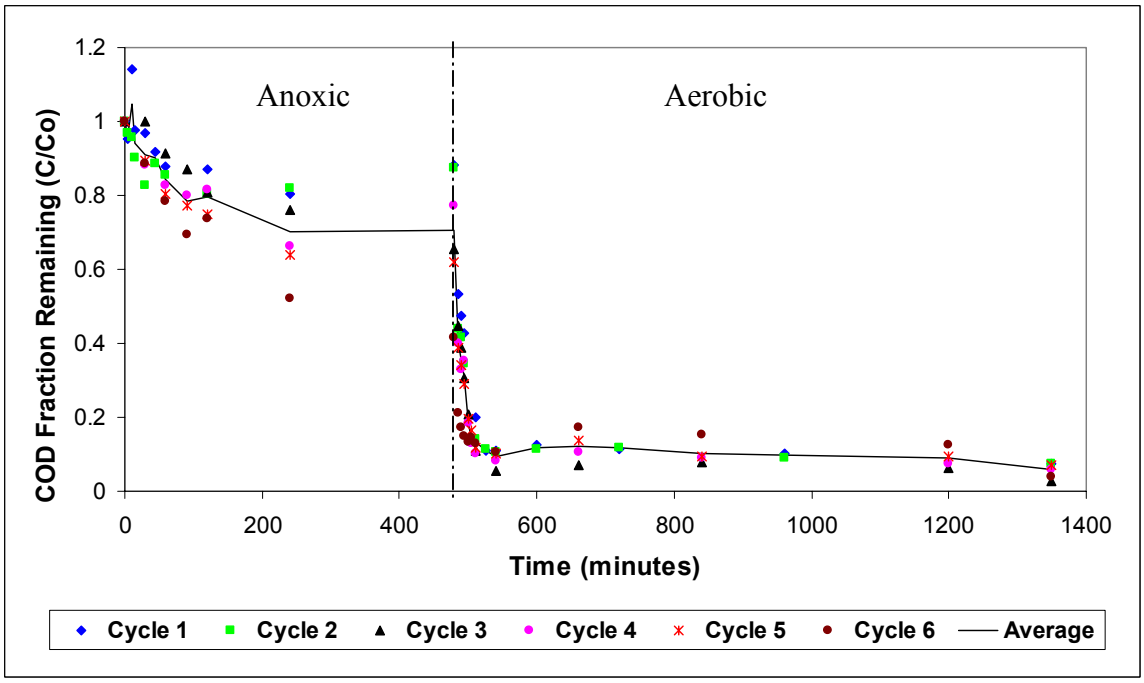

Figure 4.9 Anoxic/Aerobic Reactor 2, COD Fraction Remaining vs. Time

Using the analysis method described in 4.4, a model was developed for the removal of COD by each phase of the anoxic/aerobic process for each reactor. The rate

constants and half-lives of the phases are summarized below in Table 4.9. The two reactors show the greatest difference in the rate constants for the aerobic phase and this is to be expected since the matched pair t-tests revealed that the fraction of COD remaining in the reactors was statistically different during the beginning of the aerobic phase.

Table 4.9 Estimated Kinetic Parameters for Large Anoxic/Aerobic Reaction Vessels

Phase	Reactor	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	1	0.00263	263.6
	2	0.00207	334.9
Aerobic	1	0.07517	9.2
	2	0.05391	12.9

The model for COD removal for Reactor 1 is shown below:

$$C_{anoxic} = 0.383e^{-(0.00263)t} + 0.5561$$

$$C_{aerobic} = 0.556e^{-(0.07517)t} + 0.0614$$

The model for COD removal for Reactor 2 is shown below:

$$C_{anoxic} = 0.277e^{-(0.00207)t} + 0.6648$$

$$C_{aerobic} = 0.673e^{-(0.05391)t} + 0.0506$$

As shown in Figures 4.10 and 4.11, the model for each reactor shows good agreement with the average of the measured data, with an average error of 16 mg/L COD for Reactor 1 and 18 mg/L COD for Reactor 2. The largest error between the measured data and the model occurs in the anoxic phase, when the reactors actually out-perform the first-order model.

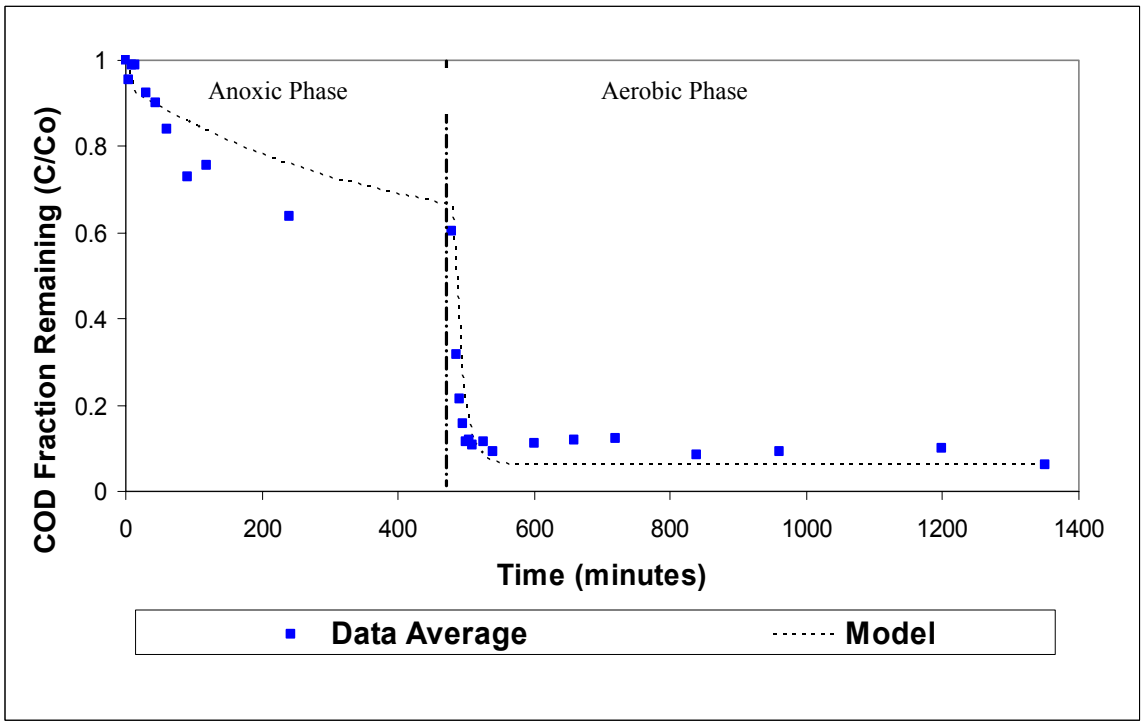

Figure 4.10 Model vs. Average Measured Data for Reactor 1

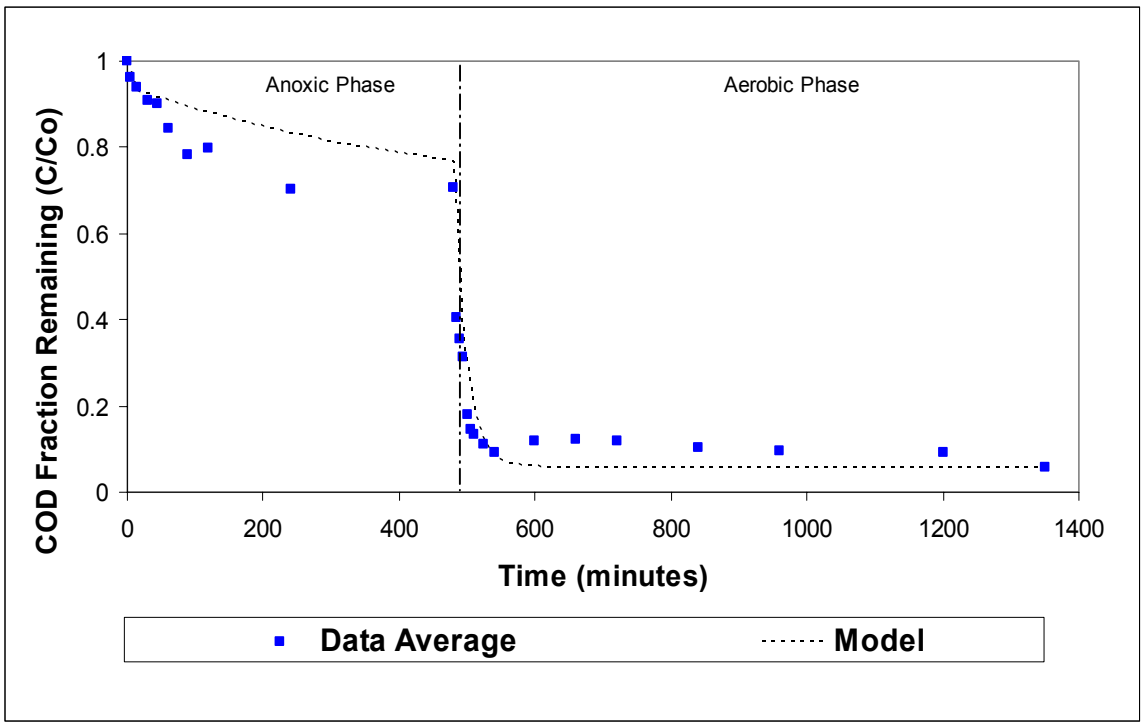

Figure 4.11 Model vs. Average Measured Data for Reactor 2

4.4.3.1. COD Removal during Feeding Period of Anoxic/Aerobic Process

As reviewed in 3.1.1, certain reaction vessels utilized in this study differed in size. The aerobic control vessels were small and feed was poured into the vessel. Due to the small volume of these reactors, mixing was achieved quickly. In contrast, the large anoxic/aerobic reaction vessels utilized a significantly larger volume and these reactors were fed at a controlled rate under anoxic conditions over a fifteen-minute time period. This feeding period was added to ensure that adequate mixing was achieved before the time-zero sample was taken. On average, the calculated initial COD concentration (based on the average of the effluent COD from the previous cycle and the influent COD) differed from the measured time-zero COD by forty-two percent during this study. It is clear from this information that the biomass was digesting or absorbing/adsorbing food in the influent during the feeding process and before the time-zero measurement was made. The preceding analysis and kinetic model apply only to the anoxic/aerobic cycle following the completion of the feeding process.

There are several hypothetical causes for the large reduction in COD during the feeding period. It is possible that the biomass may have been acting aerobically during the feeding period, due to residual oxygen in the system from the prior aerobic phase. It is also possible that the feed adsorbed to the bacteria or was absorbed by the bacteria, so that it remained undigested, but was undetectable by the test methods that were utilized in the study. In future research, this question could be answered by testing the total COD (including biomass) of the mixed liquor before and after feeding.

An abbreviated kinetic study of the anoxic/aerobic process in a small reaction vessel (Reactor 5) without the fifteen-minute feeding period was performed in order to

estimate the effect of this phenomenon. The models for the large vessels were adjusted to account for the nutrients consumed during the feeding period by adding a 58% COD reduction during the first fifteen minutes of the cycle and off-setting and scaling the remaining data to account for this modification. The adjusted models were plotted with the average measured data from Reactor 5, as shown in Figure 4.12.

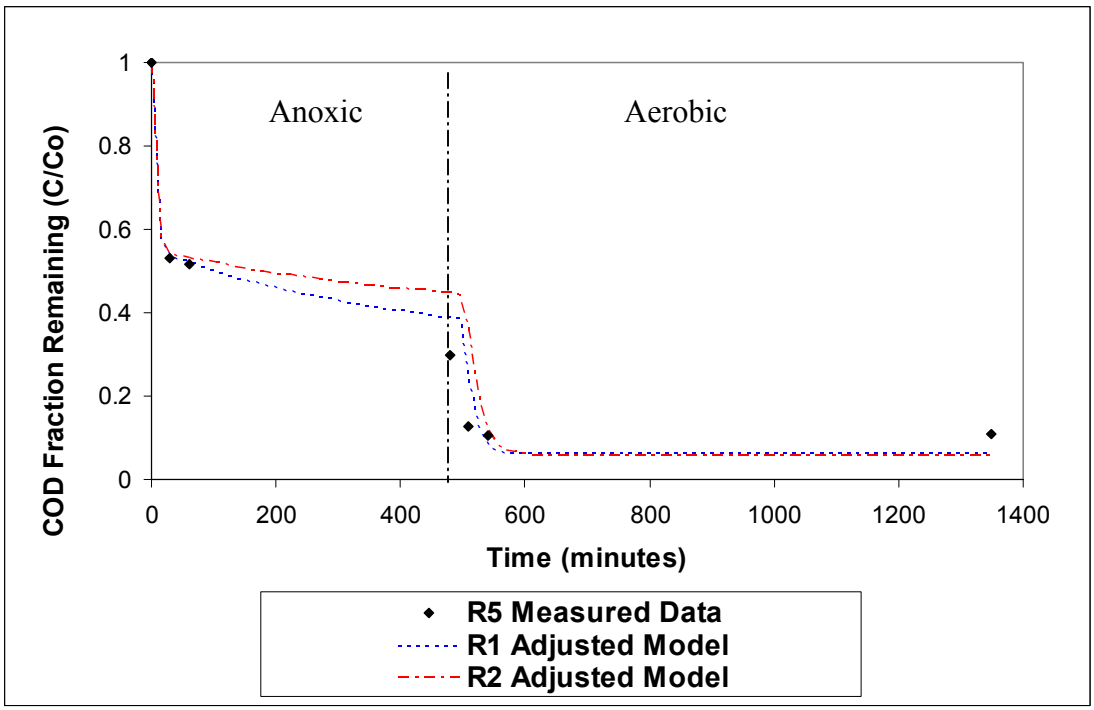

Figure 4.12 Comparison of Adjusted Models to Reactor 5 Experimental Data

An examination of the figure shows agreement between the adjusted models and the experimental data from the small anoxic/aerobic reaction vessel. Based on the experimental data from the small anoxic/aerobic reaction vessel, a new estimated rate constant for the anoxic phase (including COD removal during feeding period) was calculated to be 0.01175 minute^{-1}, which gives a half life of 59 minutes. This new model is a more accurate representation of the effective COD removal by the anoxic phase of the anoxic/aerobic process.

See Appendix I for all data and analysis related to the kinetics of COD removal for the anoxic/aerobic process.

4.4.3.2. Verification of COD Removal Characteristics of Anoxic/Aerobic Process Using Colored Influent

In order to determine if the COD removal characteristics of the anoxic/aerobic process remained stable after color was added to the influent, COD measurements from Reactors 1 and 2 taken at the beginning and end of each phase were compared between two five-day periods: (1) when the reactors were acclimated to the non-colored influent (during the COD kinetic study) and (2) when the reactors were acclimated to the colored influent (during the last week of the color removal study). The raw data are shown below in Figures 4.13-4.16 (see Appendix I).

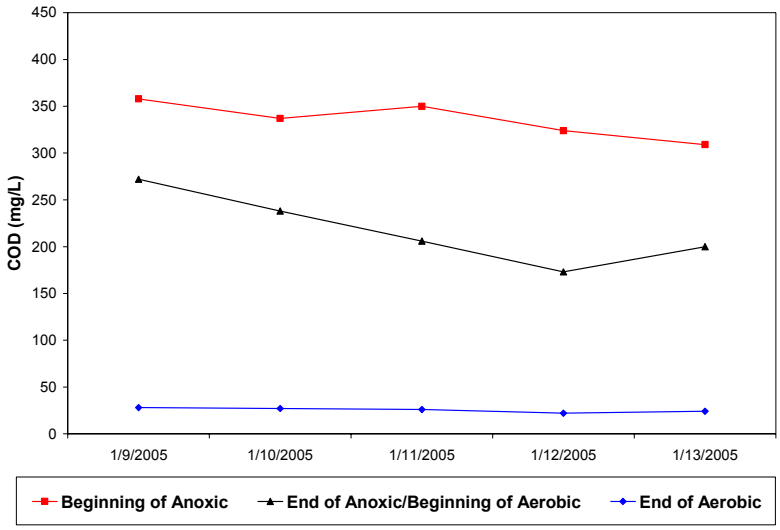

Figure 4.13 Reactor 1, COD Measurements from 5-Day Period when Acclimated to Non-Colored Influent

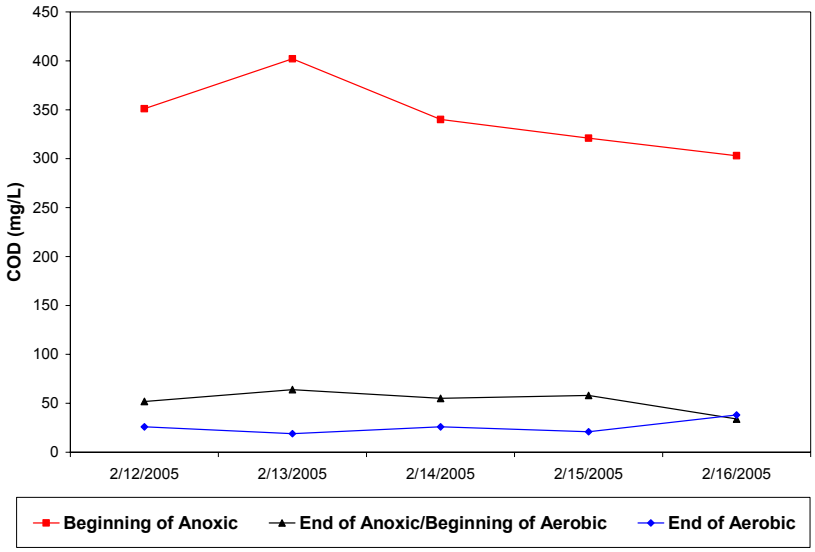

Figure 4.14 Reactor 1, COD Measurements from 5-Day Period when Acclimated to Colored Influent

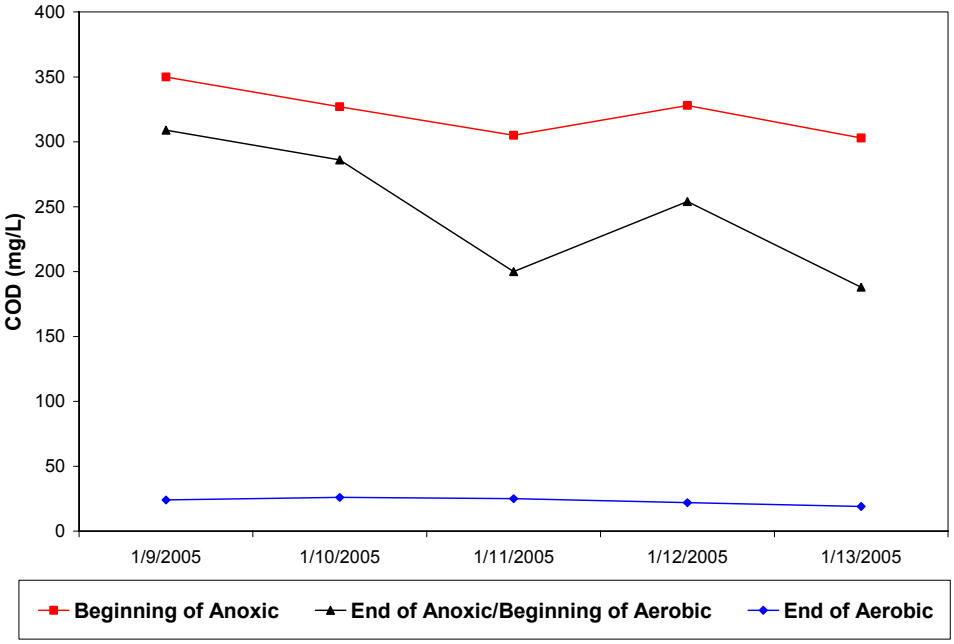

Figure 4.15 Reactor 2, COD Measurements from 5-Day Period when Acclimated to Non-Colored Influent

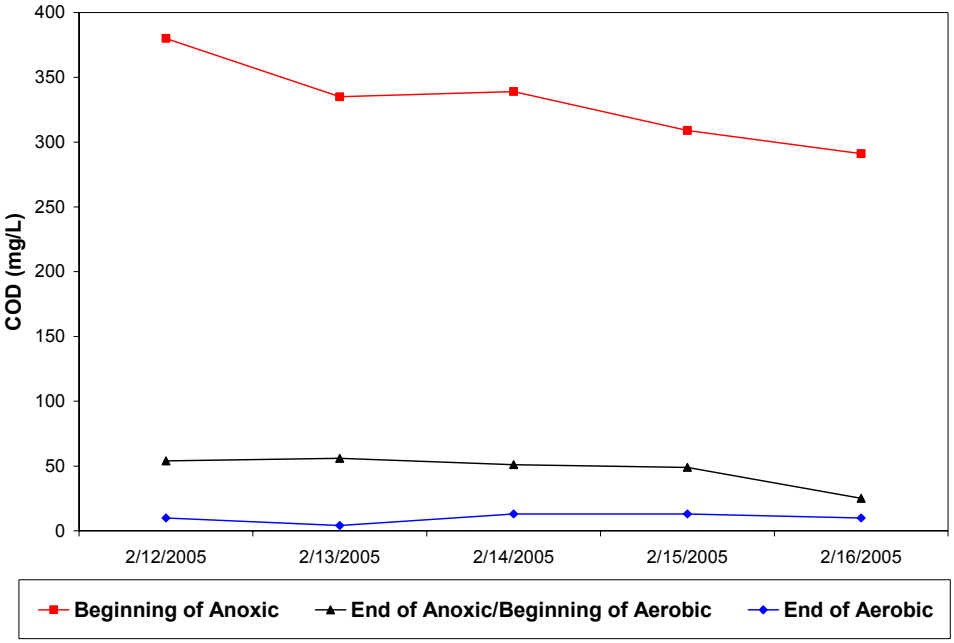

Figure 4.16 Reactor 2, COD Measurements from 5-Day Period when Acclimated to Colored Influent

The graphs above may indicate that the COD removal of the anoxic phase of the process improves when the reactors are fed influent containing anoxically degraded components such as azo dyes. These data might also indicate that the COD removal by the anoxic phase improved over time as the system continued to operate. Although the reason can not be determined at this time, it is important to note that the anoxic phase of the anoxic/aerobic system (not including feeding period) caused 85% COD removal on average when colored influent was employed.

4.4.4. COD Removal of Aerobic Process vs. Anoxic/Aerobic Sequential Process

A comparison of the estimated kinetic parameters for COD removal from the anoxic/aerobic process and the aerobic control is shown below in Table 4.10.

Table 4.10 Comparison of Kinetic Parameters for COD Removal

Phase	Reactor	Rate Constant, k (min.$^{-1}$)	Half Life, $t_{1/2}$ (min.)
Aerobic Control	Reactor 6	0.05658	12.3
Aerobic Phase of Anoxic/Aerobic	Average from Reactors 1 and 2	0.06454	10.7
Anoxic Phase of Anoxic/Aerobic (Excluding Feeding Period)	Average from Reactors 1 and 2	0.00235	295.0
Anoxic Phase of Anoxic/Aerobic (Including Feeding Period)	Reactor 5	0.01175	59.0

The kinetic rate constants and half-lives are graphed below in Figures 4.17 and 4.18, respectively. These graphs compare the phases of the anoxic/aerobic process (excluding feeding period) to the aerobic control.

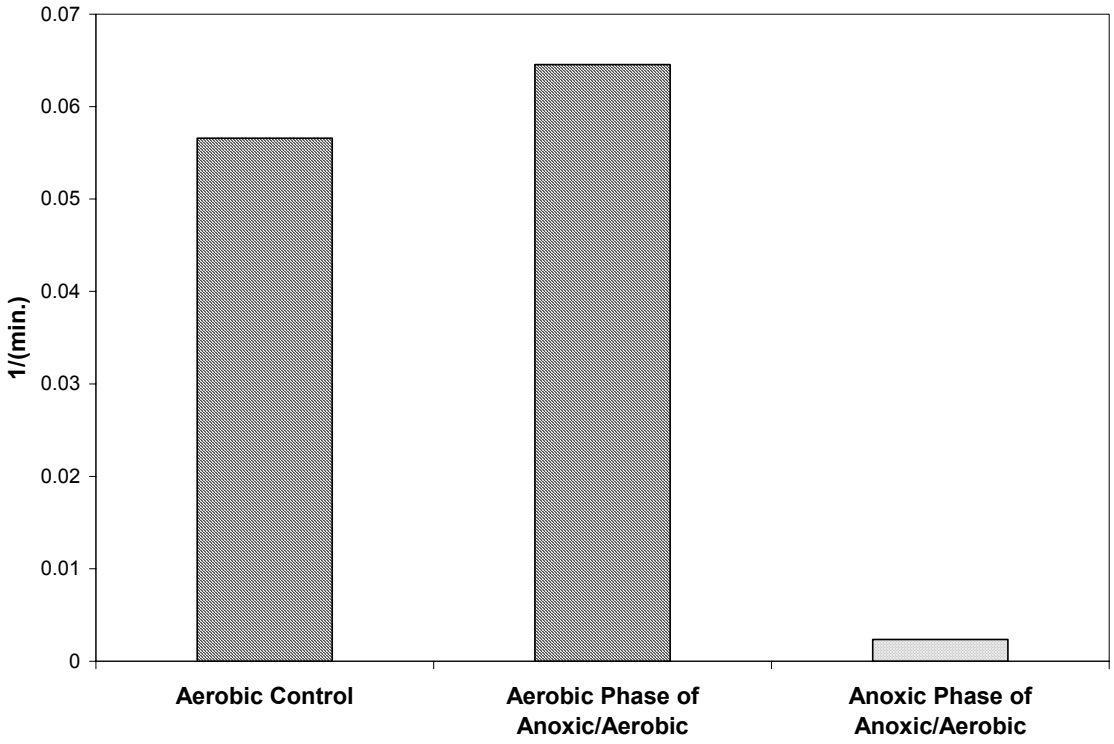

Figure 4.17 Estimated Rate Constants for COD Removal, Anoxic/Aerobic Process vs. Aerobic Control

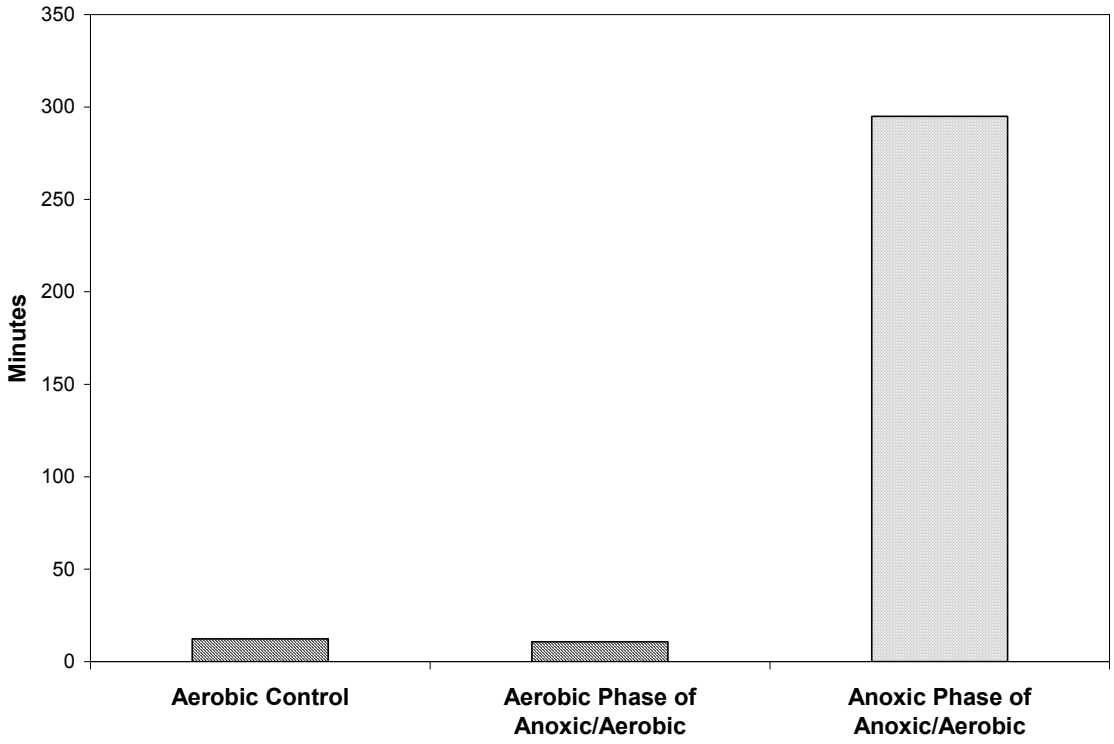

Figure 4.18 Half-Life for COD Removal, Anoxic/Aerobic Process vs. Aerobic Control

It can be noted that the aerobic phase of the anoxic/aerobic process has very similar parameters to those calculated for the aerobic control, with rate constants and half-lives differing by only ten percent. This indicates that the COD removal during the aerobic phase of the anoxic/aerobic process is not highly affected by the presence of a preceding anoxic phase. It can also be noted that anoxic respiration is less effective than aerobic respiration at removing COD from wastewater, as indicated by the lower rate constant and higher half life of the anoxic phase, whether the COD removal during the feeding period is included or excluded. However, the discussion in section 4.4.3.1 indicates that there may be an improvement in the COD removal by the anoxic phase when the reactors are fed influent containing compounds that are degraded anoxically, such as fiber reactive

azo dyes. It is recommended that a follow-up study be completed to determine the initial rate constant for COD removal by the anoxic phase after complete acclimation to colored influent has occurred.

The COD removal by the anoxic/aerobic process can also be compared to the aerobic control in terms of percent removal, as shown below in Figure 4.19. During the last week of reactor operation, the anoxic phase of the anoxic/aerobic process exhibited 85% COD removal, with an additional 10% removal during the subsequent aerobic phase. The aerobic control exhibited 97% COD removal. It can be noted that the overall percent removal by the two systems differ by only two percent.

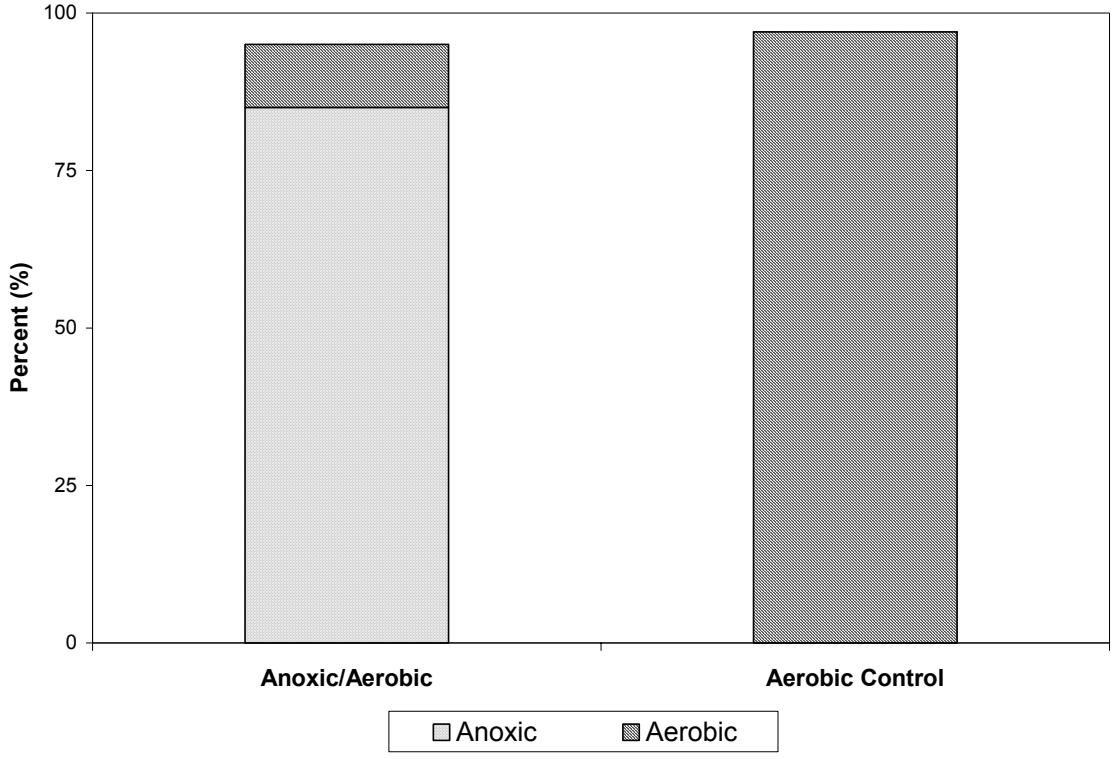

Figure 4.19 Percent COD Removal for Anoxic/Aerobic Process vs. Aerobic Control

4.5. Acclimation to Colored Influent

The reactors were fed colored influent over a five-day acclimation period before the start of the color removal studies. During this time, the concentration of dye in the synthetic influent was adjusted to achieve the proper level of ADMI to mimic effluent from a textile dyeing and finishing plant. Any variation in color level during the color kinetic study was minimized by adjusting the initial concentration to achieve maximum fit (4.6.1.1 and 4.6.2.1). Following the kinetic studies of color removal, the reactors were fed colored influent for an additional week to assess the stability of the process. During these periods, the color of the influent, reactor samples, and effluent were measured in terms of dye concentration and ADMI color value (4.5.1 and 4.5.2).

4.5.1. Characteristics of Colored Influent

To prevent oxidation of the dyes by the components of the synthetic wastewater, feed was prepared daily for each reactor and tested for COD and color. These data can be found in Appendix J. Reactor 1 was fed influent containing C. I. Reactive Red 198 and C. I. Reactive Yellow 86, since these two dyes had very different λ_{max} wavelengths and could be easily differentiated. Reactor 2 was fed influent containing only C. I. Reactive Black 5, since past research had indicated that the degradation of this dye resulted in the formation of colored by-products. Reactor 5, which was the small anoxic/aerobic reaction vessel, was fed influent containing only C. I. Reactive Violet 5, since the effect of a metal-complex dye on the effectiveness of the biomass was unknown. A summary of the colored feed characteristics is shown below in Table 4.11.

Table 4.11 Average Characteristics of Colored Influent

Reactor	COD (mg/L)	ADMI Color	Dye Concentration (g/L)
1	1153	2130	Reactive Red 198 = 0.015, Reactive Yellow 86 = 0.025
2	1131	1197	Reactive Black 5 = 0.013
5	1101	1414	Reactive Violet 5 = 0.029

During the latter part of the color study, modified aerobic control vessels were also operated. The aerobic control vessels were fed colored influent to mimic the anoxic/aerobic vessels, with Reactor 7 receiving Reactive Red 198 and Reactive Yellow 86 (for comparison with Reactor 1), Reactor 8 receiving Reactive Black 5 (for comparison with Reactor 2), and Reactor 9 receiving Reactive Violet 5 (for comparison with Reactor 5). One batch of each colored influent was prepared daily, divided, and fed to both types of reaction vessel.

4.5.2. Characteristics of Reaction Vessels

During this period of the experiment, the color of the treated wastewater was measured at the beginning and end of each phase of the anoxic/aerobic process. The color (both concentration and ADMI) was graphed to assess the stability of each reactor, as shown in Figures 4.20-4.26 below. The figures reveal that the color of the synthetic influent exhibited significant daily variation. This variation can be attributed to the necessity for daily feed preparation to prevent oxidation of the dyestuffs. It can be noted that the variation in feed color is not mirrored by the color in the reactor at the end of each phase of the anoxic/aerobic process, indicating that the biomass was adaptable to changes in influent color. All raw data can be found in Appendix J.

It should be noted that the color kinetic study was performed between January 30th and February 4th. During the week following the kinetic study, the reactors were fed colored influent, but no measurements were taken. Additional measurements were taken during the last week of reactor operation, to assess the stability of the reactors with respect to the colored influent.

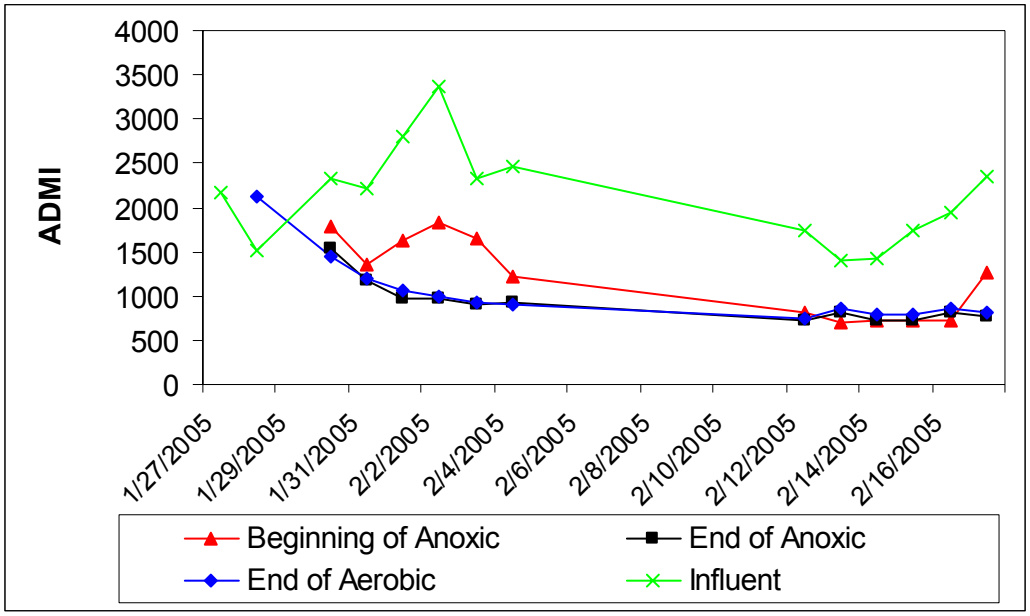

Figure 4.20 Reactor 1, ADMI

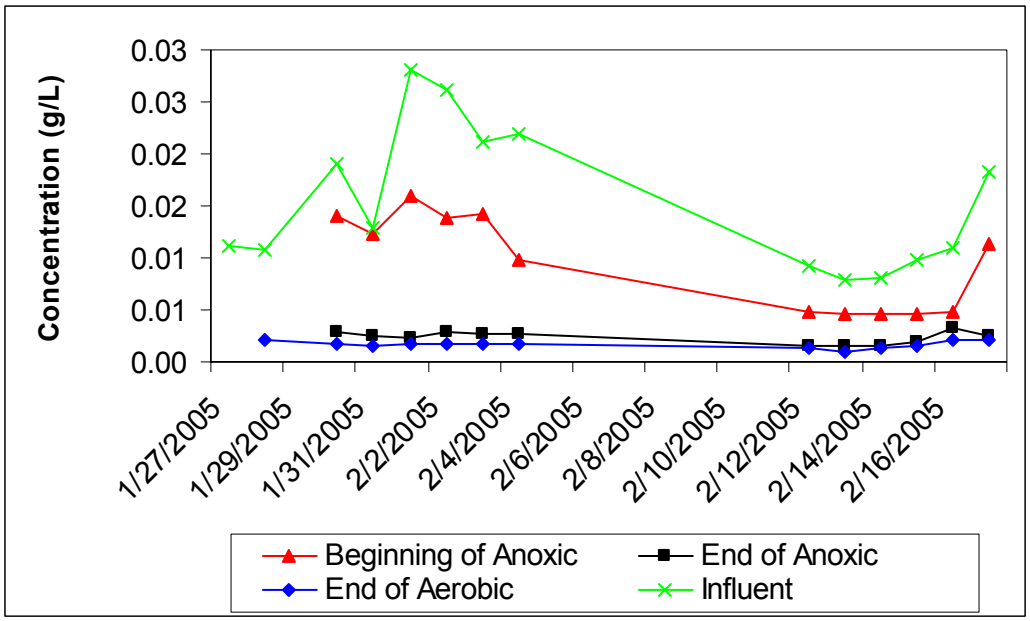

Figure 4.21 Reactor 1, Concentration of Reactive Red 198

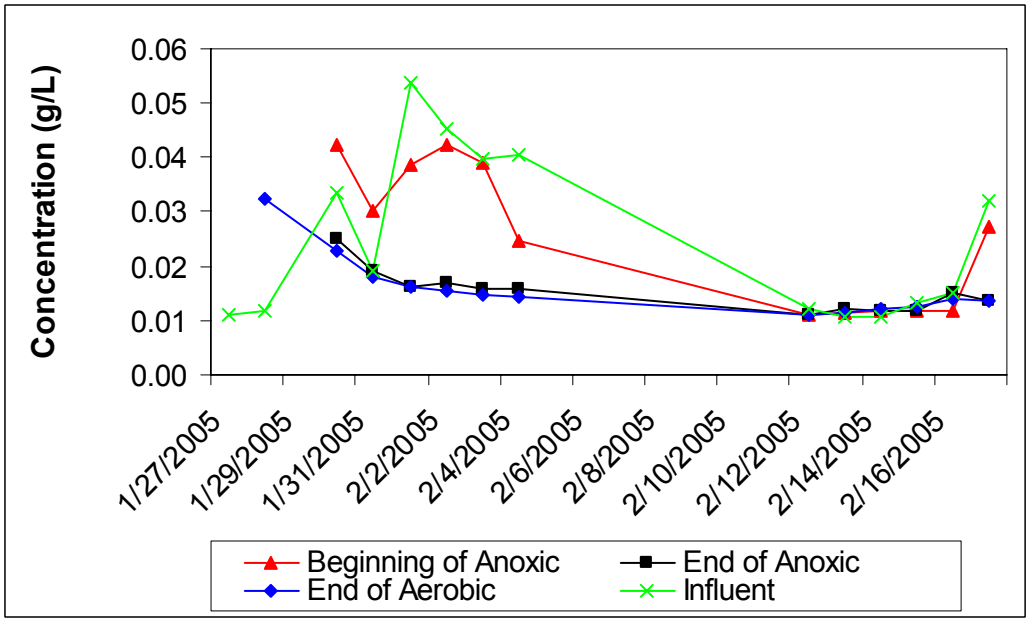

Figure 4.22 Reactor 1, Concentration of Reactive Yellow 86

Figure 4.20 (shown above) indicates that, during the last week of operation, Reactor 1 exhibited no change in ADMI color value throughout the anoxic/aerobic cycle. An examination of Figures 4.21 and 4.22 reveals that this lack of change was due to the concentration of Reactive Yellow 86, which remained constant throughout the cycle at the same concentration as was present in the influent. As discussed in 4.8.1, this dye has certain structural characteristics which may allow it to resist anoxic degradation.

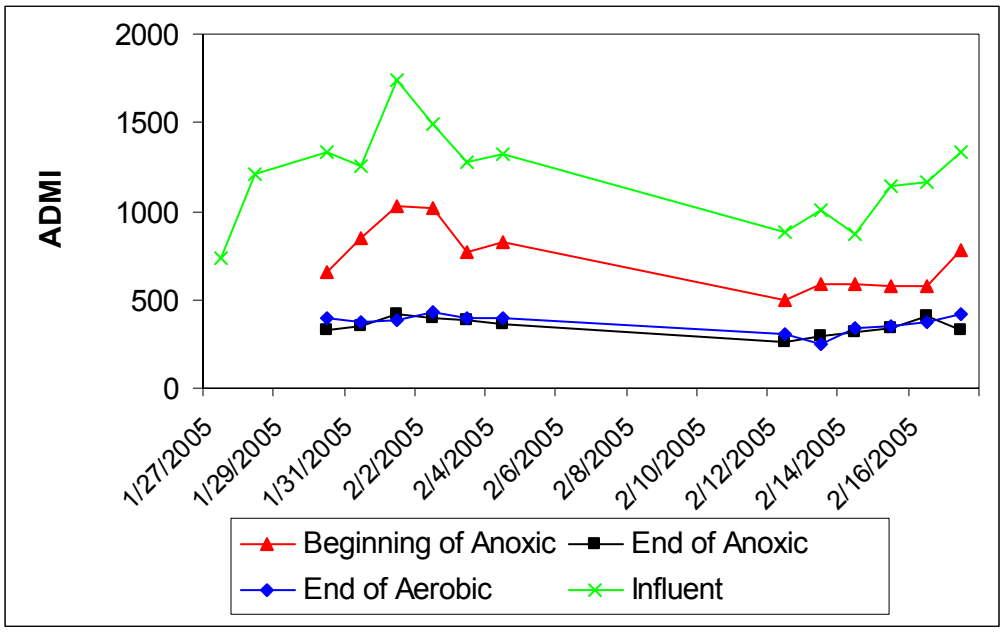

Figure 4.23 Reactor 2, ADMI

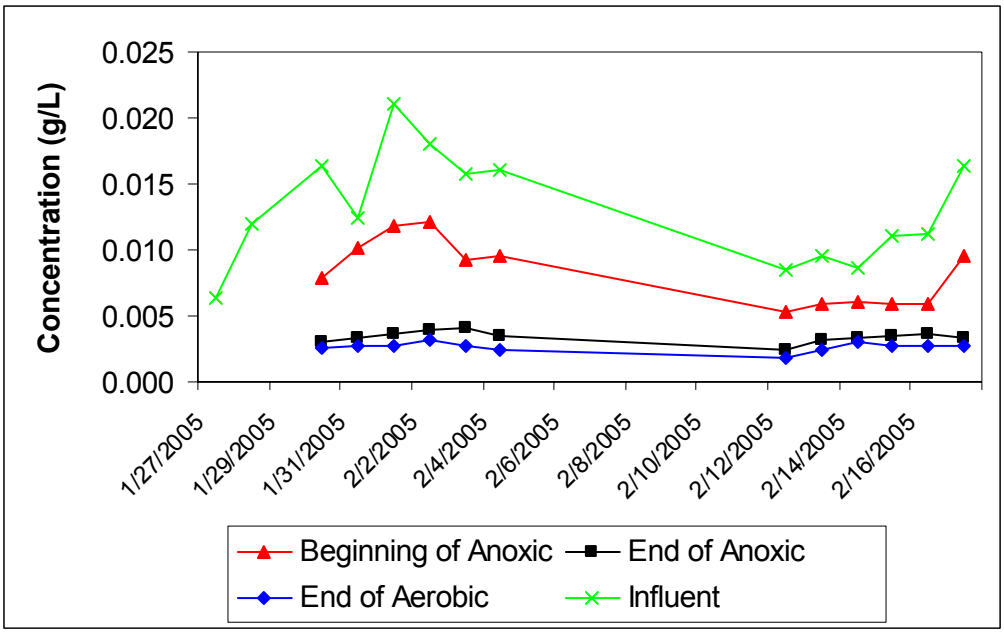

Figure 4.24 Reactor 2, Concentration of Reactive Black 5

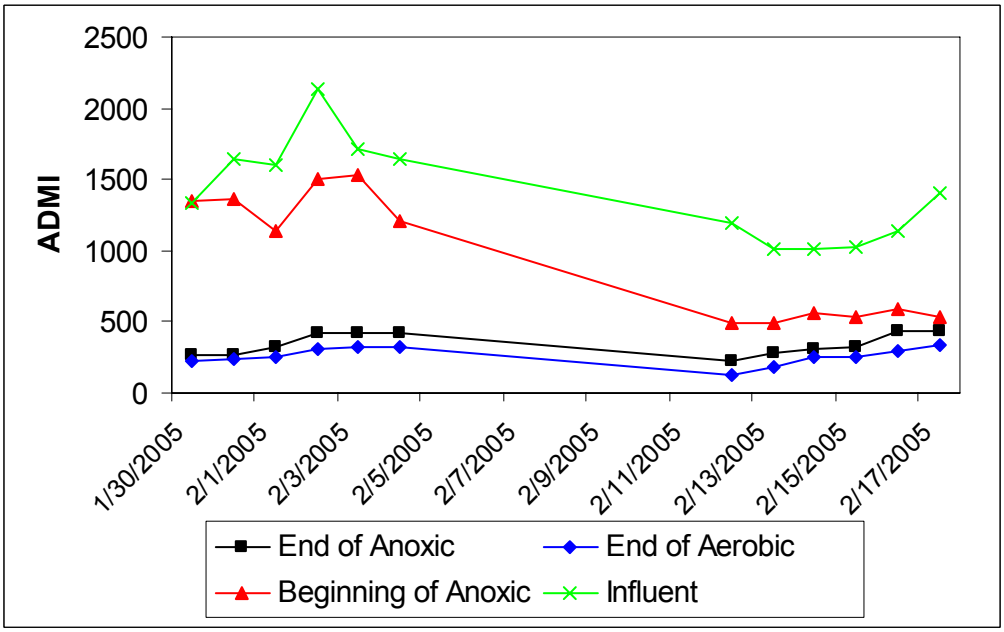

Figure 4.25 Reactor 5, ADMI

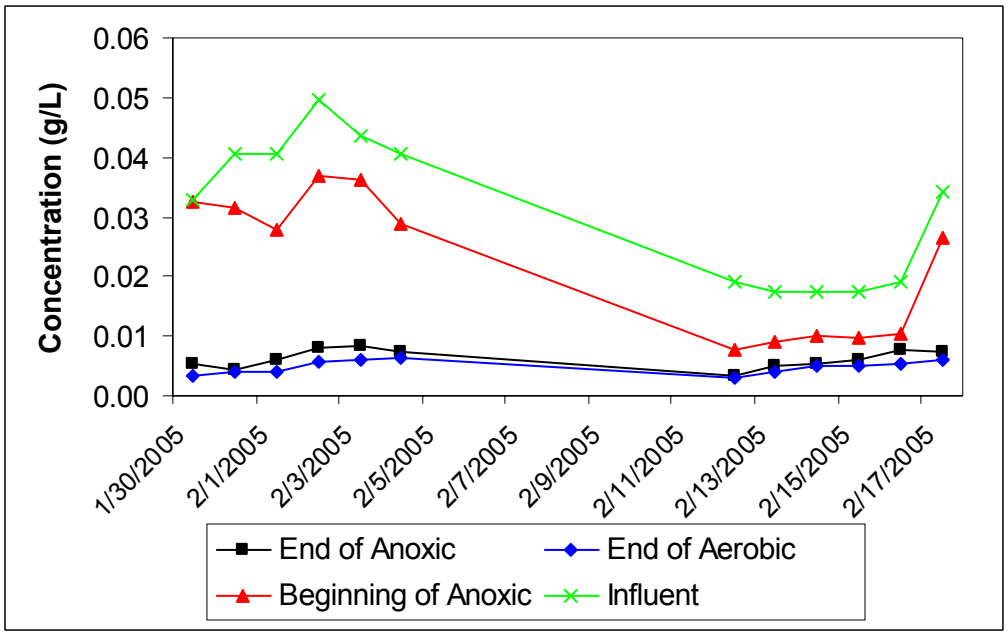

Figure 4.26 Reactor 5, Concentration of Reactive Violet 5

An examination of Figures 4.23-4.26 indicates that the degradation of Reactive Black 5 and Reactive Violet 5 remained fairly stable during the period studied.

4.6. Color Kinetics

Kinetic studies were performed to estimate the rates of color removal by a separate aerobic process and an anoxic/aerobic sequential process (3.4.1.2) for each of the four dyes studied. Color removal as measured by dye-concentration (4.6.1) and ADMI color value (4.6.2) were both assessed using the same sample set.

4.6.1. Dye Concentration-Based

The dye concentration in each sample was determined (3.3.3.1) and the data were analyzed according to a designated method (4.6.1.1) in order to estimate the rates of color removal for each of the four dyes studied. Color removal for each dye was assessed using an anoxic/aerobic reactor and an aerobic control reactor.

4.6.1.1. General Method for Analysis

The color removal for the four dyes was evaluated using concentration measurements according to the method described in section 4.4.1 for the analysis of COD removal. The rate constants were estimated using the data for the first twenty minutes of the anoxic phase and the first 120 minutes of the aerobic phase. The use of a first-order kinetic model is supported by experimental results involving the degradation of twenty different azo dyes under anaerobic conditions (32). However, the model does not perfectly correlate with the experimental data, since it was developed using the assumption that the dye degrades into colorless products. Any lack of fit between the model and the data can be explained by the production of colored by-products and non-degradable components in the dyestuff, which rendered the measurement of color alone insufficient for the development of a kinetic rate law. In future research, a model could be developed by experimenting with different concentrations of dye and biomass to determine the reaction order and utilizing High Pressure Liquid Chromatography (HPLC) to evaluate the behavior of the various reactants and products. The experimental results would also be improved by the use of purified dyes, rather than unpurified commercial dyestuffs.

Abbreviated studies were also performed in order to assess the color removal by a separate aerobic process. The modified aerobic control reaction vessels (Reactors 7, 8, and 9) were sampled at the beginning and end of eight cycles and the effluent data from each cycle were normalized based on the initial concentration for that cycle. The average fraction of concentration remaining at the end of the aerobic cycle was calculated and this

value was compared to the corresponding value for the aerobic phase of the anoxic/aerobic process.

4.6.1.2. Example Data

The data from anoxic/aerobic Reactor 1 for the concentration of C. I. Reactive Red 198 from the first cycle is shown below as an example.

Table 4.12 Example Dye Concentration Data for Anoxic/Aerobic Reactor

Phase	Time (Minutes)	Reactive Red 198 Concentration, Reactor 1 (g/L)
Anoxic	0	0.0141
	5	0.0124
	10	0.0114
	15	0.0097
	20	0.0107
	25	0.0095
	30	0.0107
	60	0.0091
	120	0.0063
	240	0.0047
	480	0.0030
Aerobic	30	0.0021
	60	0.0018
	120	0.0017
	240	0.0018
	480	0.0018
	870	0.0018

The modified aerobic control reactors were only sampled at the beginning and end of each cycle.

4.6.1.3. C. I. Reactive Red 198

Reactor 1 was fed influent containing Reactive Red 198 and the data collected were used to assess the degradation of this dye by the anoxic/aerobic process (4.6.1.3.1). Reactor 7 was fed the same influent and was sampled to compare the degradation under

an aerobic control process (4.6.1.3.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.1.3.3). The influent for Reactor 1 and 7 also contained Reactive Yellow 86 and the two dyes were distinguished during measurement by their differing λ_{max} values of 424 nm for Reactive Yellow 86 and 510 nm for Reactive Red 198.

4.6.1.3.1. Anoxic/Aerobic (Reactor 1)

Each cycle was normalized using the initial concentration at time zero and the average cycle data were calculated, as shown in Figure 4.27 below, which shows good correlation between the various cycles.

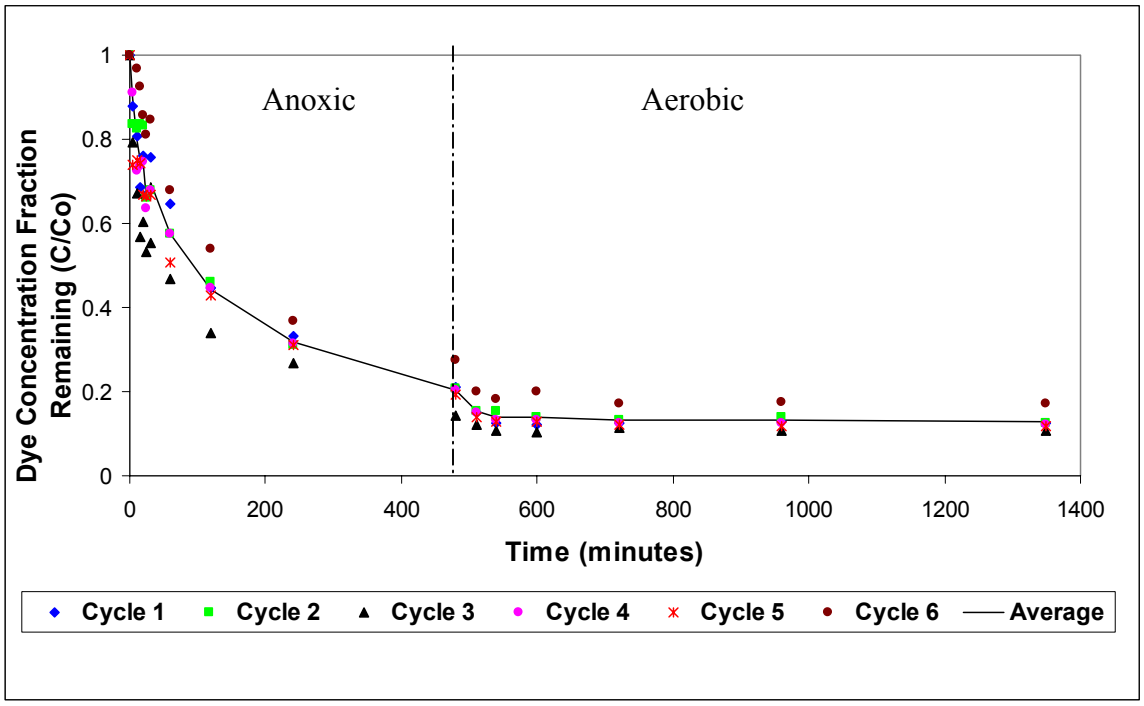

Figure 4.27 Reactive Red 198, Concentration Fraction Remaining vs. Time (Reactor 1)

Using the analysis method described in 4.6.1.1., a model was developed for the removal of color from Reactive Red 198 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.13.

Table 4.13, Reactive Red 198, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.01567	44.2
Aerobic	0.00299	231.8

The model for color removal for Reactive Red 198 is shown below:

$$C_{anoxic} = 0.80021e^{-(0.01567)t} + 0.19979$$

$$C_{aerobic} = 0.07482e^{-(0.00299)t} + 0.12498$$

As shown in Figure 4.28, the model for color removal for Reactive Red 198 shows good agreement with the average of the measured data, with an average error of 0.0006 g/L dye for the sampling scheme used.

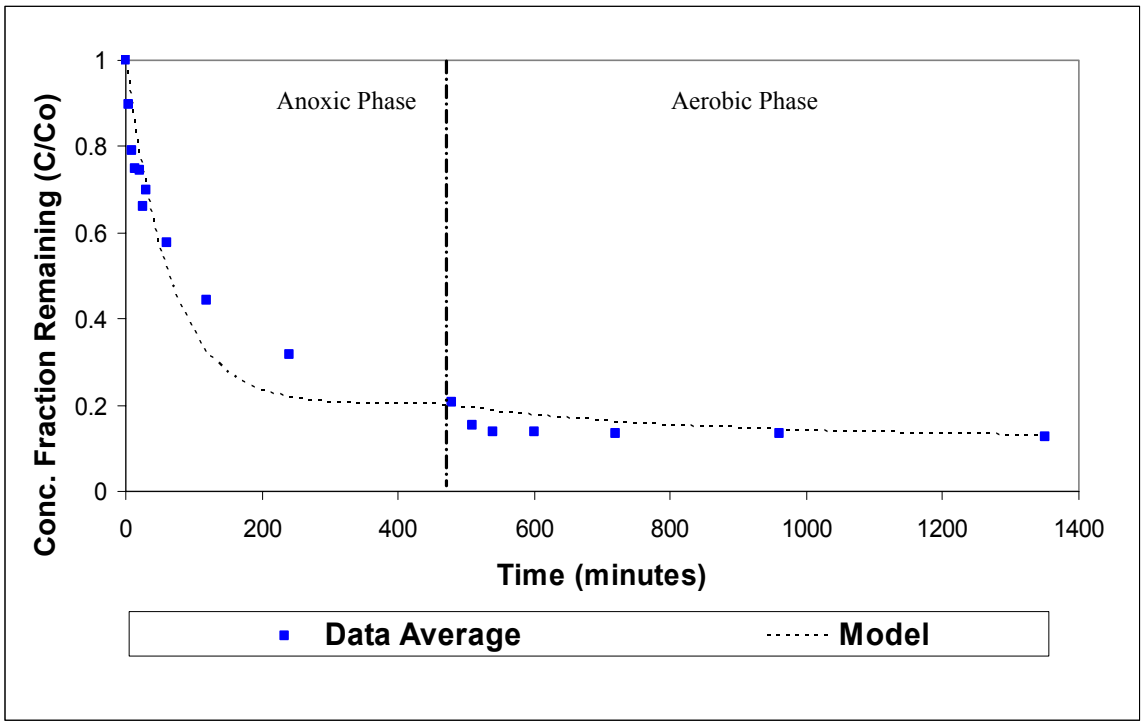

Figure 4.28, Reactive Red 198, Model vs. Average Measured Data for Anoxic/Aerobic Reactor 1

See Appendix L for all data and analysis related to concentration-based color removal for C. I. Reactive Red 198 in the anoxic/aerobic process.

4.6.1.3.2. Aerobic Control (Reactor 7)

The raw concentration measurements taken at the beginning and ending of each aerobic cycle are shown in Figure 4.29 below.

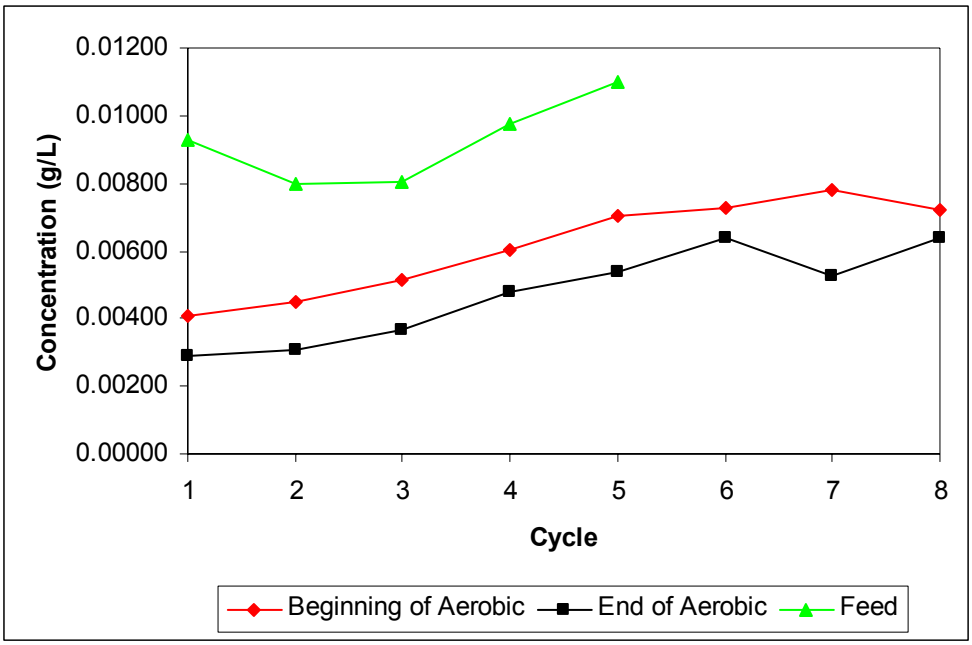

Figure 4.29 Reactive Red 198, Concentration Data for Aerobic Control (Reactor 7)

It can be noted that the concentration rose steadily throughout the first five cycles, possibly due to adsorption of dye to the biomass and the resulting saturation of the biomass with dye. Despite this upward trend, the amount of dye concentration removed by the aerobic process, indicated by the distance between the red and black line, remained fairly constant. The effluent data from each cycle were normalized by dividing the effluent concentration by the initial concentration to obtain the fraction of dye concentration remaining at the end of each cycle (see Appendix K). The average fraction of Reactive Red 198 remaining in the effluent of the aerobic control was 0.76.

4.6.1.3.3. Anoxic/Aerobic Process vs. Aerobic Control

Figure 4.30, shown below, compares the percent color removal for Reactive Red 198 for the anoxic/aerobic process vs. the aerobic control during the last week of reactor operation. The anoxic phase removed 65% of the color with an additional 9% removal

by the subsequent aerobic phase. This is significantly higher than the 12% color removal exhibited by the aerobic control.

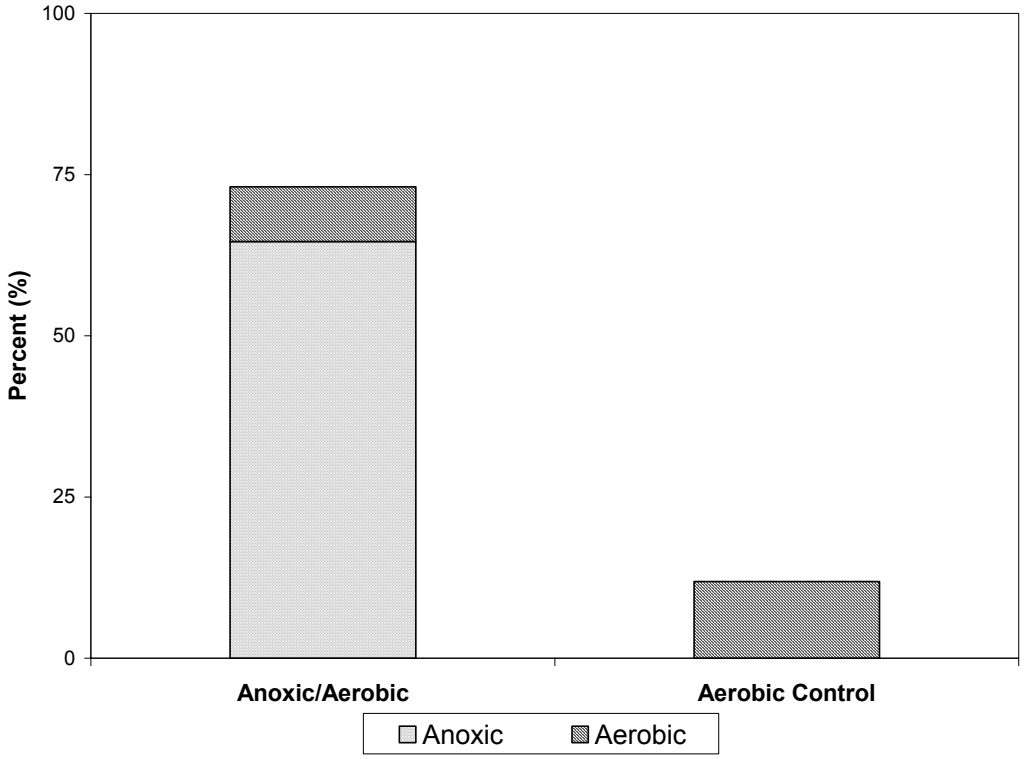

Figure 4.30 Percent Color Removal (Concentration-Based) for Reactive Red 198, Anoxic/Aerobic vs. Aerobic Control

4.6.1.4. C. I. Reactive Yellow 86

Reactor 1 was fed influent which also contained Reactive Yellow 86, in addition to Reactive Red 198, and the data collected were used to assess the degradation of Reactive Yellow 86 by the anoxic/aerobic process (4.6.1.4.1). Reactor 7 was fed the same influent and was sampled to compare the degradation under an aerobic control process (4.6.1.4.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.1.4.3).

4.6.1.4.1. Anoxic/Aerobic (Reactor 1)

Each cycle was normalized using the initial concentration at time zero and the average cycle data were calculated, as shown in Figure 4.31 below, which shows good correlation between the various cycles.

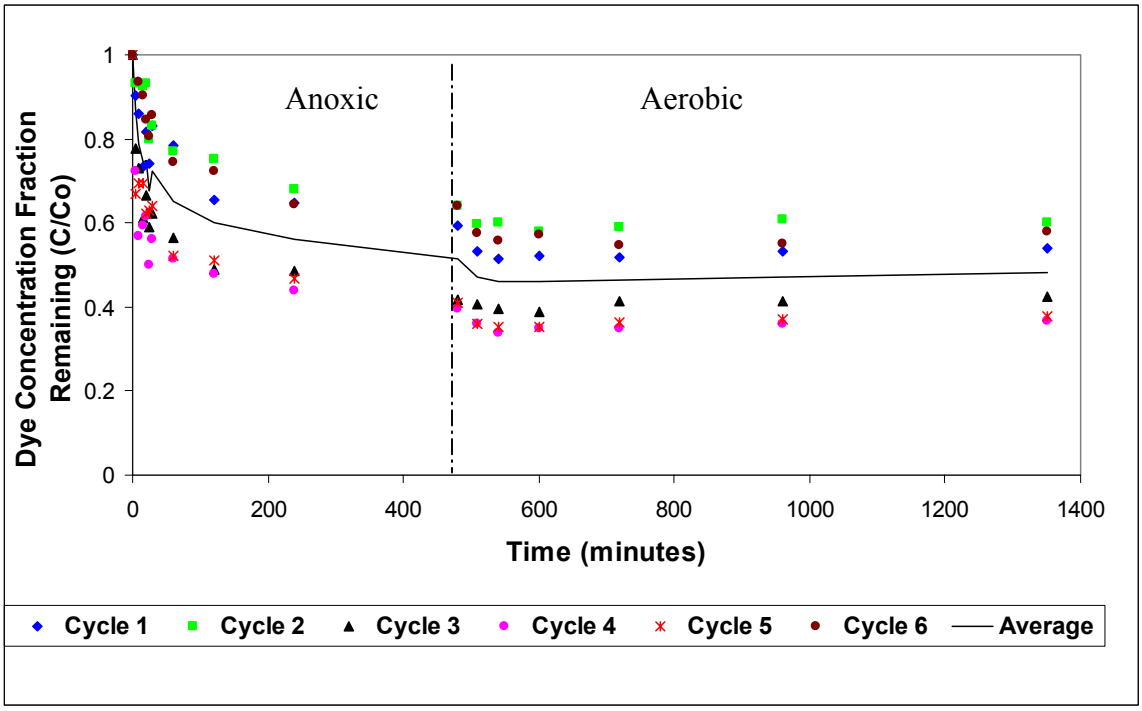

Figure 4.31 Reactive Yellow 86, Concentration Fraction Remaining vs. Time (Reactor 1)

A model was developed for the removal of color from Reactive Yellow 86 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.14.

Table 4.14, Reactive Yellow 86, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.01506	46.0
Aerobic	0.00086	806.0

The model for color removal for Reactive Yellow 86 is shown below:

$$C_{anoxic} = 0.49757e^{-(0.01506)t} + 0.50243$$

$$C_{aerobic} = 0.03274e^{-(0.00086)t} + 0.46969$$

As shown in Figure 4.32, the model for color removal for Reactive Yellow 86 shows good agreement with the average of the measured data, with an average error of 0.0023 g/L dye for the sampling scheme used.

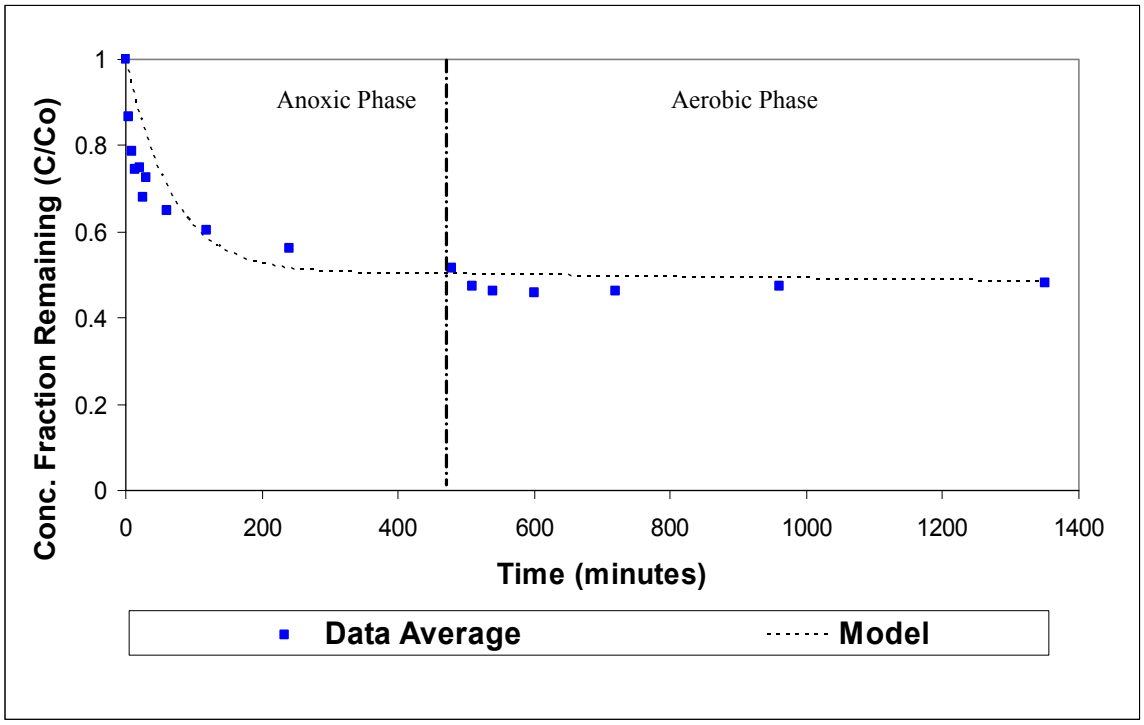

Figure 4.32, Reactive Yellow 86, Model vs. Average Measured Data for Anoxic/Aerobic Reactor 1

See Appendix N for all data and analysis related to concentration-based color removal for C. I. Reactive Yellow 86 in the anoxic/aerobic process.

4.6.1.4.2. Aerobic Control (Reactor 7)

The raw concentration measurements taken at the beginning and ending of each aerobic cycle are shown in Figure 4.33 below.

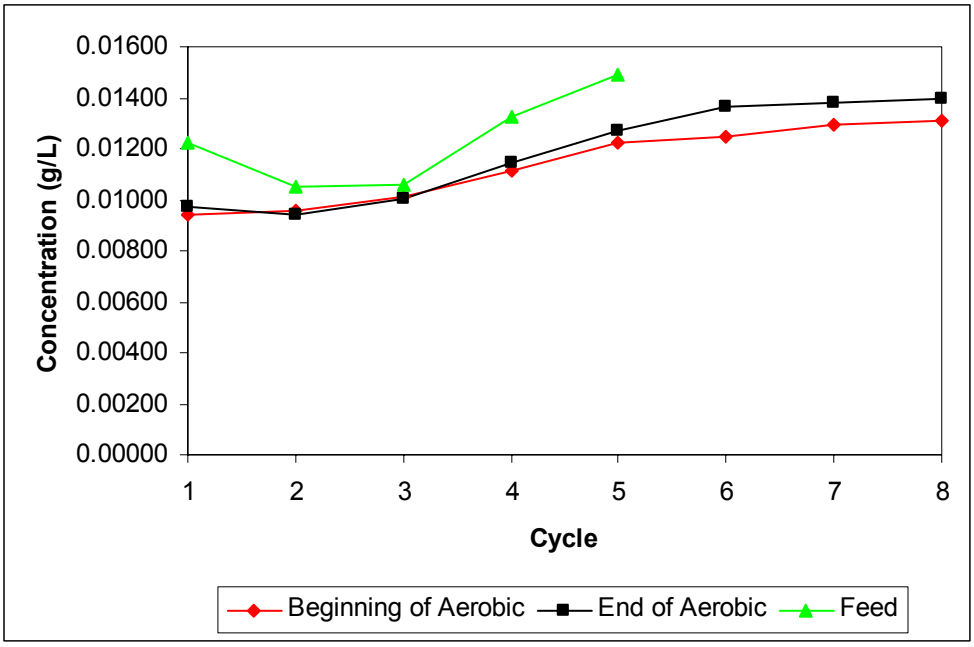

Figure 4.33 Reactive Yellow 86, Concentration Data for Aerobic Control (Reactor 7)

The average fraction of Reactive Yellow 86 remaining in the effluent of the aerobic control was 1.04, indicating that effectively no color was removed (see Appendix M).

4.6.1.4.3. Anoxic/Aerobic Process vs. Aerobic Control

Figure 4.34, shown below, compares the percent color removal for Reactive Yellow 86 for the anoxic/aerobic process vs. the aerobic control during the last week of reactor operation. The anoxic phase removed 11% of the color with an additional 1% removal by the subsequent aerobic phase. The aerobic control exhibited a 7% increase in color. This information indicates that this dye is resistant to degradation. However,

anoxic respiration is capable of a low level of degradation, with a significant portion remaining non-degradable, as indicated by the kinetic model and Figure 4.22. As discussed in 4.8.1, this dye has certain structural characteristics which may allow it to resist biological degradation.

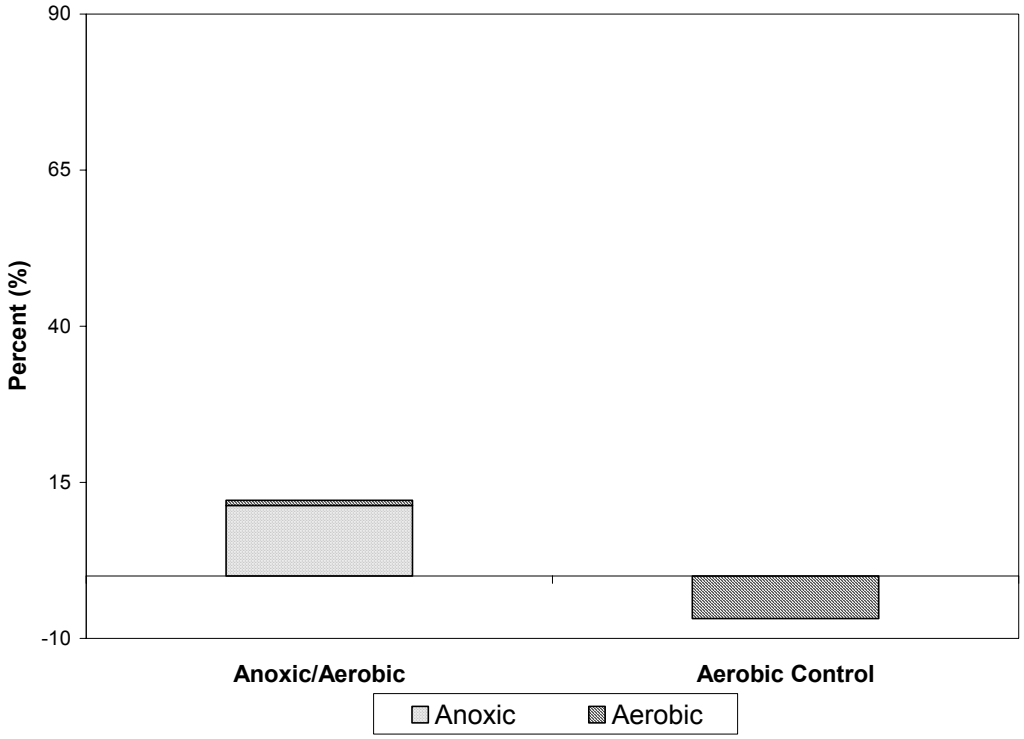

Figure 4.34 Percent Color Removal (Concentration-Based) for Reactive Yellow 86, Anoxic/Aerobic vs. Aerobic Control

4.6.1.5. C. I. Reactive Black 5

Reactor 2 was fed influent containing Reactive Black 5 and the data collected were used to assess the degradation of this dye by the anoxic/aerobic process (4.6.1.5.1). Reactor 8 was fed the same influent and was sampled to compare the degradation under an aerobic control process (4.6.1.5.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.1.5.3).

4.6.1.5.1. Anoxic/Aerobic (Reactor 2)

Each cycle was normalized using the initial concentration at time zero and the average cycle data were calculated, as shown in Figure 4.35 below, which shows good correlation between the various cycles.

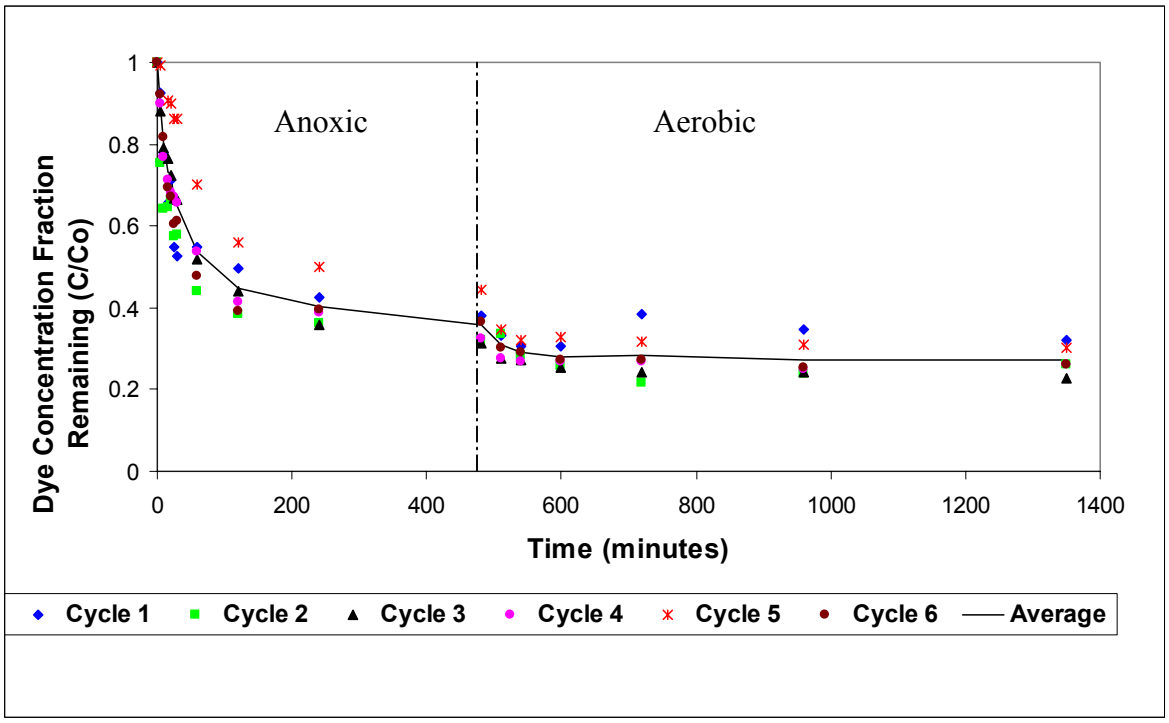

Figure 4.35 Reactive Black 5, Concentration Fraction Remaining vs. Time (Reactor 2)

A model was developed for the removal of color from Reactive Black 5 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.15.

Table 4.15 Reactive Black 5, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.01718	40.3
Aerobic	0.00186	372.7

The model for color removal for Reactive Black 5 is shown below:

$$C_{anoxic} = 0.64645e^{-(0.01718)t} + 0.35354$$

$$C_{aerobic} = 0.08538e^{-(0.00186)t} + 0.26817$$

As shown in Figure 4.36, the model for color removal for Reactive Black 5 shows good agreement with the average of the measured data, with an average error of 0.0005 g/L dye, for the sampling scheme used.

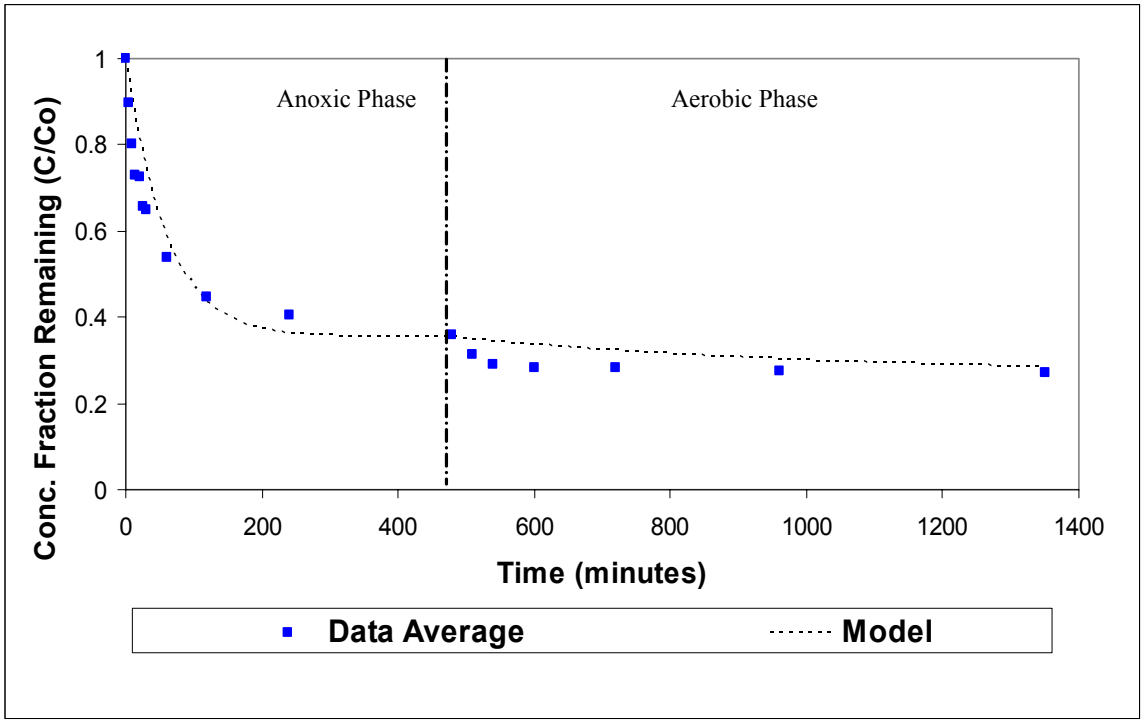

Figure 4.36 Reactive Black 5, Model vs. Average Measured Data for Anoxic/Aerobic Reactor 2

See Appendix P for all data related to color removal for C. I. Reactive Black 5 in the anoxic/aerobic process.

4.6.1.5.2. Aerobic Control (Reactor 8)

The raw concentration measurements taken at the beginning and ending of each aerobic cycle are shown in Figure 4.37 below.

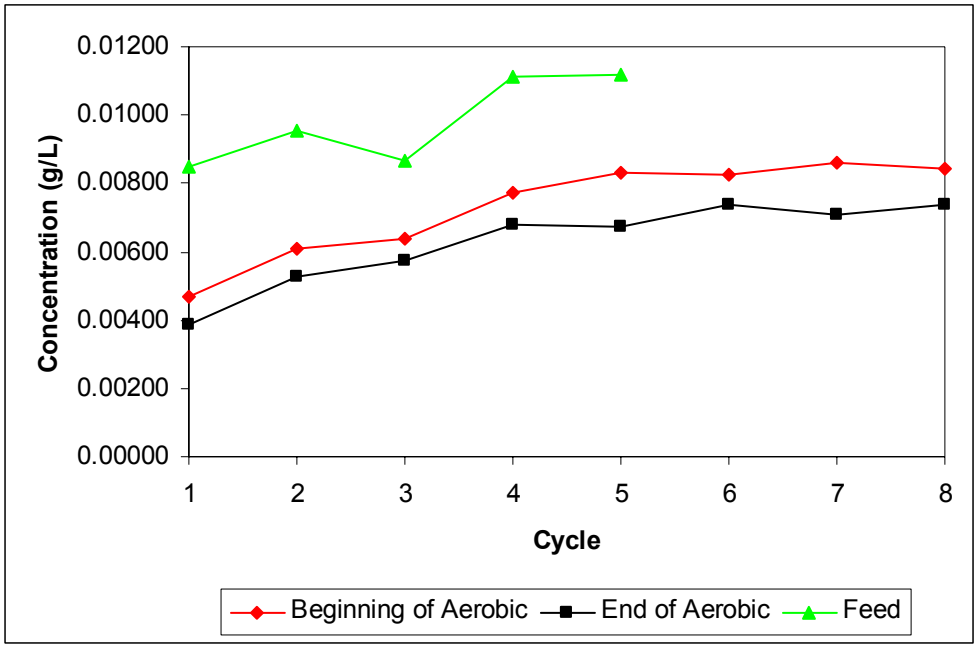

Figure 4.37 Reactive Black 5, Concentration Data for Aerobic Control (Reactor 8)

The average fraction of Reactive Black 5 remaining in the effluent of the aerobic control was 0.86 (see Appendix O) and this fraction remained fairly constant throughout the cycles observed.

4.6.1.5.3. Anoxic/Aerobic Process vs. Aerobic Control

Figure 4.38, shown below, compares the percent color removal for Reactive Black 5 for the anoxic/aerobic process vs. the aerobic control during the last week of reactor operation. The anoxic phase removed 50% of the color with an additional 10% removal

by the subsequent aerobic phase. This is significantly higher than the 13% color removal exhibited by the aerobic control.

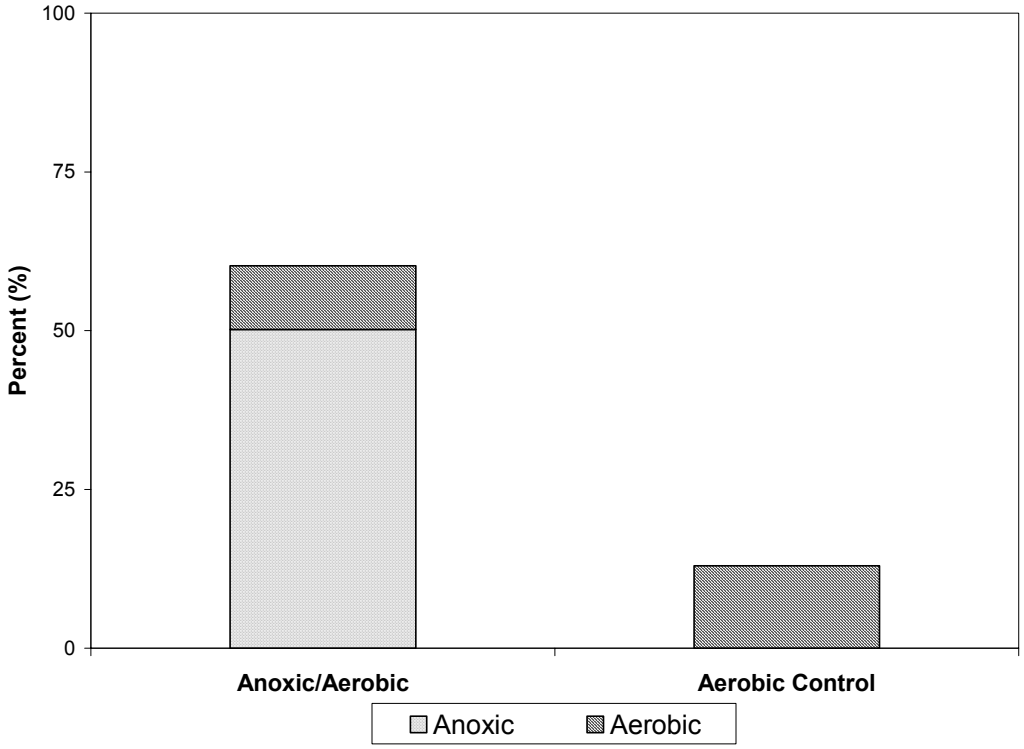

Figure 4.38 Percent Color Removal (Concentration-Based) for Reactive Black 5, Anoxic/Aerobic vs. Aerobic Control

4.6.1.6. C. I. Reactive Violet 5

Reactor 5 was fed influent containing Reactive Violet 5 and the data collected were used to assess the degradation of this dye by the anoxic/aerobic process (4.6.1.6.1). Reactor 9 was fed the same influent and was sampled to compare the degradation under an aerobic control process (4.6.1.6.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.1.6.3).

4.6.1.6.1. Anoxic/Aerobic (Reactor 5)

Each cycle was normalized using the initial concentration at time zero and the average cycle data were calculated, as shown in Figure 4.39 below, which shows good correlation between the various cycles.

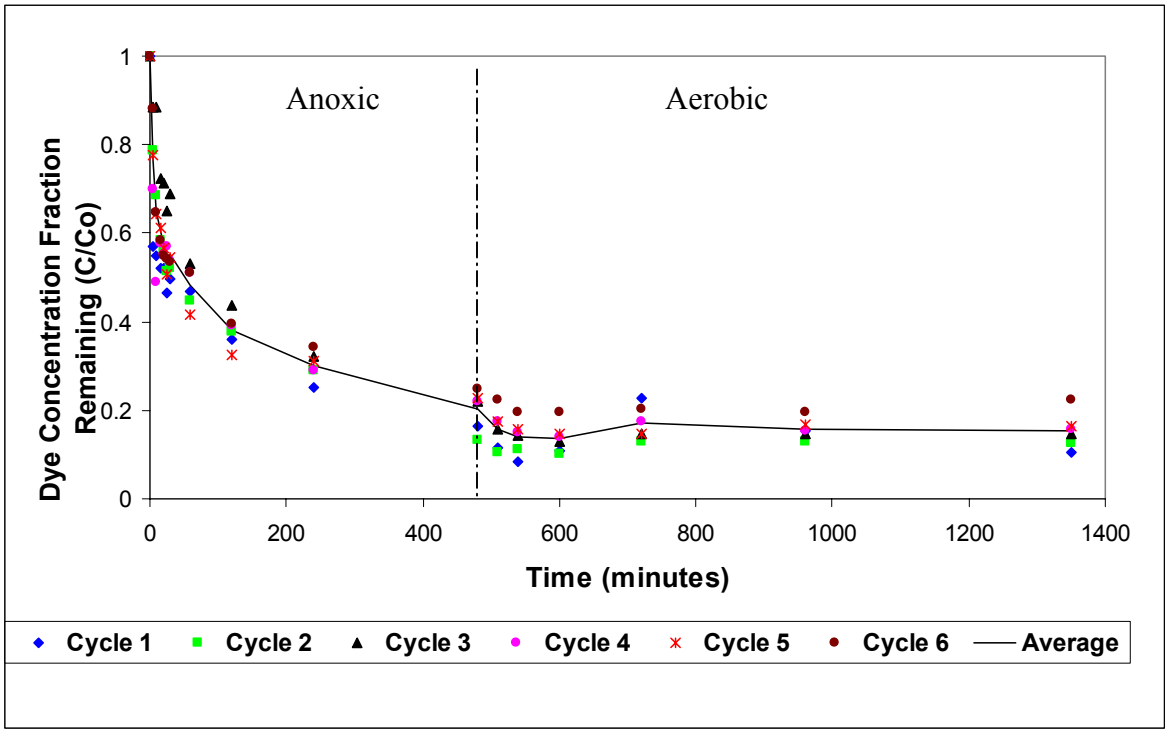

Figure 4.39 Reactive Violet 5, Concentration Fraction Remaining vs. Time (Reactor 5)

A model was developed for the removal of color from Reactive Violet 5 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.16.

Table 4.16 Reactive Violet 5, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.02696	25.7
Aerobic	0.00301	230.3

The model for color removal for Reactive Violet 5 is shown below:

$$C_{anoxic} = 0.79755e^{-(0.02696)t} + 0.20245$$

$$C_{aerobic} = 0.04939e^{-(0.00301)t} + 0.15307$$

As shown in Figure 4.40, the model for color removal for Reactive Violet 5 shows good agreement with the average of the measured data, with an average error of 0.0021 g/L dye, for the sampling scheme used.

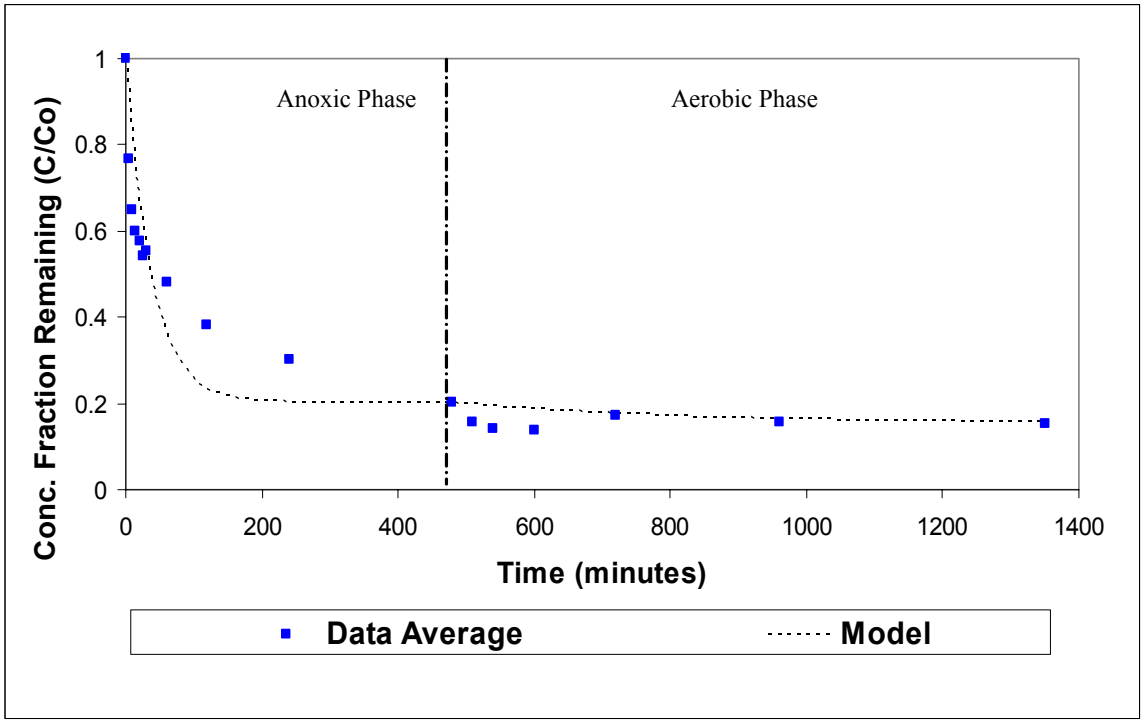

Figure 4.40 Reactive Violet 5, Model vs. Average Measured Data for Anoxic/Aerobic Reactor 5

See Appendix R for all data related to color removal for C. I. Reactive Violet 5 in the anoxic/aerobic process.

4.6.1.6.2. Aerobic Control (Reactor 9)

The raw concentration measurements taken at the beginning and ending of each aerobic cycle are shown in Figure 4.41 below.

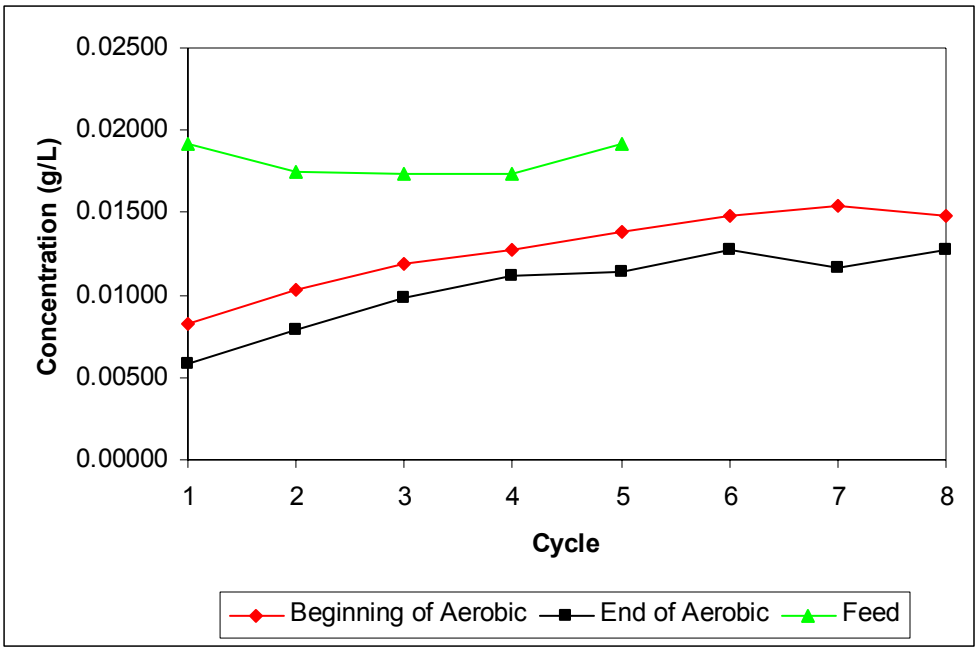

Figure 4.41 Reactive Violet 5, Concentration Data for Aerobic Control (Reactor 9)

The average fraction of Reactive Violet 5 remaining in the effluent of the aerobic control was 0.81 (see Appendix Q) and this fraction remained fairly constant over the cycles observed.

4.6.1.6.3. Anoxic/Aerobic Process vs. Aerobic Control

The average percentage of Reactive Violet 5 removed by the aerobic control process was 19%, while an average of 80% was removed by the anoxic phase of the anoxic/aerobic process. The aerobic phase of the anoxic/aerobic process removed an additional 5%. These results indicate that anoxic respiration is much more effective at degrading Reactive Violet 5 than aerobic respiration.

Figure 4.42, shown below, compares the percent color removal for Reactive Violet 5 for the anoxic/aerobic process vs. the aerobic control during the last week of reactor operation. The anoxic phase removed 53% of the color with an additional 9%

removal by the subsequent aerobic phase. This is significantly higher than the 14% color removal exhibited by the aerobic control.

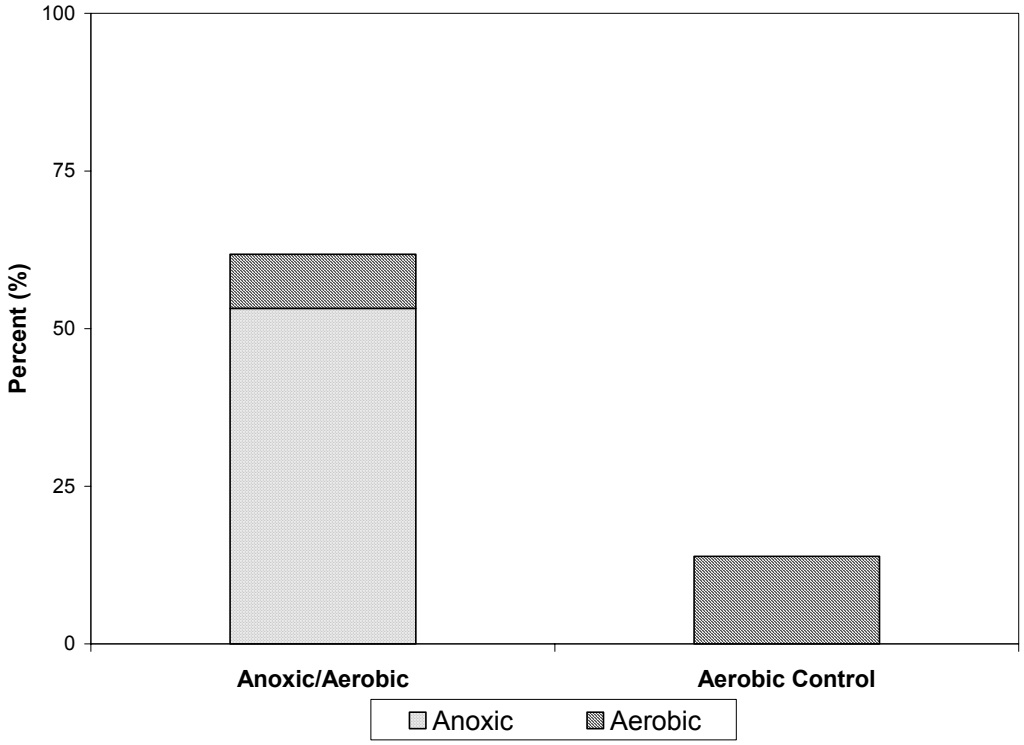

Figure 4.42 Percent Color Removal (Concentration-Based) for Reactive Violet 5, Anoxic/Aerobic vs. Aerobic Control

4.6.1.7. Color Removal during Feeding Period

Section 4.4.3.2 discussed the significant removal of COD during the fifteen-minute feeding period that precedes the anoxic phase of the anoxic/aerobic process. Any corresponding dye degradation during the feeding period was neglected in the analysis since this value showed high variation between the different dyes investigated and among the individual cycle data for each dye.

4.6.1.8. Summary of Concentration-Based Color Removal Study

For each of the four dyes studied, the color removal by the anoxic phase of the anoxic/aerobic process out-performed the aerobic phase and the aerobic control. By comparing the estimated rate constants, it is possible to assess the degradation of each dye by the two phases of the anoxic/aerobic process. As shown below in Figure 4.43, Reactive Violet 5 was degraded the most efficiently by the anoxic phase

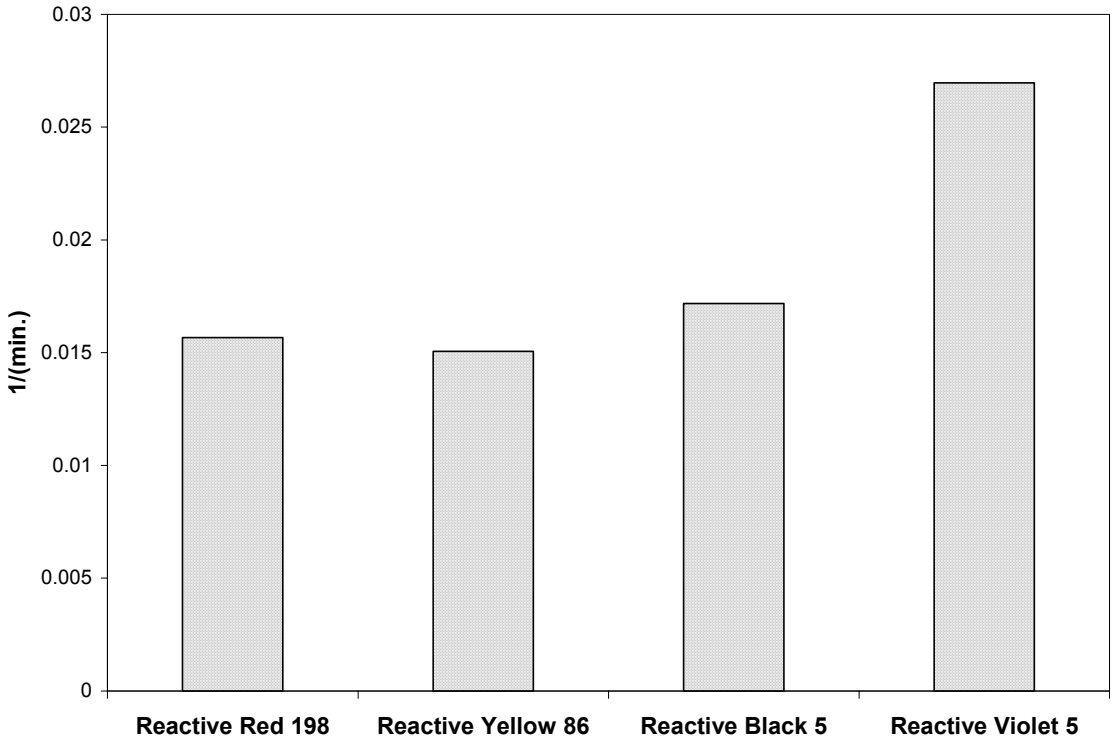

Figure 4.43 Estimated Rate Constants for Anoxic Phase of Anoxic/Aerobic Process

Figure 4.44, shown below, indicates that Reactive Red 198 and Reactive Violet 5 are degraded more quickly in the aerobic phase than the other two dyes. However, the rate constants during the aerobic phase are significantly lower than those for the anoxic phase.

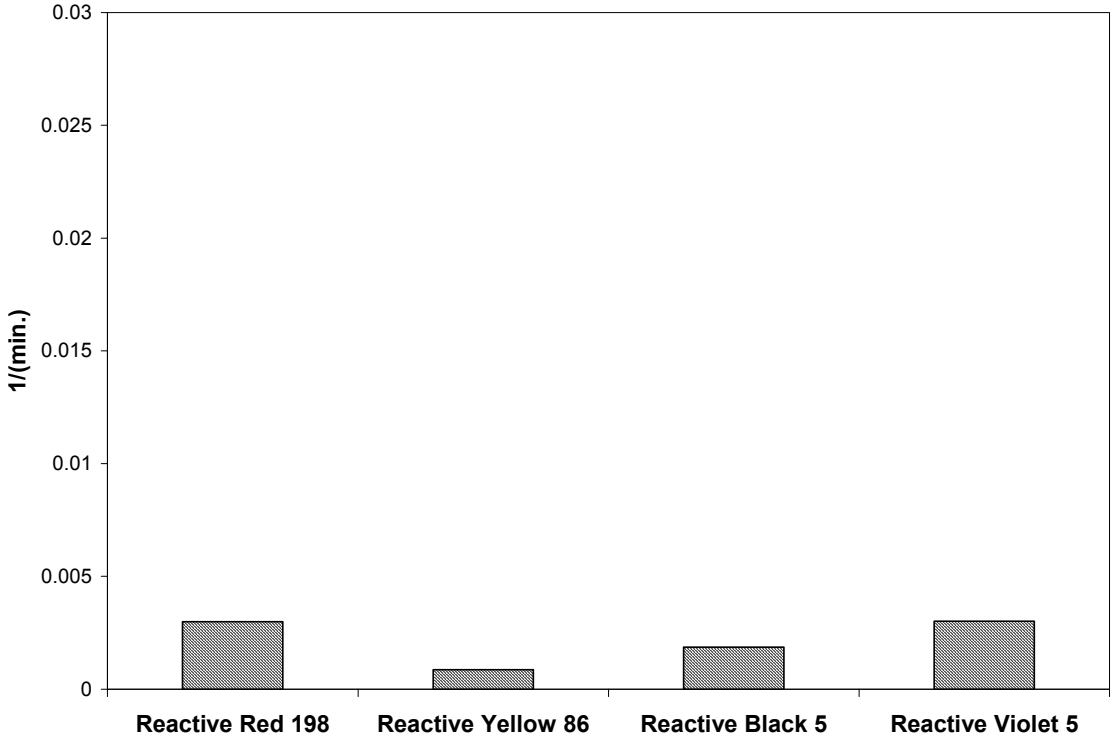

Figure 4.44 Estimated Rate Constants for Aerobic Phase of Anoxic/Aerobic Process

Figure 4.45, shown below, compares the half-life for the degradation of each dye. It can be noted that the half-lives for the anoxic phase are significantly lower than the aerobic phase for each of the dyes studied.

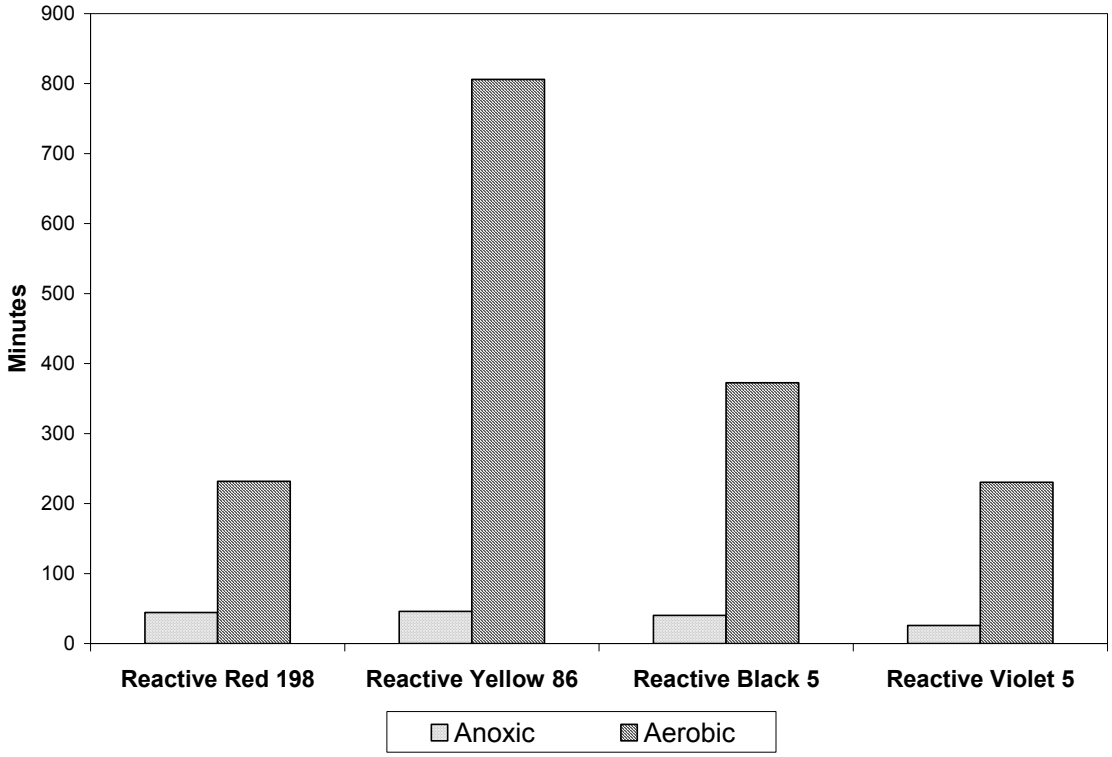

Figure 4.45 Half-Life for Concentration-Based Color Removal, Anoxic Phase vs. Aerobic Phase of Anoxic/Aerobic Process

An examination of Figure 4.46, shown below, reveals that Reactive Yellow 86 had the highest level of non-degradable material remaining in the system at the end of the anoxic/aerobic process. This level is significantly higher than the other four dyes and confirms the phenomenon in Figure 4.22, where the concentration of Reactive Yellow 86 failed to change significantly throughout the entire anoxic/aerobic cycle, once the reactor had become acclimated to the colored influent.

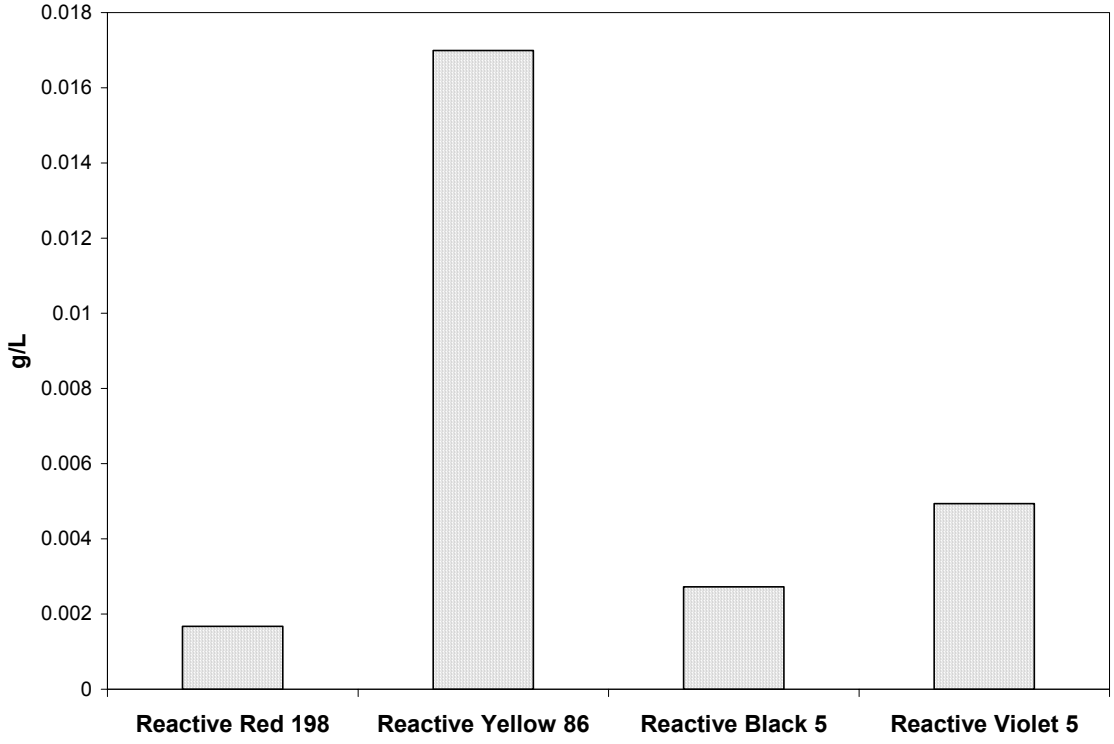

Figure 4.46 Average Non-Degradable Dye Remaining at End of Anoxic/Aerobic Process

4.6.2. ADMI-Based

The ADMI color value of each sample was determined (3.3.3.2) and the data were analyzed according to a specified method (4.6.2.1) in order to estimate the rates of color removal for each of the dyes studied. Color removal for each dye was assessed using an anoxic/aerobic reactor and an aerobic control reactor.

4.6.2.1. General Method for Analysis

For each ADMI study involving the anoxic/aerobic process, the raw data were graphed vs. time, with each cycle superimposed. The error between each data point and the corresponding data point in the first cycle was calculated and the cumulative error for

each cycle was obtained. Each cycle was then adjusted by a factor unique to that cycle in order to minimize the cumulative error and achieve maximum overlay. Using a first-order kinetic model, the average data for the adjusted cycles were then used to calculate the kinetic parameters for each phase of the process, using method described in 4.4.1.

Abbreviated studies were also performed in order to assess the color removal by a separate aerobic process. The modified aerobic control vessels (Reactors 7, 8, and 9) were sampled at the beginning and end of eight cycles and the effluent data from each cycle were normalized based on the initial ADMI for that cycle. The average fraction of ADMI remaining at the end of the aerobic cycle was calculated and this value was compared to the corresponding value for the anoxic/aerobic process.

4.6.2.2. Example Data

The data collected from the anoxic/aerobic reactor containing C. I. Reactive Violet 5 during the first cycle are shown below as an example.

Table 4.17 Example ADMI Data

Phase	Time (Minutes)	Reactive Violet 5 ADMI Color Value (Reactor 5)
Anoxic	0	1347
	5	759
	10	710
	15	696
	20	698
	25	647
	30	663
	60	649
	120	543
	240	377
	480	269
Aerobic	30	190
	60	174
	120	160
	240	400
	480	301
	870	218

The ADMI color values of samples from the modified aerobic control vessels were obtained only at the beginning and end of each aerobic cycle.

4.6.2.3. C. I. Reactive Red 198 and C. I. Reactive Yellow 86

Reactor 1 was fed influent containing Reactive Red 198 and Reactive Yellow 86. Since ADMI is a hue-independent assessment of color, the change in ADMI was assessed for these two dyes as a single variable. The data collected were used to assess the color change as related to these dyes by the anoxic/aerobic process (4.6.2.3.1). Reactor 7 was fed the same influent and was sampled to compare the color change under an aerobic control process (4.6.2.3.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.2.3.3).

4.6.2.3.1. Anoxic/Aerobic (Reactor 1)

Each cycle was adjusted to achieve the maximum overlay, with good agreement between the various cycles, as shown in Figure 4.47 below.

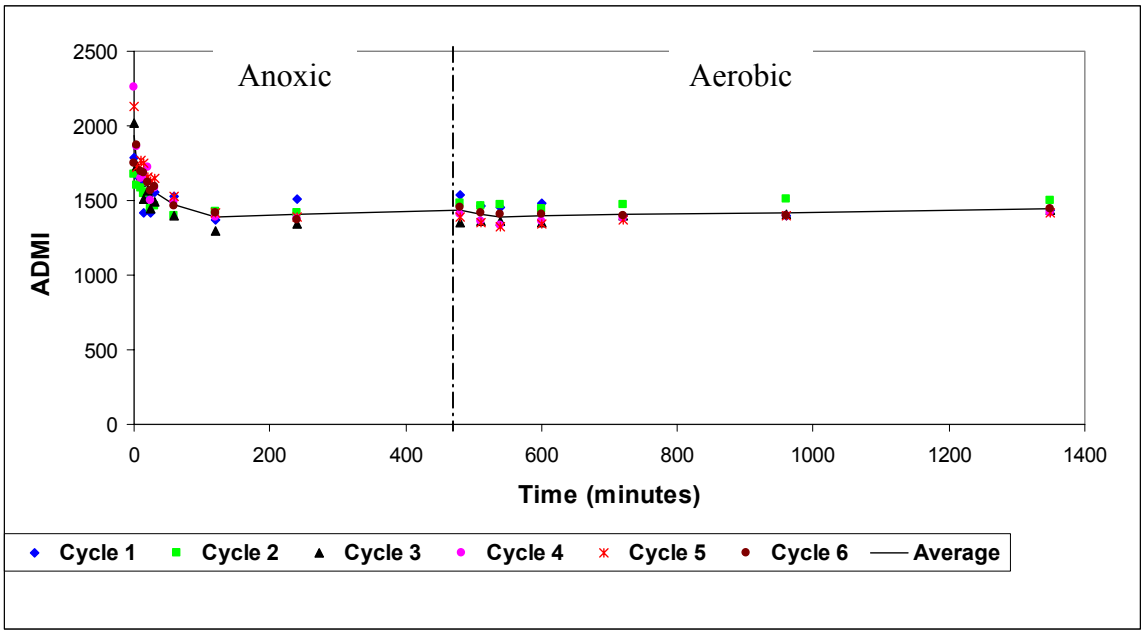

Figure 4.47 Reactor 1, Adjusted ADMI vs. Time (Reactive Red 198 and Reactive Yellow 86

Using the analysis method described in 4.6.2.1., a model was developed for the removal of ADMI color from Reactor 1 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.18.

Table 4.18 Reactor 1, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.00922	75.2
Aerobic	0.00021	3300.7

The model for color removal for Reactor 1 is shown below:

$$C_{anoxic} = 0.25738e^{-(0.00922)t} + 0.74262$$

$$C_{aerobic} = -0.00302e^{-(0.00021)t} + 0.74564$$

As shown in Figure 4.48, the model for color removal for Reactor 1 shows good agreement with the average of the measured data over a certain range, with an average error of 133 ADMI for the sampling scheme used.

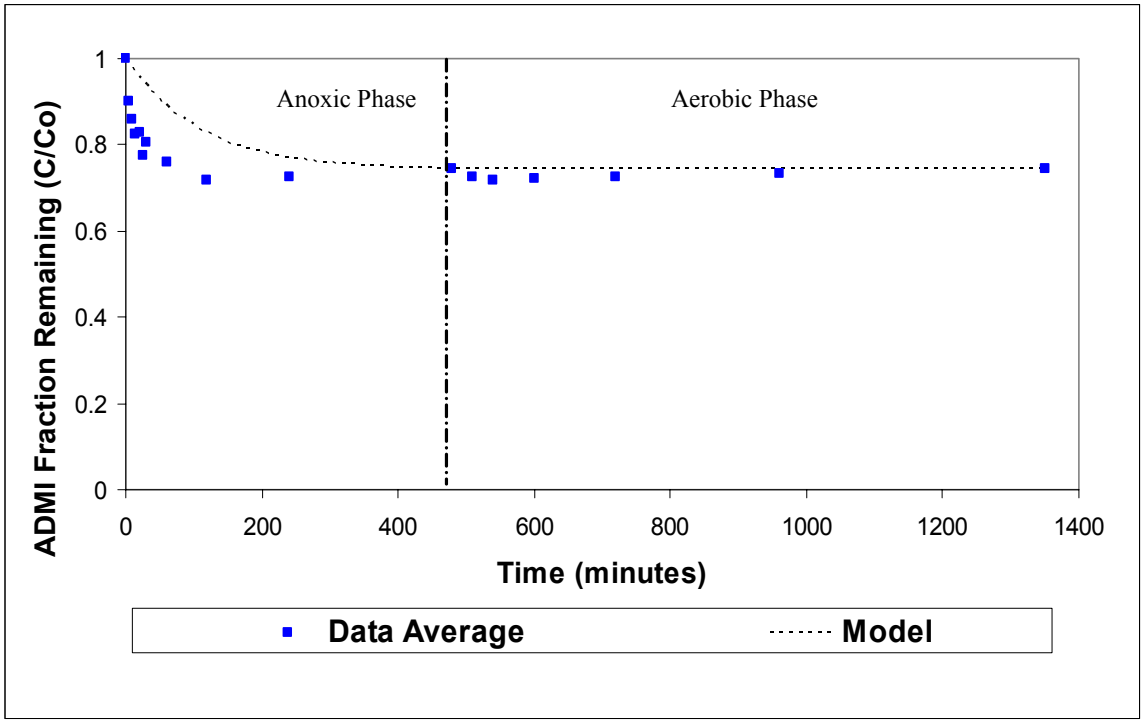

Figure 4.48 Reactor 1, Model vs. Average Measured Data for Anoxic/Aerobic Process

See Appendix T for all data related to color removal based on ADMI color value for Reactor 1.

4.6.2.3.2. Aerobic Control (Reactor 7)

The ADMI measurements taken at the beginning and ending of each aerobic cycle (see Appendix S) are shown in Figure 4.49 below.

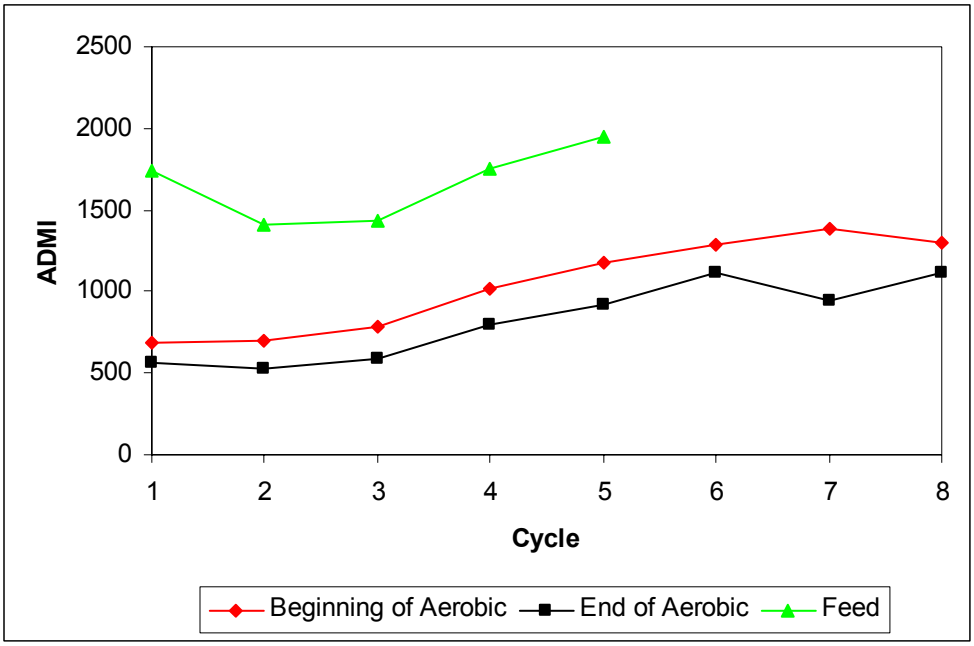

Figure 4.49 Reactor 7 (Reactive Red 198 and Reactive Yellow 86), ADMI Data for Aerobic Control

An examination of the figure above shows that, once the reactor reached a stable level, an average of 266 ADMI was removed during each aerobic cycle.

4.6.2.3.3. Anoxic/Aerobic Process vs. Aerobic Control

The samples from the aerobic control at the beginning and end of each cycle exhibited an average color change of 266 ADMI. The corresponding anoxic/aerobic reactor showed an average color change of 499 ADMI in the anoxic phase and essentially no change in ADMI during the aerobic phase. A visual examination of the samples in Figure 4.50 (shown below) confirm these measurements.

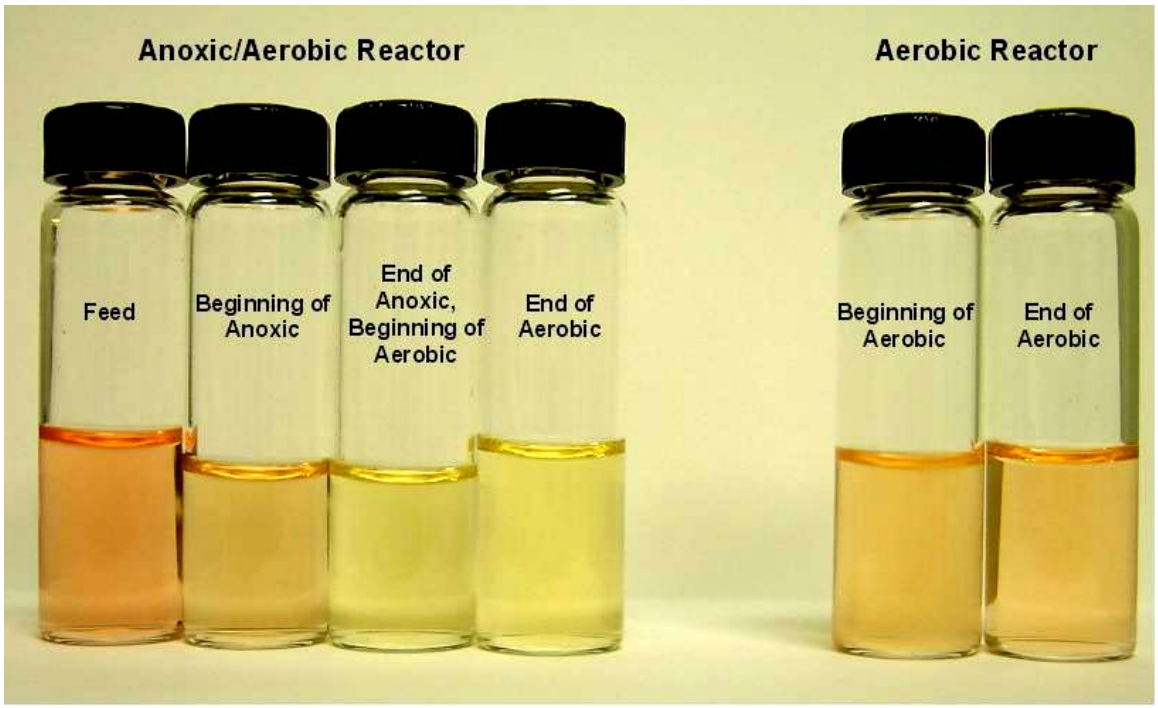

Figure 4.50 Visual Comparison of Samples Containing Reactive Red 198 and Reactive Yellow 86

This data would appear to indicate that the aerobic control exhibited better color removal than the aerobic phase of the anoxic/aerobic process. However, as shown in the concentration-based color removal studies for Reactive Red 198 (4.6.1.3) and Reactive Yellow 86 (4.6.1.4), the two dyes in the influent of these reactors have very different degradation rates. The majority of the measured color change was due to the degradation of Reactive Red 198, which exhibited a faster rate constant. In the anoxic/aerobic process, the majority of the degradation of this dye that was possible had already taken place by the beginning of the aerobic phase. Therefore, little additional color change was exhibited in the aerobic phase of the anoxic/aerobic process and a high color level remained due to the large percentage of Reactive Yellow 86 which is non-degradable under the experimental conditions used (4.6.1.4). These conclusions are supported by Figure 4.50 which shows the change in the Reactor 1 (anoxic/aerobic) samples from

orange to yellow and by the average absorbance spectra of the samples from Reactor 1 at the various phases of the anoxic/aerobic process, as shown below in Figure 4.51. The peak for Reactive Red 198, at a λ_{max} of 510 nm, is visible at the beginning of the anoxic phase, but disappears later in the cycle. However, the peak for Reactive Yellow 86, at a λ_{max} of 424 nm, is clearly visible throughout the process, indicating that a significant portion of this dye remains non-degradable.

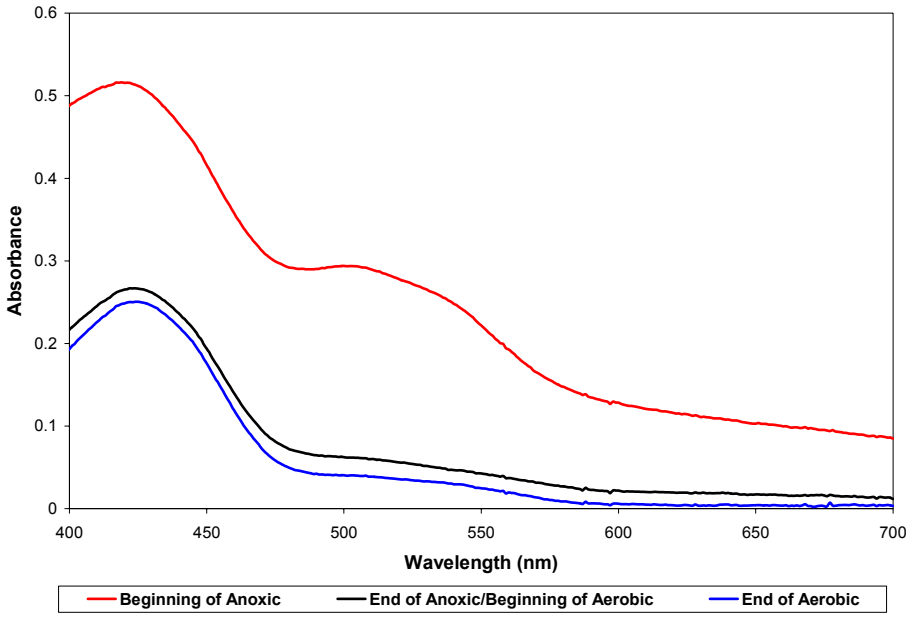

Figure 4.51 Average Absorbance Spectra, Reactor 1

The λ_{max} of the samples from this reactor also remains stable throughout the anoxic/aerobic process, as shown in Table 4.19 below.

Table 4.19 Change in λ_{max} throughout Anoxic/Aerobic Cycle

Sample	Average λ_{max}
Beginning of Anoxic	419
End of Anoxic/Beginning of Aerobic	424
End of Aerobic	425

4.6.2.4. C. I. Reactive Black 5

Reactor 2 was fed influent containing Reactive Black 5. The data collected were used to assess the color change as related to this dye by the anoxic/aerobic process (4.6.2.4.1). Reactor 8 was fed the same influent and was sampled to compare the color change under an aerobic control process (4.6.2.4.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.2.4.3).

4.6.2.4.1. Anoxic/Aerobic (Reactor 2)

Each cycle was adjusted to achieve the maximum overlay, with good agreement between the various cycles, as shown in Figure 4.52 below.

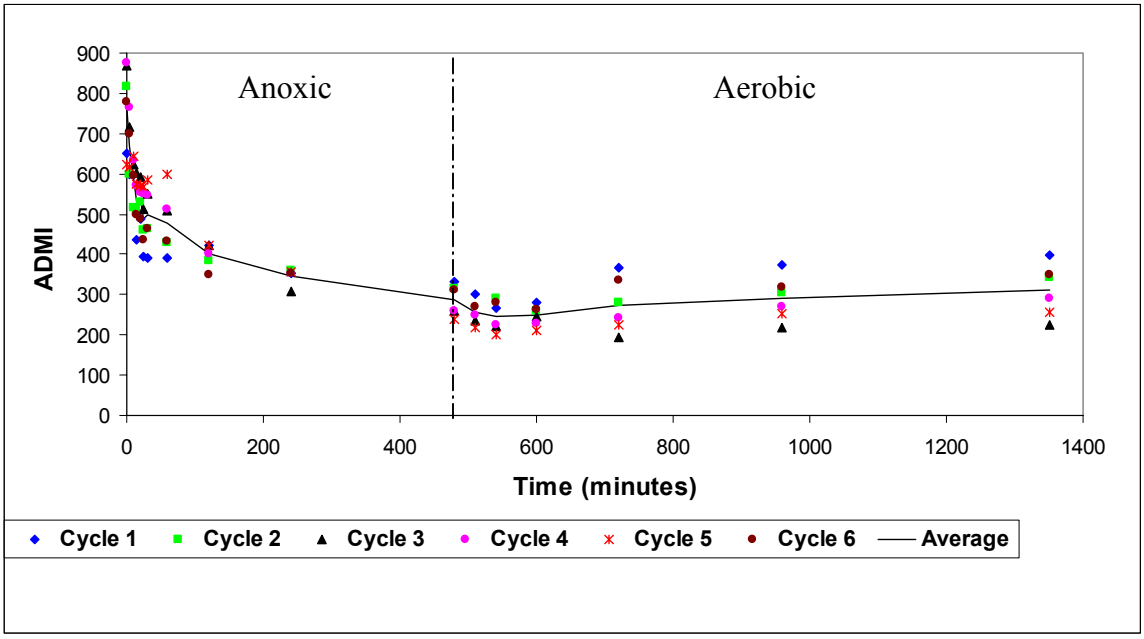

Figure 4.52 Reactive Black 5, Adjusted ADMI vs. Time

A model was developed for the removal of ADMI color due to Reactive Black 5 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.20.

Table 4.20 Reactive Black 5, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.01888	36.7
Aerobic	0.00106	653.9

The model for color removal related to Reactive Black 5 is shown below:

$$C_{anoxic} = 0.62649e^{-(0.01888)t} + 0.37351$$

$$C_{aerobic} = -0.03061e^{-(0.00106)t} + 0.40412$$

As shown in Figure 4.53, the model for color removal related to Reactive Black 5 shows good agreement with the average of the measured data over a certain range of the process, with an average error of 48 ADMI, based on the sampling scheme used.

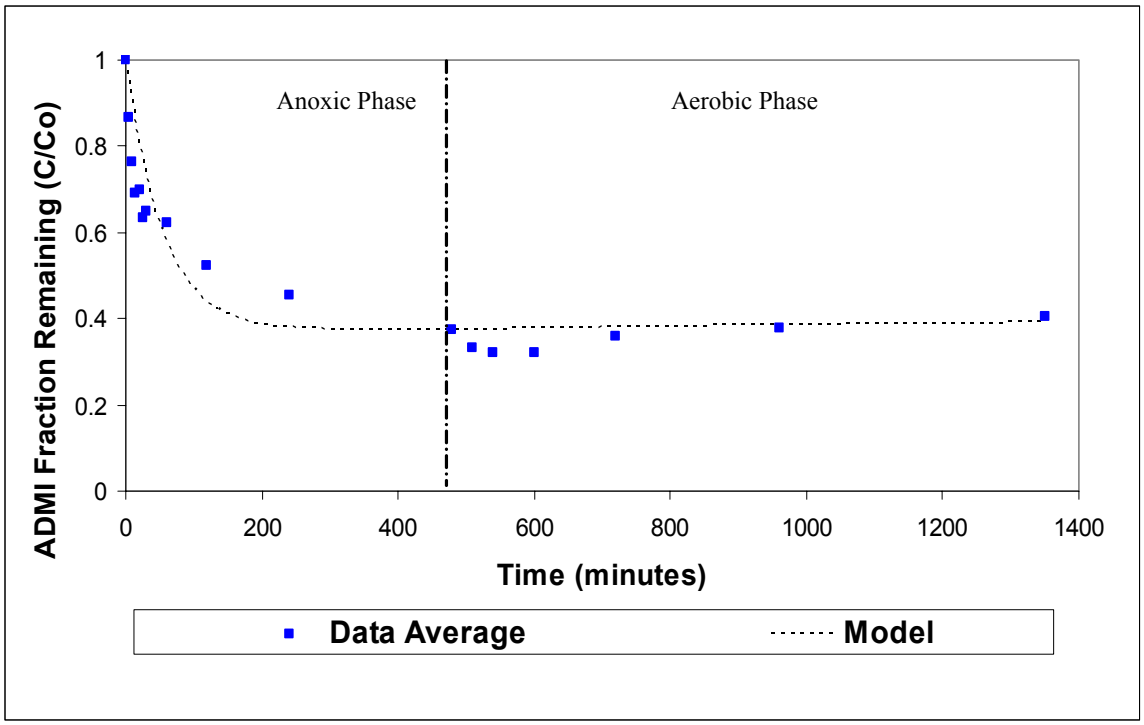

Figure 4.53 Reactive Black 5, Model vs. Average Measured Data for Anoxic/Aerobic Process

See Appendix V for all data related to color removal based on ADMI color value for Reactor 2.

4.6.2.4.2. Aerobic Control (Reactor 8)

The ADMI measurements taken at the beginning and ending of each aerobic cycle (see Appendix U) are shown in Figure 4.54 below.

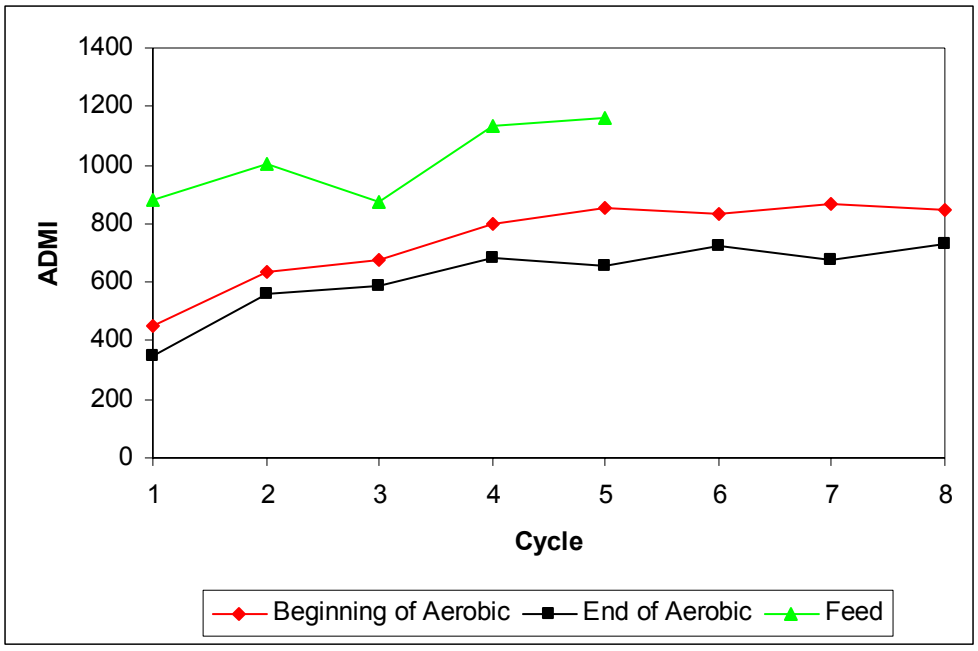

Figure 4.54 Reactive Black 5, ADMI Data for Aerobic Control

An examination of the figure above shows that, once the reactor reached a stable level, an average of 154 ADMI was removed during each aerobic cycle.

4.6.2.4.3. Anoxic/Aerobic Process vs. Aerobic Control

The samples from the aerobic control at the beginning and end of each cycle exhibited an average color change of 154 ADMI. The corresponding anoxic/aerobic reactor showed an average color change of 481 ADMI in the anoxic phase and then actually showed a slight increase in ADMI during its aerobic phase.

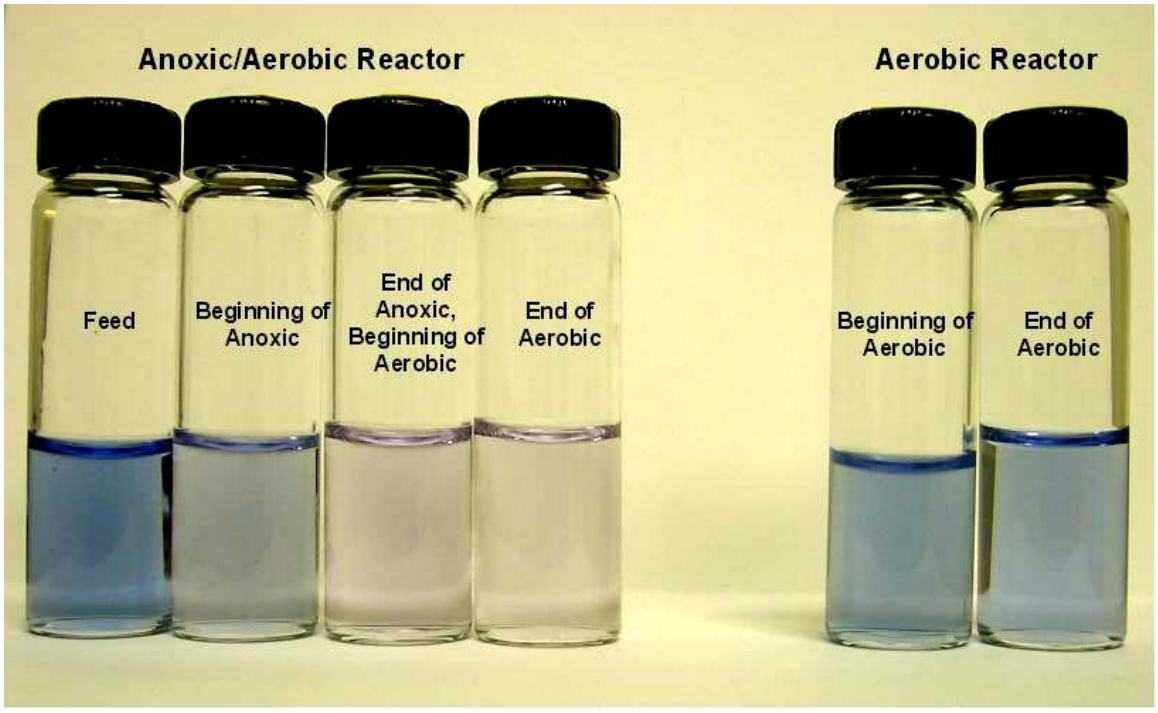

Figure 4.55 Visual Comparison of Samples Containing Reactive Black 5

These data would appear to indicate that the aerobic control exhibited better color removal than the aerobic phase of the anoxic/aerobic process. However, an examination of the samples in Figure 4.55 (above) shows slight color removal during the aerobic phase and the average absorbance spectra throughout the process (shown below in Figure 4.56) confirms that the aerobic phase was degrading the dye. This degradation is indicated by the reduction in absorbance throughout the visible spectrum (especially at the dye's λ_{max} of 594 nm). The samples exhibited a λ_{max} shift (shown below in Table 4.21), which may indicate the production of one or more by-products during the degradation of Reactive Black 5. Past research has found that the degradation of Reactive Black 5 results in the formation of one or more colorless by-products during the anoxic phase, which become colored when they are oxidized in the subsequent aerobic process and exhibit a λ_{max} similar to that of the dye (17, 32). This phenomenon noted in

past research may have been confirmed by the current research. Since ADMI is calculated by assessing the sample at three specific wavelengths, the color value increased slightly during the aerobic phase due to the λ_{max} shift closer to 540 nm, which is one of the wavelengths assessed.

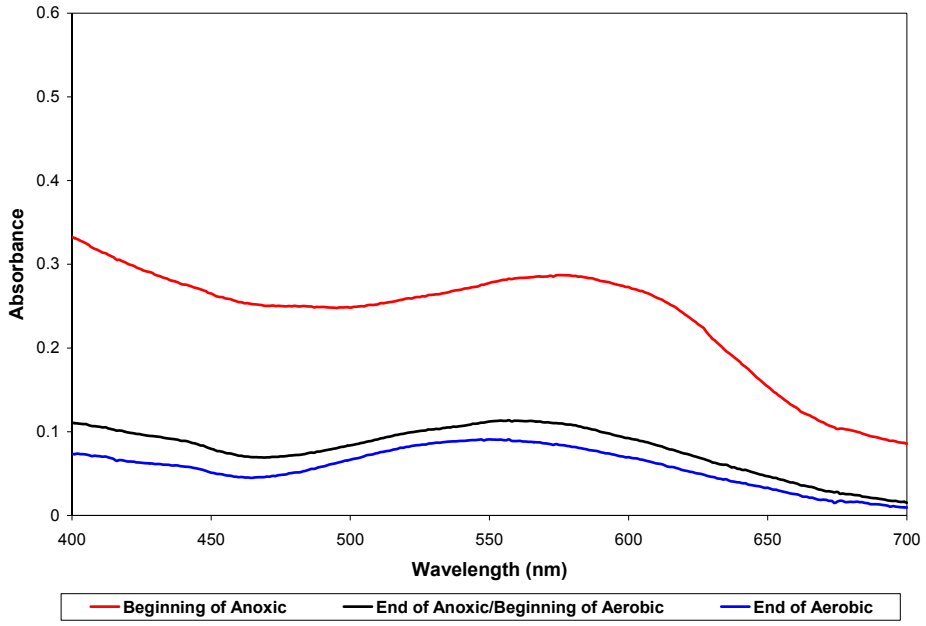

Figure 4.56 Reactive Black 5, Average Absorbance Spectra, Reactor 2

Table 4.21 Change in λ_{max} throughout Anoxic/Aerobic Cycle

Sample	Average λ_{max}
Beginning of Anoxic	575
End of Anoxic/Beginning of Aerobic	557
End of Aerobic	547

4.6.2.5. C. I. Reactive Violet 5

Reactor 5 was fed influent containing Reactive Violet 5. The data collected were used to assess the color change as related to this dye by the anoxic/aerobic process (4.6.2.5.1). Reactor 9 was fed the same influent and was sampled to compare the color

change under an aerobic control process (4.6.2.5.2). Using the data collected, the anoxic/aerobic process was compared to the aerobic control (4.6.2.5.3).

4.6.2.5.1. Anoxic/Aerobic (Reactor 5)

Each cycle was adjusted to achieve the maximum overlay, with good agreement between the various cycles, as shown in Figure 4.57 below.

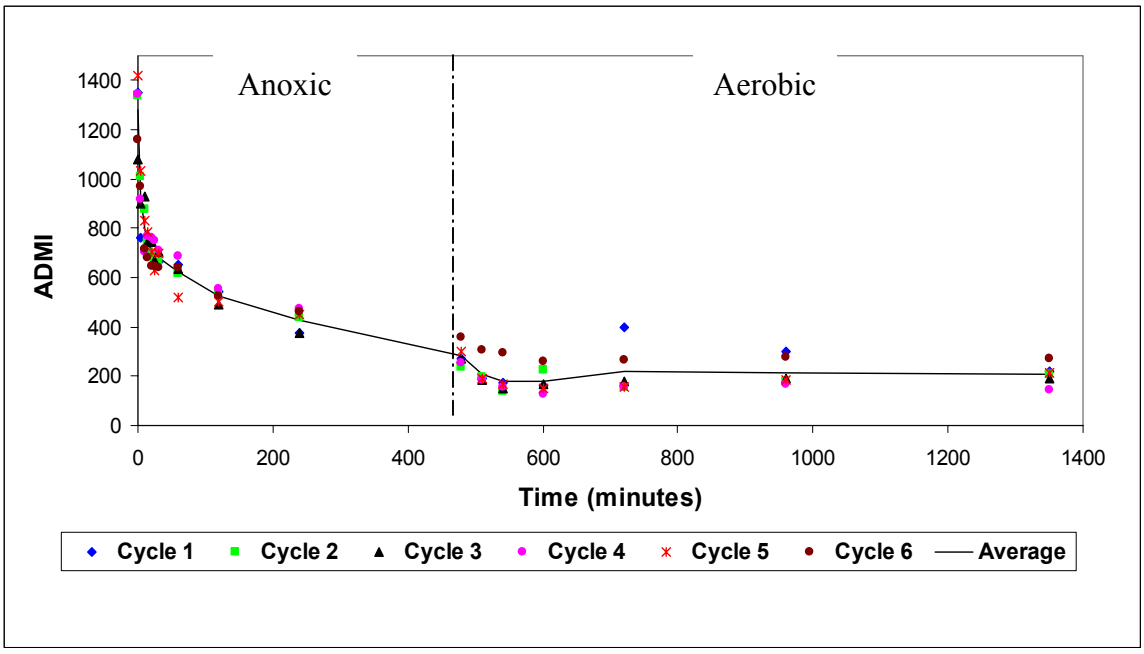

Figure 4.57 Reactive Violet 5, Adjusted ADMI vs. Time

A model was developed for the removal of ADMI color due to Reactive Violet 5 by each phase of the anoxic/aerobic process. The rate constants and half-lives of the phases are summarized below in Table 4.22.

Table 4.22, Reactive Violet 5, Estimated Kinetic Parameters for Anoxic/Aerobic Process

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Anoxic	0.02841	24.4
Aerobic	0.00335	206.9

The model for color removal for Reactor 5 is shown below:

$$C_{anoxic} = 0.77986e^{-(0.02841)t} + 0.22014$$

$$C_{aerobic} = 0.05777e^{-(0.00335)t} + 0.16237$$

As shown in Figure 4.58, the model for color removal for Reactive Violet 5 shows good agreement with the average of the measured data over a certain range, with an average error of 100 ADMI, for the sampling scheme used.

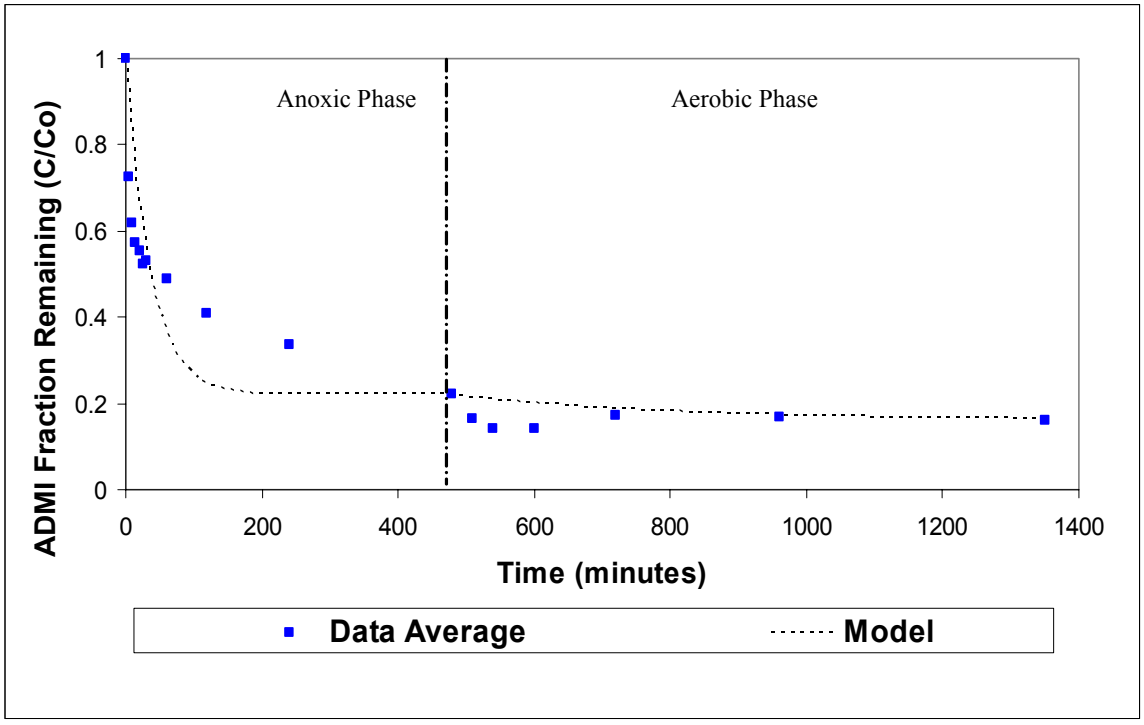

Figure 4.58 Reactive Violet 5, Model vs. Average Measured Data for Anoxic/Aerobic Process

See Appendix X for all data related to color removal based on ADMI color value for Reactor 5.

4.6.2.5.2. Aerobic Control (Reactor 9)

The ADMI measurements taken at the beginning and ending of each aerobic cycle are shown in Figure 4.59 below.

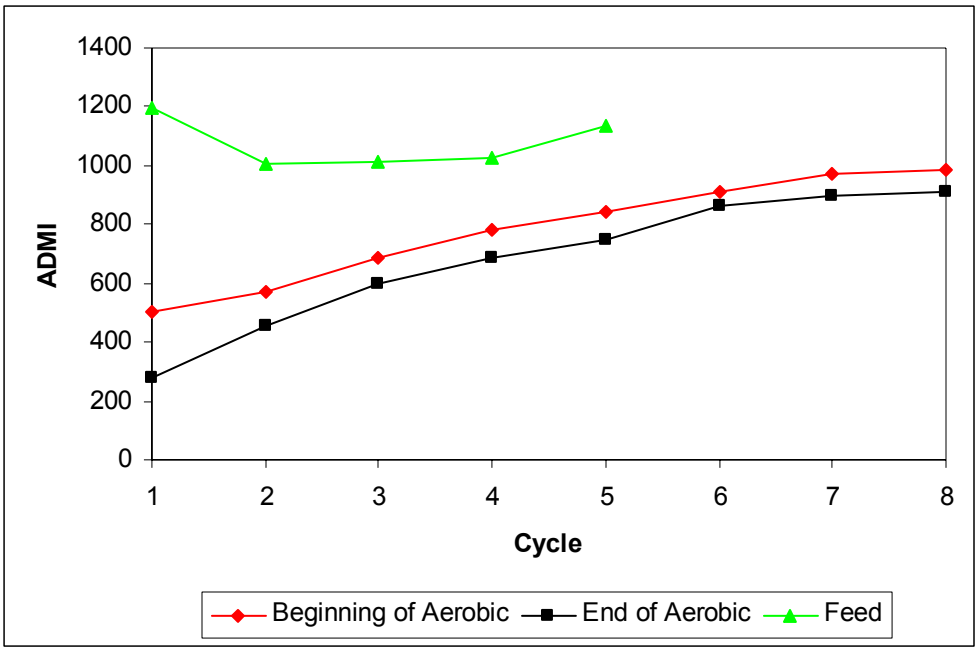

Figure 4.59 Reactive Violet 5, ADMI Data for Aerobic Control

An average of 102 ADMI was removed by the aerobic control (see Appendix W), but the trend of the graph indicates that the color level was increasing to a saturation point equal to the ADMI of the influent. This appears to contradict the concentration data for this dye, which showed that a fairly constant fraction of the concentration of Reactive Violet 5 was removed during each cycle. This can not be explained by a λ_{max} shift, since the λ_{max} remained at 565 nm throughout the cycle. However, an examination of the average spectra for the samples taken at the beginning and end of the aerobic cycle (as shown in Figure 4.60), indicates that, while there was no λ_{max} shift, there was a shift of the spectra toward the left. This shift affected the ADMI value, which is calculated by assessing the sample at three specific wavelengths. One of the wavelengths assessed is 438 nm, which was greatly affected by the shift in the spectra. The measurement at this wavelength caused the trend in the ADMI value to fail to mirror the trend in the concentration data.

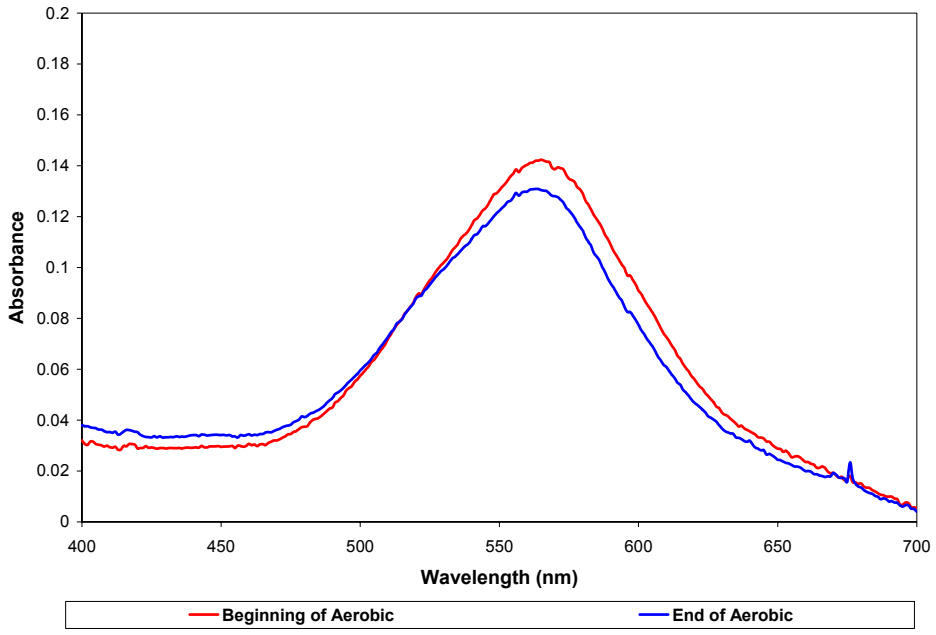

Figure 4.60 Reactive Violet 5, Average Absorbency Spectra, Reactor 9

4.6.2.5.3. Anoxic/Aerobic Process vs. Aerobic Control

The samples from the aerobic control at the beginning and end of each cycle exhibited an average color change of 102 ADMI. The corresponding anoxic/aerobic reactor showed an average color decrease of 999 ADMI in the anoxic phase and then a further decrease of 74 ADMI on average during its aerobic phase. These measurements can be confirmed by a visual examination of the samples in Figure 4.61 (shown below).

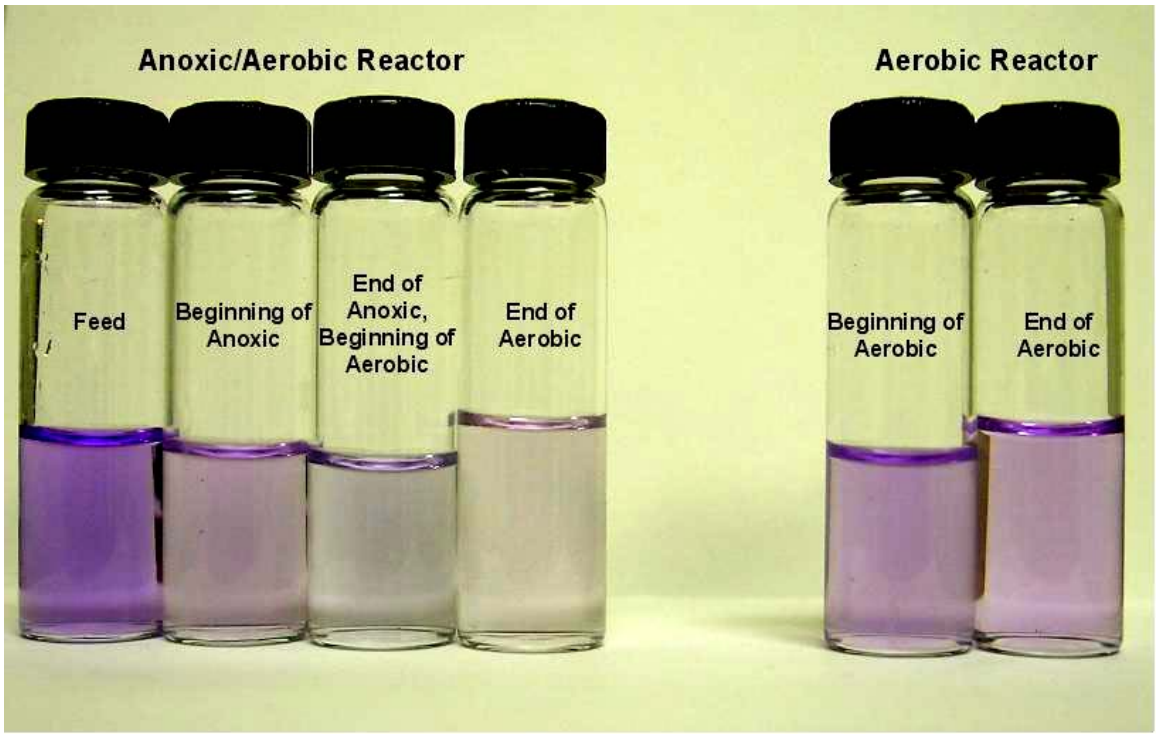

Figure 4.61 Visual Comparison of Samples Containing Reactive Violet 5

As mentioned in the previous section, the analysis of the ADMI data related to Reactive Violet 5 is complicated by shifts in the sample spectra throughout the degradation process. As seen below in Figure 4.62, the average sample spectra shows a shift to the left during the anoxic phase and then a shift back to the right during the subsequent aerobic phase.

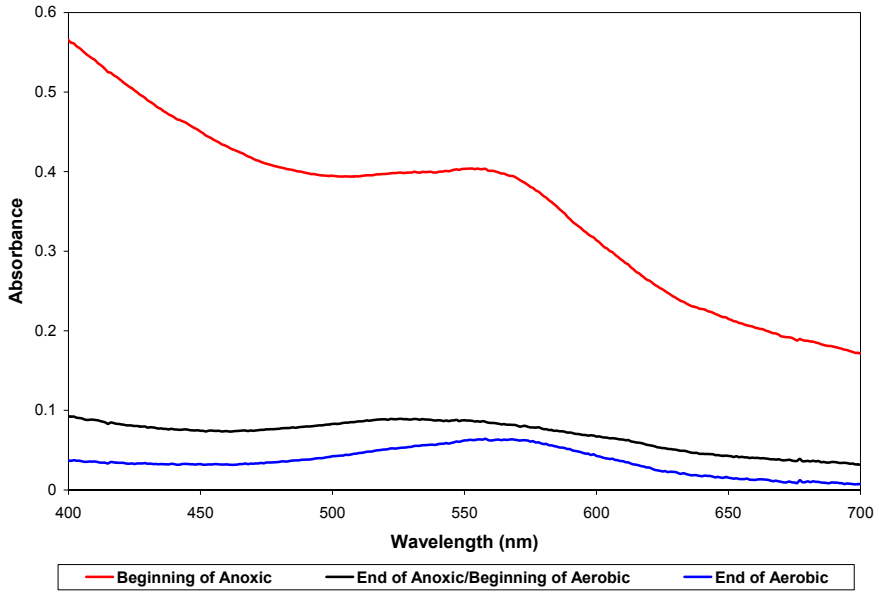

Figure 4.62 Reactive Violet 5, Average Absorbance Spectra, Reactor 5

This observation is supported by the λ_{max} information given below in Table 4.23, which shows that a shift of approximately 30 nm occurs during the anoxic phase. This λ_{max} shift indicates the production of a by-product during the anoxic phase, which may be degraded or oxidized to a different color during the aerobic phase, as evidenced by the return of the spectra to its original λ_{max}. Past research has noted the formation of colored by-products during dye degradation (17, 32).

Table 4.23 Change in λ_{max} throughout Anoxic/Aerobic Cycle

Sample	Average λ_{max}
Beginning of Anoxic	555
End of Anoxic/Beginning of Aerobic	526
End of Aerobic	558

4.6.2.6. Summary of ADMI-Based Color Change

For each of the dyes studied, the color removal by the anoxic phase out-performed the aerobic phase of the anoxic/aerobic process and the aerobic control. A comparison of the rate constants for ADMI removal for each of the reactors makes it possible to assess

the removal of color for the different dyes studied. Figure 4.63, shown below, reveals that the anoxic phase was more efficient at removing color caused by the presence of Reactive Black 5 and Reactive Violet 5.

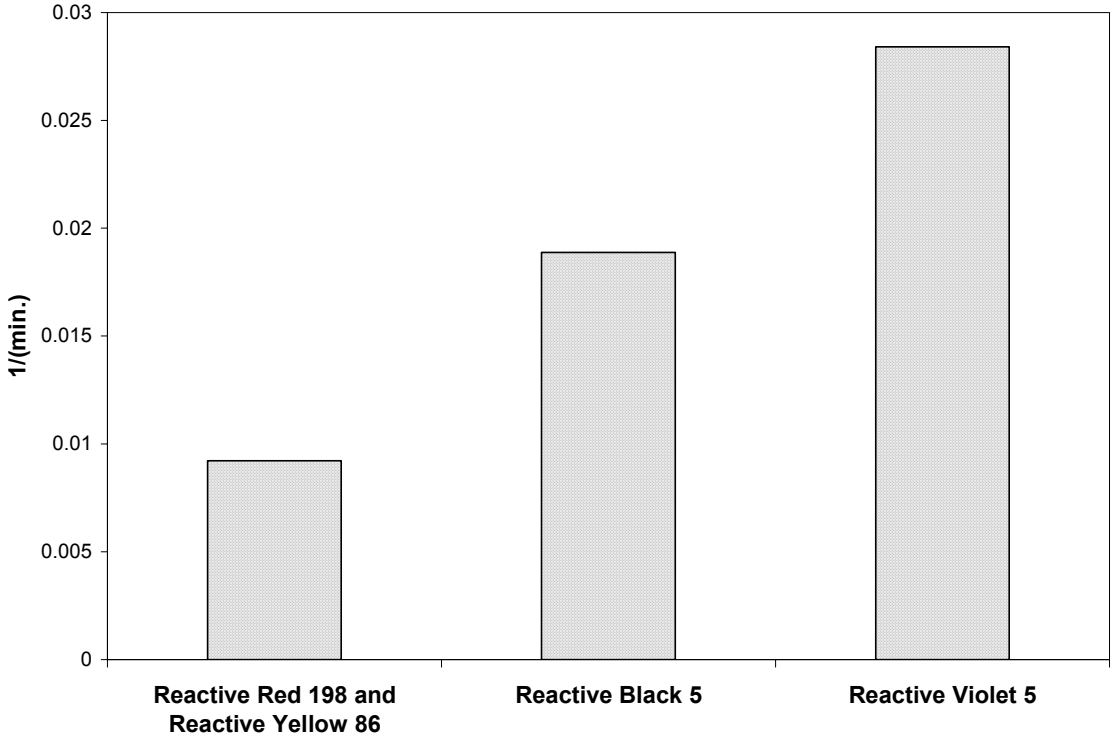

Figure 4.63 Estimated Rate Constants for Anoxic Phase of Anoxic/Aerobic Process

Figure 4.64 indicates that Reactive Violet 5 was affected the most by the aerobic phase of the anoxic/aerobic process. However, the rate constants during the aerobic phase are significantly lower than those during the anoxic phase for all dyes studied.

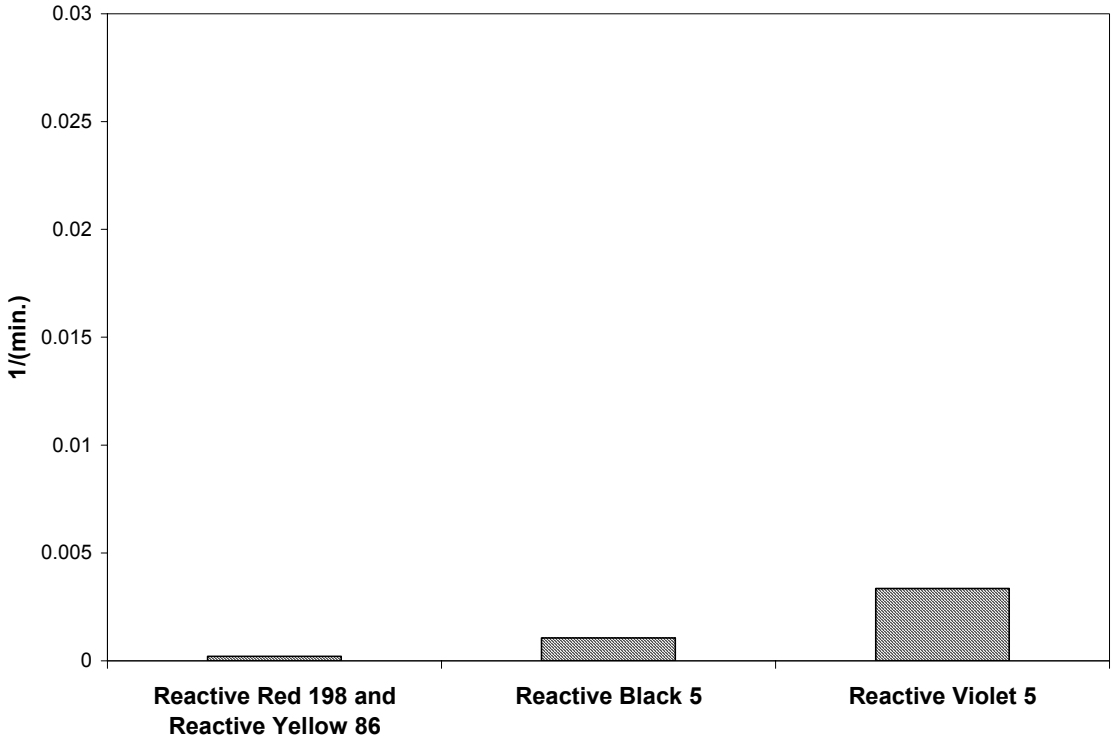

Figure 4.64 Estimated Rate Constants for Aerobic Phase of Anoxic/Aerobic Process

The half-lives for the different dyes (shown in Figure 4.65 below) confirm that the rate of degradation during the anoxic phase was higher than that of the aerobic phase. This graph also indicates that the reactor containing Reactive Red 198 and Reactive Yellow 86 exhibited almost no degradation during the aerobic phase.

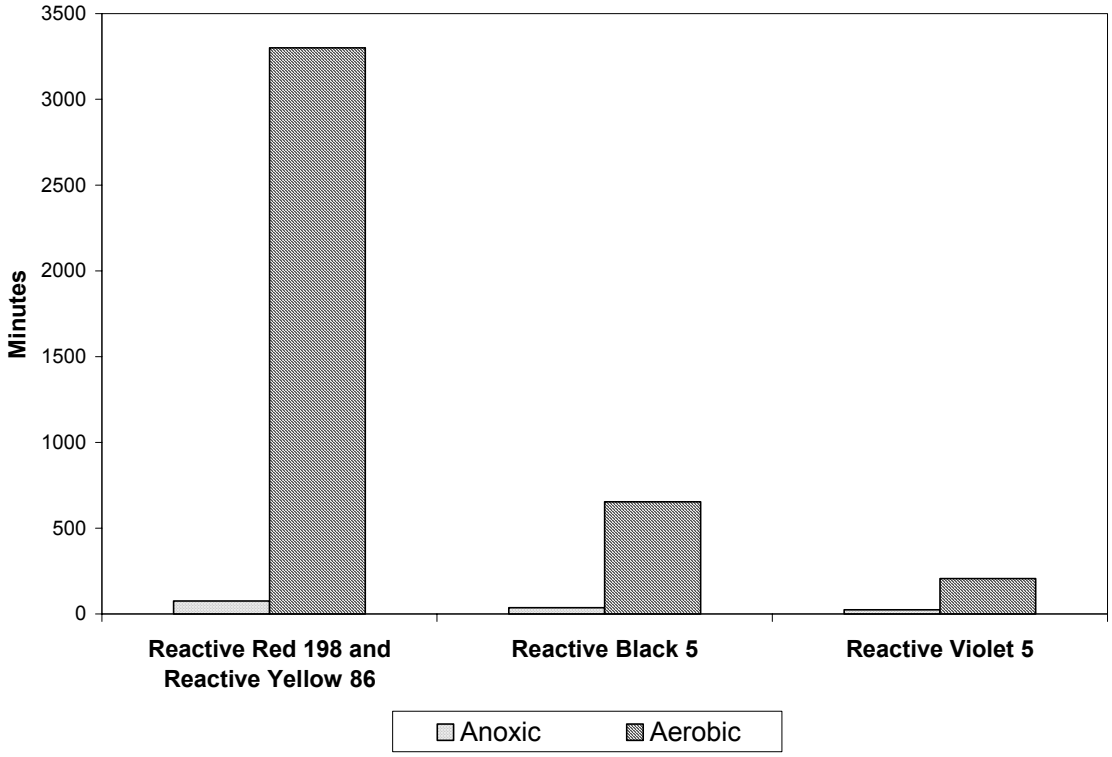

Figure 4.65 Half-Life for ADMI-Based Color Removal, Anoxic Phase vs. Aerobic Phase of Anoxic/Aerobic Process

Figure 4.66 reveals that Reactor 1, which was fed influent containing Reactive Red 198 and Reactive Yellow 86, had the largest color level remaining in the system at the end of the anoxic/aerobic process. A comparison of Figure 4.65 with Figure 4.22 reveals that this was due to a large concentration of Reactive Yellow 86 which remained non-degradable at the end of the cycle.

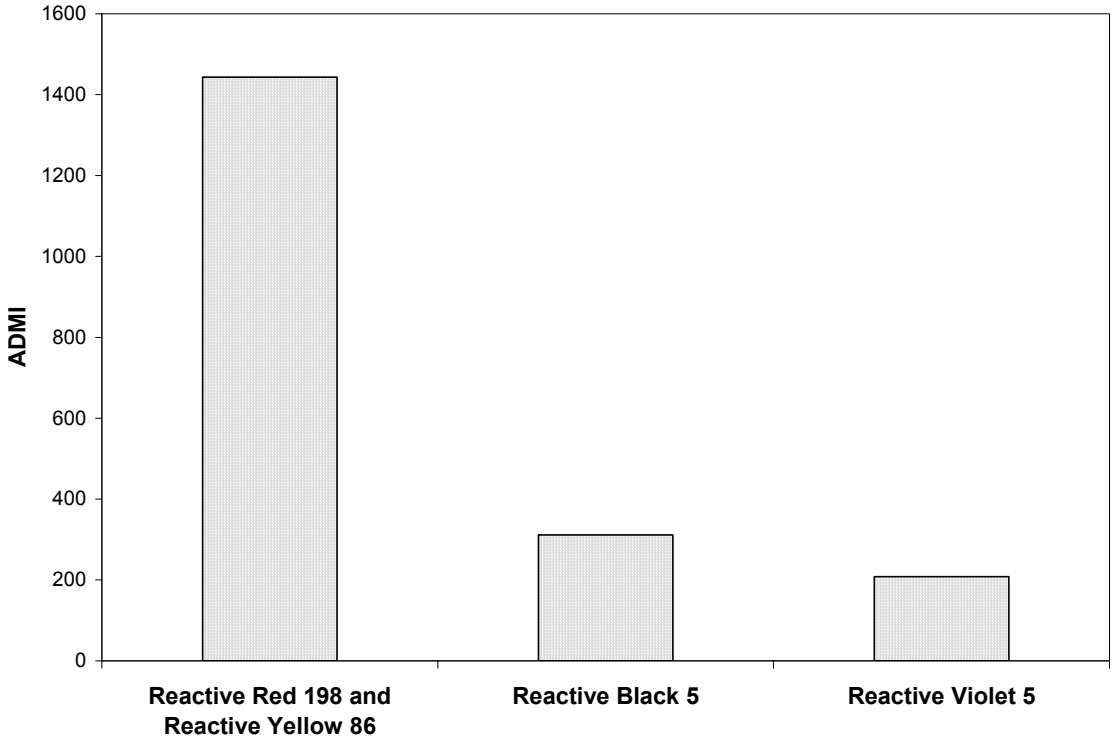

Figure 4.66 Average Non-Degradable ADMI Remaining at End of Anoxic/Aerobic Process

4.7 Color Removal Summary

The rates of dye degradation for the four dyes used in the study have been compared in the preceding sections. It is also important to compare the actual color removal by the anoxic/aerobic process, once a steady-state had been reached. The change in dye concentration in the reactors throughout the anoxic/aerobic process is summarized below in Table 4.24. These data are the average of the results from the last week of reactor operation.

Table 4.24 Color Removal by Anoxic/Aerobic Process, Concentration-Based

Dye	Beginning of Anoxic (g/L)	End of Anoxic/Beginning of Aerobic (g/L)	End of Aerobic (g/L)
Reactive Red 198	0.0058	0.0021	0.0016
Reactive Yellow 86	0.0141	0.0126	0.0124
Reactive Black 5	0.0065	0.0032	0.0026
Reactive Violet 5	0.0123	0.0058	0.0047

The concentration data in Table 4.23 was converted to percent color removal for each dye in each phase of the process and graphed below in Figure 4.67. This graph shows that Reactive Yellow 86 showed significantly less color removal than the other three dyes. It can also be noted from the graph that the majority of the color removal took place during the anoxic phase of the process, rather than the aerobic phase.

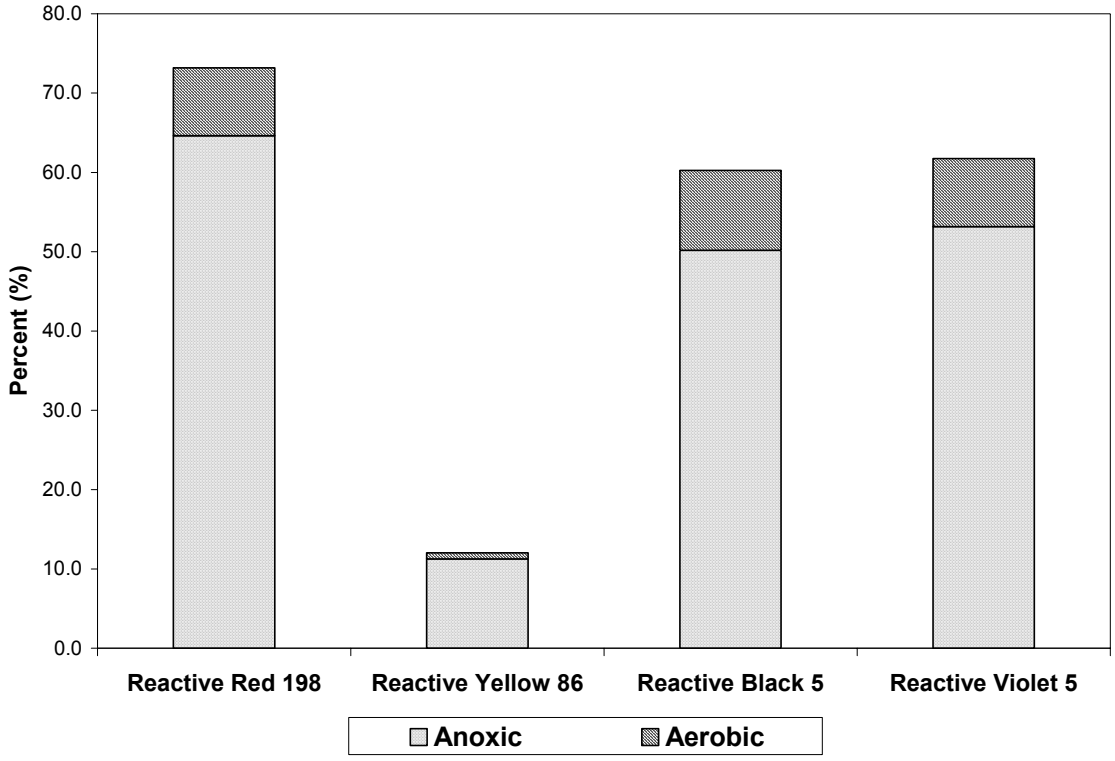

Figure 4.67 Percent Color Removal by Anoxic/Aerobic Process, Concentration-Based

In order to compare the color removal of the anoxic/aerobic process to an aerobic control system, the change in dye concentration during the last cycle of operation for the aerobic reactors is summarized below in Table 4.25 and graphed in Figure 4.68 in percent form.

Table 4.25 Color Removal by Aerobic Control, Concentration-Based

Dye	Beginning of Aerobic (g/L)	End of Aerobic (g/L)
Reactive Red 198	0.0072	0.0064
Reactive Yellow 86	0.0131	0.0140
Reactive Black 5	0.0084	0.0073
Reactive Violet 5	0.0149	0.0128

A comparison of Figures 4.67 and 4.68 reveals that the aerobic control exhibited significantly less color removal than the anoxic/aerobic process. In the case of Reactive Yellow 86, the color in the reactor actually increased throughout the aerobic cycle, which

may be an indication that there was no actual color change and the measurements fell within the range of experimental error.

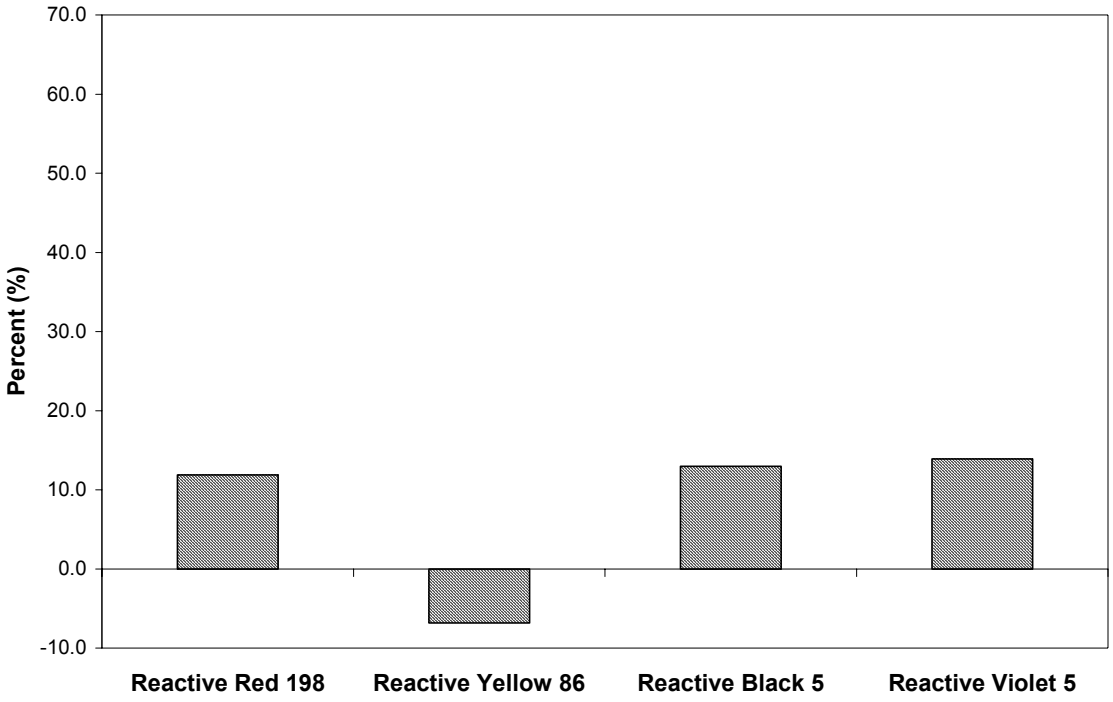

Figure 4.68 Percent Color Removal by Aerobic Control, Concentration-Based

Similar color removal data was observed for the ADMI-based measurements. The average ADMI color in the different phases of the anoxic/aerobic reactors during their last week of operation is summarized below in Table 4.26.

Table 4.26 Color Removal by Anoxic/Aerobic Process, ADMI-Based

Dye	Beginning of Anoxic (ADMI)	End of Anoxic/Beginning of Aerobic (ADMI)	End of Aerobic (ADMI)
Reactive Red 198 and Reactive Yellow 86	824	759	803
Reactive Black 5	603	323	337
Reactive Violet 5	533	334	243

The ADMI data were converted to percent removal and graphed in Figure 4.69. This figure shows that Reactive Black 5 and Reactive Violet 5 exhibited a significant decrease in ADMI during the anoxic phase. Reactive Violet 5 was the only reactor to also exhibit an ADMI decrease during the aerobic phase, while the other two reactors actually increased in color. Other researchers have found similar results when investigating anoxic/aerobic dye degradation. It has been hypothesized that certain colorless by-products of anoxic degradation are oxidized by the subsequent aerobic process to form a colored product (17, 32). A similar phenomenon may have occurred in this study and HPLC could be utilized to determine the presence of by-products in future research related to anoxic/aerobic dye degradation.

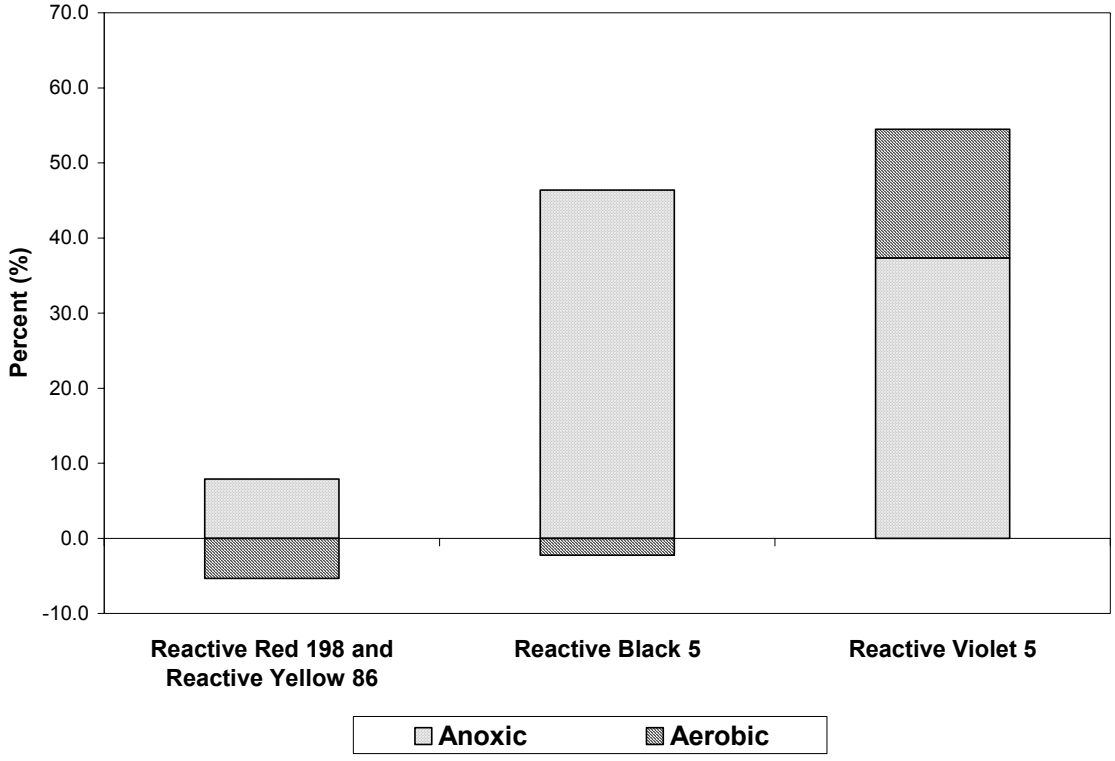

Figure 4.69 Percent Color Removal by Anoxic/Aerobic Process, ADMI-Based

Similar ADMI data for the aerobic control during the last cycle of operation is summarized below in Table 4.27 and Figure 4.70. All of the aerobic control reactors showed a slight ADMI decrease during the cycle. In the case of Reactive Black 5 and Reactive Violet 5, the ADMI decrease for the anoxic/aerobic process out-performed the aerobic control.

Table 4.27 Color Removal by Aerobic Control, ADMI-Based

Dye	Beginning of Aerobic (ADMI)	End of Aerobic (ADMI)
Reactive Red 198 and Reactive Yellow 86	1297	1117
Reactive Black 5	843	729
Reactive Violet 5	984	908

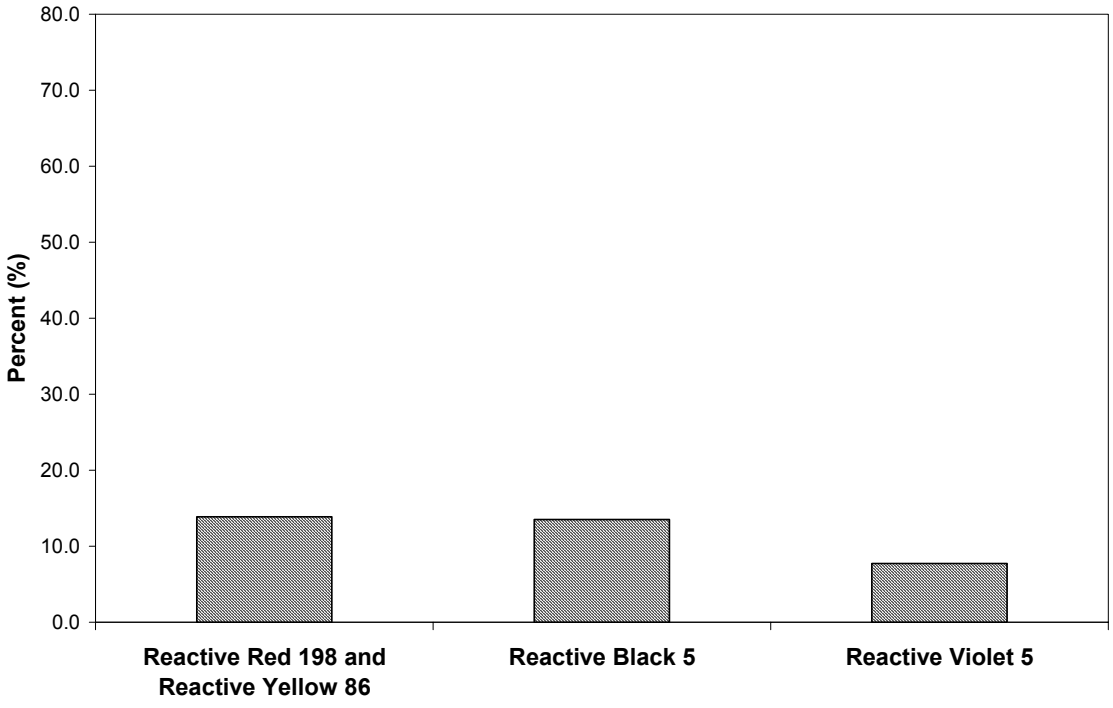

Figure 4.70 Percent Color Removal by Aerobic Control, ADMI-Based

4.8. Physical and Chemical Principles

The experimental results in the preceding sections make it possible to understand the underlying physical and chemical principles of the degradation of fiber reactive azo dye molecules by anoxic vs. aerobic respiration (4.8.1). Based on the estimated kinetic rate constants for color and COD removal, recommendations can be made for the design of a textile wastewater treatment process involving sequential anoxic and aerobic steps (4.8.2).

4.8.1. Chromophore Response to Aerobic and Anoxic Degradation

In conventional aerobic respiration, organic wastes are broken down by an oxidation-reduction reaction where the organic waste acts as the electron donor and the oxygen in the system acts as the electron acceptor. In anoxic respiration, due to the low level of oxygen present in the system, an alternate electron acceptor is required (18). The azo bond found in the dye molecule can act as this electron acceptor, which results in the cleavage of the azo bond and the formation of colorless amines (22).

The four fiber reactive azo dyes investigated in this study included Reactive Red 198, Reactive Yellow 86, Reactive Black 5, and Reactive Violet 5. The structures for these dyes are shown in Figures 1.1-1.4 in section 2.2.2. A comparison of the four dyes studied reveals that the structure of Reactive Yellow 86 has certain characteristics that differ from the other three dyes. It is the only structure with an arylazo-pyridone coupler instead of a naphthol type. It also is the only structure with an alternate electron acceptor group ($-CONH_2$) in addition to the azo bond. The pyridone system alone is more susceptible to reduction than the naphthol system. The kinetic studies of color removal,

summarized below in Table 4.28, revealed that Reactive Yellow 86 had the lowest rate constants for color removal in each phase of the anoxic/aerobic process and the largest concentration of dye remaining in the system at the end of the process due to non-degradable material. These data indicate that Reactive Yellow 86 was not reduced at the pyridone coupler, or a significant color change would have been observed. Since reduction at the carboxamido group would not lead to color loss, the lack of degradation of this dye by the anoxic/aerobic process can be attributed to the presence of an alternate electron acceptor which competed with the azo bond (9).

Table 4.28 Comparison of Kinetic Parameters for Color Removal

Dye	Anoxic Phase		Aerobic Phase		Average Non-Degradable (g/L)
	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)	
Reactive Red 198	0.01567	44.2	0.00299	231.8	0.001673
Reactive Yellow 86	0.01506	46	0.00086	806	0.016994
Reactive Black 5	0.01718	40.3	0.00186	372.7	0.002722
Reactive Violet 5	0.02696	25.7	0.00301	230.3	0.004937

4.8.2. Anoxic/Aerobic Process Design Based on Kinetic Parameters

Recommendations can be made for the design of an anoxic/aerobic sequential wastewater treatment process based on the estimated kinetic parameters for the removal of COD and color by each phase of the process. In this study, a complete 24-hour treatment cycle was made up of an eight-hour anoxic phase followed by a 16-hour aerobic phase. An examination of the estimated kinetic parameters, as shown above in Table 4.28 for color and below in Table 4.29 for COD, would indicate that the majority

of the cycle should be allotted to the anoxic phase, in order to achieve greater color removal with acceptable COD removal.

Table 4.29 Comparison of Kinetic Parameters for COD Removal

Phase	Reactor	Rate Constant, k ($min.^{-1}$)	Half Life, t1/2 (min.)
Aerobic Phase of Anoxic/Aerobic	Average from Reactors 1 and 2	0.06454	10.7
Anoxic Phase of Anoxic/Aerobic (Including Feeding Period)	Reactor 5	0.01175	59.0

However, due to the formation of aromatic amines from dye degradation during the anoxic phase (22), effluent toxicity is an issue. Since these aromatic amines must be aerobically degraded, an investigation of toxicity removal in the system must be undertaken before further design recommendations can be made.

5. Conclusions

The goal of this research was to investigate the effectiveness of a sequential anoxic/aerobic treatment process for the removal of chemical oxygen demand and fiber reactive azo dye color from wastewater. The specific objectives for this study and the related findings are summarized below.

1) Develop a viable biomass that could be effective in both an anoxic and aerobic environment: The biomass used in this experiment, once acclimated to the synthetic influent, exhibited a stable MLSS level and effluent COD. These data indicate that the anoxic/aerobic biomass was functioning effectively.
2) Compare the degradation of COD by this biomass under anoxic vs. aerobic conditions: During the last week of reactor operation, the anoxic/aerobic process exhibited 85% COD removal during the anoxic phase and an additional 10% removal during the subsequent aerobic phase. With a 95% total COD removal, the anoxic/aerobic process functioned similarly to the aerobic control, which exhibited 97% COD removal. It can be concluded that, under the experimental conditions used, the percent COD removal by the anoxic/aerobic process was comparable to a conventional aerobic process.
3) Determine the kinetic parameters for COD removal for each phase of the anoxic/aerobic process and an aerobic control process, using fully acclimated biomass: The kinetic parameters for COD removal are summarized below in Table 5.1. The aerobic control and the aerobic phase of the anoxic/aerobic process exhibited rates of COD removal that were over twice that of the anoxic phase of the anoxic/aerobic process. These rate constants show that COD removal occurs at a

faster rate under aerobic conditions as compared to anoxic conditions. The rate constants for the aerobic control and the aerobic phase of the anoxic/aerobic process are similar, with a percent difference of approximately ten percent. This indicates that, in terms of COD removal, the aerobic phase of the anoxic/aerobic process functions similarly to a conventional aerobic system.

Table 5.1 Comparison of Kinetic Parameters for COD Removal

Phase	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)
Aerobic Control	0.05658	12.3
Aerobic Phase of Anoxic/Aerobic	0.06454	10.7
Anoxic Phase of Anoxic/Aerobic	0.00235	295.0

4) Compare the degradation of fiber reactive azo dyes by this biomass under anoxic vs. aerobic conditions: In terms of concentration-based color measurement, for all four dyes studied, the color removal during the anoxic phase was five times greater than the removal during the aerobic phase of the anoxic/aerobic process and during the aerobic control process. This indicates that the anoxic phase was responsible for the majority of the color removal exhibited by the anoxic/aerobic process. In addition, under the experimental conditions used, these data show that the anoxic/aerobic process out-performs the aerobic control in terms of color removal.
5) Determine the kinetic parameters for color removal (as measured by dye concentration and ADMI color value) for each phase of the anoxic/aerobic process: The kinetic parameters for color removal are shown below in Tables 5.2 and 5.3 for concentration and ADMI-based measurements, respectively. Reactive Violet 5

exhibited the fastest degradation rate, followed by Reactive Black 5, Reactive Red 198, and Reactive Yellow 86. Reactive Yellow 86 had a significantly larger non-degradable component, as compared to the other three dyes. It can also be noted that, in terms of concentration-based measurements, the rate of degradation under anoxic conditions was at least ten times the rate under aerobic conditions. The anoxic phase exhibits both a higher percent color removal and a faster rate of color removal than the aerobic phase, which confirms the effectiveness of anoxic respiration in removing color.

Table 5.2 Comparison of Kinetic Parameters for Color Removal (Concentration-Based Measurements)

Dye	Anoxic Phase		Aerobic Phase		Average Non-Degradable (g/L)
	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)	
Reactive Red 198	0.01567	44.2	0.00299	231.8	0.001673
Reactive Yellow 86	0.01506	46	0.00086	806	0.016994
Reactive Black 5	0.01718	40.3	0.00186	372.7	0.002722
Reactive Violet 5	0.02696	25.7	0.00301	230.3	0.004937

Table 5.3 Comparison of Kinetic Parameters for Color Removal (ADMI-Based Measurements)

Dye	Anoxic Phase		Aerobic Phase		Average Non-Degradable (ADMI color)
	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)	Rate Constant, k ($min.^{-1}$)	Half Life, $t_{1/2}$ (min.)	
Reactive Red 198 and Reactive Yellow 86	0.00922	75.2	0.00021	3300.7	1443
Reactive Black 5	0.01888	36.7	0.00106	653.9	311
Reactive Violet 5	0.02841	24.4	0.00335	206.9	208

6) Compare the color removal for the dyes studied in terms of dye structure: As shown above in Tables 5.2 and 5.3, Reactive Yellow 86 exhibited lower color removal than the other three dyes studied in terms of rate and non-degradable color. The structure of this dye differs from the others in that it contains a pyridone-type coupler and a carboxamido electron acceptor group. This information indicates that certain structural features prevent degradation of a dye under both anoxic and aerobic conditions.

7) Make recommendations for the design of an anoxic/aerobic sequential wastewater treatment facility: The kinetic rate studies for COD and color removal indicate that the majority of the time in an anoxic/aerobic cycle should be devoted to the anoxic phase, in order to maximize color removal. The level of color removal that is deemed acceptable would be determined by the environmental regulations governing a specific manufacturing facility. Since certain products of dye degradation have been identified as toxic, the toxicity removal of the anoxic/aerobic system must be investigated before specific design recommendations can be made.

6. Suggestions for Further Research

The results of this study indicate the need for additional research in the area of anoxic/aerobic wastewater treatment. There are several areas of focus that could be addressed in future studies and these areas could include the following:

1) Investigate the degradation of additional dyes containing a pyridone-type structure, like Reactive Yellow 86, to confirm the resistance of such dyes to anoxic degradation.
2) Investigate the color removal of the anoxic/aerobic process when the influent contains a mixture of three or more dyes to confirm that the degradation of the individual dyes is not hampered by the presence of additional colored components.
3) Perform kinetic studies using purified dyes or use HPLC to separate the individual reactants and products in order to obtain a cleaner kinetic model for color removal and to understand the structural changes involved in the degradation of the dyes.
4) Determine the characteristics of toxicity removal by the anoxic/aerobic process and use this information, along with the rates of COD and color removal, to recommend design parameters for the process.
5) Optimize the HRT and sludge age for an anoxic/aerobic process.
6) Investigate the effectiveness of an anoxic/aerobic process for the degradation of a complex textile influent, such as effluent from a textile dyeing and finishing location, as opposed to the synthetic influent used in this study. Preliminary research has been conducted with this intent and the results are summarized below.

Approximately ten liters of effluent were obtained from a textile dyeing and finishing facility in Alexander City, Alabama. Reactor 2 was fed a portion of this effluent sample for two successive days and samples from the reactor were obtained at

the beginning and end of each phase of the process. The absorbance spectra of the samples from the second day are shown in Figure 6.1 and these spectra indicate that color removal is occurring.

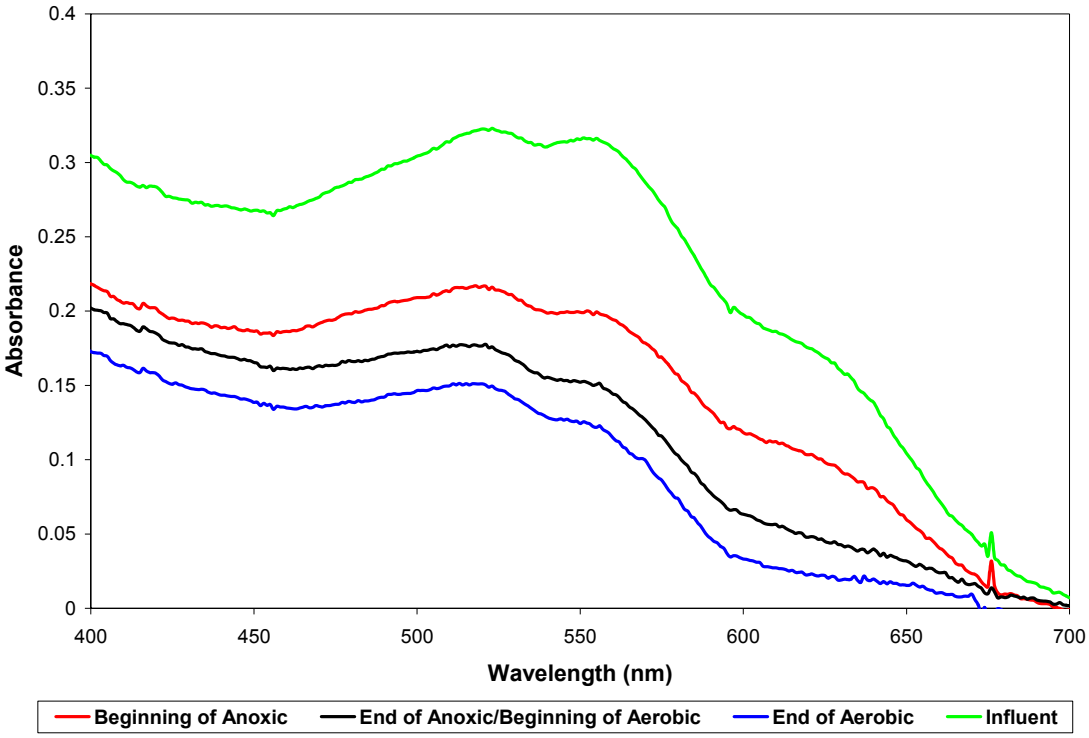

Figure 6.1 Absorbance Spectra of Samples from Complex Textile Effluent

A visual examination of the samples, shown below in Figure 6.2, confirm that color removal occurred during the anoxic/aerobic process.

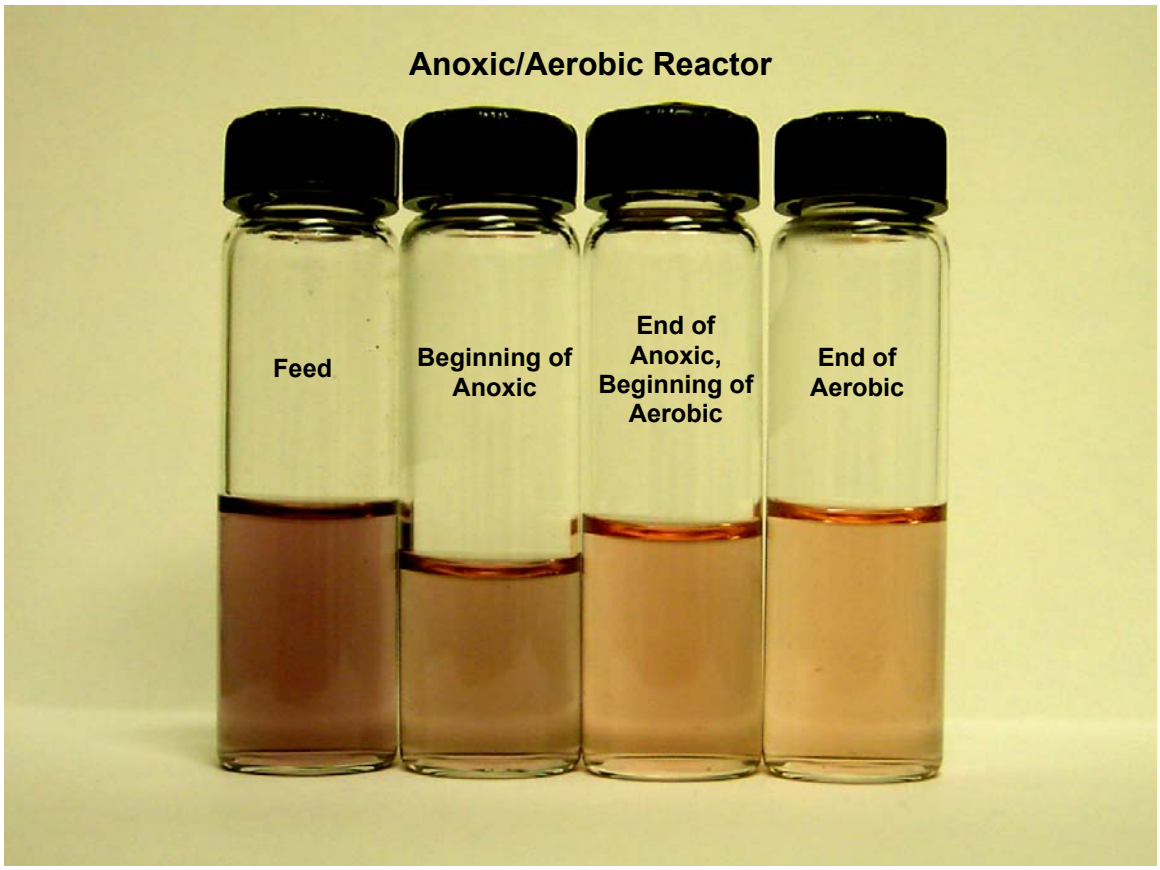

Figure 6.2 Samples from Complex Effluent

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APPENDICES

Appendix A: Creation of Calibration Curves for Dye Concentration vs. Absorbance

Table A-1 Determination of λ_{max} for Reactive Red 198

Concentration (g/L)	λ_{max} (nm)
0.0025	511
0.005	511
0.0075	509
0.0125	509
0.025	509
0.05	510
Average λ_{max}	**509.83**

Table A-2 Concentration vs. Absorbance at λ_{max} for Reactive Red 198

Concentration (g/L)	Absorbance at 510 nm
0.0025	0.0554
0.005	0.1102
0.0075	0.1631
0.0125	0.2720
0.025	0.5385
0.05	1.0738

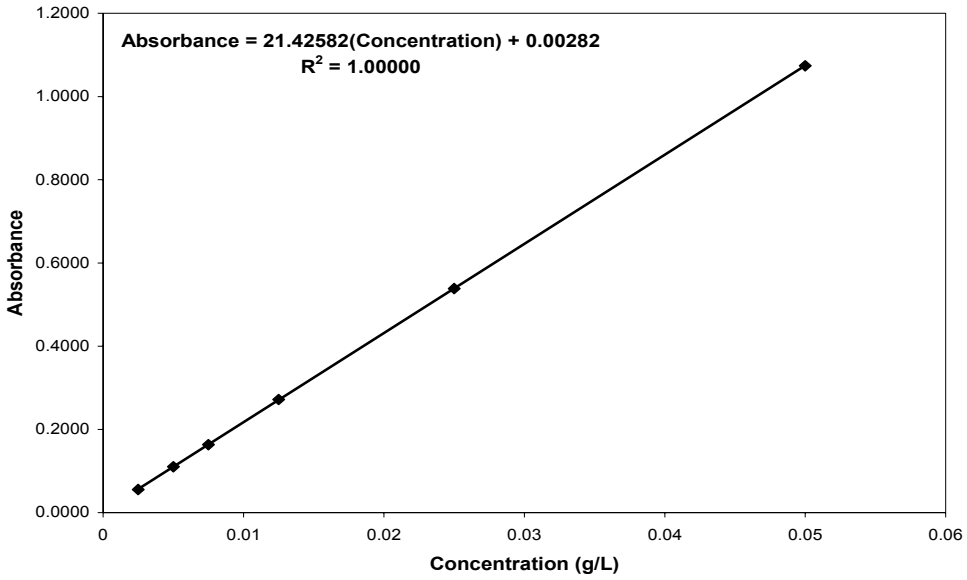


Figure A-1 Equation for Determination of Dye Concentration in Solution for Reactive Red 198

Table A-3 Determination of λ_{max} for Reactive Yellow 86

Concentration (g/L)	λ_{max} (nm)
0.0025	419
0.005	425
0.0075	424
0.0125	424
0.025	425
0.05	425
Average λ_{max}	**423.67**

Table A-4 Concentration vs. Absorbance at λ_{max} for Reactive Yellow 86

Concentration (g/L)	Absorbance at 424 nm
0.0025	0.0453
0.005	0.0776
0.0075	0.1170
0.0125	0.1942
0.025	0.3872
0.05	0.6895

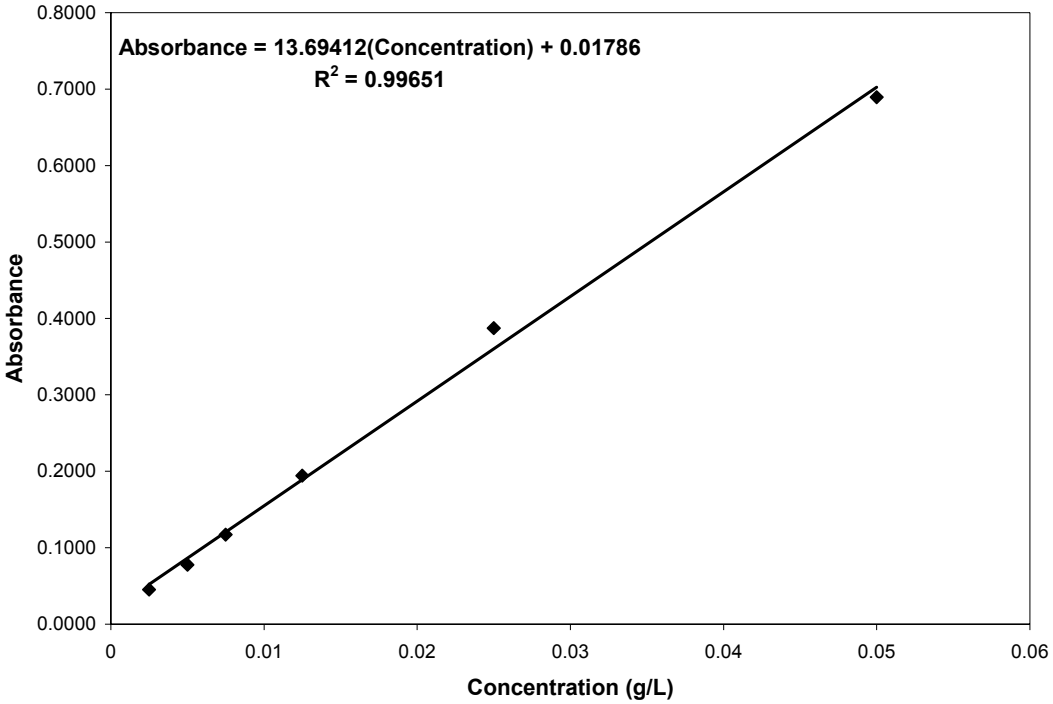


Figure A-2 Equation for Determination of Dye Concentration in Solution for Reactive Yellow 86

Table A-5 Determination of λ_{max} for Reactive Black 5

Concentration (g/L)	λ_{max} (nm)
0.0025	588
0.005	596
0.0075	596
0.01	594
0.0125	594
0.025	594
Average λ_{max}	**593.67**

Table A-6 Concentration vs. Absorbance at λ_{max} for Reactive Black 5

Concentration (g/L)	Absorbance 594 nm
0.0025	0.0662
0.005	0.1381
0.0075	0.2043
0.01	0.2709
0.0125	0.3425
0.025	0.6865

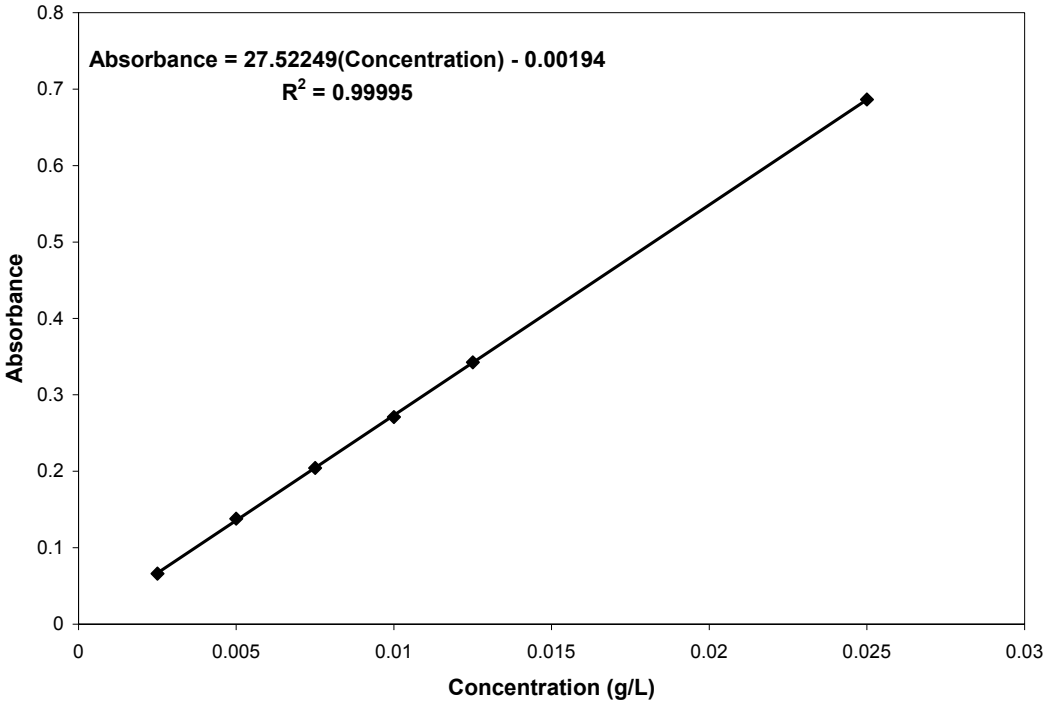


Figure A-3 Equation for Determination of Dye Concentration in Solution for Reactive Black 5

Table A-7 Determination of λ_{max} for Reactive Violet 5

Concentration (g/L)	λ_{max} (nm)
0.0025	565
0.005	562
0.0075	567
0.0125	565
0.025	565
0.05	565
Average λ_{max}	**564.83**

Table A-8 Concentration vs. Absorbance at λ_{max} for Reactive Violet 5

Concentration (g/L)	Absorbance at 565 nm
0.0025	0.0335
0.005	0.0634
0.0075	0.0949
0.0125	0.1560
0.025	0.3095
0.05	0.6143

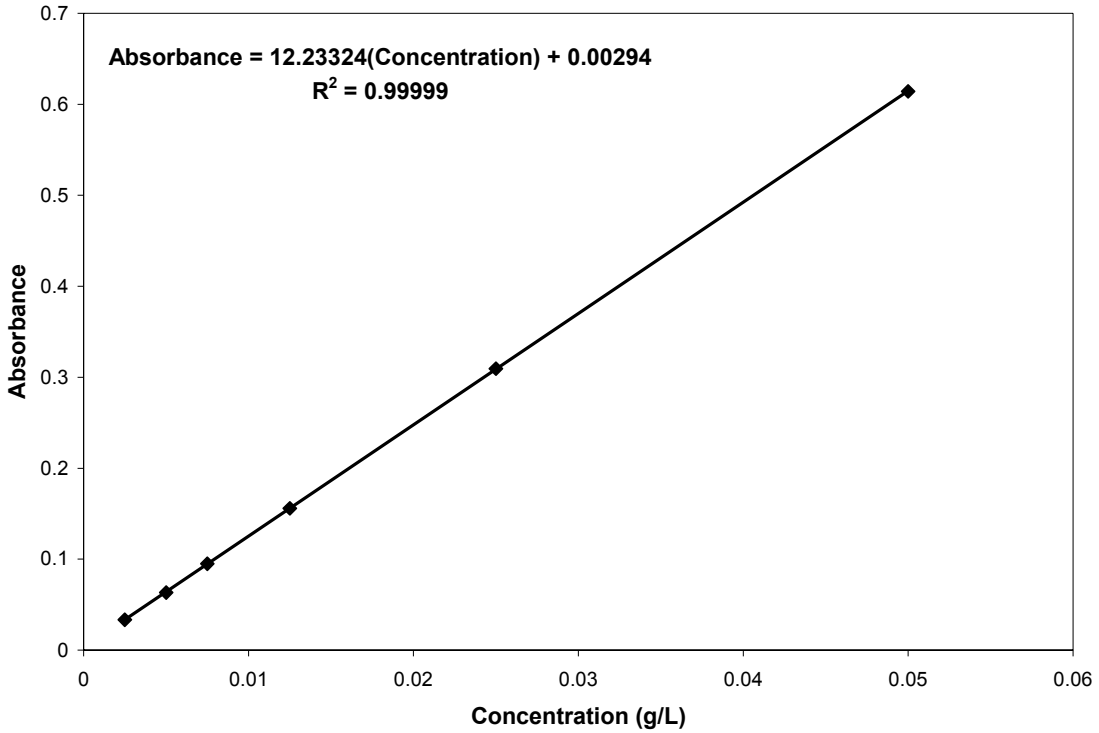


Figure A-4 Equation for Determination of Dye Concentration in Solution for Reactive Violet 5

Appendix B: ADMI Calibration Curve for Cary 3E UV-Visible Spectrophotometer

Table B-1 Transmission Data for Platinum-Cobalt ADMI Standard Solutions

Pt-Co Standard (ADMI)	%T1 (590 nm)	%T2 (540 nm)	%T3 (438 nm)	ADMI
31.25	99.5	99.3	97.9	36
62.5	99.5	99.0	96.6	60
125	99.6	98.4	93.6	120
166.7	99.7	98.2	91.6	165
250	99.6	97.5	87.5	254
500	99.5	95.2	76.6	500

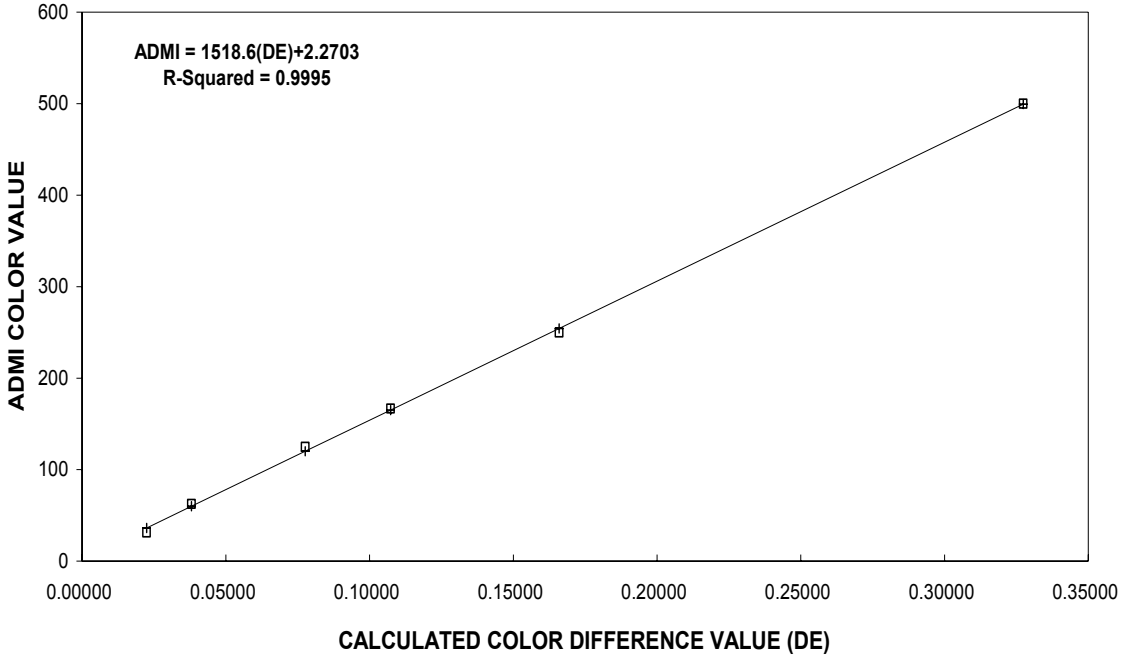


Figure B-1 ADMI Calibration Curve

Appendix C: Correlation of Dye Concentration to ADMI Color Value and Determination of Dye Concentration in Influent

Table C-1 Dye Concentration vs. ADMI for Reactive Red 198

Concentration (g/L)	%T1 (590 nm)	%T2 (540 nm)	%T3 (438 nm)	ADMI
0.00025	99.7	99.3	99.5	25
0.0005	99.8	98.4	99.1	84
0.001	99.7	96.9	98.3	163
0.0015	99.5	95.2	97.2	245
0.002	99.6	94.3	96.7	304

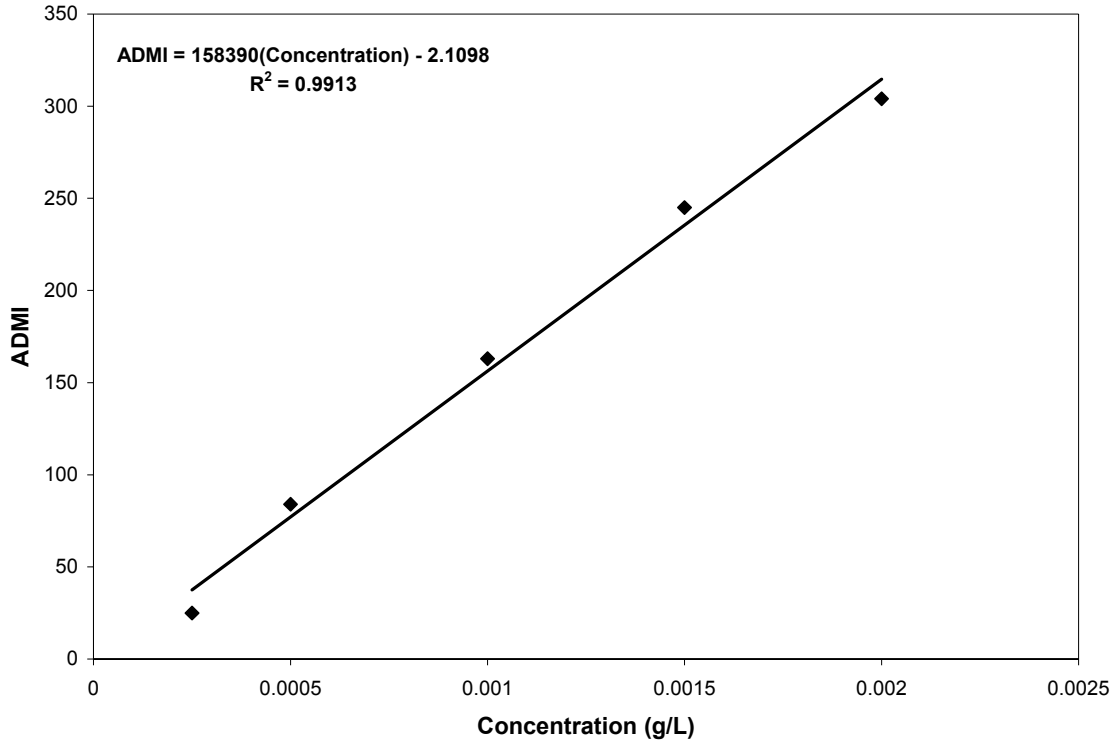


Figure C-1 Correlation Between Dye Concentration and ADMI for Reactive Red 198

Table C-2 Dye Concentration vs. ADMI for Reactive Yellow 86

Concentration (g/L)	%T1 (590 nm)	%T2 (540 nm)	%T3 (438 nm)	ADMI
0.002	99.8	100.0	95.7	118
0.0025	99.1	98.8	90.3	229
0.00375	99.5	99.7	96.0	105
0.005	99.9	99.8	84.8	413
0.00625	99.6	99.6	87.0	346

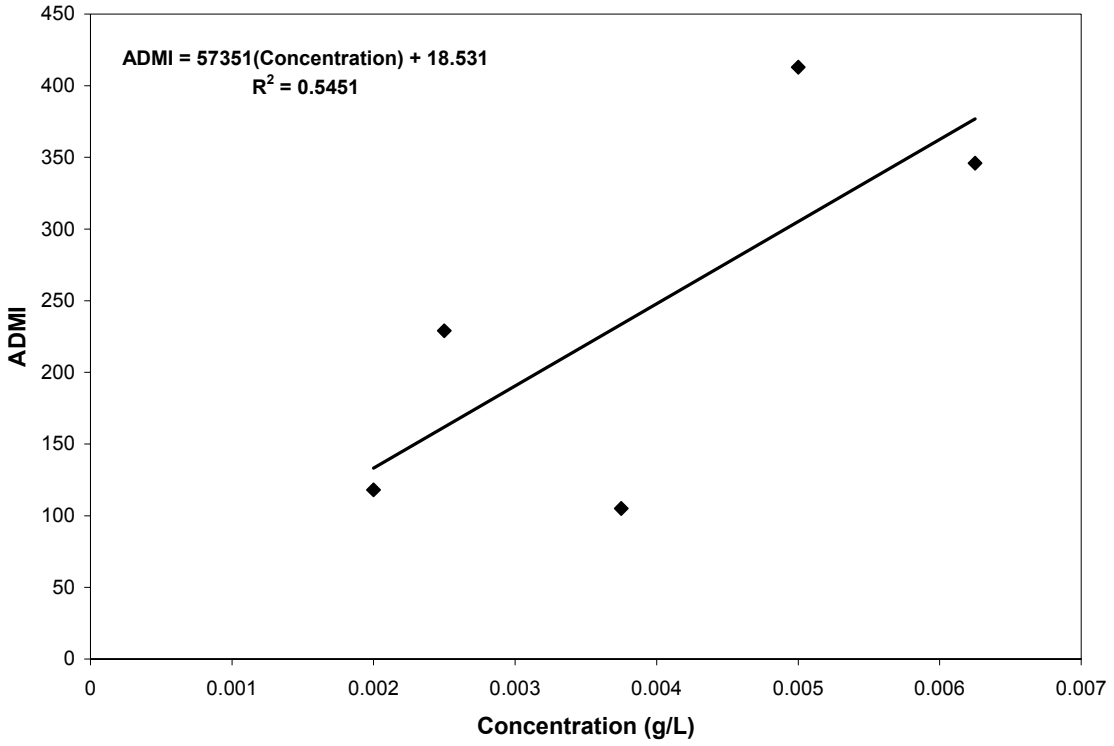


Figure C-2 Correlation Between Dye Concentration and ADMI for Reactive Yellow 86

Table C-3 Dye Concentration vs. ADMI for Reactive Black 5

Concentration (g/L)	%T1 (590 nm)	%T2 (540 nm)	%T3 (438 nm)	ADMI
0.001	92.7	94.1	96.5	110
0.002	87.5	89.9	95.7	211
0.0025	84.7	88.9	94.6	262
0.00375	79.4	83.0	92.3	355
0.005	71.7	79.0	89.2	501

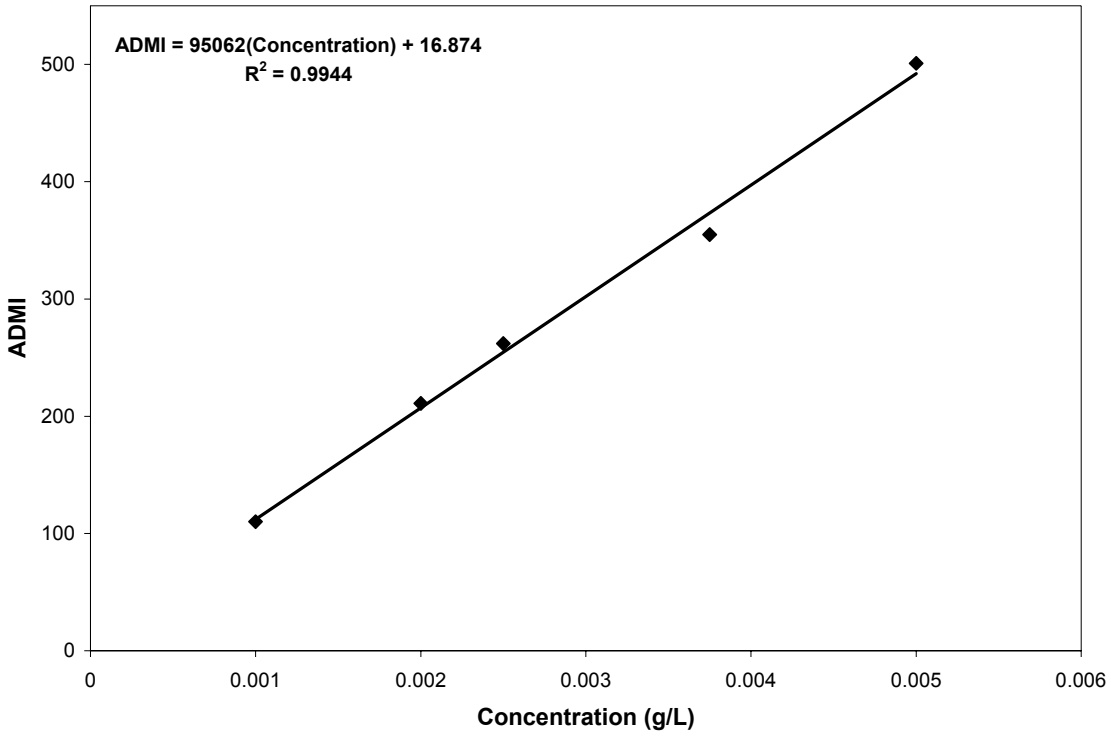


Figure C-3 Correlation Between Dye Concentration and ADMI for Reactive Black 5

Table C-4 Dye Concentration vs. ADMI for Reactive Violet 5

Concentration (g/L)	%T1 (590 nm)	%T2 (540 nm)	%T3 (438 nm)	ADMI
0.0025	94.1	93.7	98.5	166
0.00375	94.0	90.4	97.6	351
0.005	89.2	88.2	97.4	327
0.00625	90.1	84.1	96.7	622
0.0075	84.4	83.3	96.3	473

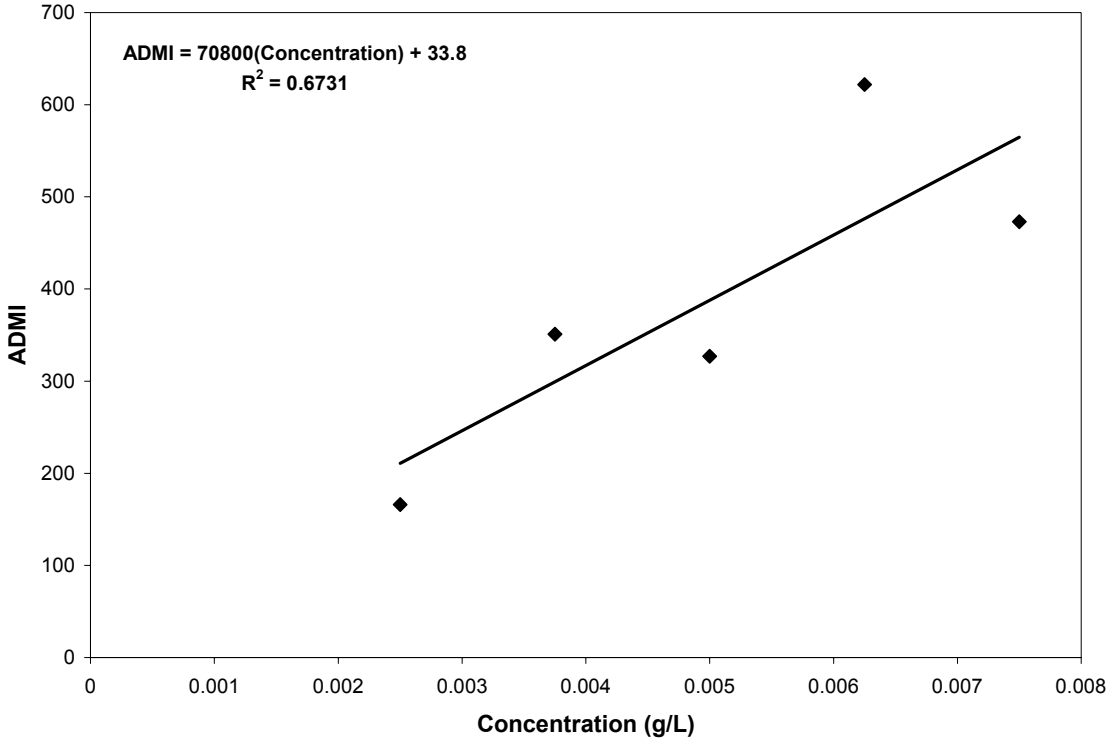


Figure C-4 Correlation Between Dye Concentration and ADMI for Reactive Violet 5

Determination of Dye Concentration for 1000 ADMI Synthetic Wastewater

Reactor 1: C. I. Reactive Red 198 and C. I. Reactive Yellow 86

Concentration of Reactive Red 198 = [(1000 ADMI) + 2.1098] / 158390 = 0.006 g/L
Concentration of Reactive Yellow 86 = [(1000 ADMI) -18.531] / 57351 = 0.017 g/L

This reactor was fed influent containing two dyes, so an ADMI color value of approximately 2000 was desired. Synthetic wastewater containing 0.01 g/L of both Reactive Red 198 and Reactive Yellow 86 had a color value of 2176 ADMI (%T1 = 99.1, %T2 = 88.8, %T3 = 88.5, Note: ¼ dilution) and these concentrations were chosen for the study.

Reactor 2: C. I. Reactive Black 5

Concentration of Reactive Black 5 = [(1000 ADMI) -16.874] / 95062 = 0.010 g/L

Synthetic wastewater containing 0.01 g/L of Reactive Black 5 had a color value of 1244 ADMI (%T1 = 82.2, %T2 = 87.3, %T3 = 93.9, Note: ¼ dilution) and this concentration was chosen for the study.

Reactor 5: C. I. Reactive Violet 5

Concentration of Reactive Violet 5 = [(1000 ADMI) -33.8] / 70800 = 0.014 g/L

Synthetic wastewater containing 0.02 g/L of Reactive Violet 5 had a color value of 1076 ADMI (%T1 = 90.5, %T2 = 90.2, %T3 = 98.2, Note: ¼ dilution) and this concentration was chosen for the study.

Color Value of Feed Mix from All Reactors

An equal parts synthetic wastewater mix from all three reactors displayed a color value of 970 ADMI (%T1 = 90.6, %T2 = 89.0, %T3 = 93.7, Note: ¼ dilution). This measurement indicated that the chosen dye concentrations were appropriate for simulating effluent from a textile dyeing and finishing plant with a color value of approximately 1000 ADMI.

Appendix D: Reactor Conditions

Table D-1 Daily Conditions for Reactor 1

Phase	End of Aerobic			Beginning of Anoxic		End of Anoxic / Beginning of Aerobic	
Date	DO	pH	Temp.	DO	pH	DO	pH
(m/d/y)	(mg/L)	(SU)	(deg. C)	(mg/L)	(SU)	(mg/L)	(SU)
12/6/2004	8.5	6.5	21.0	0.40	7.0		
12/7/2004	8.7	6.8	21.0	0.30	6.7		
12/8/2004	8.8	6.9	21.0	0.10	6.6		
12/9/2004	8.8	7.0	21.0	0.20	6.7		
12/10/2004	9.0	7.0	21.0	0.10	6.6		
12/11/2004	8.7	7.0	21.0	0.10	7.0		
12/12/2004	8.9	7.0	20.0	0.20	6.7		
12/13/2004	9.0	7.0	20.0	0.10	7.2		
12/14/2004	9.4	7.0	19.0	0.10	6.6		
12/15/2004	10.0	7.0	17.0	0.20	7.0		
12/16/2004	8.8	7.0	22.0	0.20	7.0		
12/17/2004	9.1	7.0	20.0	0.20	7.0		
12/18/2004	9.0	7.0	20.0	0.20	7.2		
12/19/2004		7.0	20.0	0.20	7.3		
12/20/2004	9.2	7.0	20.0	0.20	7.3		
12/21/2004	9.1	7.1	20.0	0.20	7.4		
12/22/2004	9.2	7.2	20.0	0.20	7.3		
12/24/2004	9.2	7.0	20.0				
12/29/2004	9.5	6.9	20.0				
12/31/2004	9.2	6.9	20.0				
1/1/2005	8.9	6.8	20.0				
1/2/2005	8.9	6.8	20.0				
1/3/2005	8.7	6.8	20.0				

Table D-1 (Cont.)

Phase	End of Aerobic			Beginning of Anoxic		End of Anoxic / Beginning of Aerobic	
Date	DO	pH	Temp.	DO	pH	DO	pH
(m/d/y)	(mg/L)	(SU)	(deg. C)	(mg/L)	(SU)	(mg/L)	(SU)
1/4/2005	9.0	6.9	20.0	0.20	6.9		
1/5/2005	9.0	6.9	20.0	0.20	6.9		
1/6/2005		6.8	21.0		6.8		
1/7/2005	9.2	6.9	20.0	0.20	6.9		
1/8/2005	9.0	6.9	21.0	0.20	6.9		
1/9/2005	9.1	7.0	20.0	0.10	6.9		
1/10/2005	6.2	6.8	22.0	0.10	6.8		
1/11/2005	8.5	6.8	21.0	0.10	6.9		
1/12/2005	8.0	6.9	22.0	0.10	6.8		
1/13/2005	7.9	6.8	23.0	0.05	6.7		
1/14/2005	7.4	6.8	20.0	0.10	6.8		
1/15/2005	9.1	6.8	20.0				
1/18/2005	8.8	6.8	20.0	0.05	6.7		
1/19/2005	9.1	6.8	19.0				
1/20/2005	8.8	6.8	21.0				
1/21/2005	8.9	6.9	21.0	0.10	6.8		
1/23/2005		7.1	21.0	0.10	6.8		
1/24/2005	9.2	6.9	19.0	0.10	6.7		
1/25/2005		6.6	19.0	0.10	6.7		
1/26/2005		6.7	20.0	0.10	6.7	0.10	6.7
1/27/2005		6.7	19.0				
1/28/2005	9.0	6.9	15.0	0.10	6.9		
1/30/2005	7.8	7.3	20.0	0.05	6.9	0.03	6.9
1/31/2005	7.8	7.0	20.0	0.02	7.0		
2/1/2005	8.0	7.1	21.0	0.01	7.0	0.02	6.9
2/2/2005	8.1	7.1	21.0	0.01	7.0	0.02	6.9
2/3/2005	8.4	7.2	19.0	0.01	7.0	0.02	6.9
2/4/2005	7.7	7.1	19.0				
2/12/2005	8.7	7.3	18.0	0.10	7.1	0.04	7.0
2/13/2005		7.0	20.0	0.02	7.1	0.03	6.9
2/14/2005		7.1	20.0	0.01	7.0	0.07	6.9
2/15/2005	7.6	7.1	19.0	0.03	7.0	0.03	6.9
2/16/2005	7.5	7.0	19.0	0.06	7.0	0.04	7.0

Table D-2 Daily Conditions for Reactor 2

	End of Aerobic			Beginning of Anoxic		End of Anoxic / Beginning of Aerobic	
Date	DO	pH	Temp.	DO	pH	DO	pH
(m/d/y)	(mg/L)	(SU)	(deg. C)	(mg/L)	(SU)	(mg/L)	(SU)
12/6/2004	8.6	6.4	22.0	0.30	7.0		
12/7/2004	8.9	6.8	21.0	0.30	6.6		
12/8/2004	8.9	7.0	21.0	0.20	6.6		
12/9/2004	8.6	7.0	21.0	0.20	6.8		
12/10/2004	8.8	7.0	21.0	0.10	6.6		
12/11/2004	8.6	7.0	21.0	0.10	7.0		
12/12/2004	8.7	7.0	20.0	0.10	6.7		
12/13/2004	9.0	7.0	20.0	0.20	7.3		
12/14/2004	9.4	7.0	19.0	0.10	6.6		
12/15/2004	10.0	7.0	17.0	0.10	7.0		
12/16/2004	8.7	7.0	22.0	0.10	7.0		
12/17/2004	9.1	7.0	20.0	0.20	7.0		
12/18/2004	9.0	7.0	20.0	0.20	7.2		
12/19/2004		7.0	20.0	0.20	7.2		
12/20/2004	9.1	7.0	20.0	0.10	7.2		
12/21/2004	0.0	7.0	20.0	0.10	7.3		
12/22/2004	9.1	7.1	20.0	0.20	7.3		
12/24/2004	9.2	7.0	20.0				
12/28/2004				0.30	6.8		
12/29/2004	9.5	6.9	20.0	0.10	7.0		
12/31/2004	9.2	7.0	20.0	0.20	6.9		
1/1/2005	9.1	7.0	20.0	0.10	6.9		
1/2/2005	9.2	7.0	20.0				
1/3/2005	9.1	7.0	20.0	0.10	6.8		
1/4/2005	9.2	7.0	20.0	0.20	6.8		
1/5/2005	9.0	7.0	20.0	0.20	6.9		
1/6/2005		6.9	21.0		6.8		
1/7/2005	9.0	6.9	20.0	0.10	6.9		
1/8/2005	8.8	6.9	21.0	0.10	6.8		
1/9/2005	9.0	7.0	20.0	0.10	6.9		

Table D-2 (Cont.)

	End of Aerobic			Beginning of Anoxic		End of Anoxic / Beginning of Aerobic	
Date	**DO**	**pH**	**Temp.**	**DO**	**pH**	**DO**	**pH**
(m/d/y)	**(mg/L)**	**(SU)**	**(deg. C)**	**(mg/L)**	**(SU)**	**(mg/L)**	**(SU)**
1/10/2005	5.8	6.8	22.0	0.10	6.8		
1/11/2005	8.5	6.8	21.0	0.10	6.9		
1/12/2005	8.0	6.9	22.0	0.10	6.8		
1/13/2005	7.5	6.8	23.0	0.05	6.8		
1/14/2005	7.0	6.8	20.0	0.05	6.8		
1/15/2005	8.9	6.8	20.0				
1/18/2005	8.4	6.7	20.0				
1/19/2005	9.0	6.8	19.0				
1/20/2005	8.4	6.7	21.0				
1/21/2005	8.5	6.8	21.0	0.10	6.8		
1/23/2005		7.3	21.0	0.10	6.8		
1/24/2005	8.7	6.8	19.0	0.10	6.7		
1/25/2005		6.8	19.0	0.10	6.7		
1/26/2005		6.9	20.0	0.10	6.7	0.10	6.7
1/27/2005		6.8	19.0				
1/28/2005	8.6	6.9	15.0	0.10	6.9		
1/30/2005	7.7	7.2	20.0	0.05	6.9	0.01	6.9
1/31/2005	7.7	7.0	20.0	0.02	6.9		
2/1/2005	8.0	7.0	21.0		7.0	0.03	6.9
2/2/2005	7.9	7.1	21.0	0.03	7.0	0.05	6.9
2/3/2005	8.1	7.1	19.0	0.02	7.0	0.03	6.9
2/4/2005	7.4	7.1	19.0	0.03			
2/12/2005	8.6	7.3	18.0	0.10	7.1	0.03	7.0
2/13/2005		7.2	20.0	0.05	7.1	0.02	6.9
2/14/2005		7.2	20.0	0.05	7.0	0.01	6.9
2/15/2005	7.9	7.2	19.0	0.03	7.1	0.03	6.9
2/16/2005	8.1	7.1	19.0	0.05	7.0	0.06	6.9

Table D-3 Daily Conditions for Reactor 5

	End of Aerobic			Beginning of Anoxic		End of Anoxic / Beginning of Aerobic	
Date	**DO**	**pH**	**Temp.**	**DO**	**pH**	**DO**	**pH**
(m/d/y)	**(mg/L)**	**(SU)**	**(deg. C)**	**(mg/L)**	**(SU)**	**(mg/L)**	**(SU)**
1/28/2005	9.4	6.9	15.0	0.30	7.1		
1/30/2005	7.4	7.3	20.0	0.02	7.0	0.01	6.9
1/31/2005	7.7	7.0	20.0	0.02	7.0		
2/1/2005	8.1	7.0	21.0	0.01	7.0	0.07	6.9
2/2/2005	8.1	7.1	21.0	0.04	7.1	0.05	6.9
2/3/2005	8.4	7.1	19.0	0.01	7.0	0.01	6.9
2/4/2005	7.4	7.2	19.0	0.03	7.1		
2/12/2005	7.4	7.5	18.0	0.10	7.1	0.02	7.0
2/13/2005		7.2	20.0	0.01	7.1	0.01	7.0
2/14/2005		7.2	20.0	0.03	7.1	0.07	7.0
2/15/2005	8.1	7.2	19.0	0.09	7.0	0.03	7.0
2/16/2005	8.4	7.1	19.0	0.07	6.9	0.04	6.9

Table D-4 Daily Conditions for Reactor 6

	End of Aerobic			Beginning of Aerobic	
Date	**DO**	**pH**	**Temp.**	**DO**	**pH**
(m/d/y)	**(mg/L)**	**(SU)**	**(deg. C)**	**(mg/L)**	**(SU)**
1/28/2005	9.6	6.9	15.0	6.30	7.2
1/30/2005	8.0	6.8	20.0	4.60	6.9
1/31/2005	7.3	6.8	20.0		6.8
2/1/2005	7.5	6.7	21.0	5.10	7.0
2/2/2005	7.6	6.7	21.0	5.30	7.0
2/3/2005	8.4	6.8	19.0	6.10	7.0
2/4/2005	7.6	6.8	19.0		

Table D-5 Daily Conditions for Reactor 7

	End of Aerobic			Beginning of Aerobic	
Date	**DO**	**pH**	**Temp.**	**DO**	**pH**
(m/d/y)	**(mg/L)**	**(SU)**	**(deg. C)**	**(mg/L)**	**(SU)**
2/12/2005	7.6	6.7	18.0	2.20	6.8
2/13/2005	7.6	7.0	20.0	4.70	6.8
2/14/2005	7.1	6.7	20.0	1.00	6.8
2/15/2005	7.5	6.7	19.0	2.60	7.0
2/16/2005	7.8	6.7	19.0	1.00	6.8

Table D-6 Daily Conditions for Reactor 8

	End of Aerobic			Beginning of Aerobic	
Date	**DO**	**pH**	**Temp.**	**DO**	**pH**
(m/d/y)	**(mg/L)**	**(SU)**	**(deg. C)**	**(mg/L)**	**(SU)**
2/12/2005	7.5	6.6	18.0	3.00	6.8
2/13/2005	7.8	6.6	20.0	1.60	6.7
2/14/2005	7.2	6.6	20.0	2.60	6.8
2/15/2005	7.7	6.7	19.0	1.40	7.0
2/16/2005	8.0	6.8	19.0	1.30	6.8

Table D-7 Daily Conditions for Reactor 9

	End of Aerobic			Beginning of Aerobic	
Date	**DO**	**pH**	**Temp.**	**DO**	**pH**
(m/d/y)	**(mg/L)**	**(SU)**	**(deg. C)**	**(mg/L)**	**(SU)**
2/12/2005	8.7	6.6	18.0	6.70	6.8
2/13/2005	8.6	6.7	20.0	5.90	6.9
2/14/2005	8.1	6.7	20.0	2.70	6.9
2/15/2005	8.2	6.7	19.0	6.10	6.9
2/16/2005	8.6	6.7	19.0	6.50	6.9

Appendix E: MLSS, TSS, and TDS Data

Table E-1 Solids Data for Reactor 1

	REACTOR	EFFLUENT (DECANT)		
Date	MLSS	TSS	Dis. Sol.	pH
(m/d/y)	(mg/L)	(mg/L)	(mg/L)	(SU)
12/6/2004	3450	0	2450	6.5
12/7/2004	3525	0	2400	6.7
12/8/2004	3450	0	2350	6.8
12/9/2004	3250	0	2600	7.0
12/10/2004	3125	0	2600	6.9
12/11/2004	3050	0	2475	7.0
12/12/2004	2975	0	2500	7.0
12/13/2004	2775	0	2500	7.0
12/14/2004	2929	0	2575	6.9
12/15/2004	2875	0	2800	7.0
12/16/2004	2725	0	2688	6.9
12/17/2004	2638	0	2550	7.0
12/18/2004	2625	0	2438	6.9
12/19/2004	2675	0	2550	7.0
12/20/2004	2488	0	2475	7.0
12/21/2004	2400	0	2538	7.0
12/22/2004	2425	0	2613	7.3
12/23/2004				7.1
12/24/2004	2613			7.0
12/28/2004	2938			
12/29/2004	2638	0	2550	6.8
12/30/2004	3163	0	2388	6.9
12/31/2004	2975	44	2534	6.9
1/1/2005	3000	19	2563	6.8
1/2/2005	3550	22	2506	6.7
1/3/2005	3600	0	2475	6.7
1/4/2005	3475	12	2500	6.8
1/5/2005	3625			6.9
1/6/2005	3262.5			6.8

Table E-1 (Cont.)

	REACTOR	EFFLUENT (DECANT)		
Date	MLSS	TSS	Dis. Sol.	pH
(m/d/y)	(mg/L)	(mg/L)	(mg/L)	(SU)
1/7/2005	3512.5	3	2431	6.7
1/8/2005	3200			6.8
1/9/2005	3287.5			7.0
1/10/2005	4862.5	6	2538	6.8
1/11/2005	4737.5			6.7
1/12/2005	4262.5			6.8
1/13/2005	4662.5			6.8
1/14/2005	4237.5	0	2631	6.7
1/15/2005	5012.5			
1/17/2005	4450			
1/18/2005	4650	0	2703	6.7
1/19/2005	4687.5			6.8
1/20/2005	4750			
1/21/2005	4762.5	0	2653	
1/23/2005				7.1
1/24/2005				6.9
1/25/2005	4550			6.6
1/26/2005	4625	0	2375	
1/28/2005	4700			6.9
1/30/2005	3900			7.4
1/31/2005	3962.5	22	2694	7.1
2/1/2005				7.2
2/2/2005	4300			7.1
2/3/2005				7.2
2/4/2005	4537.5			7.1
2/12/2005	4700			7.3
2/13/2005	4550			7.0
2/14/2005	4250			7.1
2/15/2005	4475			7.1
2/16/2005	4525			7.0

Table E-2 Solids Data for Reactor 2

	REACTOR	EFFLUENT (DECANT)		
Date	**MLSS**	**TSS**	**Dis. Sol.**	**pH**
(m/d/y)	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(SU)**
12/6/2004	3600	0	2375	6.3
12/7/2004	3650	0	2425	6.6
12/8/2004	3525	0		6.8
12/9/2004	3575	0	2675	7.0
12/10/2004	3450	0	2500	7.0
12/11/2004	3275	0	2400	6.9
12/12/2004	3200	0	2475	7.0
12/13/2004	2950	0	2550	7.0
12/14/2004	3175	0	2725	6.8
12/15/2004	3150	0	2725	7.0
12/16/2004	3000	0	2763	6.9
12/17/2004	2975	0	2175	7.0
12/18/2004	3025	0	2388	6.9
12/19/2004	3000	0	2588	7.0
12/20/2004	3025	0	2488	7.2
12/21/2004	2975	0	2513	7.0
12/22/2004	2888	0	2613	7.1
12/23/2004				7.0
12/24/2004	2900			7.0
12/28/2004	3200			
12/29/2004	2763	0	2544	6.9
12/30/2004	3275	0	2381	6.9
12/31/2004	2450	66	2409	7.0
1/1/2005	3225	38	2525	6.9
1/2/2005	2800	25	2491	6.8
1/3/2005	2825	6	2459	6.9
1/4/2005	3562.5	25	2506	6.8
1/5/2005	3412.5			6.9
1/6/2005	3500			6.9
1/7/2005	4762.5	0	2422	6.9

Table E-2 (Cont.)

	REACTOR	EFFLUENT (DECANT)		
Date	**MLSS**	**TSS**	**Dis. Sol.**	**pH**
(m/d/y)	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(SU)**
1/8/2005	3500			6.7
1/9/2005	3537.5			7.0
1/10/2005	5112.5	9	2559	6.7
1/11/2005	4812.5			6.7
1/12/2005	4700			6.8
1/13/2005	4775			6.7
1/14/2005	5175	0	2534	6.7
1/15/2005	5212.5			
1/17/2005	4687.5			
1/18/2005	4912.5	0	2678	6.7
1/19/2005	4875			6.7
1/20/2005	4975			
1/21/2005	4950	0	2656	
1/23/2005	4950			7.0
1/24/2005				6.8
1/25/2005	4750			6.8
1/26/2005	4650	0	2200	
1/28/2005	4825			6.9
1/30/2005	4150			7.3
1/31/2005	3962.5	12	2672	7.1
2/1/2005				7.1
2/2/2005	4425			7.1
2/3/2005				7.1
2/4/2005	4262.5			7.1
2/12/2005	4625			7.3
2/13/2005	4500			7.2
2/14/2005	4350			7.2
2/15/2005	4500			7.2
2/16/2005	4650			7.2

Appendix F: Characteristics of Non-Colored Influent

Table F-1 Non-Colored Influent Data

Date	TSS	Dis. Sol.	pH	COD
(m/d/y)	(mg/L)	(mg/L)	(SU)	(mg/L)
12/6/2004	0	3050	7.4	1037
12/7/2004	0	2675	6.6	667
12/8/2004	0	2500		570
12/9/2004	0	2850	6.6	708
12/10/2004	125	2475	6.4	609
12/11/2004	0	2675	7.0	890
12/12/2004	0	2525	6.4	760
12/13/2004	0	2625	7.4	1069
12/14/2004	50	2700	6.3	914
12/15/2004	75	3050	6.7	957
12/16/2004	0	2900	6.5	977
12/18/2004	0	2538	6.4	990
12/19/2004	0	2663	8.0	1190
12/20/2004			8.0	1017
12/22/2004	0	2088	7.8	785
12/23/2004			7.0	1173
12/24/2004			6.9	891
12/29/2004	0	2925	7.3	1138
12/30/2004	0	2763	7.3	1217

Table F-1 (Cont.)

Date	TSS	Dis. Sol.	pH	COD
(m/d/y)	(mg/L)	(mg/L)	(SU)	(mg/L)
12/31/2004	100	2813	7.2	1167
1/1/2005	50	2838	7.2	1147
1/2/2005	0	2763	7.0	1161
1/3/2005	0	2625	7.0	1163
1/4/2005	0	2712	7.3	1131
1/5/2005			7.3	1094
1/6/2005			7.2	1206
1/7/2005	0	2756	7.2	1145
1/8/2005			7.3	1113
1/9/2005				1083
1/10/2005	25	2712	7.2	1139
1/11/2005			7.3	1158
1/12/2005			7.3	1136
1/13/2005			7.3	1066
1/14/2005	37	2700	7.2	786
1/18/2005			7.2	1160
1/19/2005			7.3	1022
1/21/2005	50	2775		1004
1/23/2005			7.3	1037
1/24/2005				951

Appendix G: Reactor Effluent COD Data

Table G-1 Effluent COD Data

	COD (mg/L)	
Date	**Reactor 1**	**Reactor 2**
12/6/2004	43	71
12/7/2004	48	35
12/8/2004	39	44
12/9/2004	48	38
12/10/2004	45	26
12/11/2004	36	32
12/12/2004	21	30
12/13/2004	31	46
12/14/2004	29	36
12/15/2004	35	34
12/16/2004	25	18
12/17/2004	23	32
12/18/2004	66	58
12/19/2004	39	40
12/20/2004	31	33
12/21/2004	24	33
12/22/2004	25	30
12/23/2004	35	26
12/24/2004	22	23
12/29/2004	33	31
12/30/2004	24	18
12/31/2004	26	19
1/1/2005	27	22
1/2/2005	30	24
1/3/2005	36	8
1/4/2005	28	26
1/5/2005	35	17

Table G-1 (Cont.)

	COD (mg/L)	
Date	**Reactor 1**	**Reactor 2**
1/6/2005	29	22
1/7/2005	38	22
1/8/2005	33	32
1/9/2005	28	24
1/10/2005	27	26
1/11/2005	26	25
1/12/2005	22	22
1/13/2005	24	19
1/14/2005	13	21
1/15/2005	15	9
1/18/2005	14	18
1/19/2005	17	20
1/21/2005	10	10
1/23/2005	14	7
1/24/2005	33	11
1/25/2005		34
1/26/2005		39
1/27/2005	37	16
1/30/2005	22	8
1/31/2005	30	17
2/1/2005	17	12
2/2/2005	23	24
2/3/2005	30	36
2/4/2005	18	6
2/5/2005	21	18
2/13/2005	19	4
2/14/2005	26	13
2/15/2005	21	13
2/16/2005	38	10
2/17/2005	44	10

Appendix H: Kinetics of COD Removal for Aerobic Control (Reactor 6)

Table H-1 Raw COD (mg/L) Data from COD Removal Study for Aerobic Control (Reactor 6)

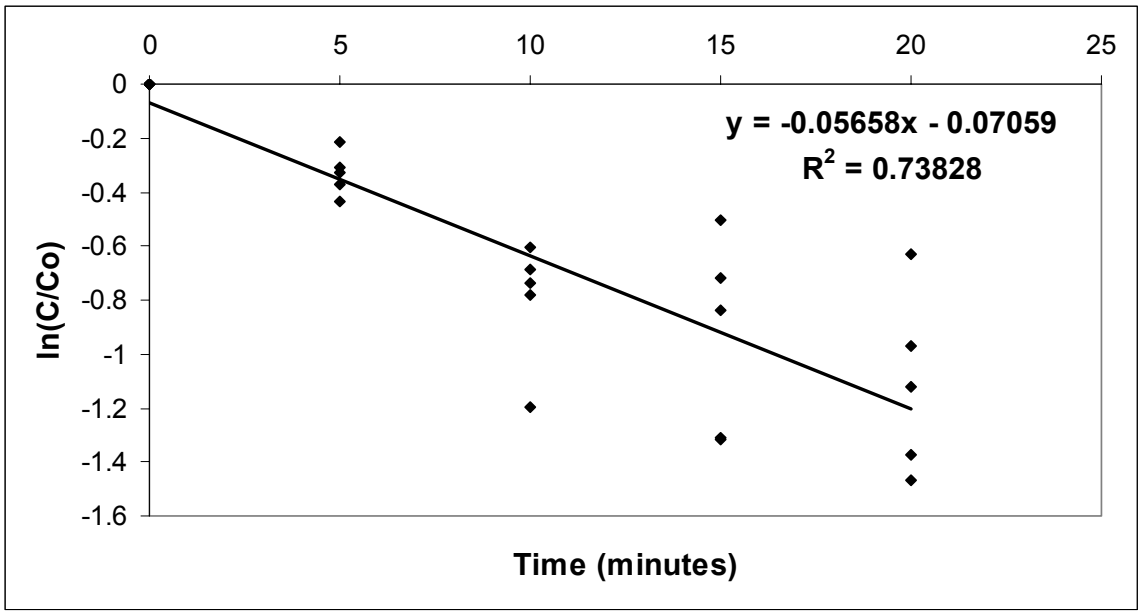
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
0	435	606	552	450	288
5	300	444	397	364	186
10	219	332	252	136	138
15	262	296	149	121	125
20	142	323	127	114	109
25	132	176	125	110	118
30	169	172	118	105	106
60	108	136	75	67	76
120	35	58	16	21	33
240	37	20	3	24	22
480	11	13	7	16	28
960	20	12	3	21	10
1380	8	14	10	21	15

Table H-2 Initial COD Concentration (mg/L) during COD Removal Study for Aerobic Control (Reactor 6)

Cycle	Effluent COD for (Cycle-1)	Influent COD	Meas. Initial COD	Calc. Initial COD	Difference	Difference (%)
1	19	893	435	456	21	4.61
2	8	1198	606	603	3	0.50
3	14	1102	552	558	6	1.08
4	10	968	450	489	39	7.98
5	21	514	288	267.5	20.5	7.66

Table H-3 *ln(C/C$_0$)* for COD Removal Study for Aerobic Control (Reactor 6)

Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Average
0	0	0	0	0	0	0
5	-0.37156	-0.31106	-0.32961	-0.21209	-0.43721	-0.32955
10	-0.68627	-0.60175	-0.78412	-1.19659	-0.73571	-0.78123
15	-0.50700	-0.71652	-1.30960	-1.31346	-0.83465	-0.88499
20	-1.11952	-0.62923	-1.46936	-1.37305	-0.97161	-1.06635
25	-1.19254	-1.23640	-1.48523	-1.40877	-0.89228	-1.22112
30	-0.94545	-1.25939	-1.54286	-1.45529	-0.99952	-1.21235
60	-1.39321	-1.49423	-1.99606	-1.90455	-1.33223	-1.58832
120	-2.52000	-2.34644	-3.54096	-3.06473	-2.16645	-2.61345
240	-2.46443	-3.41115	-5.21494	-2.93119	-2.57192	-2.98294
480	-3.67745	-3.84193	-4.36764	-3.33666	-2.33076	-3.25866
960	-3.07961	-3.92197	-5.21494	-3.06473	-3.36038	-3.48936
1380	-3.99590	-3.76782	-4.01096	-3.06473	-2.95491	-3.45233



Note: standard error for regression = 0.2484

Figure H-1 Linear Regression for Determining Rate Constant for COD Removal for Aerobic Control (Reactor 6)

Appendix I: Kinetics of COD Removal for Anoxic/Aerobic Process (Reactors 1 and 2)

Table I-1 Raw COD (mg/L) Data from COD Removal Study for Anoxic/Aerobic Process (Reactor 1)

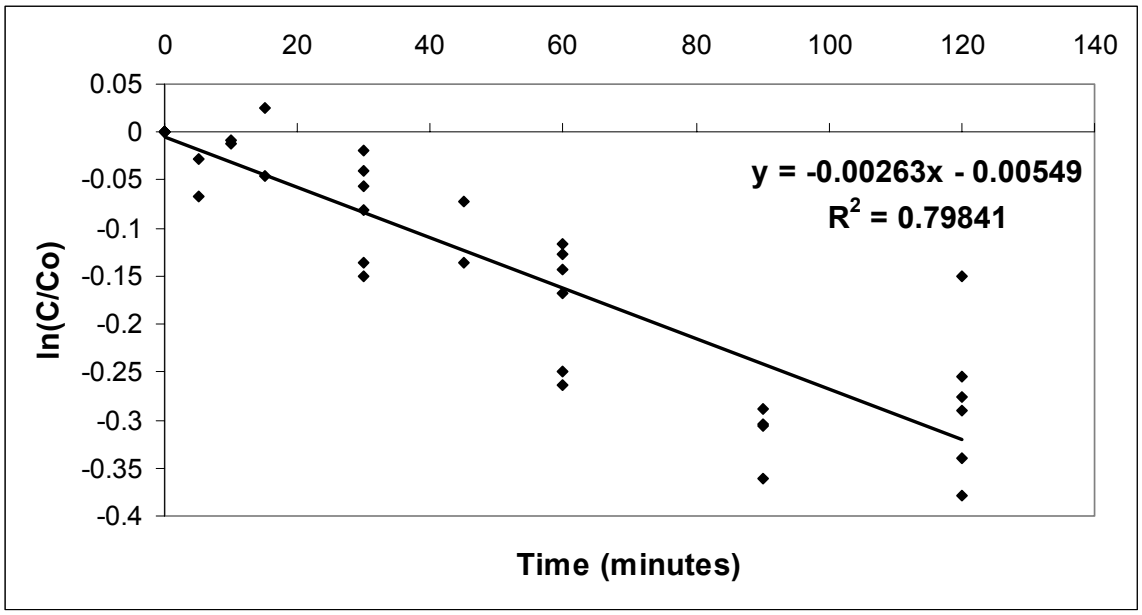
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	358	337	350	324	309	228
5	348	315				
10	355	333				
15	367	322				
30	351	294	301	306	285	219
45	333	294				
60	310	297	296	249	241	203
90			244	243	228	168
120	308	261	249	246	231	156
240	270	245	213	193	195	118
480	272	238	206	173	200	88
485	189	129	100	83	82	41
490	122	90	60	52	61	35
495	75	60	51	41	39	37
500			35	34	45	26
505			39	31	41	29
510	42	41	38	32	28	22
525	39	40				
540	36	29	15	30	38	26
600	38	40				
660			32	31	41	34
720	47	38				
840			20	28	33	21
960	34	29				
1200			21	30	33	30
1350	27	26	12	24	13	15

Table I-2 Initial COD (mg/L) Concentration during COD Removal Study for Anoxic/Aerobic Process (Reactor 1)

Cycle	Effluent COD for (Cycle-1)	Influent COD	Meas. Initial COD	Calc. Initial COD	Difference	Difference (%)
1	28	1083	358.0	555.5	197.5	35.55
2	27	1072	337.0	549.5	212.5	38.67
3	26	1129	350.0	577.5	227.5	39.39
4	22	1105	324.0	563.5	239.5	42.50
5	24	1055	309.0	539.5	230.5	42.72
6	13	750	228.0	381.5	153.5	40.24

Table I-3 $ln(C/C_0)$ for COD Removal Study for Anoxic/Aerobic Process (Reactor 1)

Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Average
0	0	0	0	0	0	0	0
5	-0.02833	-0.06751					-0.04773
10	-0.00842	-0.01194					-0.01018
15	0.02483	-0.04553					-0.00973
30	-0.01975	-0.13650	-0.15082	-0.05716	-0.08085	-0.04027	-0.07974
45	-0.07239	-0.13650					-0.10393
60	-0.14396	-0.12635	-0.16757	-0.26329	-0.24854	-0.11614	-0.17599
90			-0.36076	-0.28768	-0.30400	-0.30538	-0.31408
120	-0.15043	-0.25556	-0.34048	-0.27541	-0.29092	-0.37949	-0.27943
240	-0.28211	-0.31882	-0.49664	-0.51805	-0.46034	-0.65866	-0.44784
480	-0.27473	-0.34781	-0.53006	-0.62745	-0.43502	-0.95201	-0.50480
485	-0.63879	-0.96027	-1.25276	-1.36190	-1.32662	-1.71577	-1.15106
490	-1.07651	-1.32027	-1.76359	-1.82950	-1.62247	-1.87400	-1.53659
495	-1.56304	-1.72574	-1.92611	-2.06717	-2.06978	-1.81843	-1.84485
500			-2.30259	-2.25438	-1.92668	-2.17125	-2.15286
505			-2.19437	-2.34676	-2.01977	-2.06205	-2.14775
510	-2.14286	-2.10651	-2.22035	-2.31501	-2.40114	-2.33830	-2.24838
525	-2.21697	-2.13120					-2.17317
540	-2.29701	-2.45279	-3.14988	-2.37955	-2.09576	-2.17125	-2.37323
600	-2.24295	-2.13120					-2.18552
660			-2.39220	-2.34676	-2.01977	-1.90299	-2.14362
720	-2.03039	-2.18250					-2.10355
840			-2.86220	-2.44854	-2.23683	-2.38482	-2.45788
960	-2.35417	-2.45279					-2.40226
1200			-2.81341	-2.37955	-2.23683	-2.02815	-2.32542
1350	-2.58470	-2.56199	-3.37303	-2.60269	-3.16839	-2.72130	-2.78929

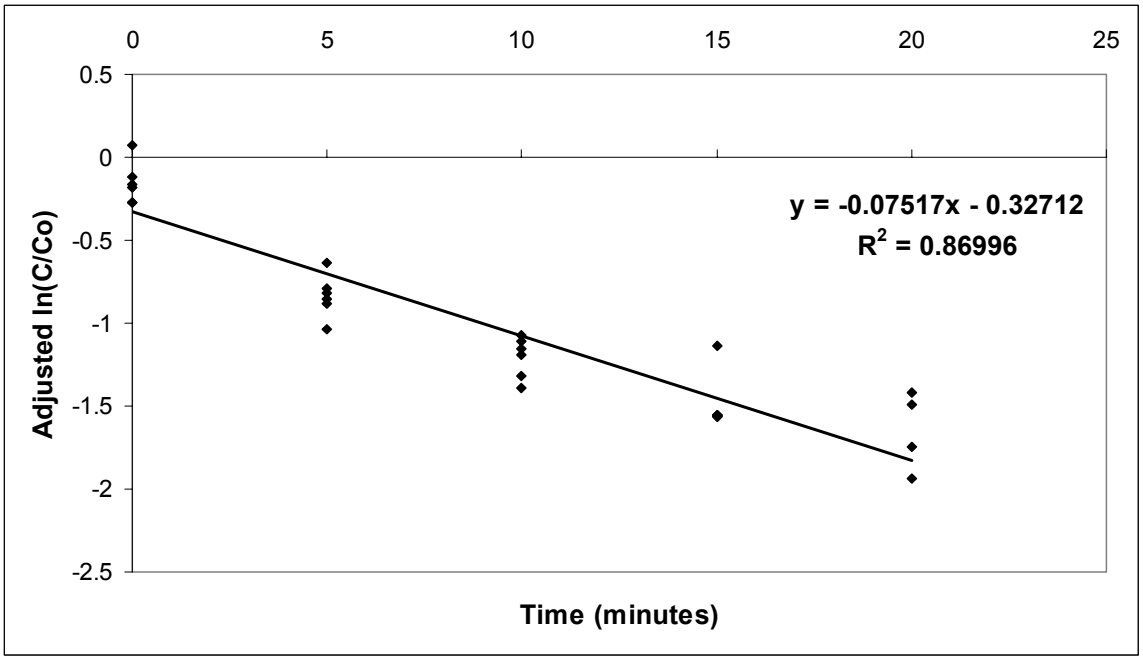


Note: standard error for regression = 0.05705

Figure I-1 Linear Regression for Determining Rate Constant of Anoxic Phase for COD Removal for Anoxic/Aerobic Process (Reactor 1)

Table I-4 Adjusted *ln(C/C$_0$)* for COD Removal Study for Aerobic Phase of Anoxic/Aerobic Process (Reactor 1)

Time (min.)	(Cycle 1) +0	(Cycle 2) +0.17	(Cycle 3) +0.37	(Cycle 4) +0.51	(Cycle 5) +0.51	(Cycle 6) +0.68
0	-0.27473	-0.17781	-0.16006	-0.11745	0.07498	-0.27201
5	-0.63879	-0.79027	-0.88276	-0.85190	-0.81662	-1.03577
10	-1.07651	-1.15027	-1.39359	-1.31950	-1.11247	-1.19400
15	-1.56304	-1.55574	-1.55611	-1.55717	-1.55978	-1.13843
20			-1.93259	-1.74438	-1.41668	-1.49125
Cumulative Error	0	0.32947	0.68266	0.61926	0.56676	0.94181



Note: standard error for regression = 0.204383

Figure I-2 Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for COD Removal for Anoxic/Aerobic Process (Reactor 1)

Table I-5 Raw COD (mg/L) Data from COD Removal Study for Anoxic/Aerobic Process (Reactor 2)

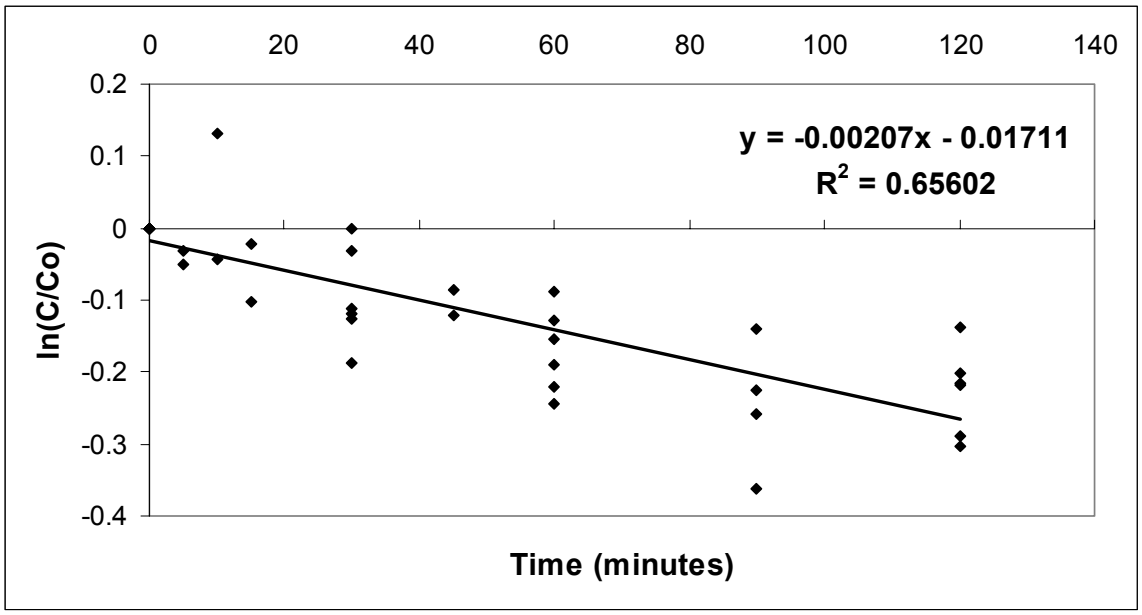
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	350	327	305	328	303	230
5	333	317				
10	399	313				
15	342	295				
30	339	271	305	289	271	204
45	321	290				
60	308	280	279	271	243	180
90			265	262	234	160
120	305	263	246	268	227	170
240	282	268	232	218	194	120
480	309	286	200	254	188	96
485	187	143	136	131	118	49
490	166	136	119	108	103	40
495	149	113	93	116	88	34
500			63	61	59	31
505			42	43	50	33
510	70	46	33	33	36	30
525	38	37				
540	38	34	17	27	31	24
600	44	37				
660			21	35	42	40
720	40	39				
840			24	30	28	35
960	36	30				
1200			19	25	29	29
1350	26	25	8	19	21	9

Table I-6 Initial COD (mg/L) Concentration during COD Removal Study for Anoxic/Aerobic Process (Reactor 2)

Cycle	Effluent COD for (Cycle-1)	Influent COD	Meas. Initial COD	Calc. Initial COD	Difference	Difference (%)
1	24	1083	350	553.5	203.5	36.77
2	26	1206	327	616	289	46.92
3	25	1187	305	606	301	49.67
4	22	1167	328	594.5	266.5	44.83
5	19	1077	303	548	245	44.71
6	21	822	230	421.5	191.5	45.43

Table I-7 $ln(C/C_0)$ for COD Removal Study for Anoxic/Aerobic Process (Reactor 2)

Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Average
0	0	0	0	0	0	0	0
5	-0.04979	-0.03106					-0.04038
10	0.13103	-0.04376					0.04745
15	-0.02312	-0.10298					-0.06226
30	-0.03193	-0.18784	0	-0.12659	-0.11161	-0.11996	-0.09435
45	-0.08649	-0.12008					-0.10314
60	-0.12783	-0.15517	-0.08910	-0.19089	-0.22067	-0.24512	-0.17003
90			-0.14058	-0.22467	-0.25841	-0.36291	-0.24349
120	-0.13762	-0.21781	-0.21498	-0.20203	-0.28878	-0.30228	-0.22572
240	-0.21603	-0.19897	-0.27357	-0.40852	-0.44587	-0.65059	-0.35368
480	-0.12459	-0.13397	-0.42199	-0.25568	-0.47729	-0.87373	-0.35063
485	-0.62682	-0.82712	-0.80766	-0.91782	-0.94305	-1.54626	-0.90825
490	-0.74595	-0.87731	-0.94119	-1.11088	-1.07900	-1.74920	-1.03871
495	-0.85399	-1.06257	-1.18771	-1.03942	-1.23640	-1.91172	-1.16683
500			-1.57718	-1.68214	-1.63620	-2.00409	-1.71198
505			-1.98264	-2.03181	-1.80171	-1.94157	-1.93569
510	-1.60944	-1.96132	-2.22380	-2.29651	-2.13021	-2.03688	-2.01650
525	-2.22035	-2.17904					-2.19948
540	-2.22035	-2.26360	-2.88710	-2.49718	-2.27975	-2.26003	-2.37648
600	-2.07374	-2.17904					-2.12501
660			-2.67579	-2.23767	-1.97606	-1.74920	-2.10356
720	-2.16905	-2.12640					-2.14750
840			-2.54226	-2.39182	-2.38153	-1.88273	-2.26641
960	-2.27441	-2.38876					-2.32995
1200			-2.77587	-2.57414	-2.34644	-2.07078	-2.40708
1350	-2.59984	-2.57108	-3.64087	-2.84857	-2.66921	-3.24085	-2.86082

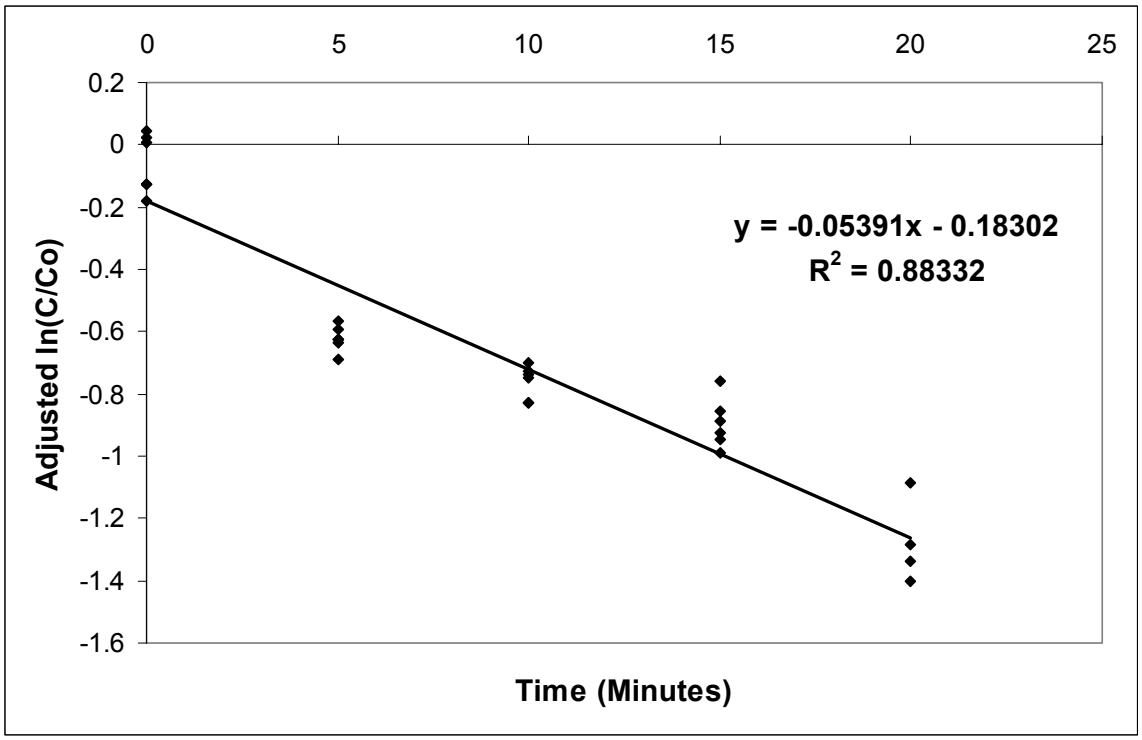


Note: standard error for regression = 0.06485

Figure I-3 Linear Regression for Determining Rate Constant of Anoxic Phase for COD Removal for Anoxic/Aerobic Process (Reactor 2)

Table I-8 Adjusted *ln(C/C$_0$)* for COD Removal Study for Aerobic Phase of Anoxic/Aerobic Process (Reactor 2)

Time (min.)	(Cycle 1) +0	(Cycle 2) +0.14	(Cycle 3) +0.24	(Cycle 4) +0.28	(Cycle 5) +0.35	(Cycle 6) +0.92
0	-0.12459	0.00603	-0.18199	0.02432	-0.12729	0.04627
5	-0.62682	-0.68712	-0.56766	-0.63782	-0.59305	-0.62626
10	-0.74595	-0.73731	-0.70119	-0.83088	-0.72900	-0.82920
15	-0.85399	-0.92257	-0.94771	-0.75942	-0.88640	-0.99172
20			-1.33718	-1.40214	-1.28620	-1.08409
Cumulative Error	0	0.26814	0.25505	0.33940	0.08583	0.39241



Note: standard error for regression = 0.137778

Figure I-4 Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for COD Removal for Anoxic/Aerobic Process (Reactor 2)

Table I-9 Raw COD (mg/L) Data Gathered during Color Kinetic Study (Reactor 1)

Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	328	317	314	181	214	272
30	258	200	362	111	164	102
60	221	197	273	106	129	87
480	122	96	108	75	61	91
510	44	41	48	28	26	23
540	44	34	36	26	30	31
1350	30	17	23	30	18	21

Table I-10 Raw COD (mg/L) Data Gathered during Color Kinetic Study (Reactor 2)

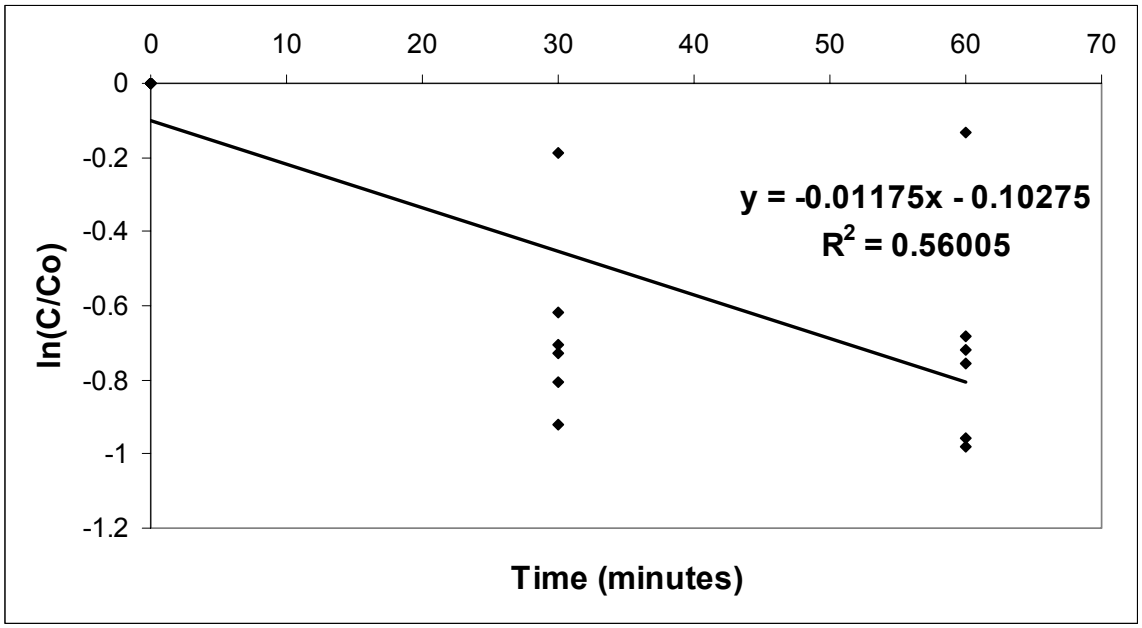
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	335	315	316	97	213	184
30	266	229	273	104	102	92
60	262	223	215	94	65	95
480	103	86	80	67	89	53
510	50	39	28	23	28	32
540	36	27	21	25	25	29
1350	17	12	24	36	6	18

Table I-11 Raw COD (mg/L) Data Gathered during Color Kinetic Study (Reactor 5)

Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	487	471	456	129	230	219
30	240	188	220	107	124	98
60	246	177	214	113	112	84
480	98	83	80	76	75	68
510	46	41	38	31	25	33
540	27	38	22	24	32	25
1350	16	17	20	46	15	25

Table I-13 $ln(C/C_0)$ for COD Removal Study for Anoxic Phase of Anoxic/Aerobic Process (Reactor 5)

Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0	0	0	0	0	0
30	-0.70763	-0.91842	-0.72887	-0.18698	-0.61780	-0.80410
60	-0.68293	-0.97871	-0.75652	-0.13242	-0.71958	-0.95825



Note: Standard error for regression = 0.270467

Figure I-5 Linear Regression for Determining Rate Constant of Anoxic Phase for COD Removal for Anoxic/Aerobic Process without Feeding Period (Reactor 5)

Table I-14 Raw COD (mg/L) Data Measurements Taken at the End of the Anoxic Phase

Phase	Date	Reactor 1 COD (mg/L)	Reactor 2 COD (mg/L)
Reactors Acclimated to Non-Colored Influent	1/9/2005	272	309
	1/10/2005	238	286
	1/11/2005	206	200
	1/12/2005	173	254
	1/13/2005	200	188
Reactors Acclimated to Colored Influent	2/12/2005	52	54
	2/13/2005	64	56
	2/14/2005	55	51
	2/15/2005	58	49
	2/16/2005	34	25

Table I-15 Matched Pair t-test Statistics for Reactor 1 vs. Reactor 2

Phase	Time	p-value
Anoxic	0	-2
	30	0.9084
	60	0.8168
	90	0.3123
	120	0.0724
	240	0.1875
Aerobic	0	0.2676
	5	0.0268
	10	0.0469
	15	0.0814
	20	0.0412
	25	0.0073
	30	0.1701
	60	0.3989
	180	0.6631
	360	0.336
	720	0.1608
	870	0.648

Note: p-value greater than 0.05 = not statistically different at 95% confidence level

Appendix J: Acclimation to Colored Influent

Table J-1 Reactor 1 Colored Influent

Date	TSS	Dis. Sol.	pH	COD	Reactive Red 198	Reactive Yellow 86	Color
(m/d/y)	(mg/L)	(mg/L)	(SU)	(mg/L)	(g/L)	(g/L)	(ADMI)
1/25/05				1054	0.03920	0.12320	6126
1/26/05	0	2287		1152	0.04880	0.14240	6835
1/27/05				1126	0.01120	0.01120	2176
1/28/05					0.01080	0.01160	1523
1/30/05			7.2	1044	0.01902	0.03345	2320
1/31/05	38	2575	7.3	964	0.01282	0.01903	2220
2/1/05				1120	0.02810	0.05372	2794
2/2/05				1536	0.02606	0.04540	3358
2/3/05				1135	0.02118	0.03964	2333
2/4/05				976	0.02184	0.04046	2455
2/12/05			7.4	1522	0.00928	0.01226	1738
2/13/05			7.7	1086	0.00796	0.01050	1403
2/14/05			7.6	1089	0.00801	0.01057	1430
2/15/05			7.6	1153	0.00975	0.01323	1750
2/16/05			7.7	1191	0.01099	0.01491	1955
2/17/05					0.01833	0.03188	2360

Table J-2 Reactor 2 Colored Influent

Date	TSS	Dis. Sol.	pH	COD	Reactive Black 5	Color
(m/d/y)	(mg/L)	(mg/L)	(SU)	(mg/L)	(g/L)	(ADMI)
1/25/05				949		
1/26/05	0	2350		1137		
1/27/05				1192	0.00640	735
1/28/05					0.01200	1212
1/30/05			7.0	1039	0.01636	1336
1/31/05	50	2612	7.3	1176	0.01237	1253
2/1/05				1137	0.02105	1735
2/2/05				1096	0.01806	1492
2/3/05				1512	0.01569	1282
2/4/05				854	0.01602	1321
2/12/05			7.4	1431	0.00849	882
2/13/05			7.7	1097	0.00952	1005
2/14/05			7.5	892	0.00869	873
2/15/05			7.6	1178	0.01111	1137
2/16/05			7.7	1138	0.01119	1159
2/17/05					0.01630	1330

Table J-3 Reactor 5 Colored Influent

Date	TSS	Dis. Sol.	pH	COD	Reactive Violet 5	Color
(m/d/y)	(mg/L)	(mg/L)	(SU)	(mg/L)	(g/L)	(ADMI)
1/25/05				1000	0.02840	1606
1/26/05					0.01960	1076
1/27/05				1138	0.01800	1890
1/28/05						
1/30/05			6.9	1029	0.03273	1332
1/31/05	25	2538	6.6	1012	0.04047	1637
2/1/05				1071	0.04044	1606
2/2/05				1080	0.04947	2131
2/3/05				947	0.04366	1720
2/4/05				813	0.04050	1639
2/12/05			7.4	1505	0.01920	1194
2/13/05			7.7	1229	0.01750	1005
2/14/05			7.5	1194	0.01734	1012
2/15/05			7.6	1147	0.01732	1024
2/16/05			7.6	1146	0.01922	1136
2/17/05					0.03435	1400

Table J-4 Reactor 1, Dye Concentration in Reactor

Date	Reactive Red 198 (g/L)			Reactive Yellow 86 (g/L)		
(m/d/y)	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic
1/25/05	0.01480	0.00560	0.00320	0.06880	0.07080	0.06480
1/26/05	0.01400	0.00440	0.00360	0.07720	0.07640	0.07600
1/28/05			0.00218			0.03250
1/30/05	0.01413	0.00298	0.00178	0.04244	0.02514	0.02296
1/31/05	0.01234	0.00254	0.00156	0.03012	0.01926	0.01810
2/1/05	0.01597	0.00227	0.00169	0.03862	0.01608	0.01638
2/2/05	0.01384	0.00280	0.00169	0.04218	0.01676	0.01545
2/3/05	0.01432	0.00277	0.00167	0.03894	0.01598	0.01475
2/4/05	0.00974	0.00269	0.00166	0.02479	0.01586	0.01432
2/12/05	0.00480	0.00157	0.00128	0.01107	0.01108	0.01114
2/13/05	0.00457	0.00156	0.00103	0.01140	0.01233	0.01124
2/14/05	0.00469	0.00160	0.00133	0.01171	0.01161	0.01199
2/15/05	0.00469	0.00188	0.00153	0.01187	0.01172	0.01245
2/16/05	0.00487	0.00321	0.00211	0.01171	0.01506	0.01406
2/17/05	0.01139	0.00256	0.00212	0.02713	0.01353	0.01380

Table J-5 Reactor 1, ADMI

Date	ADMI		
(m/d/y)	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic
1/25/05	3577	4422	4303
1/26/05	4039	4850	4935
1/28/05			2128
1/30/05	1785	1532	1438
1/31/05	1360	1171	1191
2/1/05	1637	973	1061
2/2/05	1825	978	987
2/3/05	1640	898	924
2/4/05	1216	921	909
2/12/05	803	715	747
2/13/05	711	804	849
2/14/05	727	732	781
2/15/05	722	718	783
2/16/05	716	816	848
2/17/05	1267	770	811

Table J-6 Reactor 2, Dye Concentration in Reactor

Date	Reactive Black 5 (g/L)		
(m/d/y)	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic
1/25/05	0.01560	0.00660	0.00540
1/26/05	0.01380	0.00760	0.00640
1/30/05	0.00789	0.00300	0.00252
1/31/05	0.01020	0.00327	0.00266
2/1/05	0.01175	0.00369	0.00265
2/2/05	0.01219	0.00396	0.00320
2/3/05	0.00929	0.00412	0.00280
2/4/05	0.00957	0.00349	0.00249
2/12/05	0.00523	0.00239	0.00185
2/13/05	0.00594	0.00321	0.00248
2/14/05	0.00606	0.00332	0.00296
2/15/05	0.00593	0.00350	0.00278
2/16/05	0.00597	0.00360	0.00265
2/17/05	0.00961	0.00328	0.00268

Table J-7 Reactor 2, ADMI

Date	ADMI		
(m/d/y)	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic
1/25/05	1253	695	653
1/26/05	1248	807	735
1/30/05	651	333	399
1/31/05	851	348	377
2/1/05	1028	419	383
2/2/05	1013	398	431
2/3/05	764	383	398
2/4/05	825	360	397
2/12/05	498	261	300
2/13/05	589	291	246
2/14/05	590	316	338
2/15/05	582	338	345
2/16/05	574	405	377
2/17/05	784	328	414

Table J-8 Reactor 5, Dye Concentration in Reactor

Date	Reactive Violet 5 (g/L)		
(m/d/y)	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic
1/28/05			0.00182
1/30/05	0.03256	0.00533	0.00345
1/31/05	0.03145	0.00421	0.00396
2/1/05	0.02768	0.00609	0.00407
2/2/05	0.03671	0.00804	0.00575
2/3/05	0.03626	0.00829	0.00591
2/4/05	0.02887	0.00721	0.00648
2/12/05	0.00772	0.00326	0.00292
2/13/05	0.00917	0.00503	0.00414
2/14/05	0.01001	0.00549	0.00494
2/15/05	0.00989	0.00587	0.00501
2/16/05	0.01054	0.00768	0.00531
2/17/05	0.02657	0.00726	0.00596

Table J-9 Reactor 5, ADMI

Date	ADMI		
(m/d/y)	Beginning of Anoxic	End of Anoxic / Beginning of Aerobic	End of Aerobic
1/30/05	1347	269	218
1/31/05	1365	266	236
2/1/05	1141	330	252
2/2/05	1509	419	309
2/3/05	1538	417	330
2/4/05	1213	416	326
2/12/05	493	219	132
2/13/05	497	276	184
2/14/05	561	310	255
2/15/05	529	324	251
2/16/05	585	439	294
2/17/05	536	437	341

Appendix K: Kinetics of Removal of Reactive Red 198 for Aerobic Control (Reactor 7)

Table K-1 Reactive Red 198, Raw Concentration (g/L) Data for Aerobic Control (Reactor 7)

Cycle	Beginning of Aerobic	End of Aerobic
1	0.00409	0.00290
2	0.00449	0.00306
3	0.00514	0.00369
4	0.00603	0.00476
5	0.00702	0.00539
6	0.00730	0.00637
7	0.00779	0.00528
8	0.00724	0.00638

Table K-2 Reactive Red 198, Normalized Data (C/C_0) for Effluent from Aerobic Control (Reactor 7)

Cycle	C/Co for End of Aerobic
1	0.70857
2	0.68154
3	0.71821
4	0.79002
5	0.76818
6	0.87361
7	0.67807
8	0.88134

Appendix L: Kinetics of Removal of Reactive Red 198 for Anoxic/Aerobic Process (Reactor 1)

Table L-1 Reactive Red 198, Raw Concentration (g/L) Data from Color Removal Study for Anoxic/Aerobic Process (Reactor 1)

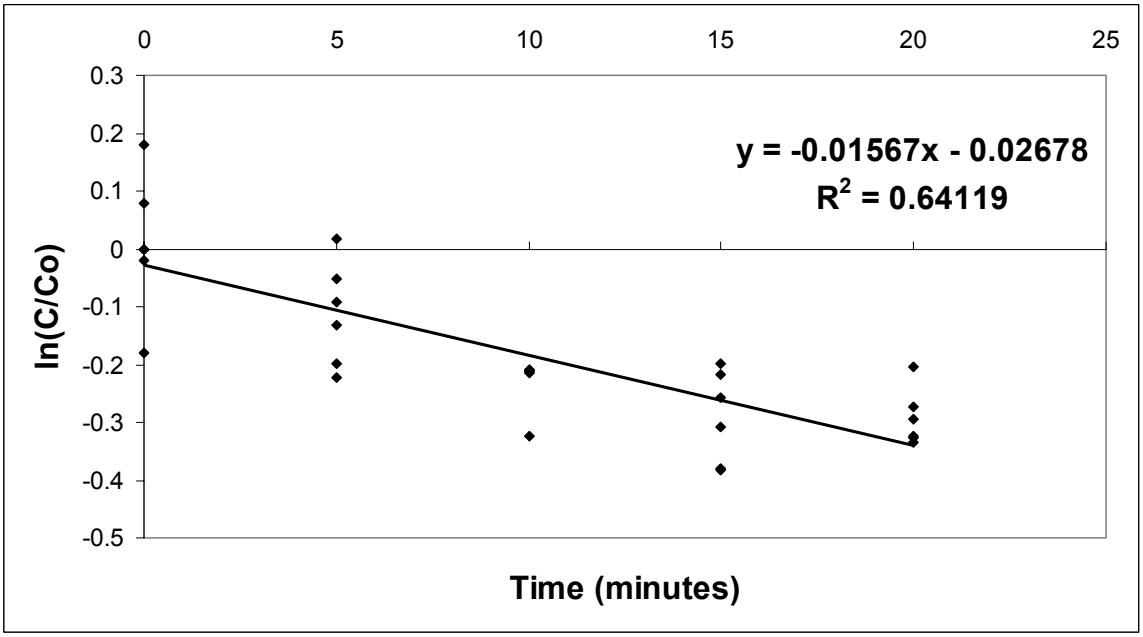
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0.01413	0.01234	0.01597	0.01384	0.01432	0.00974
5	0.01239	0.01031	0.01267	0.01263	0.01058	0.01186
10	0.01142	0.01020	0.01075	0.01002	0.01074	0.00944
15	0.00967	0.01033	0.00909	0.01017	0.01062	0.00902
20	0.01074	0.01026	0.00962	0.01031	0.00957	0.00834
25	0.00945	0.00815	0.00851	0.00880	0.00949	0.00790
30	0.01068	0.00838	0.00883	0.00937	0.00957	0.00826
60	0.00912	0.00711	0.00745	0.00794	0.00726	0.00660
120	0.00629	0.00569	0.00539	0.00619	0.00613	0.00525
240	0.00472	0.00385	0.00429	0.00435	0.00446	0.00360
480	0.00298	0.00254	0.00227	0.00280	0.00277	0.00269
510	0.00214	0.00188	0.00195	0.00210	0.00197	0.00196
540	0.00178	0.00188	0.00171	0.00182	0.00185	0.00178
600	0.00170	0.00171	0.00167	0.00184	0.00185	0.00194
720	0.00178	0.00165	0.00181	0.00171	0.00176	0.00168
960	0.00182	0.00172	0.00168	0.00173	0.00170	0.00170
1350	0.00178	0.00156	0.00169	0.00169	0.00167	0.00166

Table L-2 Reactive Red 198, $ln(C/C_0)$ for Color Removal Study for Anoxic/Aerobic Process (Reactor 1)

Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0	0	0	0	0	0
5	-0.13146	-0.17983	-0.23153	-0.09166	-0.30286	0.19686
10	-0.21306	-0.19040	-0.39593	-0.32277	-0.28809	-0.03139
15	-0.37916	-0.17751	-0.56375	-0.30807	-0.29845	-0.07613
20	-0.27438	-0.18446	-0.50714	-0.29476	-0.40345	-0.15506
25	-0.40232	-0.41503	-0.62902	-0.45237	-0.41146	-0.20918
30	-0.27986	-0.38687	-0.59284	-0.38972	-0.40316	-0.16475
60	-0.43781	-0.55142	-0.76195	-0.55550	-0.67980	-0.38834
120	-0.80922	-0.77411	-1.08589	-0.80451	-0.84780	-0.61800
240	-1.09738	-1.16378	-1.31541	-1.15707	-1.16600	-0.99607
480	-1.55781	-1.57875	-1.95025	-1.59923	-1.64191	-1.28658
510	-1.88734	-1.87973	-2.10028	-1.88631	-1.98168	-1.60408
540	-2.07031	-1.88146	-2.23521	-2.02921	-2.04413	-1.70159
600	-2.11597	-1.97522	-2.25658	-2.01791	-2.04684	-1.61219
720	-2.07075	-2.01321	-2.17478	-2.09112	-2.09659	-1.75883
960	-2.04950	-1.96815	-2.24946	-2.07709	-2.13114	-1.74612
1350	-2.07338	-2.06945	-2.24846	-2.10442	-2.14777	-1.76901

Table L-3 Reactive Red 198, Adjusted $ln(C/C_0)$ for Color Removal Study for Anoxic Phase of Anoxic/Aerobic Process (Reactor 1)

Time	(Cycle 1) +0	(Cycle 2) -0.02	(Cycle 3) +0.18	(Cycle 4) +0	(Cycle 5) +0.08	(Cycle 6) -0.18
0	0	-0.02000	0.18000	0	0.08000	-0.18000
5	-0.13146	-0.19983	-0.05153	-0.09166	-0.22286	0.01686
10	-0.21306	-0.21040	-0.21593	-0.32277	-0.20809	-0.21139
15	-0.37916	-0.19751	-0.38375	-0.30807	-0.21845	-0.25613
20	-0.27438	-0.20446	-0.32714	-0.29476	-0.32345	-0.33506
Cumulative Error	0	0.34259	0.32016	0.24097	0.38614	0.51370

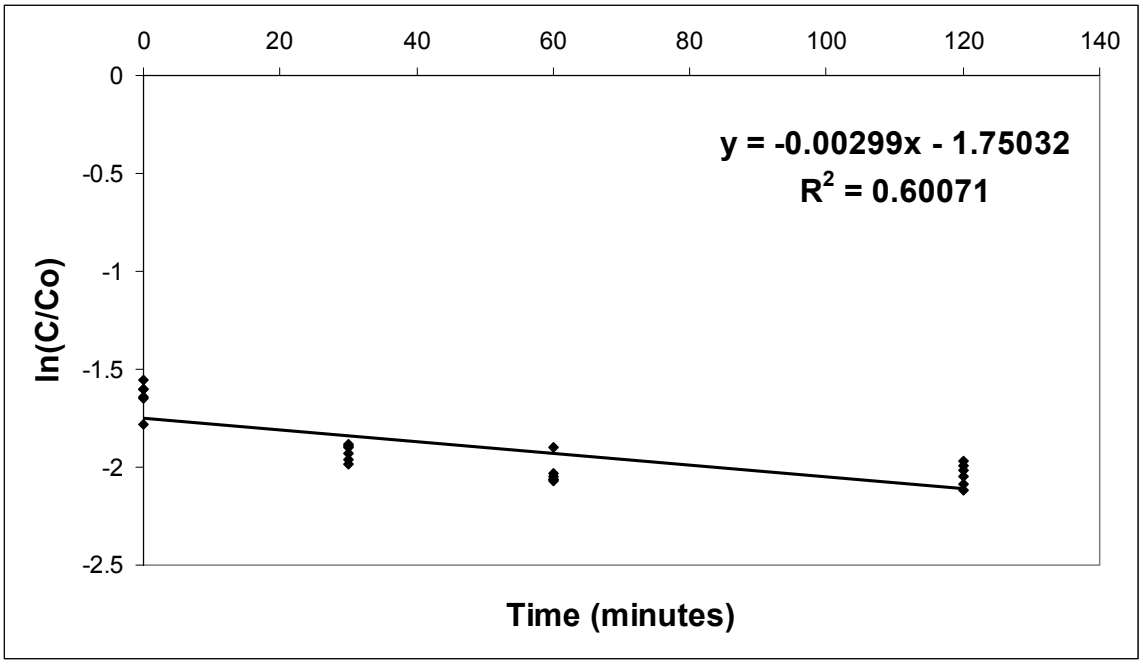


Note: standard error for regression = 0.085799

Figure L-1 Reactive Red 198, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 1)

Table L-4 Reactive Red 198, Adjusted *ln(C/C$_0$)* for Color Removal Study for Aerobic Phase of Anoxic/Aerobic Process (Reactor 1)

Time	(Cycle 1) +0	(Cycle 2) -0.02	(Cycle 3) +0.17	(Cycle 4) +0	(Cycle 5) +0	(Cycle 6) -0.36
0	-1.55781	-1.59875	-1.78025	-1.59923	-1.64191	-1.64658
30	-1.88734	-1.89973	-1.93028	-1.88631	-1.98168	-1.96408
60	-2.07031	-1.90146	-2.06521	-2.02921	-2.04413	-2.06159
120	-2.11597	-1.99522	-2.08658	-2.01791	-2.04684	-1.97219
Cumulative Error	0	0.34294	0.29988	0.18162	0.27375	0.31801



Note: standard error for regression = 0.113137

Figure L-2 Reactive Red 198, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 1)

Appendix M: Kinetics of Removal of Reactive Yellow 86 for Aerobic Control (Reactor 7)

Table M-1 Reactive Yellow 86, Raw Concentration (g/L) Data for Aerobic Control (Reactor 7)

Cycle	Beginning of Aerobic	End of Aerobic
1	0.00940	0.00970
2	0.00953	0.00944
3	0.01011	0.01007
4	0.01113	0.01144
5	0.01222	0.01270
6	0.01250	0.01364
7	0.01297	0.01384
8	0.01307	0.01396

Table M-2 Reactive Yellow 86, Normalized Data (C/C_0) for Effluent from Aerobic Control (Reactor 7)

Cycle	C/Co for End of Aerobic
1	1.03213
2	0.99056
3	0.99629
4	1.02778
5	1.03970
6	1.09111
7	1.06729
8	1.06821

Appendix N: Kinetics of Removal of Reactive Yellow 86 for Anoxic/Aerobic Process (Reactor 1)

Table N-1 Reactive Yellow 86, Raw Concentration (g/L) Data from Color Removal Study for Anoxic/Aerobic Process (Reactor 1)

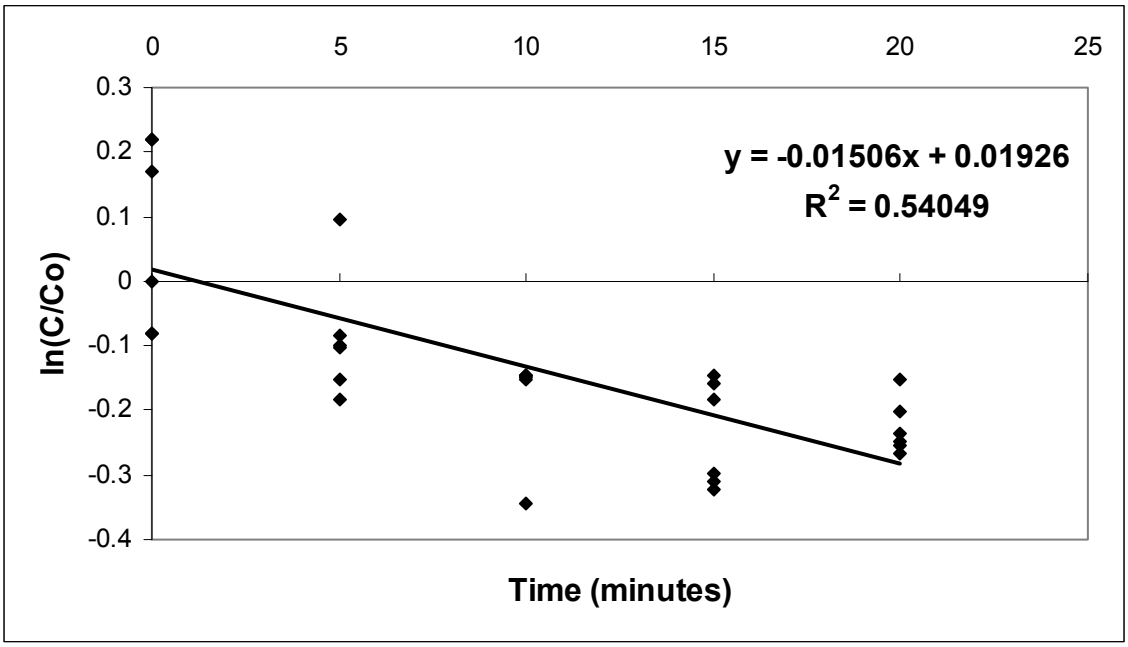
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0.04244	0.03012	0.03862	0.04218	0.03894	0.02479
5	0.03836	0.02802	0.02998	0.03057	0.02606	0.02952
10	0.03653	0.02804	0.02819	0.02396	0.02703	0.02318
15	0.03116	0.02785	0.02364	0.02510	0.02698	0.02235
20	0.03464	0.02802	0.02576	0.02588	0.02422	0.02094
25	0.03145	0.02410	0.02274	0.02115	0.02457	0.01996
30	0.03527	0.02503	0.02405	0.02370	0.02497	0.02119
60	0.03335	0.02320	0.02179	0.02168	0.02034	0.01849
120	0.02775	0.02266	0.01886	0.02017	0.01988	0.01794
240	0.02750	0.02050	0.01872	0.01853	0.01821	0.01600
480	0.02514	0.01926	0.01608	0.01676	0.01598	0.01586
510	0.02261	0.01800	0.01566	0.01514	0.01398	0.01429
540	0.02190	0.01812	0.01530	0.01431	0.01371	0.01380
600	0.02209	0.01740	0.01497	0.01464	0.01368	0.01414
720	0.02193	0.01774	0.01595	0.01476	0.01413	0.01358
960	0.02255	0.01830	0.01602	0.01518	0.01437	0.01366
1350	0.02296	0.01810	0.01638	0.01545	0.01475	0.01432

Table N-2 Reactive Yellow 86, $ln(C/C_0)$ for Color Removal Study for Anoxic/Aerobic Process (Reactor 1)

Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0	0	0	0	0	0
5	-0.10093	-0.07230	-0.25331	-0.32193	-0.40164	0.17480
10	-0.14974	-0.07178	-0.31483	-0.56542	-0.36502	-0.06707
15	-0.30894	-0.07846	-0.49113	-0.51921	-0.36685	-0.10345
20	-0.20301	-0.07223	-0.40512	-0.48834	-0.47463	-0.16881
25	-0.29955	-0.22297	-0.52953	-0.69024	-0.46045	-0.21672
30	-0.18511	-0.18535	-0.47382	-0.57652	-0.44407	-0.15668
60	-0.24087	-0.26134	-0.57229	-0.66534	-0.64938	-0.29339
120	-0.42475	-0.28456	-0.71694	-0.73773	-0.67222	-0.32340
240	-0.43371	-0.38485	-0.72431	-0.82262	-0.75983	-0.43769
480	-0.52367	-0.44731	-0.87653	-0.92315	-0.89032	-0.44667
510	-0.62968	-0.51497	-0.90258	-1.02454	-1.02417	-0.55088
540	-0.66173	-0.50850	-0.92579	-1.08088	-1.04389	-0.58602
600	-0.65269	-0.54862	-0.94809	-1.05807	-1.04586	-0.56136
720	-0.66012	-0.52927	-0.88465	-1.04969	-1.01333	-0.60197
960	-0.63212	-0.49848	-0.88003	-1.02184	-0.99691	-0.59584
1350	-0.61413	-0.50964	-0.85781	-1.00429	-0.97051	-0.54850

Table N-3 Reactive Yellow 86, Adjusted $ln(C/C_0)$ for Color Removal Study for Anoxic Phase of Anoxic/Aerobic Process (Reactor 1)

Time	(Cycle 1) +0	(Cycle 2) -0.08	(Cycle 3) +0.17	(Cycle 4) +0.22	(Cycle 5) +0.22	(Cycle 6) -0.08
0	0	-0.08000	0.17000	0.22000	0.22000	-0.08000
5	-0.10093	-0.15230	-0.08331	-0.10193	-0.18164	0.09480
10	-0.14974	-0.15178	-0.14483	-0.34542	-0.14502	-0.14707
15	-0.30894	-0.15846	-0.32113	-0.29921	-0.14685	-0.18345
20	-0.20301	-0.15223	-0.23512	-0.26834	-0.25463	-0.24881
Cumulative Error	0	0.33467	0.23683	0.49174	0.51914	0.44968

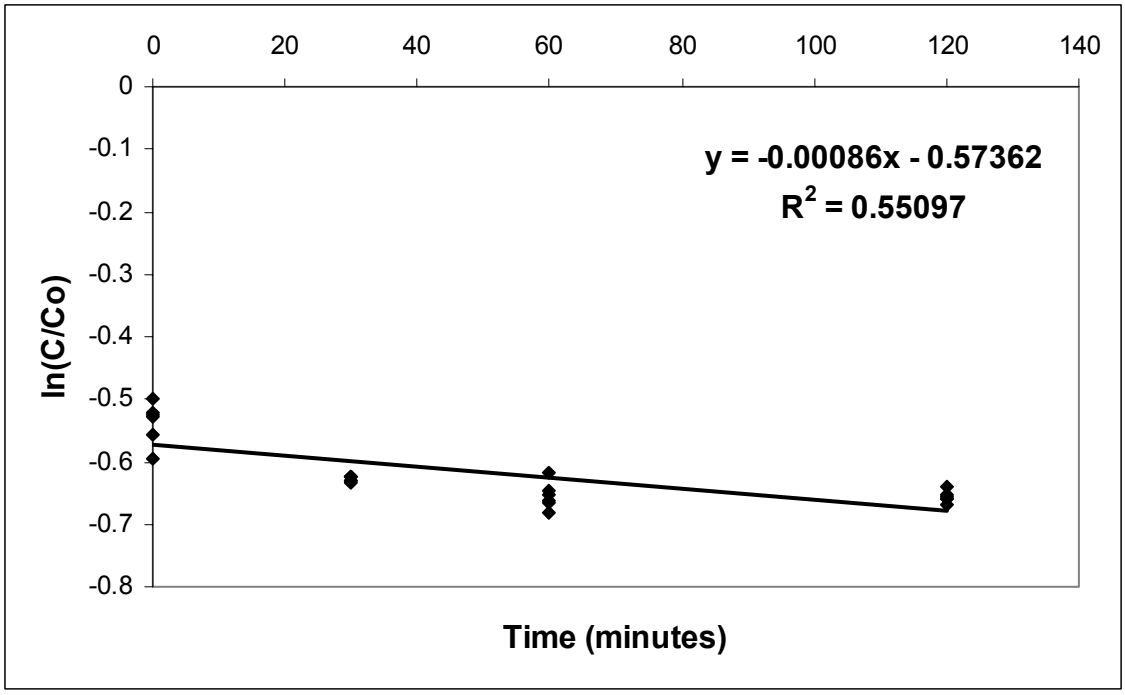


Note: standard error for regression = 0.1016129

Figure N-1 Reactive Yellow 86, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 1)

Table N-4 Reactive Yellow 86, Adjusted *ln(C/C$_0$)* for Color Removal Study for Aerobic Phase of Anoxic/Aerobic Process (Reactor 1)

Time	(Cycle 1) +0	(Cycle 2) -0.11	(Cycle 3) +0.28	(Cycle 4) +0.4	(Cycle 5) +0.39	(Cycle 6) -0.08
0	-0.52367	-0.55731	-0.59653	-0.52315	-0.50032	-0.52667
30	-0.62968	-0.62497	-0.62258	-0.62454	-0.63417	-0.63088
60	-0.66173	-0.61850	-0.64579	-0.68088	-0.65389	-0.66602
120	-0.65269	-0.65862	-0.66809	-0.65807	-0.65586	-0.64136
Cumulative Error	0	0.08749	0.11130	0.03021	0.03885	0.01982



Note: standard error for regression = 0.03616

Figure N-2 Reactive Yellow 86, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 1)

Appendix O: Kinetics of Removal of Reactive Black 5 for Aerobic Control (Reactor 8)

Table O-1 Reactive Black 5, Raw Concentration (g/L) Data for Aerobic Control (Reactor 8)

Cycle	Beginning of Aerobic	End of Aerobic
1	0.00469	0.00389
2	0.00611	0.00528
3	0.00640	0.00571
4	0.00770	0.00679
5	0.00833	0.00675
6	0.00827	0.00736
7	0.00858	0.00709
8	0.00844	0.00735

Table O-2 Reactive Black 5, Normalized Data (C/C_0) for Effluent from Aerobic Control (Reactor 8)

Cycle	C/Co for End of Aerobic
1	0.82920
2	0.86446
3	0.89148
4	0.88160
5	0.80983
6	0.88964
7	0.82604
8	0.87031

Appendix P: Kinetics of Removal of Reactive Black 5 for Anoxic/Aerobic Process (Reactor 2)

Table P-1 Reactive Black 5, Raw Concentration (g/L) Data from Color Removal Study for Anoxic/Aerobic Process (Reactor 2)

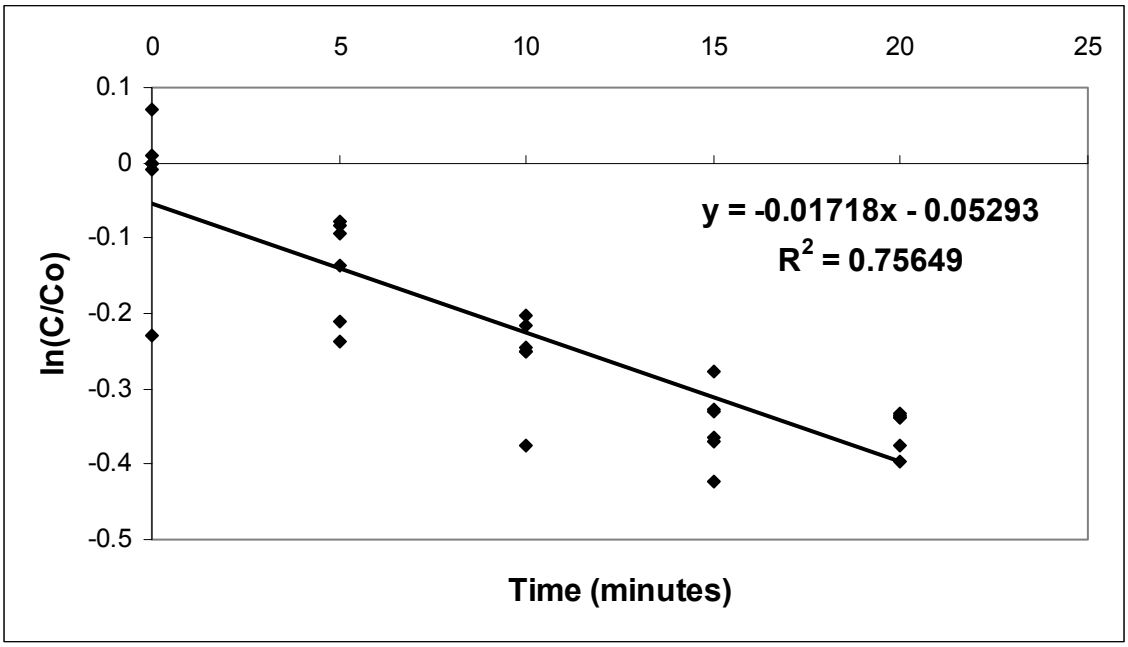
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0.00789	0.01020	0.01175	0.01219	0.00929	0.00957
5	0.00730	0.00770	0.01035	0.01097	0.00921	0.00881
10	0.00614	0.00654	0.00930	0.00938	0.00942	0.00782
15	0.00518	0.00657	0.00901	0.00869	0.00841	0.00665
20	0.00564	0.00679	0.00851	0.00830	0.00834	0.00644
25	0.00433	0.00587	0.00785	0.00821	0.00801	0.00577
30	0.00416	0.00592	0.00780	0.00800	0.00802	0.00585
60	0.00433	0.00450	0.00607	0.00657	0.00651	0.00457
120	0.00391	0.00390	0.00520	0.00503	0.00520	0.00375
240	0.00336	0.00369	0.00420	0.00475	0.00463	0.00379
480	0.00300	0.00327	0.00369	0.00396	0.00412	0.00349
510	0.00261	0.00344	0.00322	0.00338	0.00322	0.00288
540	0.00243	0.00288	0.00319	0.00326	0.00299	0.00280
600	0.00241	0.00262	0.00297	0.00328	0.00303	0.00262
720	0.00304	0.00221	0.00285	0.00326	0.00294	0.00261
960	0.00272	0.00244	0.00284	0.00304	0.00288	0.00242
1350	0.00252	0.00266	0.00265	0.00320	0.00280	0.00249

Table P-2 Reactive Black 5, $ln(C/C_0)$ for Color Removal Study for Anoxic/Aerobic Process (Reactor 2)

Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0	0	0	0	0	0
5	-0.07727	-0.28072	-0.12668	-0.10493	-0.00815	-0.08321
10	-0.25064	-0.44480	-0.23381	-0.26165	0.01417	-0.20213
15	-0.42177	-0.44040	-0.26591	-0.33803	-0.09881	-0.36378
20	-0.33672	-0.40681	-0.32232	-0.38406	-0.10722	-0.39559
25	-0.60084	-0.55190	-0.40411	-0.39570	-0.14812	-0.50630
30	-0.63970	-0.54438	-0.40947	-0.42074	-0.14696	-0.49180
60	-0.59941	-0.81883	-0.66007	-0.61789	-0.35491	-0.73942
120	-0.70226	-0.96097	-0.81626	-0.88520	-0.57921	-0.93833
240	-0.85462	-1.01758	-1.02977	-0.94239	-0.69570	-0.92669
480	-0.96599	-1.13729	-1.15891	-1.12398	-0.81315	-1.01015
510	-1.10608	-1.08775	-1.29335	-1.28211	-1.05789	-1.20067
540	-1.17964	-1.26635	-1.30356	-1.31872	-1.13187	-1.22797
600	-1.18553	-1.35941	-1.37509	-1.31309	-1.11916	-1.29428
720	-0.95284	-1.53059	-1.41526	-1.31985	-1.15007	-1.30044
960	-1.06373	-1.43175	-1.42136	-1.38934	-1.17071	-1.37540
1350	-1.13986	-1.34322	-1.48788	-1.33788	-1.19873	-1.34673

Table P-3 Reactive Black 5, Adjusted $ln(C/C_0)$ for Color Removal Study for Anoxic Phase of Anoxic/Aerobic Process (Reactor 2)

Time	(Cycle 1) +0	(Cycle 2) +0.07	(Cycle 3) -0.10	(Cycle 4) +0.01	(Cycle 5) -0.23	(Cycle 6) +0
0	0	0.07000	-0.01000	0.01000	-0.23000	0
5	-0.07727	-0.21072	-0.13668	-0.09493	-0.23815	-0.08321
10	-0.25064	-0.37480	-0.24381	-0.25165	-0.21583	-0.20213
15	-0.42177	-0.37040	-0.27591	-0.32803	-0.32881	-0.36378
20	-0.33672	-0.33681	-0.33232	-0.37406	-0.33722	-0.39559
Cumulative Error	0	0.37906	0.22653	0.15974	0.51915	0.17131

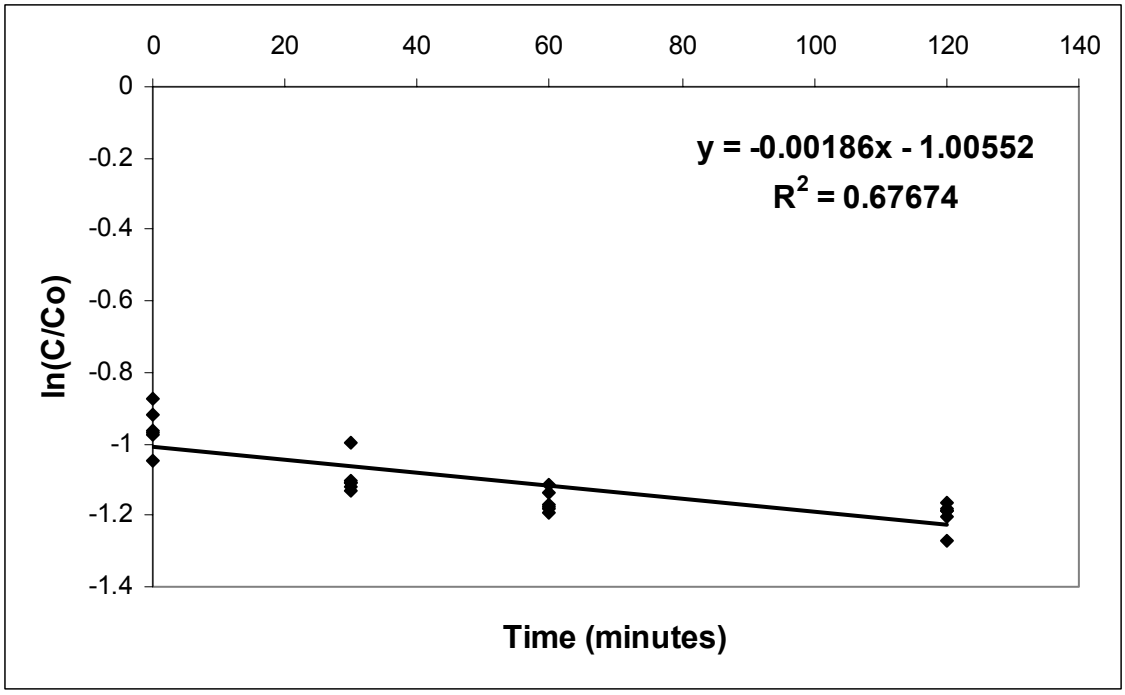


Note: standard error for regression = 0.07133

Figure P-1 Reactive Black 5, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 2)

Table P-4 Reactive Black 5, Adjusted *ln(C/C$_0$)* for Color Removal Study for Aerobic Phase of Anoxic/Aerobic Process (Reactor 2)

Time	(Cycle 1) +0	(Cycle 2) +0.09	(Cycle 3) +0.19	(Cycle 4) +0.15	(Cycle 5) -0.06	(Cycle 6) +0.09
0	-0.96599	-1.04729	-0.96891	-0.97398	-0.87315	-0.92015
30	-1.10608	-0.99775	-1.10335	-1.13211	-1.11789	-1.11067
60	-1.17964	-1.17635	-1.11356	-1.16872	-1.19187	-1.13797
120	-1.18553	-1.26941	-1.18509	-1.16309	-1.17916	-1.20428
Cumulative Error	0	0.27680	0.07216	0.06737	0.12325	0.11084



Note: standard error for regression = 0.05947

Figure P-2 Reactive Black 5, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 2)

Appendix Q: Kinetics of Removal of Reactive Violet 5 for Aerobic Control (Reactor 9)

Table Q-1 Reactive Violet 5, Raw Concentration (g/L) Data for Aerobic Control (Reactor 9)

Cycle	Beginning of Aerobic	End of Aerobic
1	0.00825	0.00585
2	0.01033	0.00792
3	0.01184	0.00984
4	0.01276	0.01120
5	0.01382	0.01146
6	0.01479	0.01270
7	0.01541	0.01161
8	0.01486	0.01280

Table Q-2 Reactive Violet 5, Normalized Data (C/C_0) for Effluent from Aerobic Control (Reactor 9)

Cycle	C/Co for End of Aerobic
1	0.70909
2	0.76676
3	0.83115
4	0.87730
5	0.82955
6	0.85873
7	0.75339
8	0.86113

Appendix R: Kinetics of Removal of Reactive Violet 5 for Anoxic/Aerobic Process (Reactor 5)

Table R-1 Reactive Violet 5, Raw Concentration (g/L) Data from Color Removal Study for Anoxic/Aerobic Process (Reactor 5)

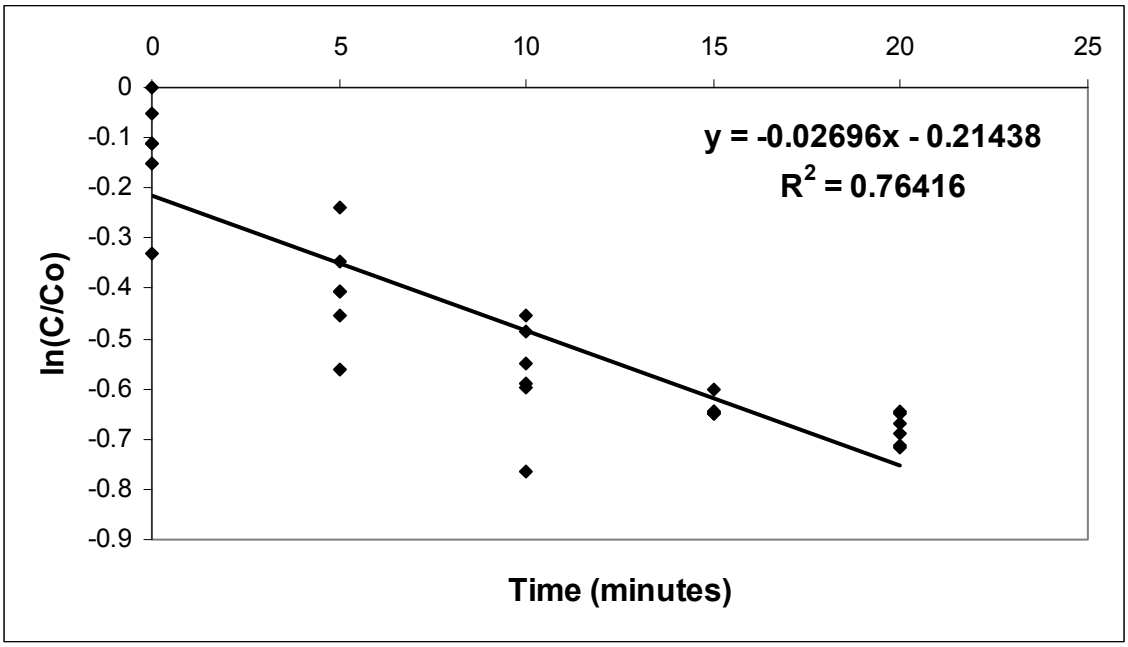
Time (min.)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0.03256	0.03145	0.02768	0.03671	0.03626	0.02887
5	0.01861	0.02478	0.02447	0.02569	0.02810	0.02541
10	0.01790	0.02160	0.02447	0.01794	0.02339	0.01863
15	0.01702	0.01832	0.02008	0.02115	0.02213	0.01690
20	0.01699	0.01765	0.01974	0.02023	0.02060	0.01581
25	0.01518	0.01619	0.01802	0.02094	0.01836	0.01569
30	0.01612	0.01639	0.01907	0.01977	0.01972	0.01547
60	0.01523	0.01409	0.01467	0.01880	0.01513	0.01474
120	0.01175	0.01184	0.01209	0.01442	0.01178	0.01145
240	0.00818	0.00910	0.00887	0.01060	0.01126	0.00986
480	0.00533	0.00421	0.00609	0.00804	0.00829	0.00721
510	0.00375	0.00329	0.00432	0.00638	0.00632	0.00651
540	0.00269	0.00350	0.00399	0.00550	0.00568	0.00567
600	0.00347	0.00323	0.00354	0.00515	0.00535	0.00560
720	0.00735	0.00404	0.00402	0.00639	0.00530	0.00590
960	0.00498	0.00406	0.00408	0.00565	0.00610	0.00561
1350	0.00345	0.00396	0.00407	0.00575	0.00591	0.00648

Table R-2 Reactive Violet 5, $ln(C/C_0)$ for Color Removal Study for Anoxic/Aerobic Process (Reactor 5)

Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	0	0	0	0	0	0
5	-0.55953	-0.23814	-0.12330	-0.35715	-0.25490	-0.12749
10	-0.59814	-0.37578	-0.12310	-0.71579	-0.43872	-0.43780
15	-0.64879	-0.54056	-0.32086	-0.55130	-0.49383	-0.53525
20	-0.65045	-0.57740	-0.33798	-0.59582	-0.56537	-0.60198
25	-0.76291	-0.66416	-0.42935	-0.56155	-0.68091	-0.60965
30	-0.70324	-0.65197	-0.37240	-0.61901	-0.60909	-0.62370
60	-0.75993	-0.80297	-0.63453	-0.66919	-0.87404	-0.67214
120	-1.01901	-0.97724	-0.82852	-0.93415	-1.12438	-0.92458
240	-1.38082	-1.24027	-1.13775	-1.24210	-1.16949	-1.07432
480	-1.80936	-2.01051	-1.51320	-1.51864	-1.47566	-1.38715
510	-2.16154	-2.25691	-1.85769	-1.74932	-1.74755	-1.48984
540	-2.49237	-2.19541	-1.93777	-1.89865	-1.85327	-1.62730
600	-2.23768	-2.27466	-2.05667	-1.96371	-1.91310	-1.63952
720	-1.48773	-2.05097	-1.93005	-1.74871	-1.92332	-1.58802
960	-1.87727	-2.04720	-1.91536	-1.87150	-1.78309	-1.63794
1350	-2.24342	-2.07127	-1.91659	-1.85443	-1.81420	-1.49455

Table R-3 Reactive Violet 5, Adjusted $ln(C/C_0)$ for Color Removal Study for Anoxic Phase of Anoxic/Aerobic Process (Reactor 5)

Time	(Cycle 1) +0	(Cycle 2) -0.11	(Cycle 3) -0.33	(Cycle 4) -0.05	(Cycle 5) -0.15	(Cycle 6) -0.11
0	0	-0.11000	-0.33000	-0.05000	-0.15000	-0.11000
5	-0.55953	-0.34814	-0.45330	-0.40715	-0.40490	-0.23749
10	-0.59814	-0.48578	-0.45310	-0.76579	-0.58872	-0.54780
15	-0.64879	-0.65056	-0.65086	-0.60130	-0.64383	-0.64525
20	-0.65045	-0.68740	-0.66798	-0.64582	-0.71537	-0.71198
Cumulative Error	0	0.47248	0.60088	0.42215	0.38393	0.54745

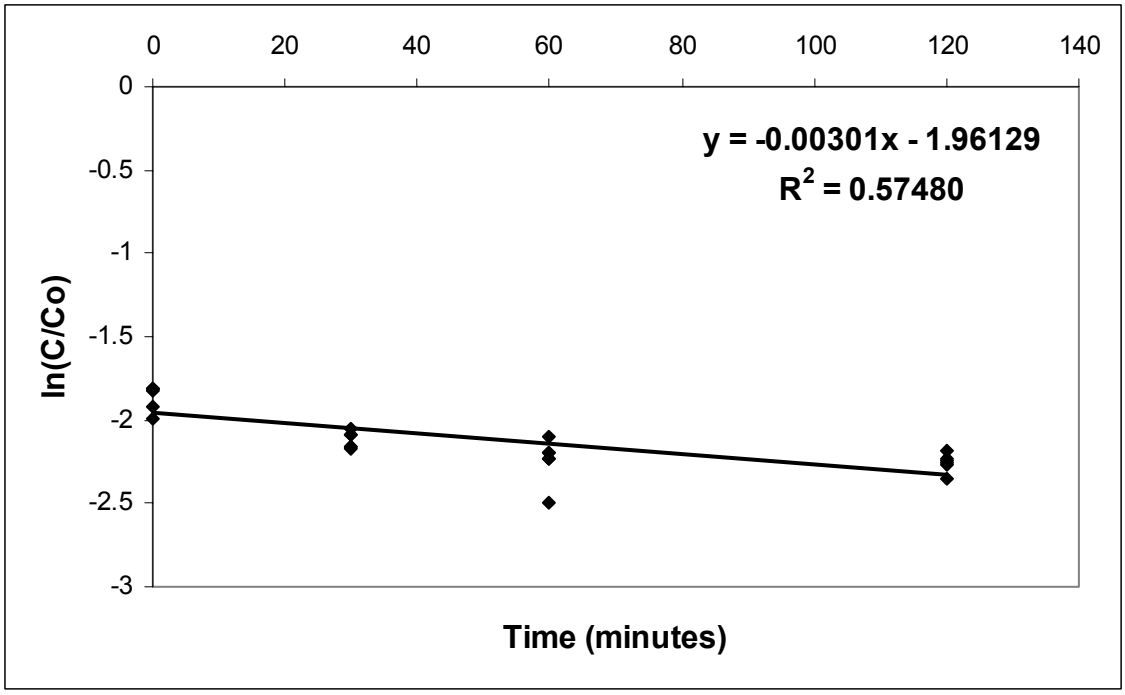


Note: standard error for regression = 0.10962

Figure R-1 Reactive Violet 5, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 5)

Table R-4 Reactive Violet 5, Adjusted *ln(C/C$_0$)* for Color Removal Study for Aerobic Phase of Anoxic/Aerobic Process (Reactor 5)

Time	(Cycle 1) +0	(Cycle 2) +0.09	(Cycle 3) -0.30	(Cycle 4) -0.30	(Cycle 5) -0.34	(Cycle 6) -0.60
0	-1.80936	-1.92051	-1.81320	-1.81864	-1.81566	-1.98715
30	-2.16154	-2.16691	-2.15769	-2.04932	-2.08755	-2.08984
60	-2.49237	-2.10541	-2.23777	-2.19865	-2.19327	-2.22730
120	-2.23768	-2.18466	-2.35667	-2.26371	-2.25310	-2.23952
Cumulative Error	0	0.55649	0.38128	0.44125	0.39481	0.51640



Note: standard error for regression = 0.12010

Figure R-2 Reactive Violet 5, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for Color Removal for Anoxic/Aerobic Process (Reactor 5)

Appendix S: Kinetics of Removal of ADMI due to Reactive Red 198 and Reactive Yellow 86 for Aerobic Control (Reactor 7)

Table S-1 Reactor 7, Raw ADMI Data

Cycle	Beginning of Aerobic	End of Aerobic
1	687	564
2	699	522
3	784	585
4	1018	792
5	1176	918
6	1287	1118
7	1387	939
8	1297	1117

Appendix T: Kinetics of Removal of ADMI due to Reactive Red 198 and Reactive Yellow 86 for Anoxic/Aerobic Process (Reactor 1)

Table T-1 Reactor 1, Raw ADMI Data

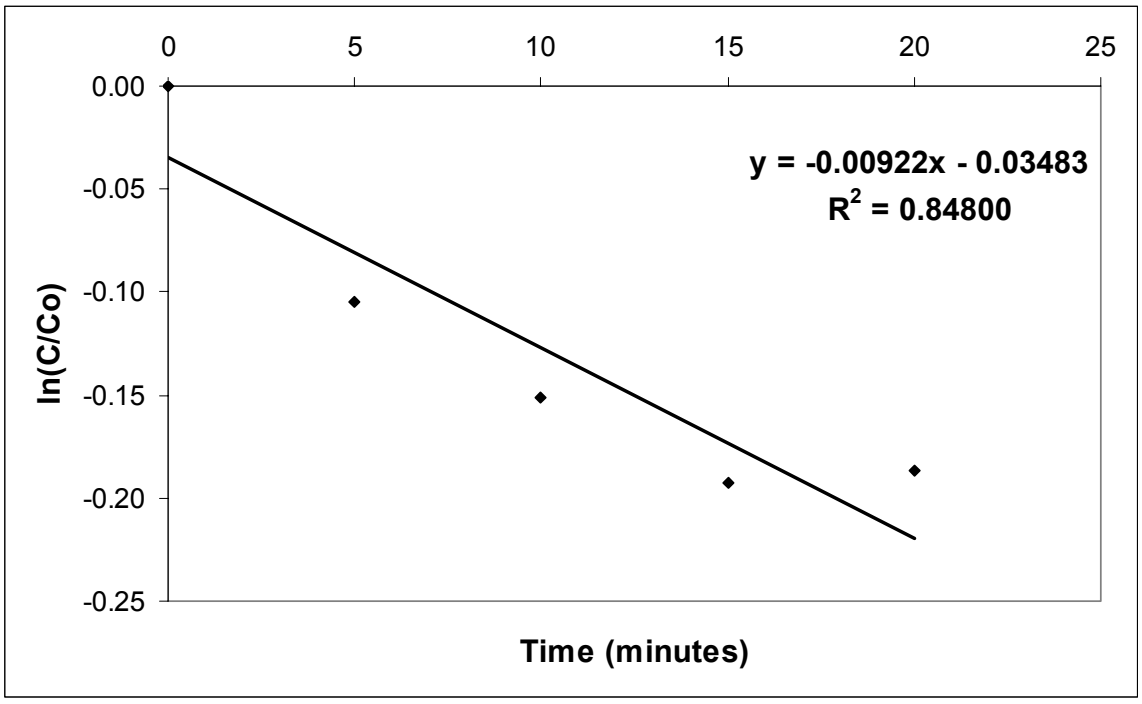
Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	1785	1360	1637	1825	1640	1216
5	1668	1288	1353	1436	1232	1333
10	1610	1272	1291	1220	1276	1161
15	1413	1232	1135	1240	1260	1152
20	1524	1243	1185	1288	1162	1085
25	1418	1134	1069	1066	1139	1028
30	1555	1151	1111	1154	1155	1057
60	1527	1087	1025	1059	1034	924
120	1373	1117	917	958	925	879
240	1511	1108	966	949	898	836
480	1532	1171	973	978	898	921
510	1464	1151	986	933	857	878
540	1455	1156	983	904	831	869
600	1483	1130	974	927	847	870
720	1399	1158	1023	953	877	862
960	1402	1196	1028	972	907	857
1350	1438	1191	1061	987	924	909

Table T-2 Reactor 1, Adjusted ADMI Data

Adjustment	0	312	377	430	494	537
Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	1785	1672	2014	2255	2134	1753
5	1668	1600	1730	1866	1726	1870
10	1610	1584	1668	1650	1770	1698
15	1413	1544	1512	1670	1754	1689
20	1524	1555	1562	1718	1656	1622
25	1418	1446	1446	1496	1633	1565
30	1555	1463	1488	1584	1649	1594
60	1527	1399	1402	1489	1528	1461
120	1373	1429	1294	1388	1419	1416
240	1511	1420	1343	1379	1392	1373
480	1532	1483	1350	1408	1392	1458
510	1464	1463	1363	1363	1351	1415
540	1455	1468	1360	1334	1325	1406
600	1483	1442	1351	1357	1341	1407
720	1399	1470	1400	1383	1371	1399
960	1402	1508	1405	1402	1401	1394
1350	1438	1503	1438	1417	1418	1446

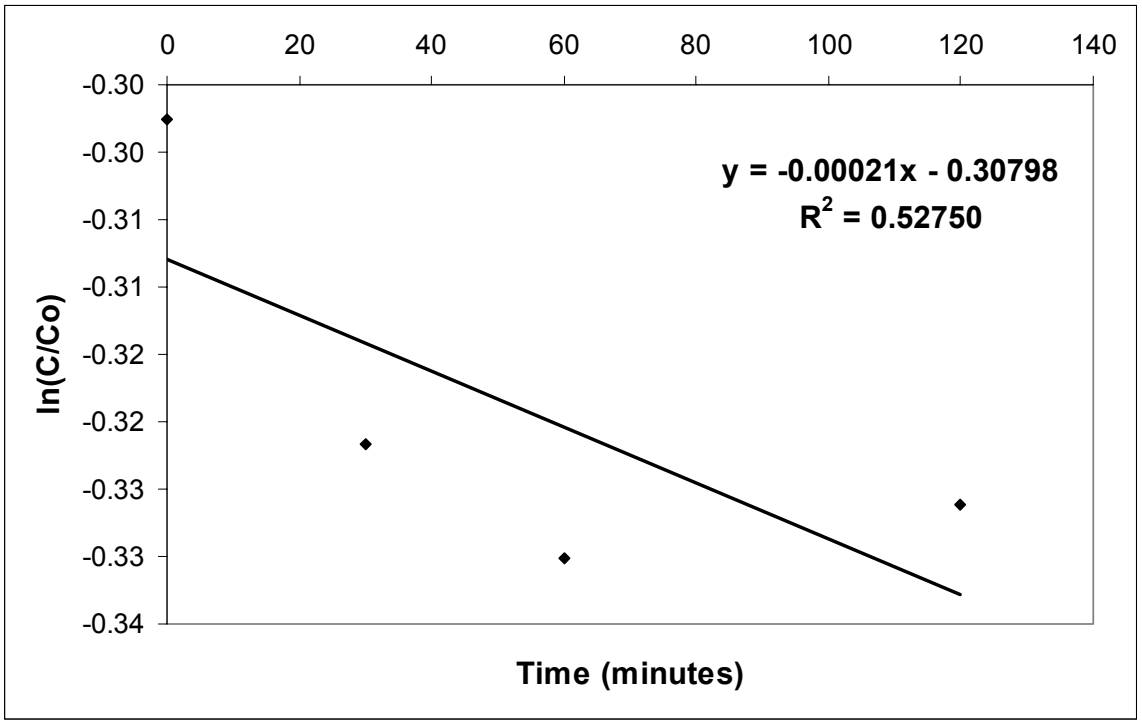
Table T-3 Reactor 1, *ln(Average C/C$_0$)* for Adjusted ADMl Data

Time	ln (Avg C/Co)
0	0
5	-0.10461
10	-0.15150
15	-0.19233
20	-0.18658
25	-0.25457
30	-0.21853
60	-0.27665
120	-0.33364
240	-0.32176
480	-0.29757
510	-0.32161
540	-0.33008
600	-0.32612
720	-0.32137
960	-0.31057
1350	-0.29351



Note: Standard error for regression = 0.053519

Figure T-1 Reactor 1, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for ADMl Removal for Anoxic/Aerobic Process



Note: Standard error for regression = 0.012292

Figure T-2 Reactor 1, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for ADMI Removal for Anoxic/Aerobic Process

Appendix U: Kinetics of Removal of ADMI due to Reactive Black 5 for Aerobic Control (Reactor 8)

Table U-1 Reactor 8, Raw ADMI Data

Cycle	Beginning of Aerobic	End of Aerobic
1	452	346
2	638	563
3	676	589
4	798	686
5	856	652
6	832	726
7	869	676
8	843	729

Appendix V: Kinetics of Removal of ADMI due to Reactive Black 5 for Anoxic/Aerobic Process (Reactor 2)

Table V-1 Reactor 2, Raw ADMI Data

Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	651	851	1028	1013	764	825
5	600	634	876	906	758	746
10	515	550	780	771	787	642
15	434	548	760	710	715	546
20	487	564	749	692	715	533
25	395	497	669	690	709	483
30	390	497	709	685	728	511
60	392	466	668	650	740	479
120	423	418	581	541	564	397
240	353	396	466	493	499	400
480	333	348	419	398	383	360
510	301	1138	394	388	361	317
540	265	327	381	363	343	326
600	282	293	404	368	352	309
720	368	314	353	381	368	383
960	374	340	377	409	395	365
1350	399	377	383	431	398	397

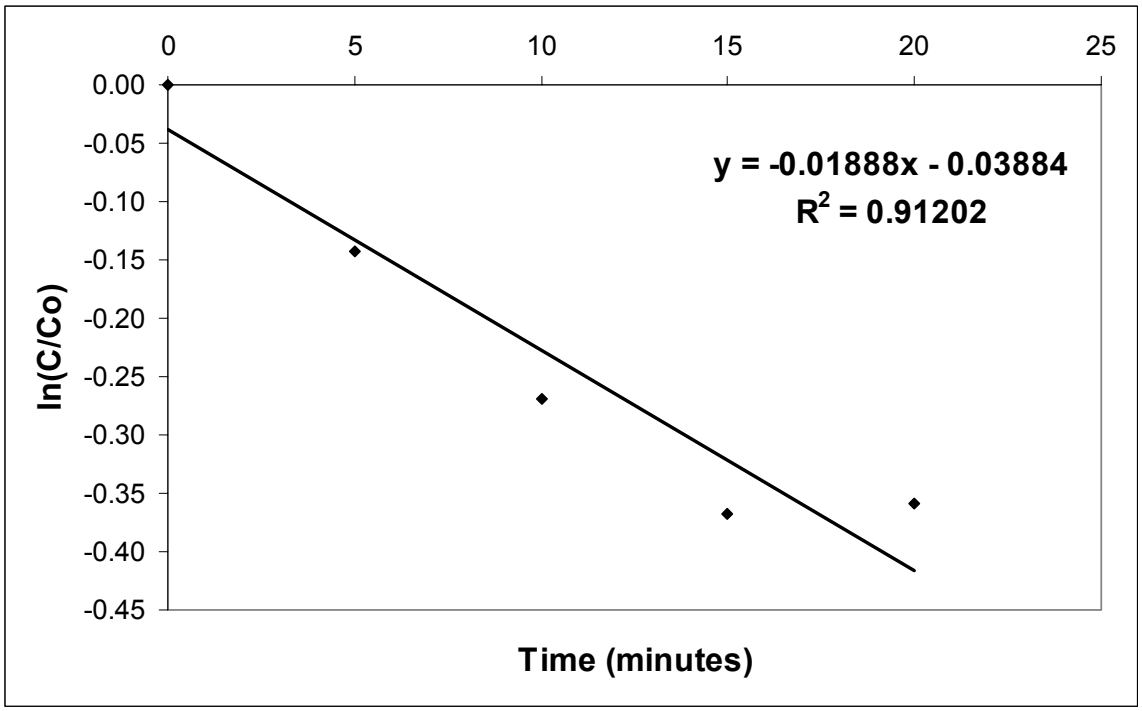
Note: Data point from Cycle 2 at 510 minutes was dropped from analysis

Table V-2 Reactor 2, Adjusted ADMI Data

Adjustment	0	-35	-158	-139	-142	-47
Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	651	816	870	874	622	778
5	600	599	718	767	616	699
10	515	515	622	632	645	595
15	434	513	602	571	573	499
20	487	529	591	553	573	486
25	395	462	511	551	567	436
30	390	462	551	546	586	464
60	392	431	510	511	598	432
120	423	383	423	402	422	350
240	353	361	308	354	357	353
480	333	313	261	259	241	313
510	301		236	249	219	270
540	265	292	223	224	201	279
600	282	258	246	229	210	262
720	368	279	195	242	226	336
960	374	305	219	270	253	318
1350	399	342	225	292	256	350

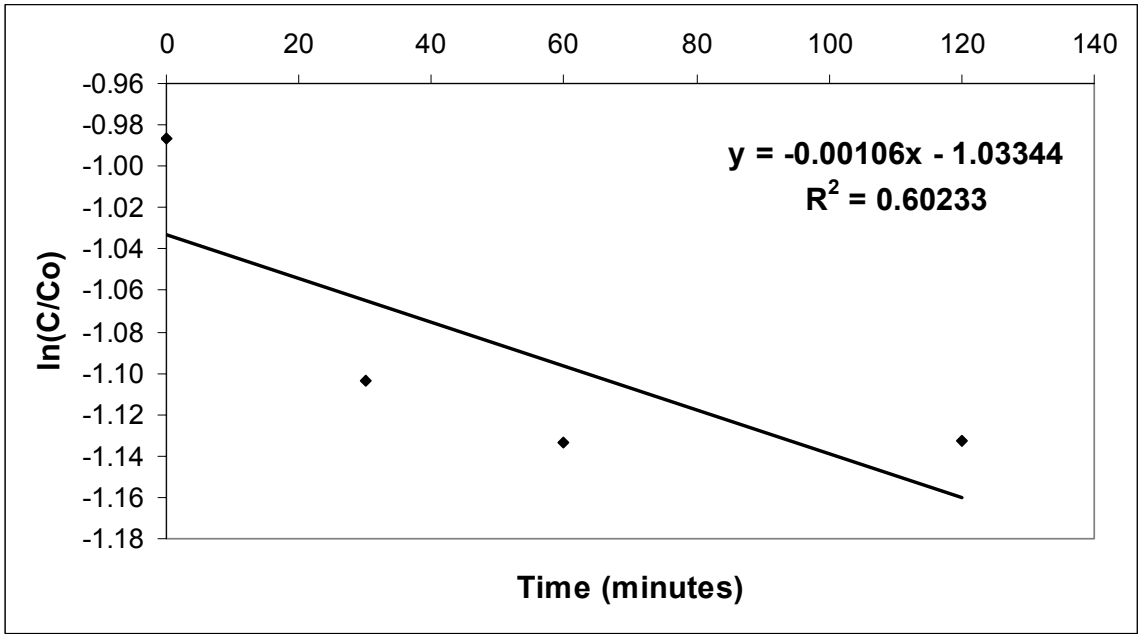
Table V-3 Reactor 2, *ln(Average C/C$_0$)* for Adjusted ADMI Data

Time	ln (Avg C/Co)
0	0
5	-0.14241
10	-0.26879
15	-0.36738
20	-0.35942
25	-0.45630
30	-0.42993
60	-0.47273
120	-0.65142
240	-0.79283
480	-0.98639
510	-1.10357
540	-1.13317
600	-1.13228
720	-1.02991
960	-0.97468
1350	-0.90605



Note: Standard error for regression = 0.053519

Figure V-1 Reactor 2, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for ADMI Removal for Anoxic/Aerobic Process



Notes: Standard error for regression = 0.053816

Figure V-2 Reactor 2, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for ADMI Removal for Anoxic/Aerobic Process

Appendix W: Kinetics of Removal of ADMI due to Reactive Violet 5 for Aerobic Control (Reactor 9)

Table W-1 Reactor 9, Raw ADMI Data

Cycle	Beginning of Aerobic	End of Aerobic
1	502	279
2	572	454
3	687	601
4	784	683
5	839	746
6	910	865
7	970	895
8	984	908

Appendix X: Kinetics of Removal of ADMI due to Reactive Violet 5 for Anoxic/Aerobic Process (Reactor 5)

Table X-1 Reactor 5, Raw ADMI Data

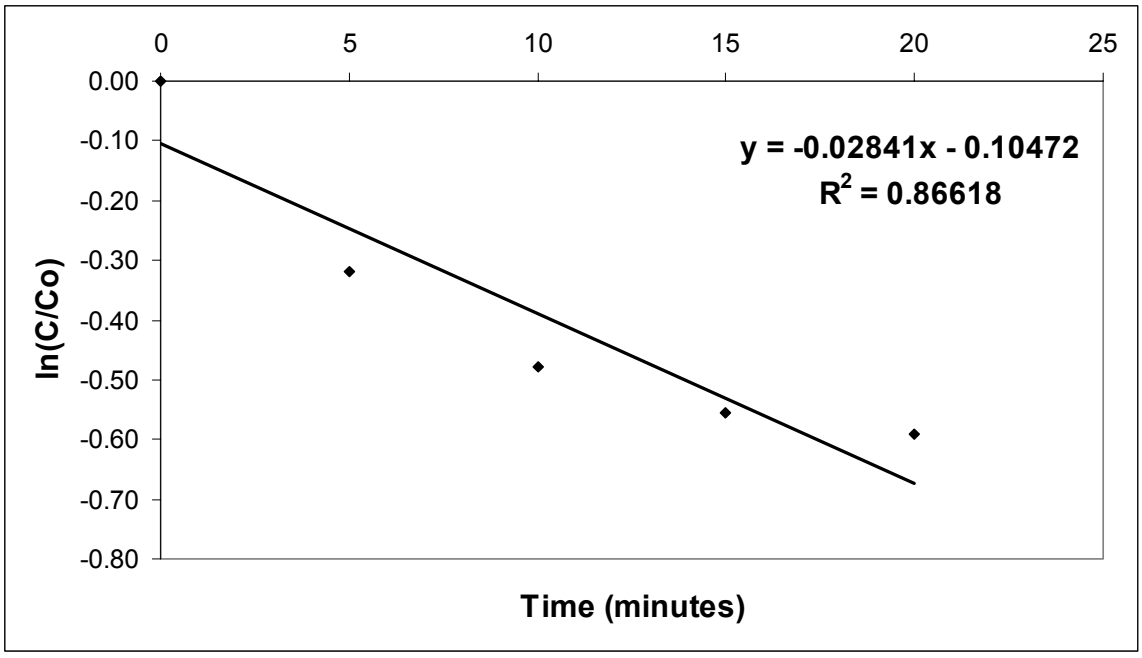
Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	1347	1365	1141	1509	1538	1213
5	759	1038	963	1079	1149	1026
10	710	909	992	865	946	772
15	696	774	804	928	905	733
20	698	727	807	921	821	702
25	647	701	733	913	749	701
30	663	696	765	872	817	694
60	649	646	695	851	640	696
120	543	566	549	713	620	578
240	377	466	438	634	568	516
480	269	266	330	419	417	416
510	190	228	248	344	308	358
540	174	165	213	317	288	350
600	160	252	229	288	267	317
720	400	187	240	316	274	323
960	301	207	253	327	303	331
1350	218	236	252	309	330	326

Table X-2 Reactor 5, Adjusted ADMI Data

Adjustment	0	-29	-61	-162	-118	-55
Time	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
0	1347	1336	1080	1347	1420	1158
5	759	1009	902	917	1031	971
10	710	880	931	703	828	717
15	696	745	743	766	787	678
20	698	698	746	759	703	647
25	647	672	672	751	631	646
30	663	667	704	710	699	639
60	649	617	634	689	522	641
120	543	537	488	551	502	523
240	377	437	377	472	450	461
480	269	237	269	257	299	361
510	190	199	187	182	190	303
540	174	136	152	155	170	295
600	160	223	168	126	149	262
720	400	158	179	154	156	268
960	301	178	192	165	185	276
1350	218	207	191	147	212	271

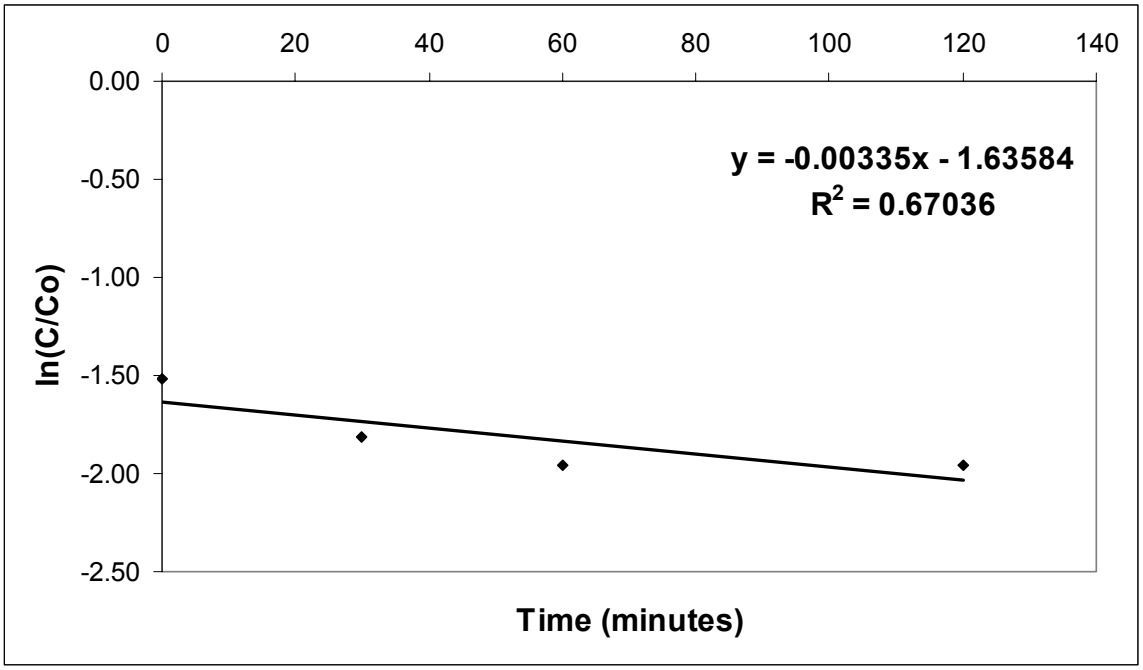
Table X-3 Reactor 5, *ln(Average C/C$_0$)* for Adjusted ADMI Data

Time	ln (Avg C/Co)
0	0
5	-0.31909
10	-0.47782
15	-0.55464
20	-0.59239
25	-0.64868
30	-0.63310
60	-0.71761
120	-0.89429
240	-1.09412
480	-1.51416
510	-1.81525
540	-1.96150
600	-1.95531
720	-1.76666
960	-1.77950
1350	-1.81955



Note: Standard error for regression = 0.101927

Figure X-1 Reactor 5, Linear Regression for Determining Rate Constant of Anoxic Phase (using Adjusted Data) for ADMI Removal for Anoxic/Aerobic Process



Note: Standard error for regression = 0.14728

Figure X-2 Reactor 5, Linear Regression for Determining Rate Constant of Aerobic Phase (using Adjusted Data) for ADMI Removal for Anoxic/Aerobic Process