3-2021

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Megan C. Shade

Recommended Citation

Shade, Megan C., "The Effect of Molar Peroxide Ratio on the Oxidation of Bisphenol A in an Ultraviolet Light Emitting Diode/Hydrogen Peroxide Advanced Oxidation Process" (2021). *Theses and Dissertations*. 4963.
https://scholar.afit.edu/etd/4963

THE EFFECT OF MOLAR PEROXIDE RATIO ON THE OXIDATION OF BISPHENOL A IN AN ULTRAVIOLET LIGHT EMITTING DIODE/HYDROGEN PEROXIDE ADVANCED OXIDATION PROCESS

THESIS

Megan C. Shade

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

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THESIS

Presented to the Faculty

Department of Systems Engineering and Management

Graduate School of Engineering and Management

Air Force Institute of Technology

Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the

Degree of Master of Science in Environmental Engineering and Science

Megan C. Shade, BS

March 2021

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AFIT-ENV-MS-21-M-271

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Megan C. Shade

NH-02

Committee Membership:

Dr. Willie F. Harper, Jr.
Chair

Dr. Adam C. Burdsall
Member

Lt. Col. John E. Stubbs
Member

Abstract

Bisphenol A (BPA) is a compound widely used in industry that is detrimental to human health and ecological systems. It enters the environment through various process and subsequently creates an exposure hazard. Ultraviolet light emitting diodes (UVLED) and hydrogen peroxide (H_2O_2) can be combined to create an advanced oxidation process that produces hydroxyl radicals. These highly reactive radicals have the potential to degrade contaminants in water. Further knowledge of the optimal molar peroxide ratio to effectively degrade contaminants and any subsequent reaction byproducts is needed. This research utilized 50, 100, 250, 500, and 1000:1 H_2O_2:BPA molar ratios in a Continuous Flow Stirred-Tank Reactor (CFSTR) with UVLED as the mechanism for BPA degradation. High Performance Liquid Chromatography (HPLC) and Mass Spectrometry (MS) were used for the analysis of mass ratio concentrations and potential reaction byproducts, respectively. This study saw the highest degradation and rate constants at the 500:1 molar ratio. The 100 and 250:1 ratios had similar rate constants and degradation, both slightly lower than the 500:1 ratio. The 50 and 1000:1 ratios were also similar to each other and had the lowest degradation and rate constants. These results illustrate that the reactions at the 50, 100, and 250:1 ratios were hydrogen peroxide limited. The 1000:1 results exhibited evidence of radical scavenging that limited the degradation of BPA. Further research at molar peroxide ratios near the 100, 250, and the 500:1 ratio could provide the best potential for BPA removal versus cost or regulatory requirements.

To my family, your unwavering support, wisdom, and love brought me to this point. Your compassion, and concern for others inspired me to make a difference in the world. To my friends who believed in me and cheered me on. And to my pitbulls, my study partners that never left my side. It has been an honor to have you in my life.

Acknowledgements

First, I would like to thank Dr. Willie Harper, Jr., my thesis advisor, for this educational opportunity, as well as his support and guidance throughout my thesis research. Second, I would like to thank Dr. Daniel Felker and Dr. Adam Burdsall for their mentorship throughout the research process. Lastly, I would like to thank Lt Col John Stubbs, my advisor, for his direction and encouragement throughout my education at AFIT.

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Glossary of Acronyms and Abbreviations

AFIT – Air Force Institute of Technology

AOP – Advanced Oxidation Process

BPA – Bisphenol A

CEC – Contaminants of Emerging Concern

CFSTR – Continuous Flow Stirred-Tank Reactor

DI Water – Deionized water

$HO\cdot$ – Hydroxyl Radical

HPLC – High Performance Liquid Chromatography

H_2O_2 – Hydrogen Peroxide

LED – Light Emitting Diode

MS – Mass Spectroscopy

UV – Ultraviolet

WPAFB – Wright Patterson Air Force Base

WWTP – Wastewater Treatment Plant

THE EFFECT OF MOLAR PEROXIDE RATIO ON THE OXIDATION OF BISPHENOL A IN AN ULTRAVIOLET LIGHT EMITTING DIODE/HYDROGEN PEROXIDE ADVANCED OXIDATION PROCESS

I. Introduction

1.1 Chapter Overview

This chapter summarizes the need for this research, defines the problem, the hypothesis, and how this experiment was conducted.

1.2 General Issue

Global water resources have been inundated with various pollutants. Pathogens, pesticides, pharmaceuticals, solvents, chlorinated organics, and algal toxins are some of the many hazardous substances that are harmful to both human health and the environment. Current wastewater treatment plants (WWTP) provide minimal removal of these compounds. When the wastewater effluent is discharged, it introduces these pollutants into waterways (Kang et al., 2018). This presents a need for further research into treatment technologies that can remediate various pollutants without creating toxic byproducts. Contaminants of concern (CEC) in water sources have increased due to rises in chemical production and human populations. Additionally, improvements in analytical technology have highlighted chemical levels that were previously undetected, further expanding the number of compounds now found throughout the environment (Baken et al., 2018). These CEC originate from pharmaceutical and personal care products, pesticides, industrial compounds, and illicit drugs, and have known/potential adverse health and environmental effects (Borull et al., 2019).

BPA is widely used in various industry processes and products that has resulted in pervasive exposure to both humans and the environment. It is a known endocrine disruptor that has also exhibited additional potential adverse effects to human health and ecological systems (Wang et al., 2009). Wastewater treatment generally has low BPA removal rates leading to the release of the compound during discharge (Kang et al., 2018). This has led to an intensified need for treatment and remediation technologies.

Safe drinking water is essential for the military, not only in the United States, but abroad as well. Environmental security has been a priority for the military since the 1990s, and water issues are considered a threat to national security (O'Lear et al., 2013). Further understanding of technology with the potential to protect, as well as treat water resources is essential to human health and military capabilities.

Ultraviolet (UV) Light Emitting Diodes (LED) and Hydrogen peroxide (H_2O_2) have the potential to be utilized in the application of an Advanced Oxidation Process (AOP) during the water treatment process. When H_2O_2 is exposed to UV light it creates two hydroxyl radicals ($HO\cdot$) that are highly reactive (Vega & Valdés, 2018). This research studied the results of BPA degradation when treated with various molar ratios of H_2O_2 to BPA.

Mercury lamps have been utilized in water treatment, but they pose additional environmental concerns. LED technology presents an alternative to the traditional mercury lamps.

1.3 Problem Statement

The Air Force Institute of Technology (AFIT) at Wright-Patterson Air Force Base (WPAFB) is researching the degradation potential of contaminants during H_2O_2 UV LED AOP. BPA is a contaminant that has been routinely observed in source/drinking water, and can enter the environment through wastewater discharge and sludge (Kleywegt et al., 2011). The effects of UV LED-AOPs on BPA removal are not fully understood and require additional research.

1.4 Research Objectives

The purpose of this research was to study the effect of molar peroxide ratio on BPA removal during an AOP and investigate the production of reaction byproducts. BPA removal kinetics are expected to be influenced by hydroxyl radical scavenging. Radical scavenging can interfere with the radical-BPA reactions, thereby inhibiting the degradation mechanisms.

1.5 Methodology

During the course of this research, one control experiment, and 15 AOP experiments were conducted. The control test was completed without the addition of H_2O_2. The 15 AOP experiments consisted of five molar ratios (50, 100, 250, 500, and 1000:1 H_2O_2 to BPA). These AOP experiments consisted of two 60-minute segments. The first hour was completed without UV light, and the solution was recycled back to the original flask. Samples were taken at time 0, 10, 20, 30, 40, 50, and 60 minutes. After the initial 60 minutes, the UV light was turned on and samples were collected at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes. The solution was pumped into a waste container after passing through the reactor. Each molar peroxide ratio was replicated for three trials. Each sample was collected and filtered into High Performance Liquid Chromatography (HPLC) vials. The samples were analyzed using HPLC and Mass Spectroscopy (MS). The HPLC data was used to determine BPA concentrations and the MS data was used to determine possible by-products. Tukey pairwise comparisons were used for statistical analysis utilizing Jupyter Notebook 6.0.1.

1.6 Assumptions and Limitations

There were several assumptions made for this research:

1. The components of the experiment were working at the same efficiency for each trial.
2. The stir bar maintained a consistently mixed solution inside the reactor. Observations were made to determine if it was likely the stir bar was continuing to operate; checking the reactor for vibrations and listening for noise associated with the stir bar spinning inside the reactor.

II. Literature Review

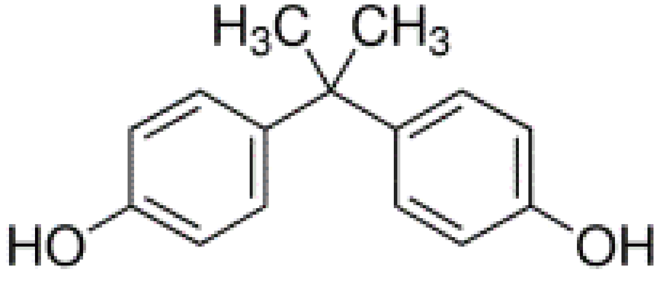
2.1 Chapter Overview

This chapter summarizes BPA fate in the environment, potential problems of BPA, and the AOP process.

2.2 Background

Bisphenol A is a known endocrine disruptor that may have additional adverse effects to human health and ecological systems (Wang et al., 2009). It has been utilized in the production of wide-ranging items, and during industrial processes, including the food and beverage industry (Hu et al., 2019). Because BPA is widely used, is present in various environmental media, and has detrimental effects, it is necessary to further research remediation and treatment options. BPA has a molecular weight of 228.29 g/mol and molecular formula $C_{15}H_{16}O_2$. The molecular structure of BPA (Figure 1) has two benzene rings each containing a hydroxyl group, which form a phenol, connected by a central carbon atom. Two methyl groups are also located at the central carbon atom.

Figure 1: BPA molecular structure



Due to the pervasive use of BPA in industry, this chemical is released into the environment via various mechanisms. The processes that produce BPA, and the subsequent wastewater discharges are categorized as production sources. Landfill leaching, degradation of plastics already in the environment, WWTP discharges, and disposal or burning of waste are considered consumer sources (Corrales et al., 2015). BPA has been detected in the influent and effluent of wastewater treatment plants, as well as in sewage sludge. Sewage sludge utilized as fertilizer can introduce BPA into the food supply and groundwater (Hu et al., 2019). BPA has also been observed in source water and drinking water (Kleywegt et al., 2011)

Mercury lamps have routinely been used to generate UV light for water treatment processes and previous AOP research, but UV LED options are increasingly seen as a better option. UV LED lamps are highly energy efficient compared to the standard mercury lamps (Martín-Sómer et al., 2017). Mercury is a known toxin and is highly detrimental to human health (Bjørklund et al., 2017). Mercury lamps are also very fragile and have higher operating costs than LEDs (Huang et al., 2017).

2.3 BPA Degradation Research

Previous studies of BPA degradation have utilized both hydroxyl and sulfate radicals during AOP research, with both radicals showing sufficient ability to remove BPA from water (Qui et al., 2019). These studies have varied in their approach, as well as the parameters the researchers were analyzing. Carbonate and nitrate constituents are found in natural waters; BPA degradation levels and reaction byproducts varied when combined with these constituents (Kang et al., 2018). Titanium dioxide (TiO_2), when used as the photocatalyst, has also shown to degrade BPA in an AOP. The removal rates decreased as the amounts of TiO_2 oversaturated the solution (Wang et al., 2009). BPA degradation has also been demonstrated with UV light only, increasing as the drive current increases (Stubbs, 2017).

BPA removal has also been conducted utilizing adsorption technologies. Different adsorptive media, such as clays, activated carbon, natural polymers, and nanomaterials have had success in removing BPA from water sources (Bhatnagar and Anastopoulos, 2017).

The limited research completed thus far showcases the need for additional data collection under this study's parameters.

III. Methodology

3.1 Chapter Overview

This chapter details the materials and methods used to conduct the AOP experiments.

3.2 Materials and Equipment

250 mL Pyrex® Vista™ No. 70640 volumetric flasks were used for solution preparation and storage. PharMed® BPT tubing circulated the solution from the flasks to the Continuous Stirred-Tank Reactor (CSTR), and from the CSTR to the flask. To maintain constant mixing, a stir bar and stir plate were utilized with both the solution flask and the reactor. A Cole-Parmer® MasterFlex® No. 77200-50 peristaltic pump propelled the solution through at a rate of 2 mL per minute. The pump was primed with a 45 mL of solution using a 60 mL syringe. Electricity was provided to the reactor by Keysight E3620A Dual Output DC Power Supply. A Mettler-Toledo pH meter was used to determine the pH of the H_2O_2 - BPA solution before it was circulated through the reactor. Each sample was captured in a syringe and filtered with a Millex® - FG Hydrophobic Fluoropore™ 0.2 µm filter into HPLC vials. All samples and standards were vortex mixed for 30 seconds on a Daigger Vortex Genie 2® mixer. HPLC and MS were conducted on an Agilent technologies 6130 Quadrupole LC/MS.

3.3 Hydrogen Peroxide/BPA Molar Ratio Experiment

Five molar ratios, 50, 100, 250, 500, and 1000:1 H_2O_2 to BPA were utilized to study the effects molar peroxide ration on BPA degradation. 31 mL of 81 mg/L BPA solution was pipetted into a 250 mL flask and filled with Deionized (DI) water to create a 10 mg/L BPA solution. 30% hydrogen peroxide stock solution was added to the flask at volumes of 55, 11, 277, 111, 554, 1108 µL to produce the 50, 100, 250, 500, and 1000:1 molar ratios respectively. A stir bar was added to the solution before the flask was wrapped in foil, hand mixed for 10 minutes, and then placed on a stir plate at 850 rpm for one hour. 100, 200, 400, 600, 800, and 1000 µL of the H_2O_2 – BPA solution were pipetted into HPLC vials to create standards of 10, 20, 40, 60, 80, and 100% respectively. A blank was created using DI water. All standards were filtered and vortex mixed for 30 seconds.

To prepare the reactor setup, the tubing was connected to the entry and exit ports of the reactor and primed with 45 mL of solution. The stir plate for the reactor was turned on. The UVLED electrical source was preadjusted to 0.068 amps. The flask containing the H_2O_2 – BPA solution was placed on a stir plate adjacent to the reactor and maintained at 850 rpm.

To obtain the control samples, the pump was turned on at time zero minutes and the first sample was collected. Control samples were collected at time 0, 10, 20, 30, 40, 50, and 60 minutes. Each sample was filtered into a HPLC vial and vortex mixed for 30 seconds. During the control portion of the experiment, the effluent was recycled back into the solution flask.

After the control samples were collected, the UV light was turned on and the first sample was collected at time 0 minutes. Experiment samples were taken at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes. Each sample was filtered into a HPLC vial and vortex mixed. During the run portion of the experiment, the effluent was cycled into a waste container. Once the standards and samples were obtained, they were placed into the HPLC tray. The HPLC program was loaded and verified before starting the analysis.

Reaction rates were acquired using a reaction rate derivation in MATLAB code created by Dr. Harper.

Equation 1: Equation for reaction rate constants

$$C_n/C_0 = \frac{(1 + \tau k) * e^{(1/\tau + k)*(-1)t}}{\tau k + 1}$$

Figure 2: Continuous Flow Stirred-Tank Reactor

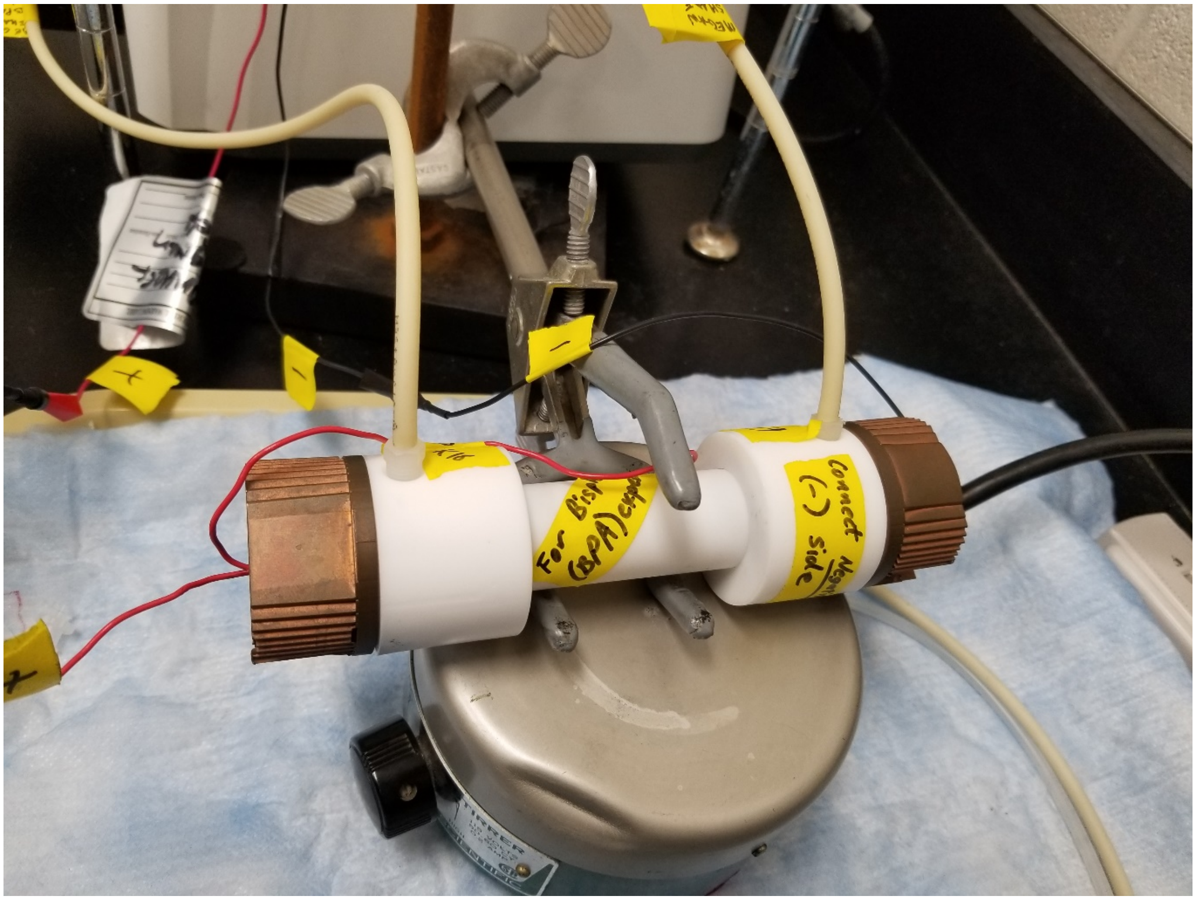
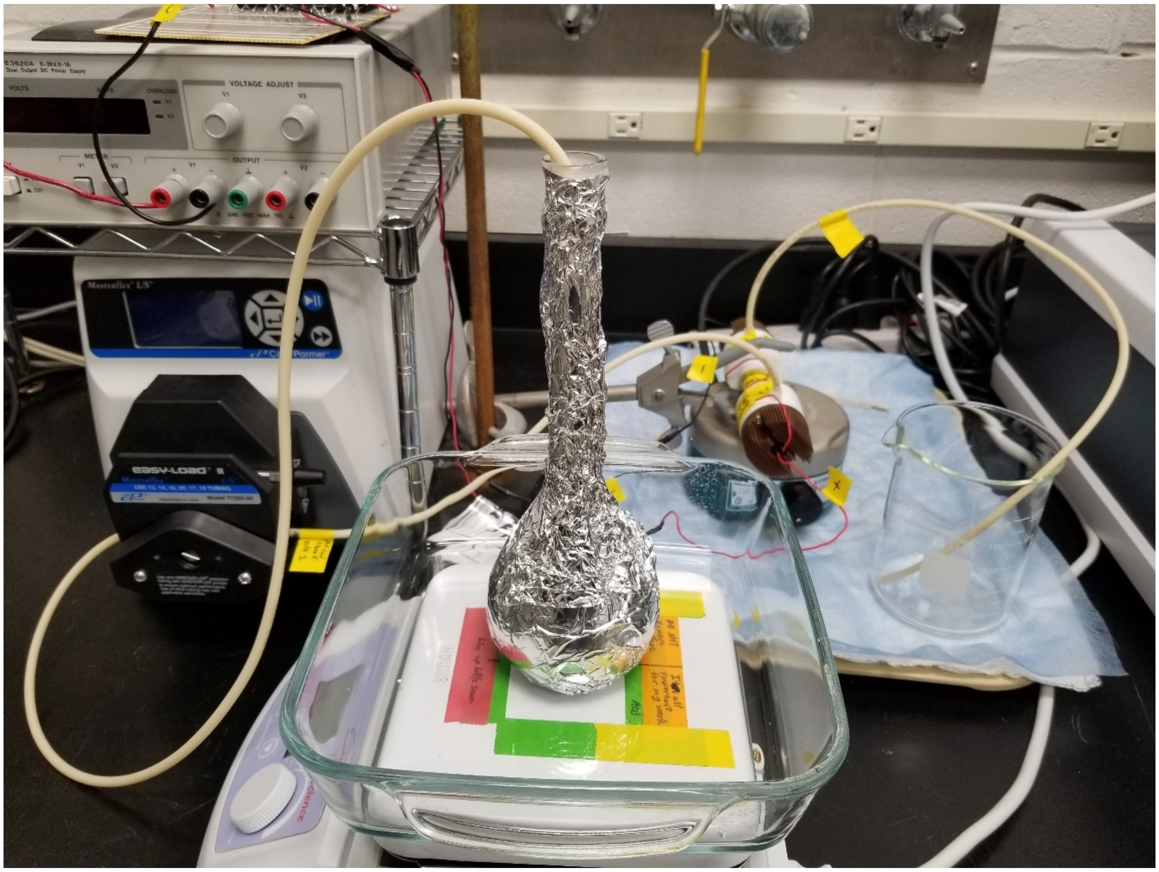


Figure 3: AOP Experiment setup – effluent recycled into solution flask

The recycled reactor set up was utilized during the control portion of each AOP.

Figure 4: AOP Experiment setup – effluent cycled into waste container



The non-recycled reactor setup was utilized for the initial control without H_2O_2, and all AOP runs during UV exposure.

IV. Analysis and Results

4.1 Chapter Overview

This chapter discusses the results and statistical analysis of the AOP experiments.

4.2 Results

Figure 5 shows the mass ratios of a BPA solution without any added H_2O_2, a 0:1 ratio. The x-axis is the time elapsed for the duration of the experiment. The y-axis is the relative concentration (C_n/C_0) of BPA. For the control, four samples were taken with no UV light. The control was conducted to illustrate if the treatment had an effect on BPA degradation. The UV light was turned on and eight samples were taken for the trial.

The relative concentrations of the control at time 0, 20, 40, and 60 minutes were 0.84, 0.88, 0.85, 0.86 respectively. The relative concentrations remain overall consistent during the 60-minute control time. The results of the relative concentrations of the control illustrate the experiment did not degrade BPA.

The relative concentrations of the trial at time 5, 10, 15, 20, 25, 35, 45, and 60 minutes were 1.04, 1.04, 1.00, 1.00, 1.00, 0.99, 1.01, and 1.02 respectively. The results of the relative concentrations of the trial illustrate the experiment did not degrade BPA when exposed to UV light without H_2O_2 added to the solution.

Figure 5: Initial control – Bisphenol A solution with no Hydrogen Peroxide

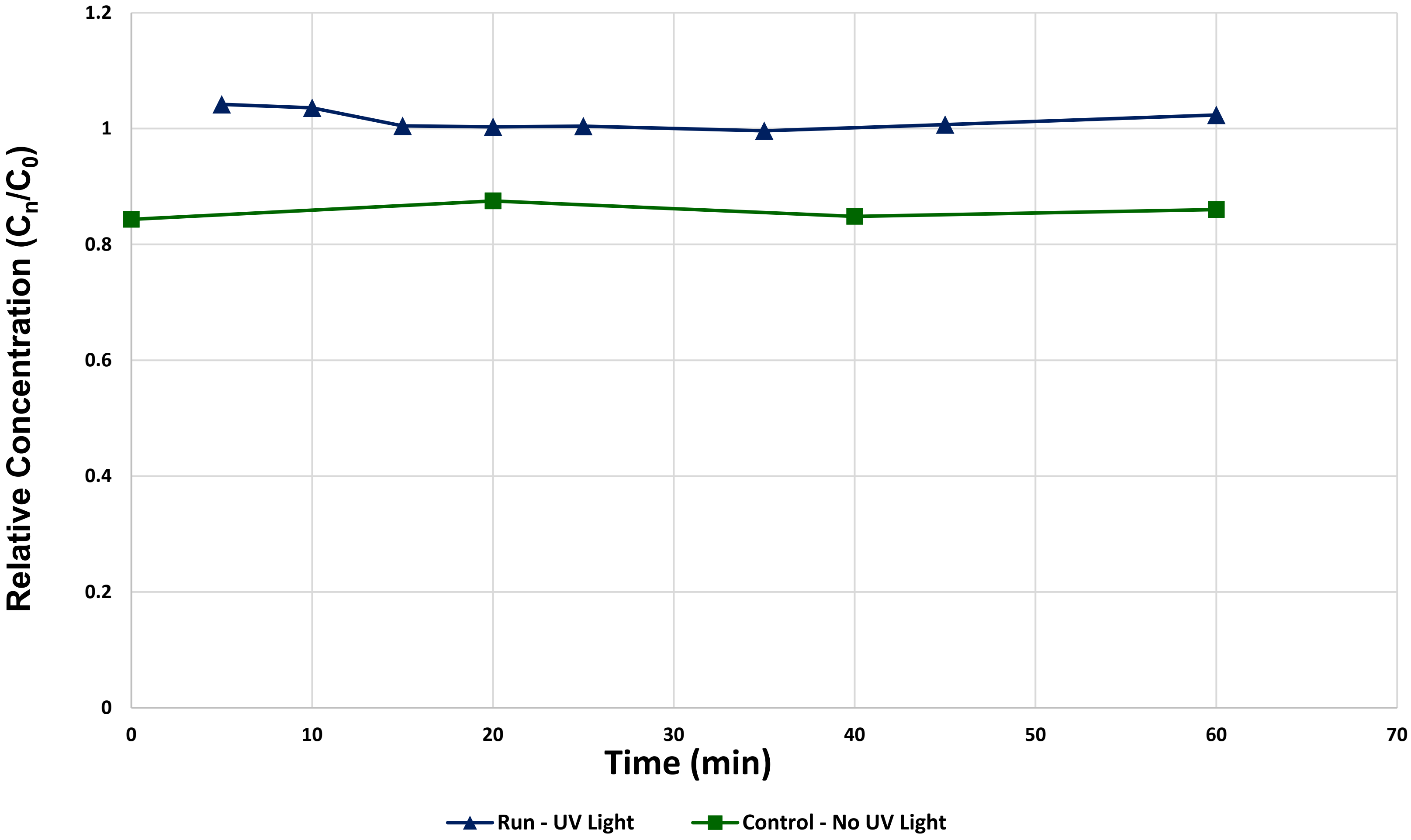


Figure 6 shows the degradation of BPA in three trials at the 50:1 H_2O_2 to BPA molar ratio. The x-axis is the time elapsed for the duration of the experiment. The y-axis is relative concentration (C_n/C_0) of BPA. For the control, seven samples were taken with no UV light. The UV light was turned on and eleven samples were taken for the trial.

The average relative concentrations of the controls at time 0, 10, 20, 30, 40, 50, and 60 minutes were 0.90, 0.90, 0.89, 0.91, 0.90, 0.89, and 0.91, respectively. The control did not degrade BPA with the UV light off. The average relative concentrations of the trials at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes were 0.98, 0.73, 0.65, 0.55, 0.42, 0.38, 0.33, 0.34, 0.31, 0.30, 0.29 respectively.

The majority of degradation occurred during the first ten minutes, leveling out throughout the remainder of the experiment as the solution in the reactor reached equilibrium. The results of the relative concentrations of the trial illustrate the experiment degraded BPA. The lack of degradation during the control compared to the degradation exhibited during the trials shows that the H_2O_2-UV treatment was effective.

Figure 6: Hydrogen Peroxide:Bisphenol A 50:1 Mass Ratio vs Time

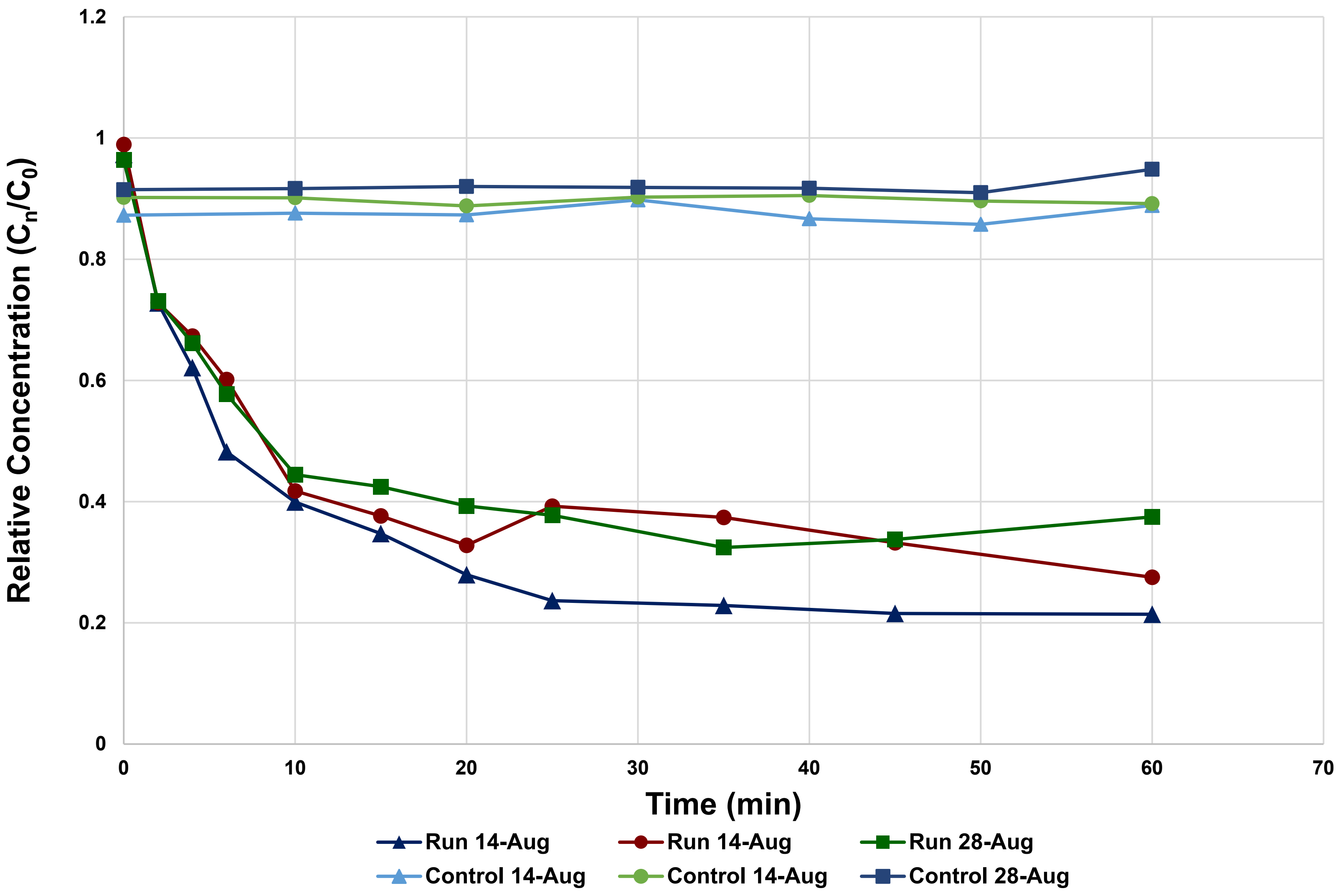


Figure 7 shows the degradation of BPA in three trials at the 100:1 H_2O_2 to BPA molar ratio. The x-axis is the time elapsed for the duration of the experiment. The y-axis is the relative concentration (C_n/C_0) of BPA. For the control, seven samples were taken with no UV light. The UV light was turned on and eleven samples were taken for the trial.

The average relative concentrations of the controls at time 0, 10, 20, 30, 40, 50, and 60 minutes were 0.91, 0.93, 0.92, 0.93, 0.93, 0.94, and 0.94, respectively. The control did not degrade BPA with the UV light off. The average relative concentrations of the trials at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes were 0.98, 0.69, 0.50, 0.39, 0.29, 0.25, 0.25, 0.22, 0.25, 0.24, 0.21 respectively.

The majority of degradation occurs during the first ten minutes, leveling out throughout the remainder of the experiment as the solution in the reactor reached equilibrium. The results of the relative concentrations of the trial illustrate the experiment degraded BPA. The lack of degradation during the control compared to the degradation exhibited during the trials shows that the H_2O_2-UV treatment was effective.

The 26 June trial experienced pump issues at the 25- and 35-minute sample times. The 25 min sample was collected at 27 minutes and the 35 min sample was collected at 36 minutes.

. **Figure 7: Hydrogen Peroxide:Bisphenol A 100:1 Mass Ratio vs Time**

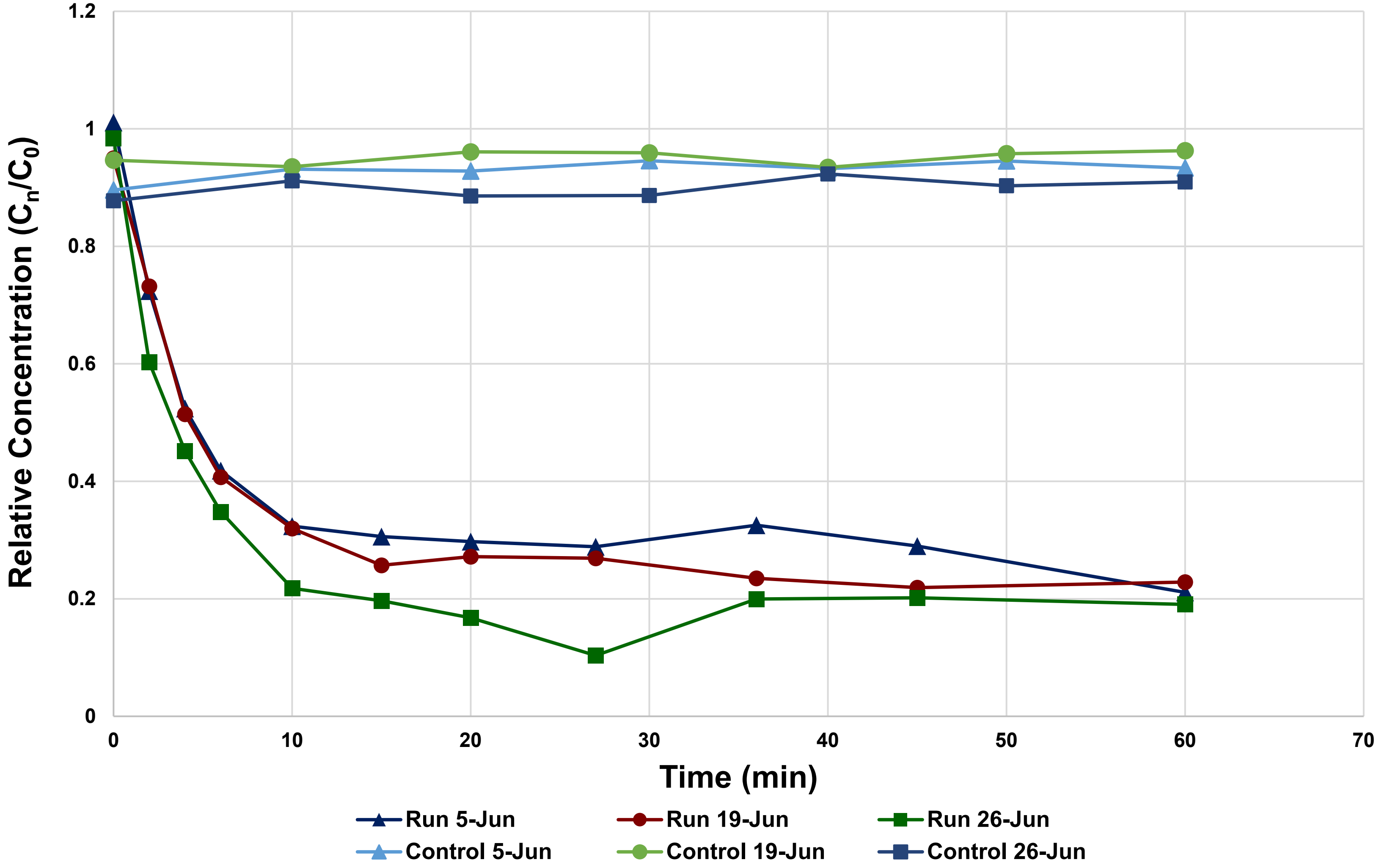


Figure 8 shows the degradation of BPA in three trials at the 250:1 H_2O_2 to BPA molar ratio. The x-axis is the time elapsed for the duration of the experiment. The y-axis is the relative concentration (C_n/C_0) of BPA. For the control, seven samples were taken with no UV light. The UV light was turned on and eleven samples were taken for the trial.

The average relative concentrations of the controls at time 0, 10, 20, 30, 40, 50, and 60 minutes were 0.89, 0.90, 0.91, 0.90, 0.90, 0.89, and 0.91, respectively. The control did not degrade BPA with the UV light off. The average relative concentrations of the trials at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes were 0.97, 0.57, 0.49, 0.39, 0.30, 0.24, 0.24, 0.24, 0.24, 0.25, 0.24 respectively. This molar ratio had degradation comparable to the 100:1 ratio.

The majority of degradation occurs during the first ten minutes, leveling out throughout the remainder of the experiment as the solution in the reactor reached equilibrium. The results of the relative concentrations of the trial illustrate the experiment degraded BPA. The lack of degradation during the control compared to the degradation exhibited during the trials shows that the H_2O_2-UV treatment was effective.

Figure 8: Hydrogen Peroxide:Bisphenol A 250:1 Mass Ratio vs Time

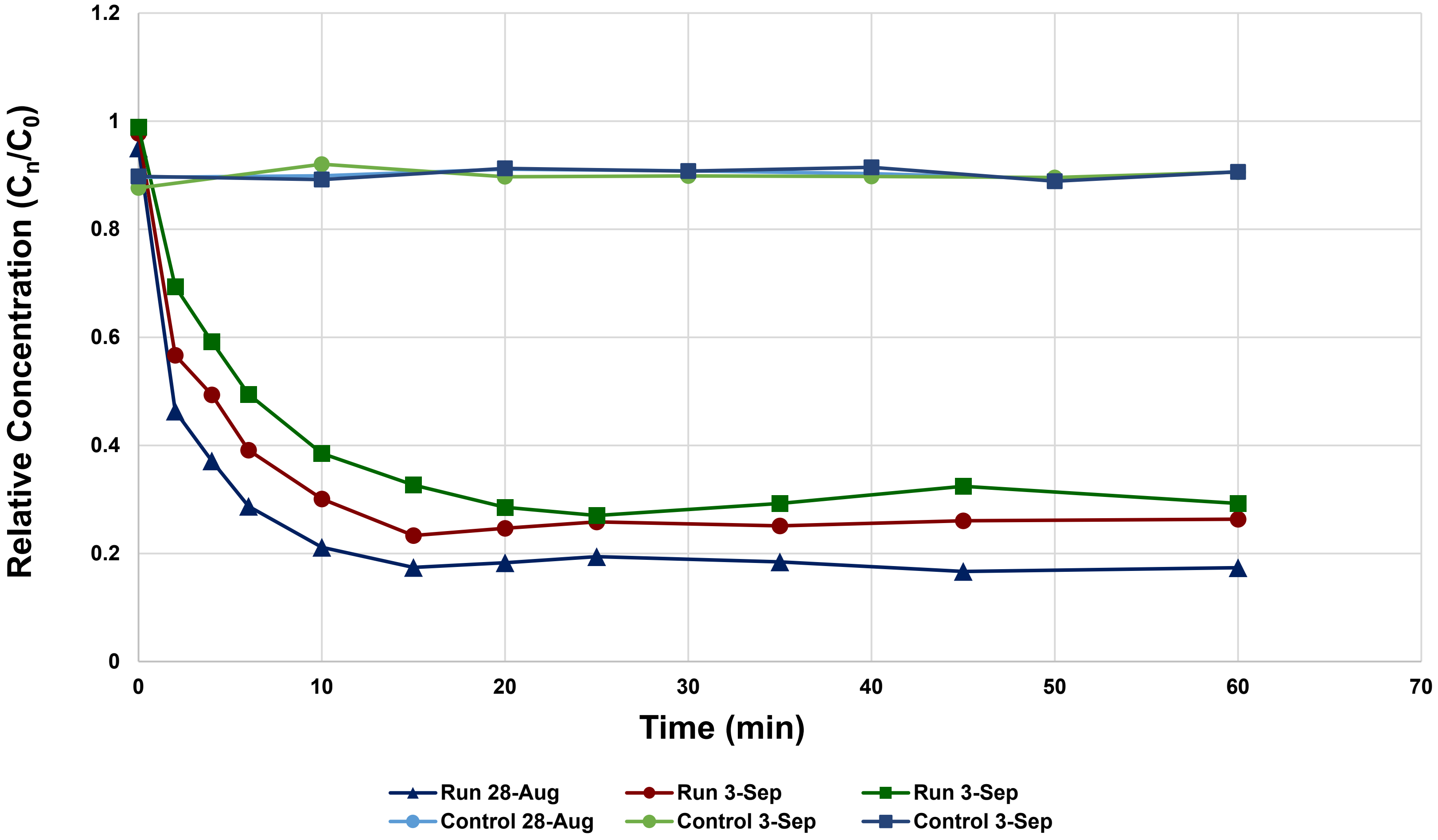


Figure 9 shows the degradation of BPA in three trials at the 500:1 H_2O_2 to BPA molar ratio. The x-axis is the time elapsed for the duration of the experiment. The y-axis is the relative concentration (Cn/C0) of BPA. For the control, seven samples were taken with no UV light. The UV light was turned on and eleven samples were taken for the trial.

The average relative concentrations of the controls at time 0, 10, 20, 30, 40, 50, and 60 minutes were 0.85, 0.86, 0.89, 0.88, 0.90, 0.87, and 0.86, respectively. The control did not degrade BPA with the UV light off. The average relative concentrations of the trials at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes were 0.96, 0.60, 0.42, 0.29, 0.22, 0.19, 0.19, 0.13, 0.13, 0.19, 0.18 respectively. This molar ratio had the highest degradation compared to the other ratios.

The majority of degradation occurs during the first ten minutes, leveling out throughout the remainder of the experiment as the solution in the reactor reached equilibrium. The results of the relative concentrations of the trial illustrate the experiment degraded BPA. The lack of degradation during the control compared to the degradation exhibited during the trials shows that the H_2O_2-UV treatment was effective.

The 500:1 results indicate that the 100:1 and 250:1 results were limited due to the levels of hydrogen peroxide. The addition of more hydrogen peroxide facilitates more radical production, resulting in greater BPA degradation.

The 10 July trial experienced pump issues at the 25- and 35-minute sample times. The 25 min sample was collected at 26 minutes and the 35 min sample was collected at 36 minutes

Figure 9: Hydrogen Peroxide:Bisphenol A 500:1 Mass Ratio vs Time

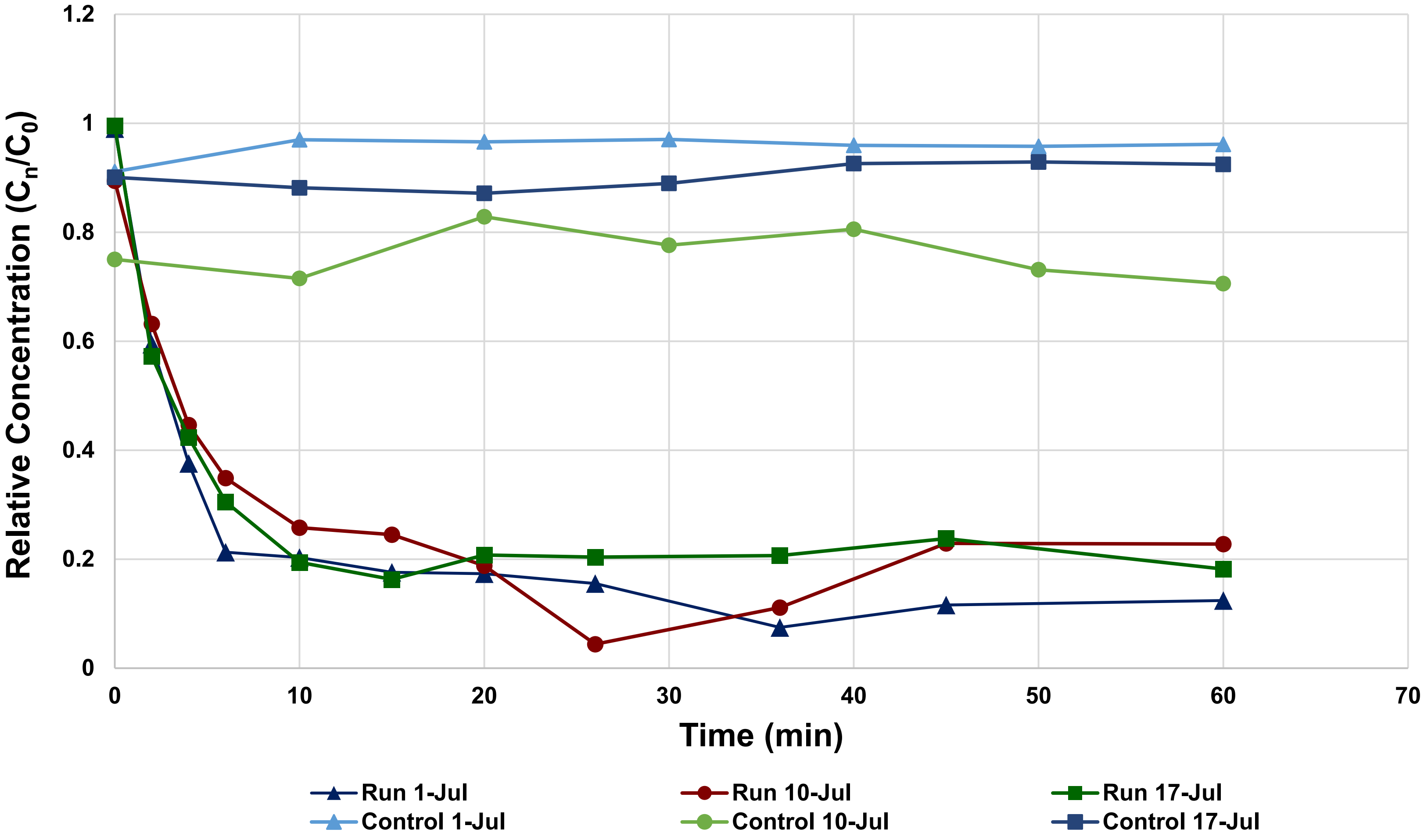


Figure 10 shows the degradation of BPA in three trials at the 1000:1 H_2O_2 to BPA molar ratio. The x-axis is the time elapsed for the duration of the experiment. The y-axis is the relative concentration (C_n/C_0) of BPA. For the control, seven samples were taken with no UV light. The UV light was turned on and eleven samples were taken for the trial.

The average relative concentrations of the controls at time 0, 10, 20, 30, 40, 50, and 60 minutes were 0.89, 0.91, 0.90, 0.90, 0.90, 0.92, and 0.91, respectively. The control did not degrade BPA with the UV light off. The average relative concentrations of the trials at time 0, 2, 4, 6, 10, 15, 20, 25, 35, 45, and 60 minutes were 0.98, 0.69, 0.56, 0.48, 0.34, 0.32, 0.29, 0.28, 0.31, 0.30, 0.30 respectively. This molar ratio had degradation comparable to the 50:1 ratio, both having the lowest BPA removal.

The majority of degradation occurs during the first ten minutes, leveling out throughout the remainder of the experiment as the solution in the reactor reached equilibrium. The results of the relative concentrations of the trial illustrate the experiment degraded BPA. The lack of degradation during the control compared to the degradation exhibited during the trials shows that the H_2O_2-UV treatment was effective.

These results strongly suggest that radical scavenging occurred. Because the solution was comprised of DI water, H_2O_2, and BPA, there are three possible radical scavengers: bicarbonate, H_2O_2, and other radicals. Radical-radical reactions are the most thermodynamically favorable with an activation energy of 8 kJ/mol. Radical-H_2O_2 reactions have the next lowest activation energy at 14 kJ/mol followed by radical-bicarbonate at 23.6 kJ/mol (Buxton et al., 1988)

Figure 10: Hydrogen Peroxide:Bisphenol A 1000:1 Mass Ratio vs Time

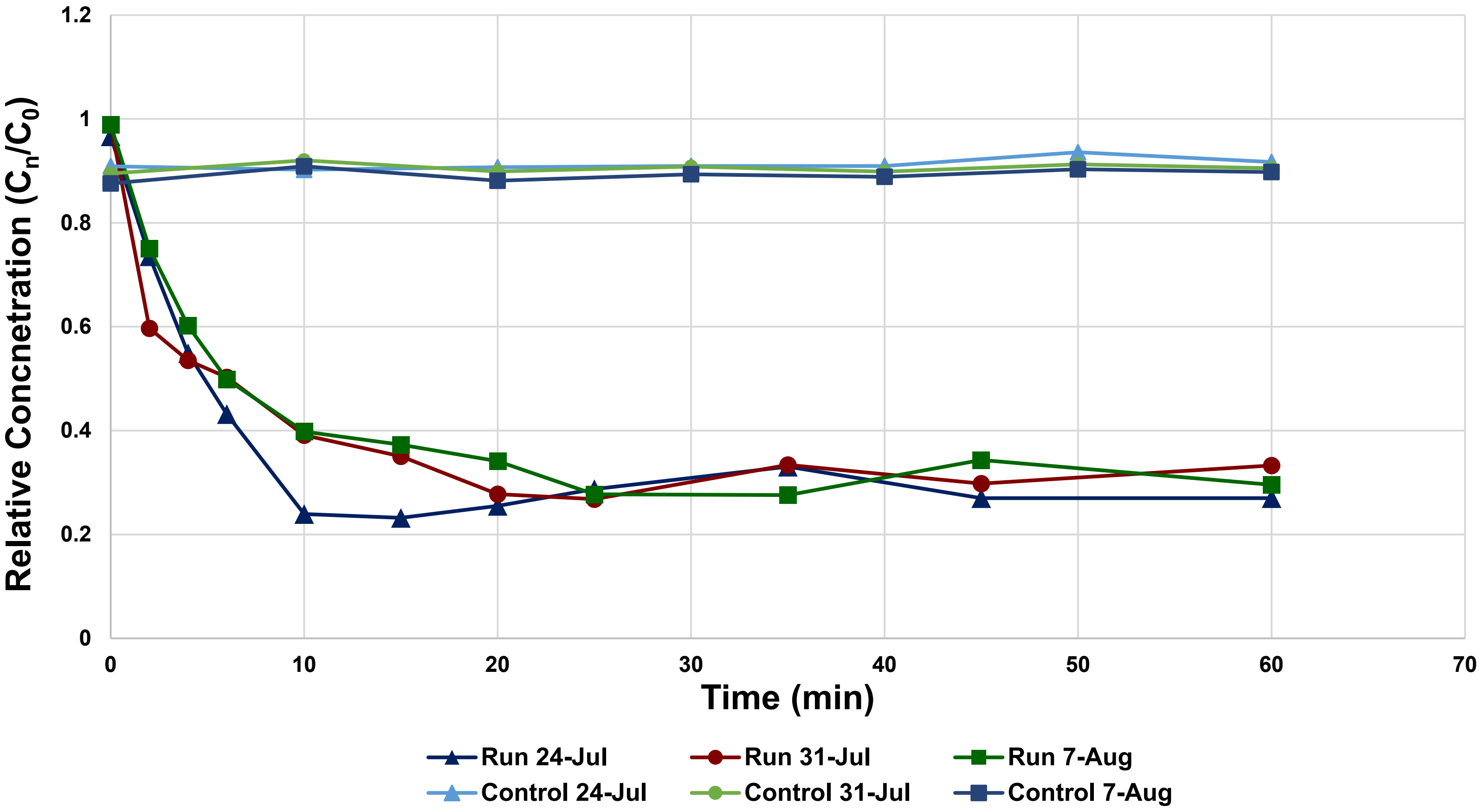


Figure 11 shows the averages of the five molar ratios in comparison to each other. The x-axis represents the time elapsed for the duration of the experiment. The y-axis represents the relative concentration. The 500:1 ratio had the highest degradation followed by 100 and 250 ratios. The 50 and 1000 ratios had the lowest degradation of all the ratios. The error bars have a value of one standard deviation.

A previous AOP study conducted at AFIT by Col John E. Stubbs, utilized the same reactor setup as this research, and demonstrated that BPA removal is a function of molar peroxide ratio (Stubbs, 2017).

Figure 11: Comparison of averages of the five molar ratios

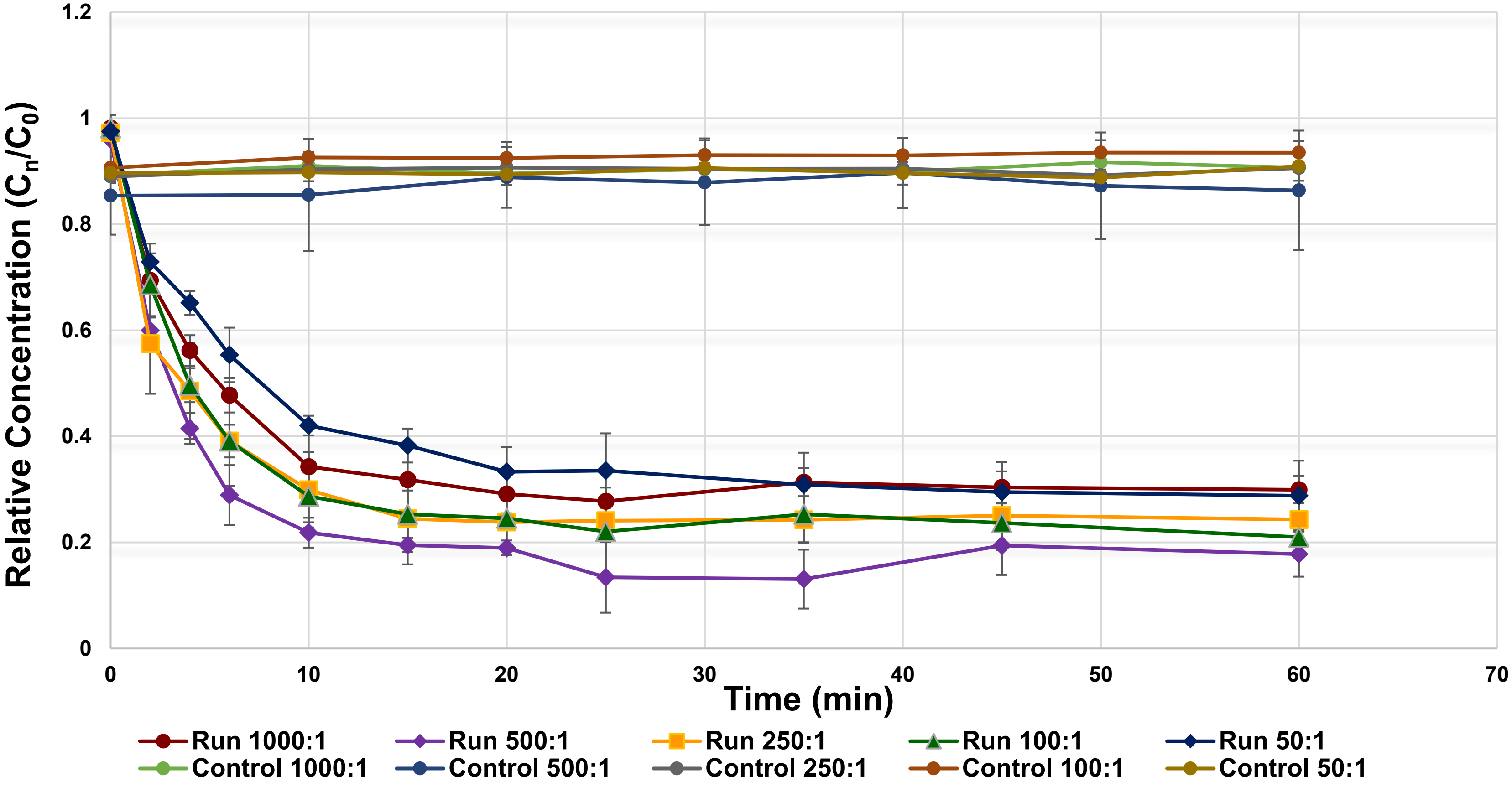


Table 1 shows the rate constants generated for each experiment and the average for each ratio. The 500:1 molar ratio had the highest average rate constant. The 100 and 250 molar ratios averages were very close to each other and were the second highest rate. The 50 and 1000 ratios were also similar to each other and were the lowest rates out of the five molar ratios.

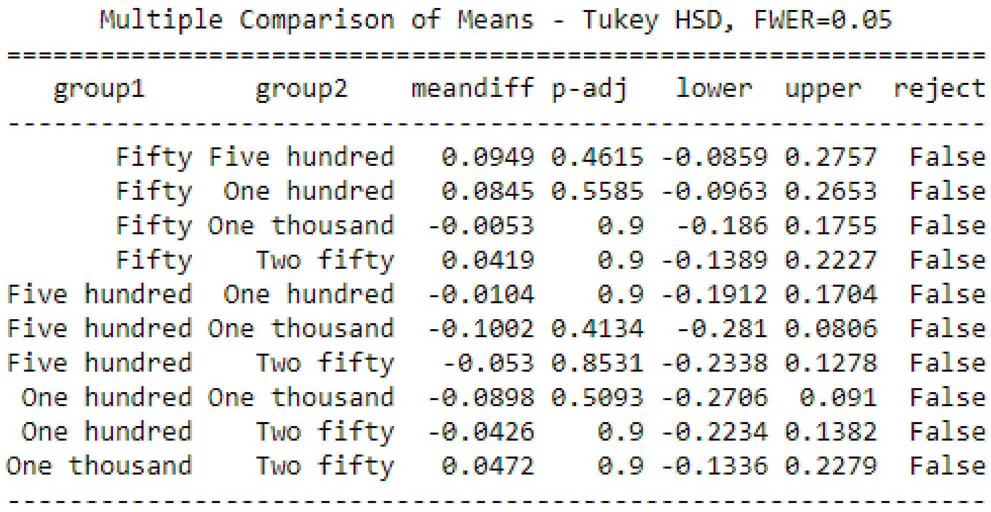
Table 1: Reaction rate constants

	1000:1	**500:1**	**250:1**	**100:1**	**50:1**
	0.17	0.31	0.3	0.17	0.16
	0.15	0.26	0.2	0.19	0.12
	0.14	0.26	0.15	0.26	0.11
AVG	0.15	0.28	0.22	0.21	0.13

Tukey pairwise comparison statistical analysis was utilized to determine statistical differences between overall degradation of the molar ratios and the rate constants of the molar ratios. The significance level for the analysis was 0.05 which corresponds to a 95% confidence interval.

Figure 12 shows the Tukey statistical analysis output. There was not a statistical difference between the overall degradation among the various molar ratios. The same general degradation occurred for each molar ratio.

Figure 12: Tukey pairwise comparison of overall degradation



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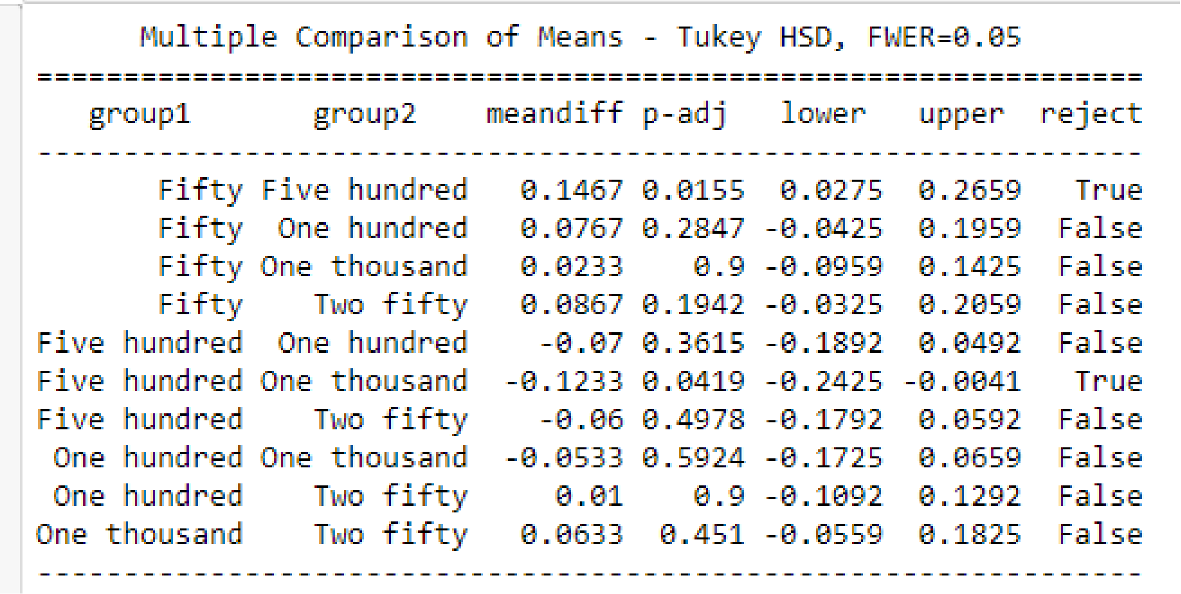
     Multiple Comparison of Means - Tukey HSD, FWER=0.05
===============================================================
   group1       group2    meandiff p-adj   lower  upper  reject
---------------------------------------------------------------
       Fifty Five hundred   0.0949 0.4615 -0.0859 0.2757  False
       Fifty  One hundred   0.0845 0.5585 -0.0963 0.2653  False
       Fifty One thousand  -0.0053    0.9  -0.186 0.1755  False
       Fifty    Two fifty   0.0419    0.9 -0.1389 0.2227  False
Five hundred  One hundred  -0.0104    0.9 -0.1912 0.1704  False
Five hundred One thousand  -0.1002 0.4134  -0.281 0.0806  False
Five hundred    Two fifty   -0.053 0.8531 -0.2338 0.1278  False
 One hundred One thousand  -0.0898 0.5093 -0.2706  0.091  False
 One hundred    Two fifty  -0.0426    0.9 -0.2234 0.1382  False
One thousand    Two fifty   0.0472    0.9 -0.1336 0.2279  False
---------------------------------------------------------------
```

Figure 13 shows the Tukey statistical analysis output. There was a statistical difference of rate constants between the 500:1 ratio and the 50 and 1000 ratios. A similar reaction rate can be reached at the 100:1 ratio as the 250 and 500:1 ratios while utilizing less H_2O_2.

Figure 13: Tukey pairwise comparison of rate constants



```
      Multiple Comparison of Means - Tukey HSD, FWER=0.05
================================================================
   group1       group2    meandiff p-adj   lower   upper  reject
----------------------------------------------------------------
       Fifty Five hundred   0.1467 0.0155  0.0275  0.2659   True
       Fifty  One hundred   0.0767 0.2847 -0.0425  0.1959  False
       Fifty One thousand   0.0233    0.9 -0.0959  0.1425  False
       Fifty    Two fifty   0.0867 0.1942 -0.0325  0.2059  False
Five hundred  One hundred    -0.07 0.3615 -0.1892  0.0492  False
Five hundred One thousand  -0.1233 0.0419 -0.2425 -0.0041   True
Five hundred    Two fifty    -0.06 0.4978 -0.1792  0.0592  False
 One hundred One thousand  -0.0533 0.5924 -0.1725  0.0659  False
 One hundred    Two fifty     0.01    0.9 -0.1092  0.1292  False
One thousand    Two fifty   0.0633  0.451 -0.0559  0.1825  False
----------------------------------------------------------------
```

Figure 14 shows the MS chromatogram of potential reaction byproducts at time 17.285. There are notable peaks at 259 and 260 amu. The peak at 260 amu may be due to the addition of two oxygen to BPA (Dr. D. Felker, personal correspondence, December 2020).

Figure 14 MS Chromatogram at time 17.258

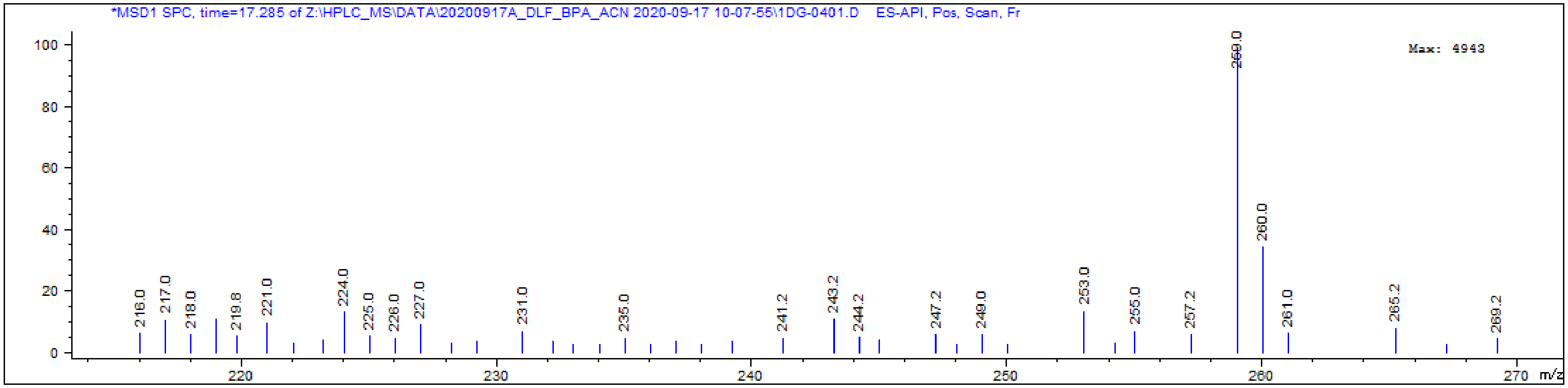
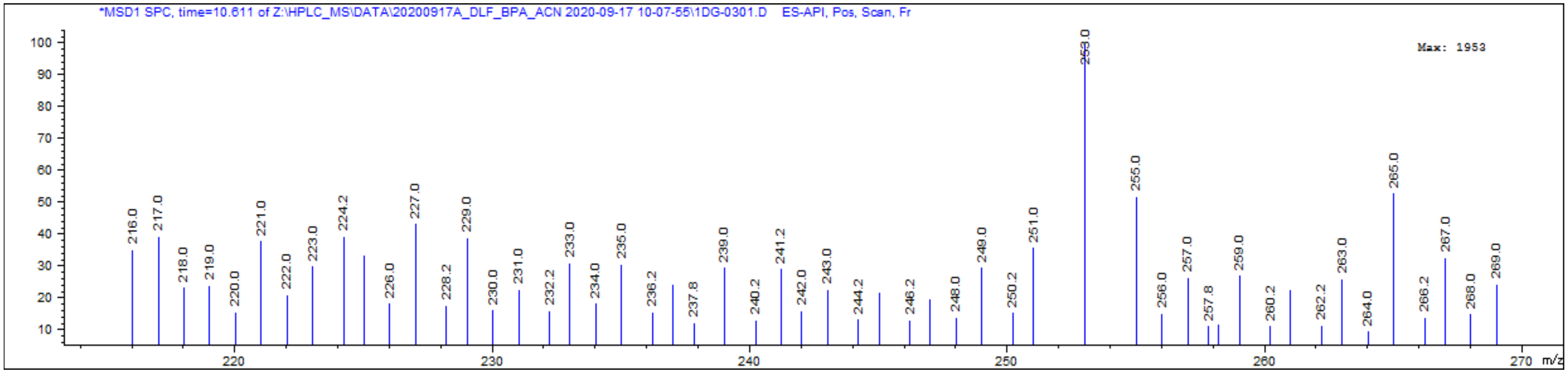


Figure 15 shows the MS chromatogram of potential reaction byproducts at time 10.311. There is a notable peak at 253 amu. This may be due to the addition of CN to BPA (Dr. D. Felker, personal correspondence, December 2020). Both chromatograms had significant peaks that could not be determined with previous research.

Figure 15 MS Chromatogram at time 10.611



V. Conclusions and Recommendations

5.1 Chapter Overview

This chapter evaluates future research possibilities and recommendations for improvement.

5.2 Research Conclusions

Statistical analysis did not show a statistical difference between the overall degradation of any of the molar ratios. There was a statistical difference of the degradation rate constants between the 500:1 ratio and the 50 and 1000:1 ratios. The data suggests that peroxide-limited reactions and radical scavenging impacted BPA degradation. The reactions of the lower molar ratios, 50, 100, and 250:1, were limited by the amount of H_2O_2. Less H_2O_2 in the solution resulted in fewer radicals produced, subsequently reducing radical-BPA reactions and inhibiting BPA degradation. Due to the highly reactive nature of hydroxyl radicals, they indiscriminately react with other compounds. More favorable thermodynamic reactions facilitate radical scavenging, also inhibiting BPA degradation.

5.3 Research Significance

This research provided additional data that may continue to improve the technology that will enable an optimal water treatment process for contaminant degradation. This study was the first UV LED H_2O_2 AOP trial that investigated BPA degradation kinetics under the parameters utilized. This research illustrated that BPA degradation occurs utilizing UV LED and H_2O_2 and that a molar ratio of 100:1 may obtain the same rate constant as the 250 and 500:1 ratios with the benefit of using less H_2O_2.

5.4 Recommendations for Future Research

Additional research trials centered around the 100:1 molar ratio may narrow down the optimal ratio for degradation and rate constant. Additional trials will also increase the sample size, lending itself to a stronger statistical analysis. Implementing LED testing will ensure that the LEDs are working consistently across each experiment. Future studies should also consider more powerful LEDs, the effect of co-contaminants, and larger scale testing.

Appendix A. Data for 29 March – 0:1 ratio with 10.048 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L
Blank	0		0	0	0
Standard	10		1	19.6	1.00481
Standard	20		0.998	39.7	2.00962
Standard	40		1.001	91.8	4.01924
Standard	60		1.014	139.8	6.02886
Standard	80		1.051	166.5	8.03848
Standard	100		1.079	215	10.0481

Control						**Cn/C0**	**Average Control**
C1	84.3247	0	1.095	183	8.473030181	0.843247	8.60837432
C2	87.50215	20	1.098	189.9	8.792303534	0.8750215	
C3	84.83125	40	1.095	184.1	8.523928831	0.8483125	
C4	86.02855	60	1.096	186.7	8.644234733	0.8602855	

Test						**Cn/C0**
R1	89.25205	5	1.099	193.7	8.968135236	1.041791969
R2	88.7455	10	1.097	192.6	8.917236586	1.035879279
R3	86.0746	15	1.098	186.8	8.648861883	1.004703276
R4	85.93645	20	1.098	186.5	8.634980432	1.003090724
R5	86.02855	25	1.099	186.7	8.644234733	1.004165759
R6	85.3378	35	1.102	185.2	8.574827482	0.996103
R7	86.2588	45	1.099	187.2	8.667370483	1.006853345
R8	87.68635	60	1.101	190.3	8.810812134	1.023516382

Appendix B. Data for 14 Aug, Exp 1. – 50:1 ratio with 10.05268 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.084	16.1	1.005268		
Standard	20		1.082	36.1	2.010536		
Standard	40		1.086	70.4	4.021072		
Standard	60		1.085	110.2	6.031608		
Standard	80		1.084	135.5	8.042144		
Standard	100		1.081	173	10.05268		
Control						**Cn/C0**	**Average Control**
C1	87.2559	0	1.082	151.8	8.771556408	0.872559	8.807187414
C2	87.6021	10	1.086	152.4	8.806358786	0.876021	
C3	87.3136	20	1.083	151.9	8.777356804	0.873136	
C4	89.7947	30	1.084	156.2	9.026773848	0.897947	
C5	86.6789	40	1.084	150.8	8.713552445	0.866789	
C6	85.7557	50	1.083	149.2	8.620746103	0.857557	
C7	88.8715	60	1.082	154.6	8.933967506	0.888715	
Test						**Cn/C0**	
R1	85.2364	0	1.083	148.3	8.568542536	0.97290339	
R2	63.772	2	1.083	111.1	6.41079509	0.72790492	
R3	54.4246	4	1.084	94.9	5.471130879	0.62121204	
R4	42.2499	6	1.084	73.8	4.247247247	0.48224786	
R5	34.9797	10	1.085	61.2	3.516397306	0.3992645	
R6	30.4214	15	1.083	53.3	3.058165994	0.34723526	
R7	24.4783	20	1.084	43	2.460725168	0.27939966	
R8	20.7278	25	1.084	36.5	2.083699405	0.23659079	
R9	20.0354	35	1.084	35.3	2.014094649	0.22868761	
R10	18.8814	45	1.084	33.3	1.898086722	0.21551565	
R11	18.766	60	1.082	33.1	1.886485929	0.21419845	

Appendix C. Data for 14 Aug, Exp 2. – 50:1 ratio with 10.05268 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.088	18.1	1.005268		
Standard	20		1.086	34.8	2.010536		
Standard	40		1.087	72.2	4.021072		
Standard	60		1.086	107.1	6.031608		
Standard	80		1.085	146.2	8.042144		
Standard	100		1.086	187.2	10.05268		
Control						**Cn/C0**	**Average Control**
C1	90.19392	0	1.084	166.2	9.066906157	0.9019392	9.02830387
C2	90.14016	10	1.084	166.1	9.061501836	0.9014016	
C3	88.79616	20	1.084	163.6	8.926393817	0.8879616	
C4	90.24768	30	1.084	166.3	9.072310478	0.9024768	
C5	90.51648	40	1.085	166.8	9.099332082	0.9051648	
C6	89.60256	50	1.084	165.1	9.007458629	0.8960256	
C7	89.17248	60	1.083	164.3	8.964224062	0.8917248	
Test						**Cn/C0**	
R1	88.84992	0	1.082	163.7	8.931798138	0.98931076	
R2	65.41056	2	1.083	120.1	6.575514283	0.72832222	
R3	60.46464	4	1.085	110.9	6.078316772	0.67325124	
R4	54.01344	6	1.084	98.9	5.42979828	0.60141953	
R5	37.50912	10	1.086	68.2	3.770671804	0.41765008	
R6	33.79968	15	1.086	61.3	3.397773671	0.37634684	
R7	29.44512	20	1.088	53.2	2.960023689	0.32786044	
R8	35.2512	25	1.086	64	3.543690332	0.39250898	
R9	33.58464	35	1.087	60.9	3.376156388	0.37395245	
R10	29.82144	45	1.085	53.9	2.997853935	0.33205062	
R11	24.71424	60	1.087	44.4	2.484443462	0.27518385	

Appendix D. Data for 28 Aug, Exp. 1 – 50:1 ratio with 10.051068 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.076	19	1.0051068		
Standard	20		1.08	42	2.0102136		
Standard	40		1.084	83.7	4.0204272		
Standard	60		1.09	126.3	6.0306408		
Standard	80		1.088	158.7	8.0408544		
Standard	100		1.087	205.8	10.051068		
Control						**Cn/C0**	**Average Control**
C1	91.46526	0	1.087	187.2	9.193235479	0.9146526	9.254359
C2	91.66098	10	1.088	187.6	9.212907429	0.9166098	
C3	92.00349	20	1.09	188.3	9.247333342	0.9200349	
C4	91.8567	30	1.092	188	9.23257938	0.918567	
C5	91.70991	40	1.092	187.7	9.217825417	0.9170991	
C6	90.97596	50	1.089	186.2	9.144055603	0.9097596	
C7	94.84143	60	1.09	194.1	9.532576621	0.9484143	
Test						**Cn/C0**	
R1	88.72518	0	1.087	181.6	8.917828175	0.96363542	
R2	67.29384	2	1.089	137.8	6.763749618	0.73087175	
R3	60.88401	4	1.092	124.7	6.119493246	0.66125522	
R4	53.15307	6	1.088	108.9	5.34245121	0.57729025	
R5	40.92057	10	1.085	83.9	4.112954317	0.44443427	
R6	39.11016	15	1.088	80.2	3.930988777	0.42477159	
R7	36.17436	20	1.087	74.2	3.635909522	0.39288615	
R8	34.75539	25	1.083	71.3	3.493287883	0.37747486	
R9	29.86239	35	1.087	61.3	3.001489125	0.32433247	
R10	31.08564	45	1.085	63.8	3.124438815	0.33761807	
R11	34.51074	60	1.088	70.8	3.468697945	0.37481774	

Appendix E. Data for 5 June – 100:1 ratio with 10.044 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.104	19.3	1.0044		
Standard	20		1.104	44.9	2.0088		
Standard	40		1.106	83	4.0176		
Standard	60		1.103	133.6	6.0264		
Standard	80		1.103	165.4	8.0352		
Standard	100		1.104	209.7	10.044		
Control						**Cn/C0**	**Average Control**
C1	89.5731	0	1.104	189	8.996722164	0.895731	9.343099
C2	93.1371	10	1.104	196.5	9.354690324	0.931371	
C3	92.80446	20	1.104	195.8	9.321279962	0.928045	
C4	94.5627	30	1.103	199.5	9.497877588	0.945627	
C5	93.23214	40	1.104	196.7	9.364236142	0.932321	
C6	94.51518	50	1.101	199.4	9.493104679	0.945152	
C7	93.32718	60	1.103	196.9	9.373781959	0.933272	
Test						**Cn/C0**	
R1	94.03998	0	1.101	198.4	9.445375591	1.010947	
R2	67.19118	2	1.104	141.9	6.748682119	0.722317	
R3	48.51582	4	1.104	102.6	4.872928961	0.521554	
R4	38.63166	6	1.103	81.8	3.88016393	0.415297	
R5	29.79294	10	1.104	63.2	2.992402894	0.320279	
R6	28.12974	15	1.104	59.7	2.825351086	0.3024	
R7	27.3219	20	1.105	58	2.744211636	0.293715	
R8	26.51406	25	1.1	56.3	2.663072186	0.285031	
R9	29.9355	35	1.107	63.5	3.00672162	0.321812	
R10	26.6091	45	1.105	56.5	2.672618004	0.286053	
R11	19.2435	60	1.109	41	1.93281714	0.206871	

Appendix F. Data for 19 June – 100:1 ratio with 10.05888 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.12	24.6	1.005888		
Standard	20		1.119	40.8	2.011776		
Standard	40		1.117	76.2	4.023552		
Standard	60		1.12	119.9	6.035328		
Standard	80		1.122	157.3	8.047104		
Standard	100		1.118	200.2	10.05888		
Control						**Cn/C0**	**Average Control**
C1	94.65302	0	1.124	187.8	9.521033698	0.9465302	9.565467
C2	93.53784	10	1.122	185.6	9.40885908	0.9353784	
C3	96.07234	20	1.122	190.6	9.663801394	0.9607234	
C4	95.92027	30	1.122	190.3	9.648504855	0.9592027	
C5	93.43646	40	1.123	185.4	9.398661388	0.9343646	
C6	95.7682	50	1.121	190	9.633208316	0.957682	
C7	96.2751	60	1.119	191	9.684196779	0.962751	
Test						**Cn/C0**	
R1	90.29368	0	1.122	179.2	9.082532919	0.9495128	
R2	69.30802	2	1.122	137.8	6.971610562	0.7288312	
R3	48.37305	4	1.124	96.5	4.865787052	0.5086827	
R4	38.08298	6	1.123	76.2	3.830721259	0.4004741	
R5	29.66844	10	1.124	59.6	2.984312777	0.3119882	
R6	23.63633	15	1.123	47.7	2.377550071	0.2485556	
R7	25.05565	20	1.124	50.5	2.520317767	0.2634809	
R8	24.8022	25	1.12	50	2.494823535	0.2608157	
R9	21.50735	35	1.118	43.5	2.163398528	0.2261676	
R10	19.98665	45	1.12	40.5	2.01043314	0.2101762	
R11	20.89907	60	1.12	42.3	2.102212372	0.219771	

Appendix G. Data for 26 June – 100:1 ratio with 10.043 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.119	21.9	1.0043		
Standard	20		1.113	41.8	2.0086		
Standard	40		1.112	84.6	4.0172		
Standard	60		1.118	143.9	6.0258		
Standard	80		1.117	167.1	8.0344		
Standard	100		1.115	207.3	10.043		
Control						**Cn/C0**	**Average Control**
C1	87.75806	0	1.114	187.6	8.813541966	0.877581	9.0343247
C2	91.14638	10	1.117	194.8	9.153830943	0.911464	
C3	88.55808	20	1.117	189.3	8.893887974	0.885581	
C4	88.6522	30	1.115	189.5	8.903340446	0.886522	
C5	92.32288	40	1.115	197.3	9.271986838	0.923229	
C6	90.2993	50	1.117	193	9.068758699	0.902993	
C7	90.95814	60	1.119	194.4	9.134926	0.909581	
Test						**Cn/C0**	
R1	88.51102	0	1.12	189.2	8.889161739	0.983932	
R2	53.78074	2	1.122	115.4	5.401199718	0.597853	
R3	40.03922	4	1.12	86.2	4.021138865	0.445096	
R4	30.62722	6	1.118	66.2	3.075891705	0.340467	
R5	18.7681	10	1.115	41	1.884880283	0.208635	
R6	16.83864	15	1.121	36.9	1.691104615	0.187187	
R7	14.20328	20	1.123	31.3	1.42643541	0.157891	
R8	8.36784	27	1.121	18.9	0.840382171	0.093021	
R9	17.121	36	1.117	37.5	1.71946203	0.190325	
R10	17.30924	45	1.117	37.9	1.738366973	0.192418	
R11	16.27392	60	1.12	35.7	1.634389786	0.180909	

Appendix H. Data for 28 Aug, Exp. 2 – 250:1 ratio with 10.051068 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.086	17.9	1.0051068		
Standard	20		1.088	42.3	2.0102136		
Standard	40		1.088	82.3	4.0204272		
Standard	60		1.086	120	6.0306408		
Standard	80		1.087	169.7	8.0408544		
Standard	100		1.087	201.8	10.051068		
Control						**Cn/C0**	**Average Control**
C1	89.5943	0	1.087	183.8	9.005184017	0.895943	9.0693845
C2	89.8859	10	1.086	184.4	9.034492931	0.898859	
C3	91.1009	20	1.09	186.9	9.156613408	0.911009	
C4	90.8093	30	1.085	186.3	9.127304493	0.908093	
C5	90.2747	40	1.087	185.2	9.073571484	0.902747	
C6	89.3513	50	1.085	183.3	8.980759922	0.893513	
C7	90.6149	60	1.087	185.9	9.107765217	0.906149	
Test						**Cn/C0**	
R1	85.7549	0	1.089	175.9	8.619283312	0.9503714	
R2	41.8205	2	1.086	85.5	4.203406893	0.4634721	
R3	33.5099	4	1.087	68.4	3.368102836	0.3713706	
R4	25.9283	6	1.086	52.8	2.606071064	0.2873482	
R5	19.0757	10	1.092	38.7	1.917311578	0.2114048	
R6	15.7223	15	1.086	31.8	1.580259064	0.174241	
R7	16.4999	20	1.087	33.4	1.658416169	0.1828587	
R8	17.5205	25	1.09	35.5	1.760997369	0.1941694	
R9	16.6457	35	1.089	33.7	1.673070626	0.1844746	
R10	15.0419	45	1.089	30.4	1.511871597	0.1667006	
R11	15.6737	60	1.088	31.7	1.575374245	0.1737024	

Appendix I. Data for 3 Sept, Exp. 1 – 250:1 ratio with 10.046889 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.061	17	1.0046889		
Standard	20		1.065	36.8	2.0093778		
Standard	40		1.067	77.9	4.0187556		
Standard	60		1.068	120.5	6.0281334		
Standard	80		1.071	160.9	8.0375112		
Standard	100		1.071	205.9	10.046889		
Control						**Cn/C0**	**Average Control**
C1	87.63605	0	1.08	178.1	8.804696667	0.8763605	9.030231385
C2	92.0359	10	1.085	187.2	9.246744713	0.920359	
C3	89.7151	20	1.086	182.4	9.013576513	0.897151	
C4	89.86015	30	1.085	182.7	9.028149526	0.8986015	
C5	89.76345	40	1.085	182.5	9.018434184	0.8976345	
C6	89.57005	50	1.085	182.1	8.999003501	0.8957005	
C7	90.5854	60	1.085	184.2	9.101014588	0.905854	
Test						**Cn/C0**	
R1	87.8778	0	1.086	178.6	8.828985022	0.97771415	
R2	50.9384	2	1.087	102.2	5.117724506	0.56673238	
R3	44.3628	4	1.083	88.6	4.457081273	0.49357332	
R4	35.1763	6	1.087	69.6	3.534123815	0.39136581	
R5	27.0535	10	1.086	52.8	2.718035116	0.30099285	
R6	20.9614	15	1.089	40.2	2.105968591	0.23321314	
R7	22.17015	20	1.087	42.7	2.227410362	0.24666149	
R8	23.23385	25	1.089	44.9	2.33427912	0.25849605	
R9	22.55695	35	1.09	43.5	2.266271728	0.25096497	
R10	23.42725	45	1.089	45.3	2.353709803	0.26064778	
R11	23.669	60	1.086	45.8	2.377998157	0.26333746	

Appendix J. Data for 3 Sept, Exp. 2 – 250:1 ratio with 10.046889 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.086	16.7	1.0046889		
Standard	20		1.088	40.1	2.0093778		
Standard	40		1.085	79.9	4.0187556		
Standard	60		1.088	121.6	6.0281334		
Standard	80		1.089	157.8	8.0375112		
Standard	100		1.086	202.3	10.046889		
Control						**Cn/C0**	**Average Control**
C1	89.77728	0	1.088	180.4	9.019823669	0.8977728	9.0701847
C2	89.18424	10	1.088	179.2	8.960241598	0.8918424	
C3	91.25988	20	1.088	183.4	9.168778845	0.9125988	
C4	90.76568	30	1.089	182.4	9.11912712	0.9076568	
C5	91.45756	40	1.091	183.8	9.188639535	0.9145756	
C6	88.88772	50	1.089	178.6	8.930450563	0.8888772	
C7	90.61742	60	1.088	182.1	9.104231602	0.9061742	
Test						**Cn/C0**	
R1	89.28308	0	1.088	179.4	8.970171943	0.98897346	
R2	62.6457	2	1.089	125.5	6.293943942	0.69391574	
R3	53.45358	4	1.087	106.9	5.370421849	0.59209619	
R4	44.65682	6	1.089	89.1	4.486621136	0.49465598	
R5	34.77282	10	1.087	69.1	3.493586628	0.3851726	
R6	29.48488	15	1.088	58.4	2.962313165	0.32659899	
R7	25.77838	20	1.088	50.9	2.589925225	0.28554272	
R8	24.39462	25	1.087	48.1	2.450900393	0.27021505	
R9	26.42084	35	1.091	52.2	2.654472468	0.29265914	
R10	29.2872	45	1.089	58	2.942452475	0.32440932	
R11	26.42084	60	1.091	52.2	2.654472468	0.29265914	

Appendix K. Data for 1 July – 500:1 ratio with 10.0432 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.112	20.6	1.00432		
Standard	20		1.115	43.5	2.00864		
Standard	40		1.116	80.8	4.01728		
Standard	60		1.117	118.4	6.02592		
Standard	80		1.117	164.6	8.03456		
Standard	100		1.117	203.5	10.0432		
Control						**Cn/C0**	**Average Control**
C1	91.1195	0	1.12	185.2	9.151313624	0.911195	9.606833
C2	96.9862	10	1.12	197.1	9.740518038	0.969862	
C3	96.5918	20	1.118	196.3	9.700907658	0.965918	
C4	97.0355	30	1.12	197.2	9.745469336	0.970355	
C5	95.9509	40	1.122	195	9.636540789	0.959509	
C6	95.7537	50	1.12	194.6	9.616735598	0.957537	
C7	96.1481	60	1.12	195.4	9.656345979	0.961481	
Test						**Cn/C0**	
R1	94.7184	0	1.12	192.5	9.512758349	0.9902075	
R2	56.7081	2	1.122	115.4	5.695307899	0.5928393	
R3	35.7063	4	1.117	72.8	3.586055122	0.3732817	
R4	20.0782	6	1.118	41.1	2.016493782	0.209902	
R5	19.1415	10	1.119	39.2	1.922419128	0.2001096	
R6	16.5286	15	1.122	33.9	1.660000355	0.1727937	
R7	16.2821	20	1.119	33.4	1.635243867	0.1702167	
R8	14.5566	25	1.116	29.9	1.461948451	0.152178	
R9	6.8165	35	1.119	14.2	0.684594728	0.0712612	
R10	10.7605	45	1.119	22.2	1.080698536	0.1124927	
R11	11.5493	60	1.12	23.8	1.159919298	0.120739	

Appendix L. Data for 10 July – 500:1 ratio with 10.04772 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.112	23.9	1.004772		
Standard	20		1.11	42.9	2.009544		
Standard	40		1.112	82.6	4.019088		
Standard	60		1.109	122.6	6.028632		
Standard	80		1.111	159.3	8.038176		
Standard	100		1.113	204.2	10.04772		
Control						**Cn/C0**	**Average Control**
C1	75.01628	0	1.111	152.4	7.537425769	0.750163	7.6254726
C2	71.52538	10	1.108	145.4	7.186669911	0.715254	
C3	82.84587	20	1.108	168.1	8.324121049	0.828459	
C4	77.60952	30	1.111	157.6	7.797987263	0.776095	
C5	80.55185	40	1.11	163.5	8.093624343	0.805519	
C6	73.12122	50	1.114	148.6	7.347015446	0.731212	
C7	70.57785	60	1.113	143.5	7.09146475	0.705779	
Test						**Cn/C0**	
R1	67.68539	0	1.111	137.7	6.800838468	0.891858	
R2	47.23869	2	1.111	96.7	4.746411303	0.622442	
R3	32.77639	4	1.109	67.7	3.293279893	0.431879	
R4	25.19615	6	1.11	52.5	2.531638603	0.331998	
R5	18.11461	10	1.107	38.3	1.820105292	0.238688	
R6	17.11721	15	1.11	36.3	1.719889333	0.225545	
R7	12.67878	20	1.109	27.4	1.273928314	0.167062	
R8	1.45803	26	1.104	4.9	0.146498772	0.019212	
R9	6.69438	36	1.107	15.4	0.672632558	0.088209	
R10	15.87046	45	1.108	33.8	1.594619384	0.209117	
R11	15.77072	60	1.112	33.6	1.584597788	0.207803	

Appendix M. Data for 17 July – 500:1 ratio with 10.043578 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.087	21.5	1.0043578		
Standard	20		1.09	34.5	2.0087156		
Standard	40		1.091	78	4.0174312		
Standard	60		1.098	119.4	6.0261468		
Standard	80		1.1	156	8.0348624		
Standard	100		1.102	198	10.043578		
Control						**Cn/C0**	**Average Control**
C1	90.07215	0	1.103	177.5	9.046466642	0.9007215	9.0718116
C2	88.15429	10	1.106	173.7	8.853844876	0.8815429	
C3	87.14489	20	1.104	171.7	8.752465	0.8714489	
C4	88.96181	30	1.105	175.3	8.934948778	0.8896181	
C5	92.59565	40	1.104	182.5	9.299916332	0.9259565	
C6	92.89847	50	1.102	183.1	9.330330295	0.9289847	
C7	92.44424	60	1.104	182.2	9.284709351	0.9244424	
Test						**Cn/C0**	
R1	89.92074	0	1.104	177.2	9.03125966	0.99552989	
R2	51.71495	2	1.106	101.5	5.194031341	0.57254621	
R3	38.23946	4	1.105	74.8	3.840609992	0.42335645	
R4	27.59029	6	1.104	53.7	2.771052297	0.30545743	
R5	17.54676	10	1.102	33.8	1.762322527	0.19426357	
R6	14.72044	15	1.102	28.2	1.478458873	0.16297284	
R7	18.75804	20	1.105	36.2	1.883978379	0.20767389	
R8	18.40475	25	1.104	35.5	1.848495422	0.20376255	
R9	18.6571	35	1.108	36	1.873840391	0.20655636	
R10	21.48342	45	1.109	41.6	2.157704045	0.2378471	
R11	16.43642	50	1.102	31.6	1.650804663	0.18197078	

Appendix N. Data for 24 July – 1000:1 ratio with 10.0444 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.09	20.6	1.00444		
Standard	20		1.09	40	2.00888		
Standard	40		1.087	84.9	4.01776		
Standard	60		1.088	124.2	6.02664		
Standard	80		1.088	166.9	8.03552		
Standard	100		1.093	207.1	10.0444		
Control						**Cn/C0**	**Average Control**
C1	90.89852	0	1.089	188.9	9.130210943	0.9089852	9.16953563
C2	90.2254	10	1.09	187.5	9.062600078	0.902254	
C3	90.7062	20	1.089	188.5	9.110893553	0.907062	
C4	90.9466	20	1.089	189	9.13504029	0.909466	
C5	90.9466	30	1.089	189	9.13504029	0.909466	
C6	93.591	40	1.088	194.5	9.400654404	0.93591	
C7	91.71588	60	1.087	190.6	9.212309851	0.9171588	
Test						**Cn/C0**	
R1	88.25412	0	1.09	183.4	8.864596829	0.96674436	
R2	67.147	2	1.09	139.5	6.744513268	0.73553488	
R3	50.12668	4	1.09	104.1	5.034924246	0.54909261	
R4	39.40484	6	1.09	81.8	3.957979749	0.43164451	
R5	21.85564	10	1.09	45.3	2.195267904	0.23940884	
R6	21.18252	15	1.09	43.9	2.127657039	0.23203542	
R7	23.29804	20	1.09	48.3	2.34014833	0.25520903	
R8	26.23092	25	1.09	54.4	2.634738528	0.28733609	
R9	30.17348	35	1.09	62.6	3.030745025	0.33052328	
R10	24.64428	45	1.09	51.1	2.47537006	0.26995588	
R11	24.64428	50	1.09	51.1	2.47537006	0.26995588	

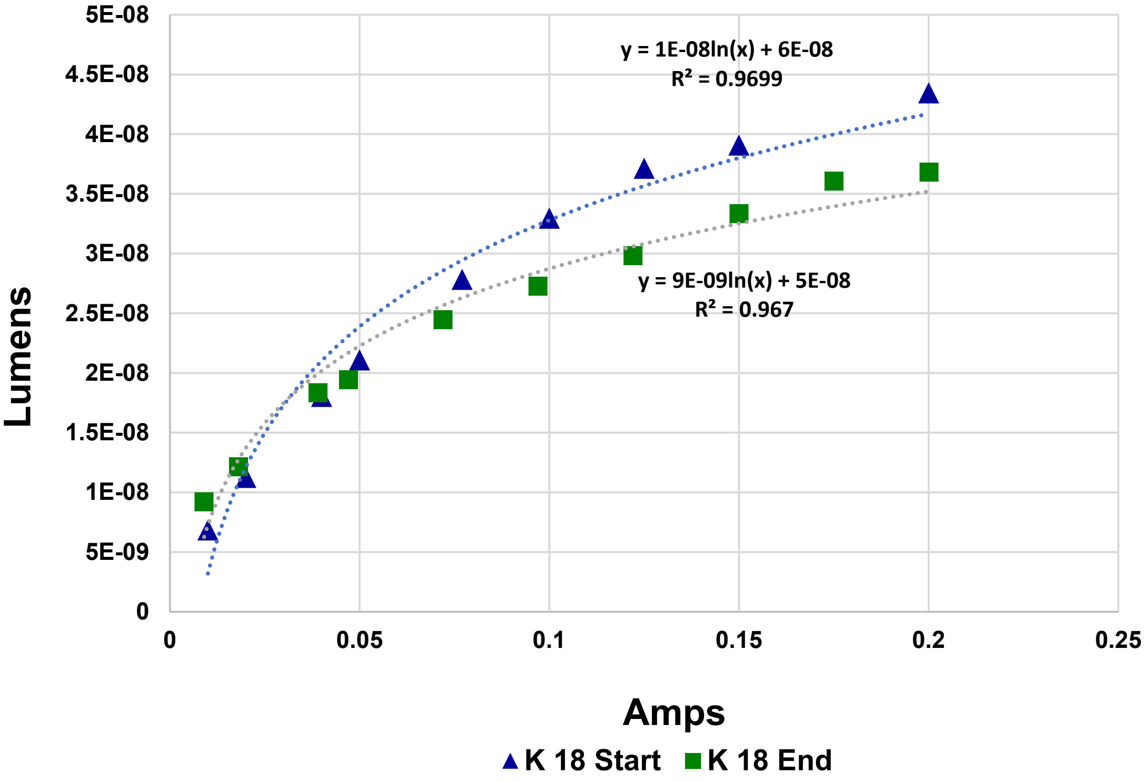
Appendix O. Data for 31 July – 1000:1 ratio with 10.049332 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.086	20.5	1.0049332		
Standard	20		1.088	38.1	2.0098664		
Standard	40		1.089	82.9	4.0197328		
Standard	60		1.088	122.2	6.0295992		
Standard	80		1.088	163.4	8.0394656		
Standard	100		1.086	206.1	10.049332		
Control						**Cn/C0**	**Average Control**
C1	89.5067	0	1.091	183.7	8.994825445	0.895067	9.099963
C2	92.0287	10	1.091	188.9	9.248269598	0.920287	
C3	89.8947	20	1.089	184.5	9.033816853	0.898947	
C4	90.8162	30	1.088	186.4	9.126421448	0.908162	
C5	89.8462	40	1.087	184.4	9.028942927	0.898462	
C6	91.2527	50	1.09	187.3	9.170286782	0.912527	
C7	90.5252	60	1.089	185.8	9.097177892	0.905252	
Test						**Cn/C0**	
R1	89.5552	0	1.089	183.8	8.999699371	0.988982	
R2	54.0532	2	1.088	110.6	5.431985525	0.5969239	
R3	48.4757	4	1.089	99.1	4.871484032	0.5353301	
R4	45.5172	6	1.092	93	4.574174545	0.5026586	
R5	35.4292	10	1.087	72.2	3.560397933	0.3912541	
R6	31.7432	15	1.089	64.6	3.189979555	0.3505486	
R7	25.1472	20	1.087	51	2.527125617	0.2777072	
R8	24.2742	25	1.088	49.2	2.439394948	0.2680665	
R9	30.2397	35	1.087	61.5	3.038887849	0.3339451	
R10	26.9902	45	1.087	54.8	2.712334805	0.29806	
R11	30.1427	60	1.091	61.3	3.029139997	0.3328739	

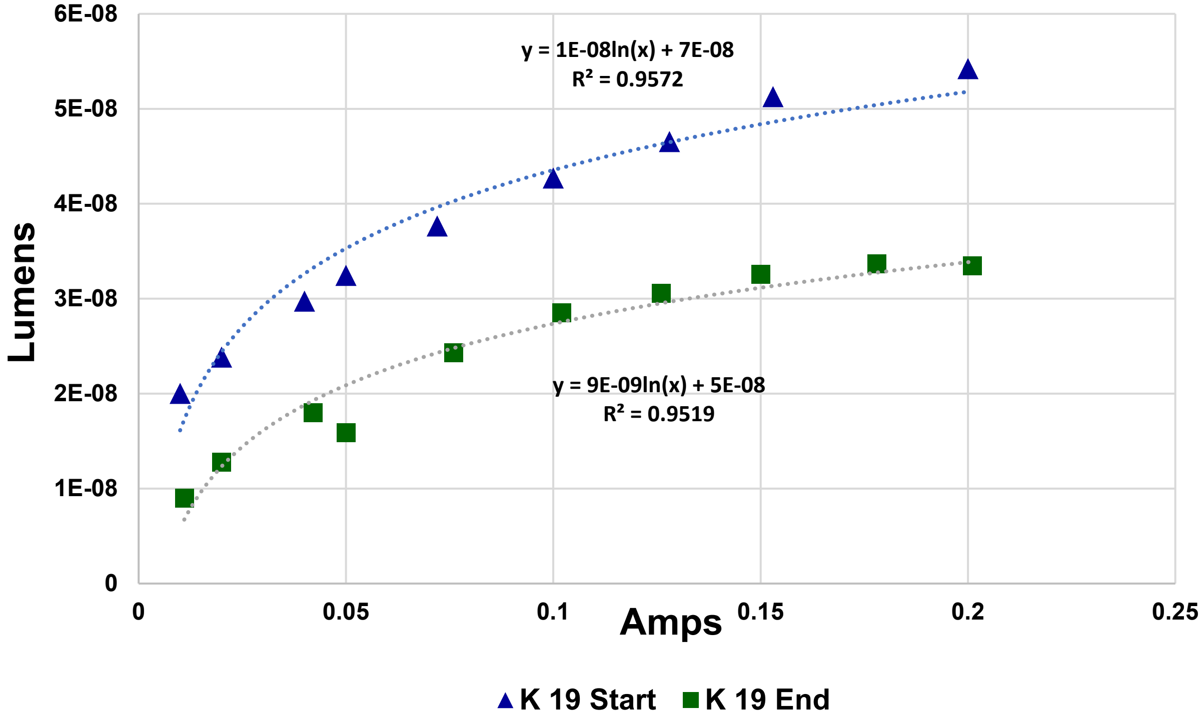
Appendix P. Data for 7 Aug – 1000:1 ratio with 10.051849 mg/L BPA solution

Sample	Concentration %	Time (min)	RT (min)	Peak Area	Concentration mg/L		
Blank	0		0	0	0		
Standard	10		1.088	19.5	1.0051849		
Standard	20		1.083	44.9	2.0103698		
Standard	40		1.08	82.5	4.0207396		
Standard	60		1.083	125.4	6.0311094		
Standard	80		1.084	167.5	8.0414792		
Standard	100		1.083	208.7	10.051849		
Control						**Cn/C0**	**Average Control**
C1	87.5774	0	1.09	183	8.803148006	0.875774	8.973078391
C2	90.88319	10	1.091	189.9	9.135441025	0.9088319	
C3	88.10441	20	1.093	184.1	8.856122256	0.8810441	
C4	89.35007	30	1.093	186.7	8.981334118	0.8935007	
C5	88.87097	40	1.092	185.7	8.933175709	0.8887097	
C6	90.30827	50	1.093	188.7	9.077650935	0.9030827	
C7	89.78126	60	1.094	187.6	9.024676685	0.8978126	
Test						**Cn/C0**	
R1	88.24814	0	1.093	184.4	8.870569778	0.98857598	
R2	66.9761	2	1.091	140	6.732336438	0.75028169	
R3	53.65712	4	1.091	112.2	5.39353268	0.60107941	
R4	44.41049	6	1.092	92.9	4.464075395	0.49749653	
R5	35.40341	10	1.094	74.1	3.558697314	0.39659715	
R6	33.15164	15	1.092	69.4	3.332352794	0.3713723	
R7	30.32495	20	1.09	63.5	3.048218183	0.33970707	
R8	24.62366	25	1.09	51.6	2.475133121	0.27583991	
R9	24.47993	35	1.092	51.3	2.460685599	0.27422981	
R10	30.51659	45	1.091	63.9	3.067481547	0.34185387	
R11	26.2526	60	1.091	55	2.638871711	0.29408767	

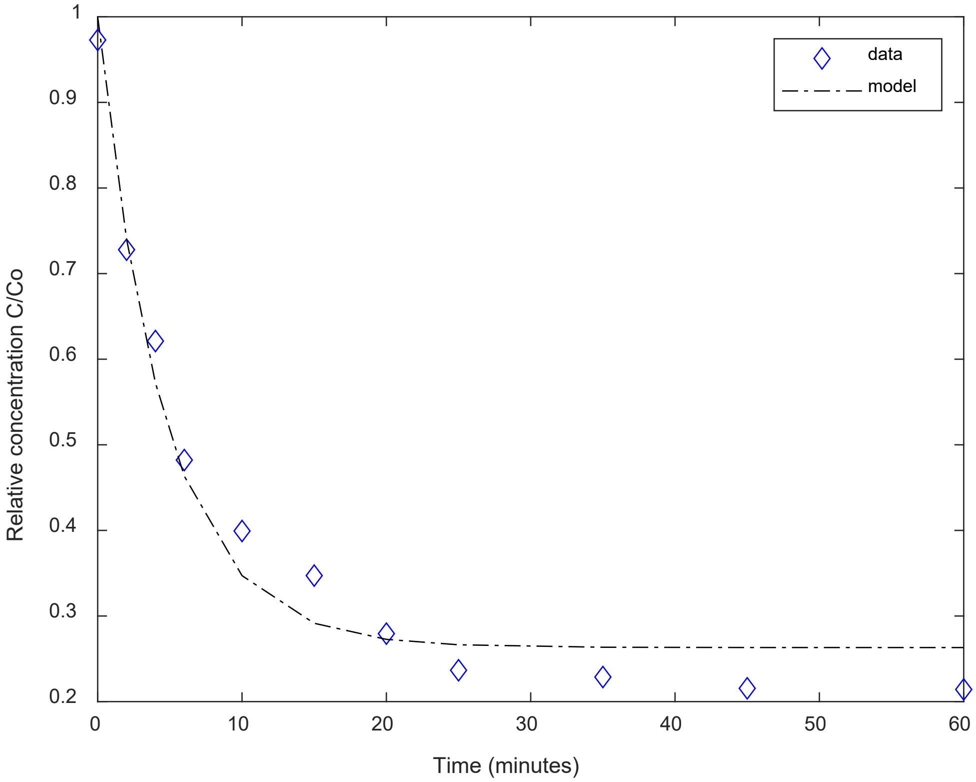
Appendix Q. Start and end data of lumens vs amps for bulb K 18



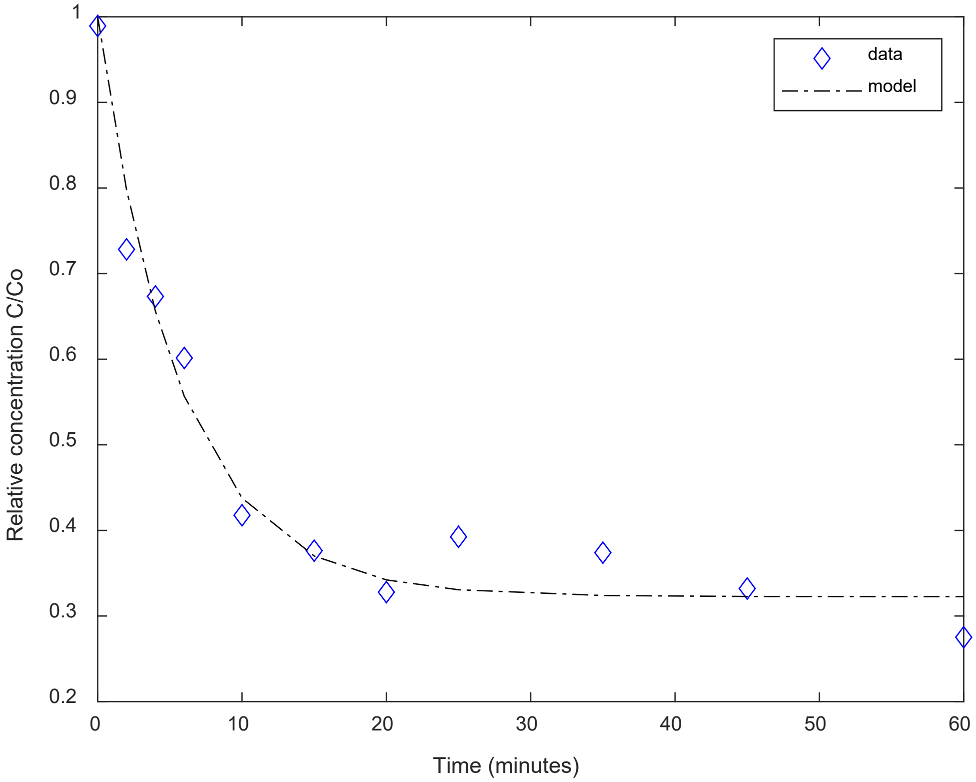
Appendix R. Start and end data of lumens vs amps for bulb K 19



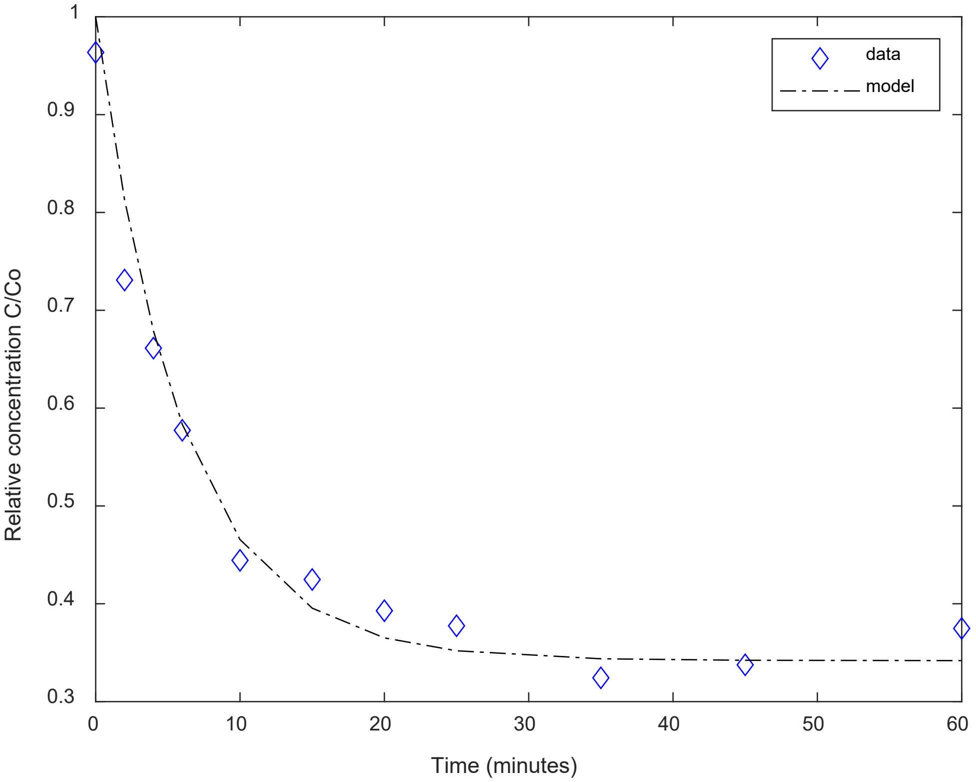
Appendix S. MATLAB Model – 50:1 ratio, 14 Aug Exp. 1



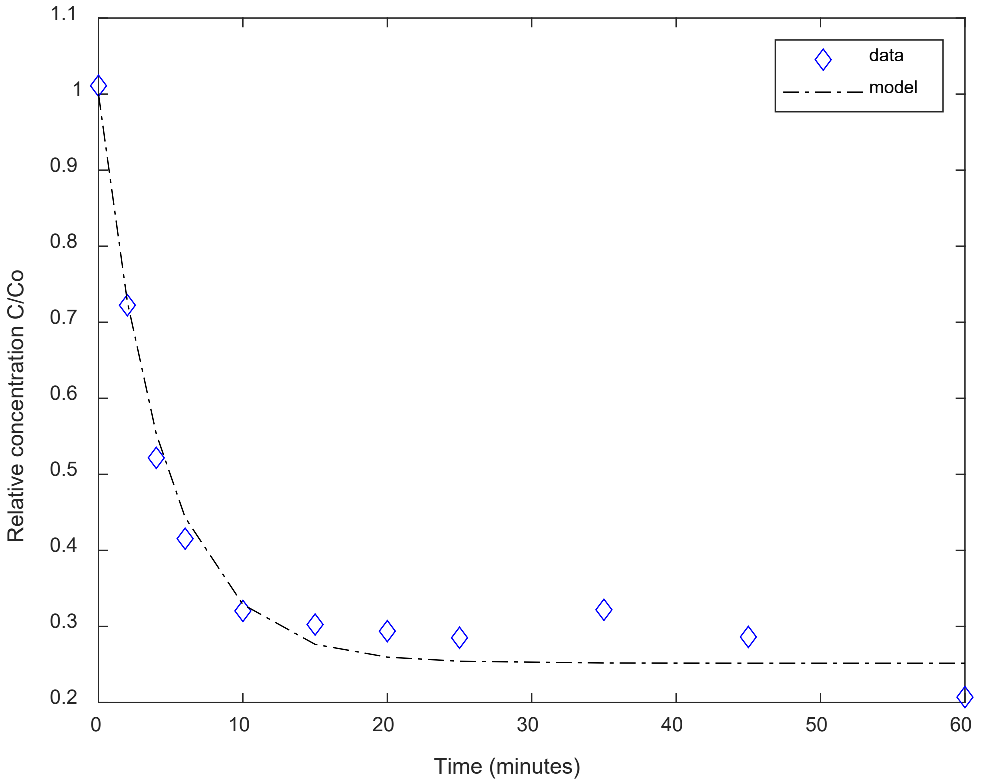
Appendix T. MATLAB Model – 50:1 ratio, 14 Aug Exp. 2



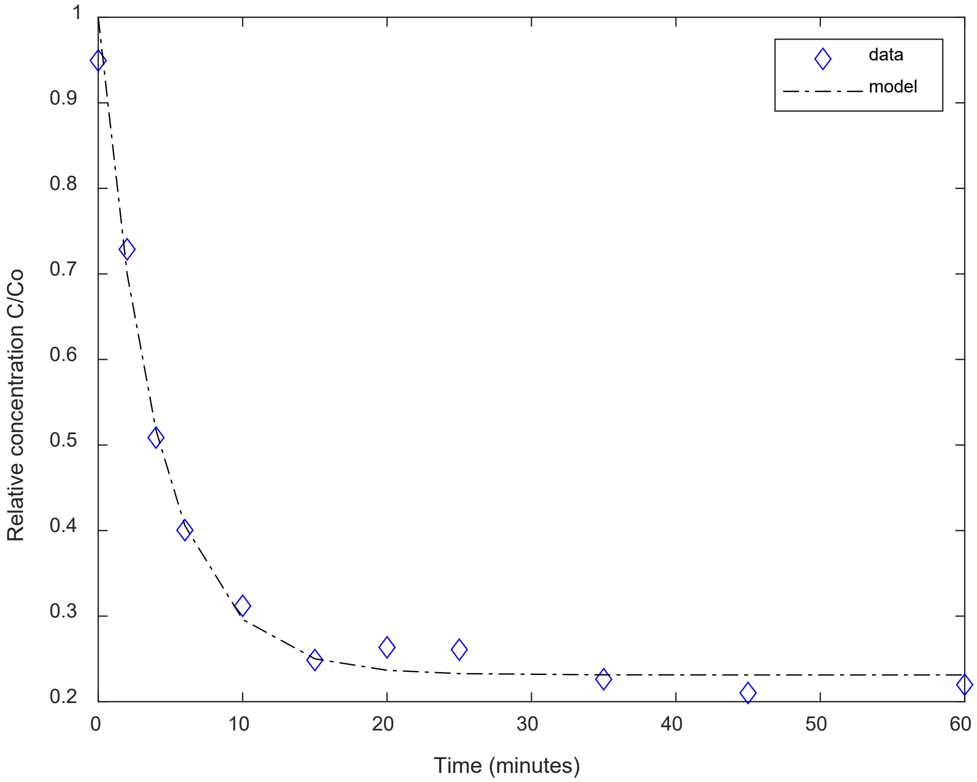
Appendix U. MATLAB Model – 50:1 ratio, 28 Aug



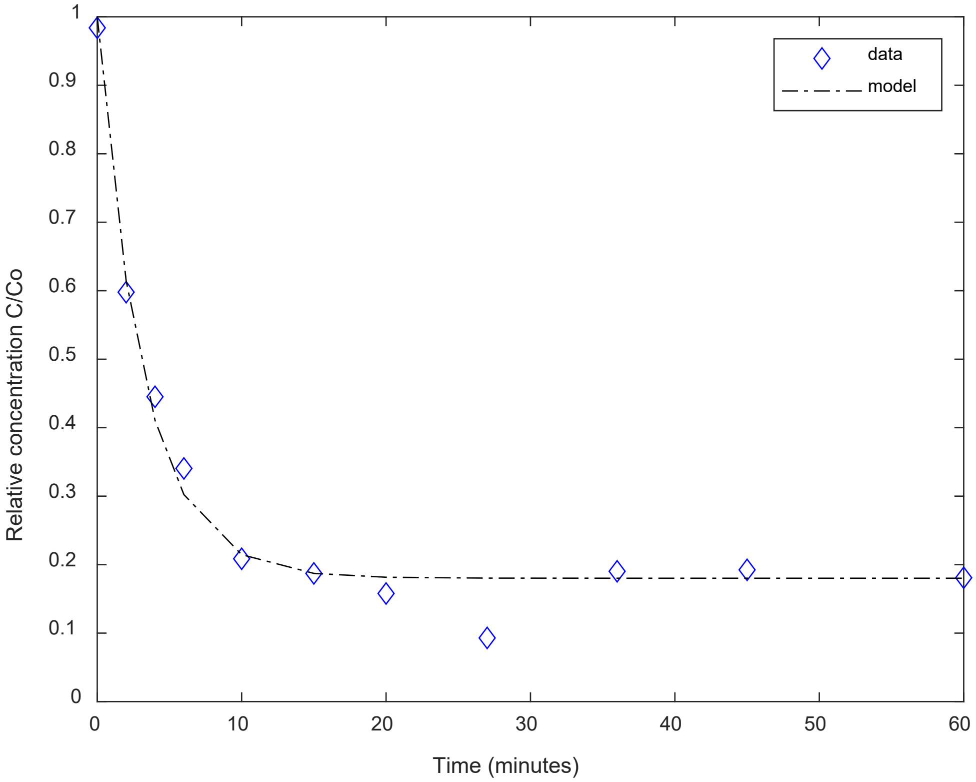
Appendix V. MATLAB Model – 100:1 ratio, 5 Jun



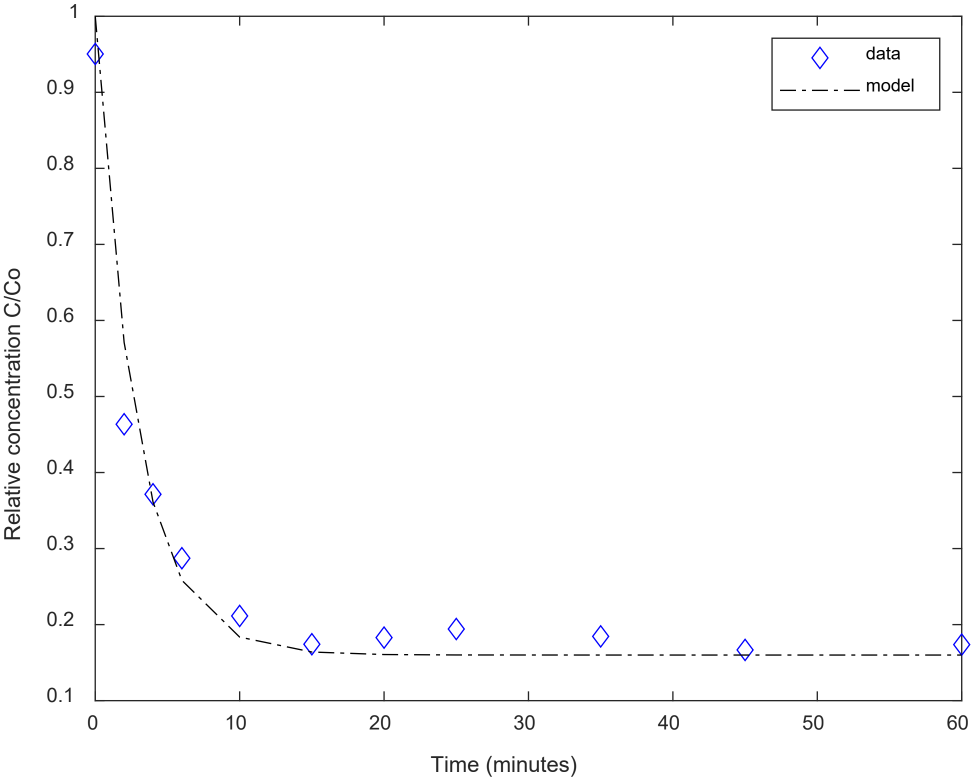
Appendix W. MATLAB Model – 100:1 ratio, 19 Jun



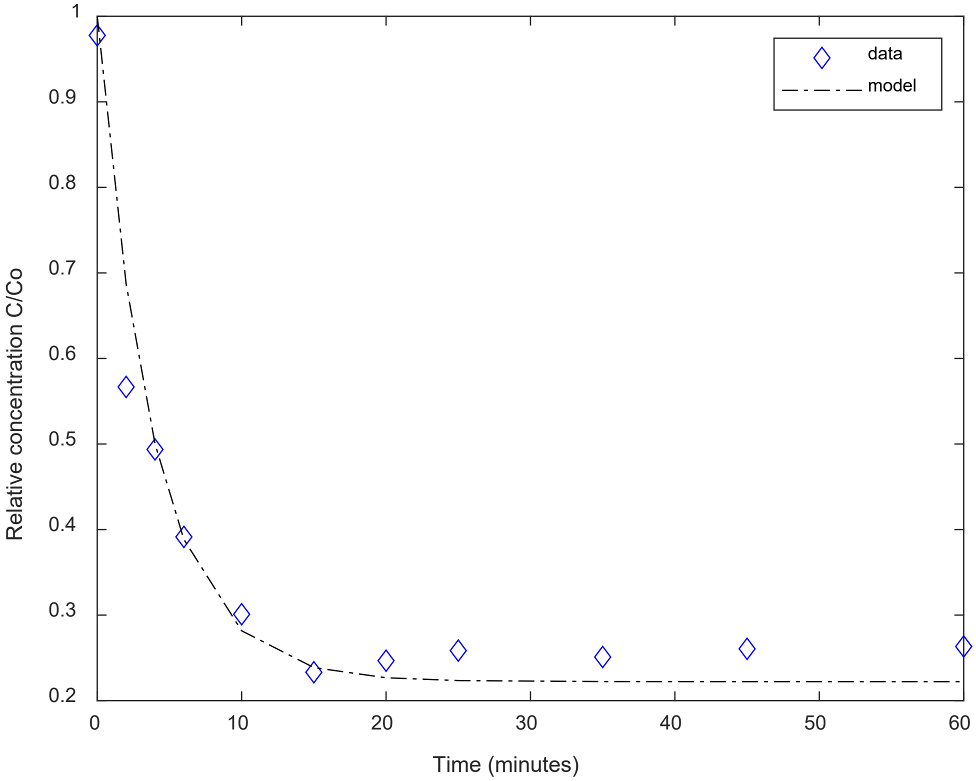
Appendix X. MATLAB Model – 100:1 ratio, 26 Jun



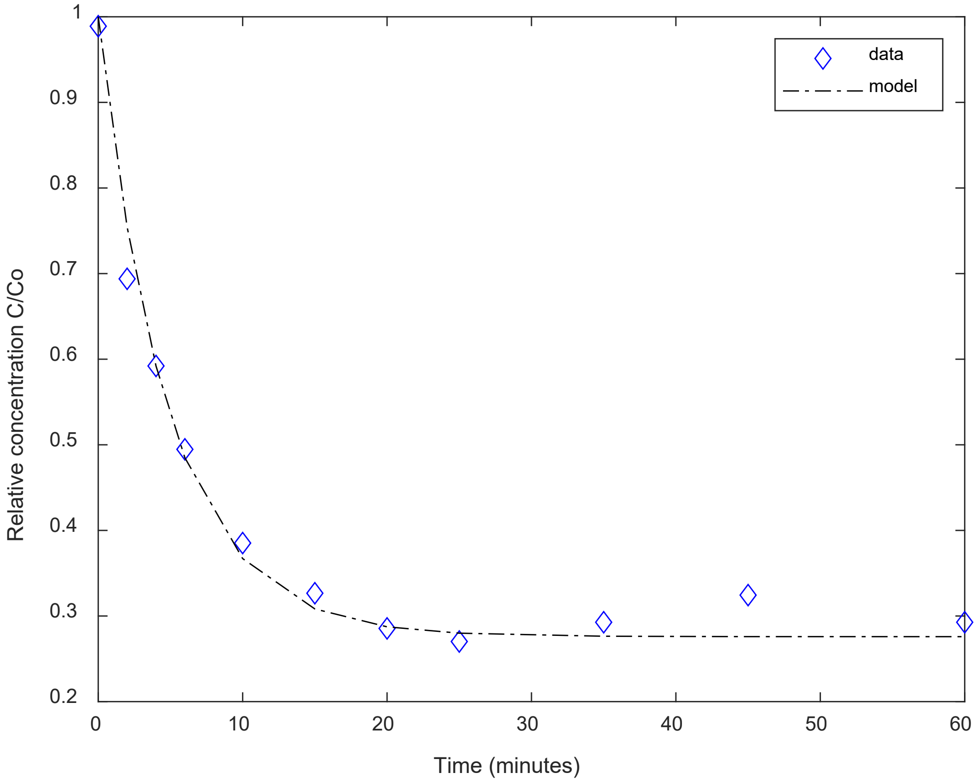
Appendix Y. MATLAB Model – 250:1 ratio, 28 Aug



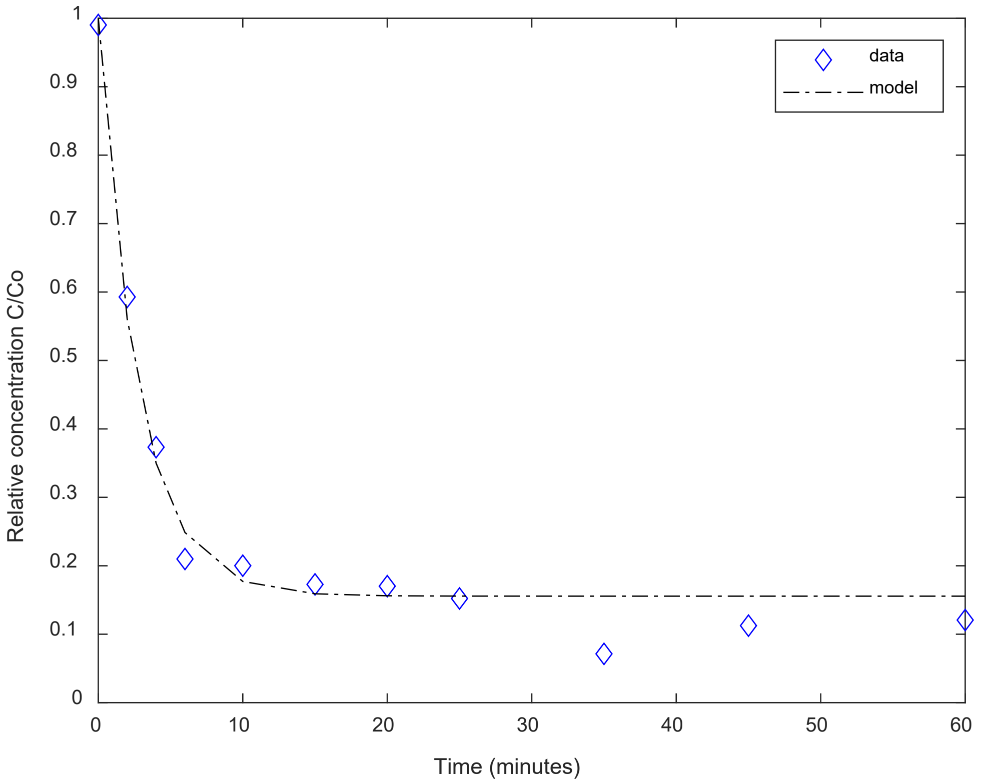
Appendix Z. MATLAB Model – 250:1 ratio, 3 Sept Exp. 1



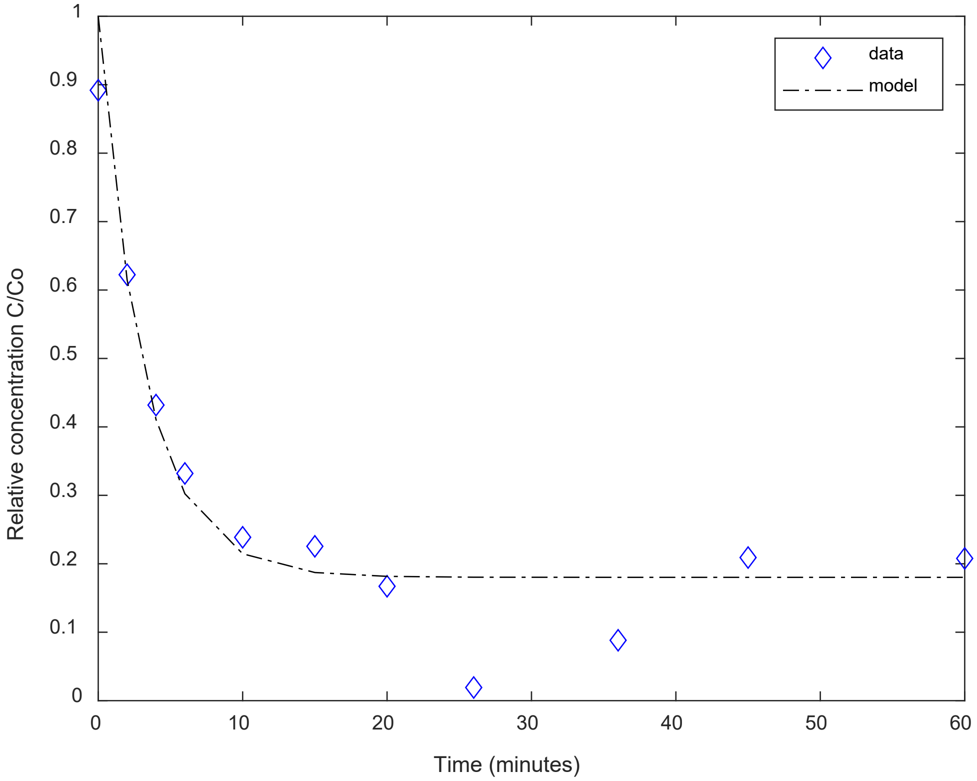
Appendix AA. MATLAB Model – 250:1 ratio, 3 Sept Exp. 2



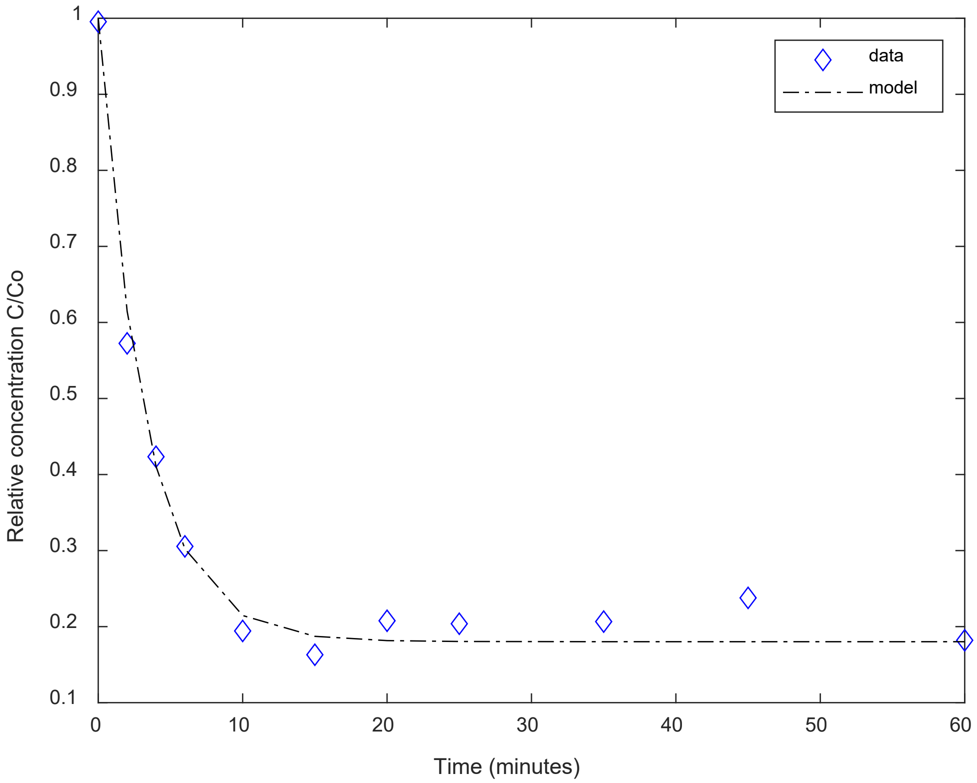
Appendix BB. MATLAB Model – 500:1 ratio, 1 July



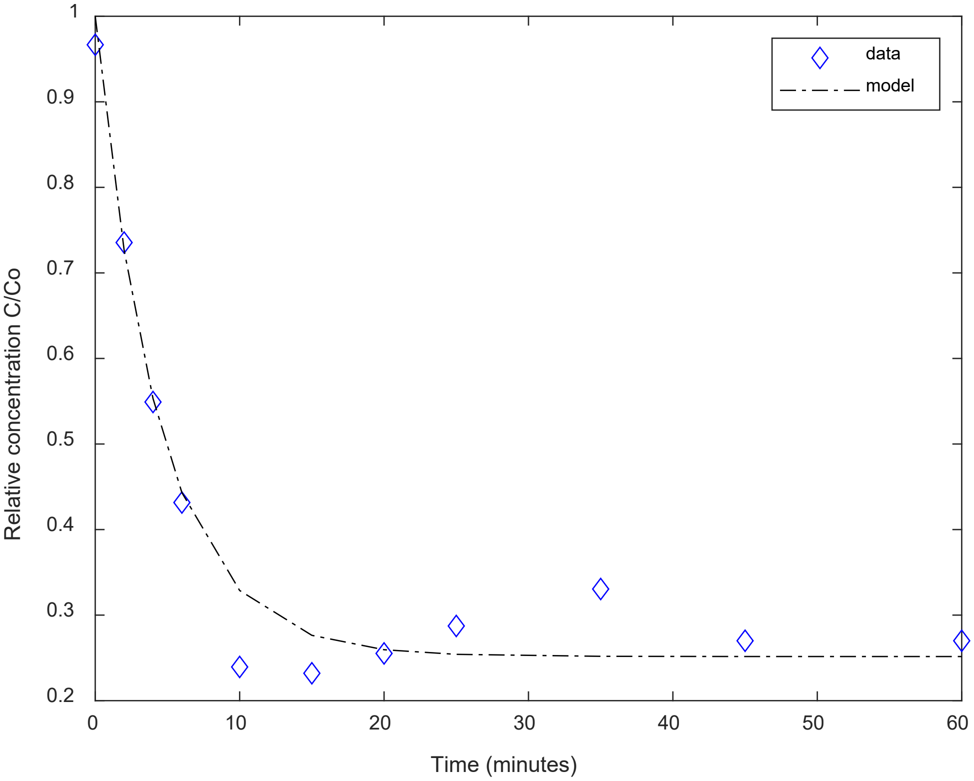
Appendix CC. MATLAB Model – 500:1 ratio, 10 July



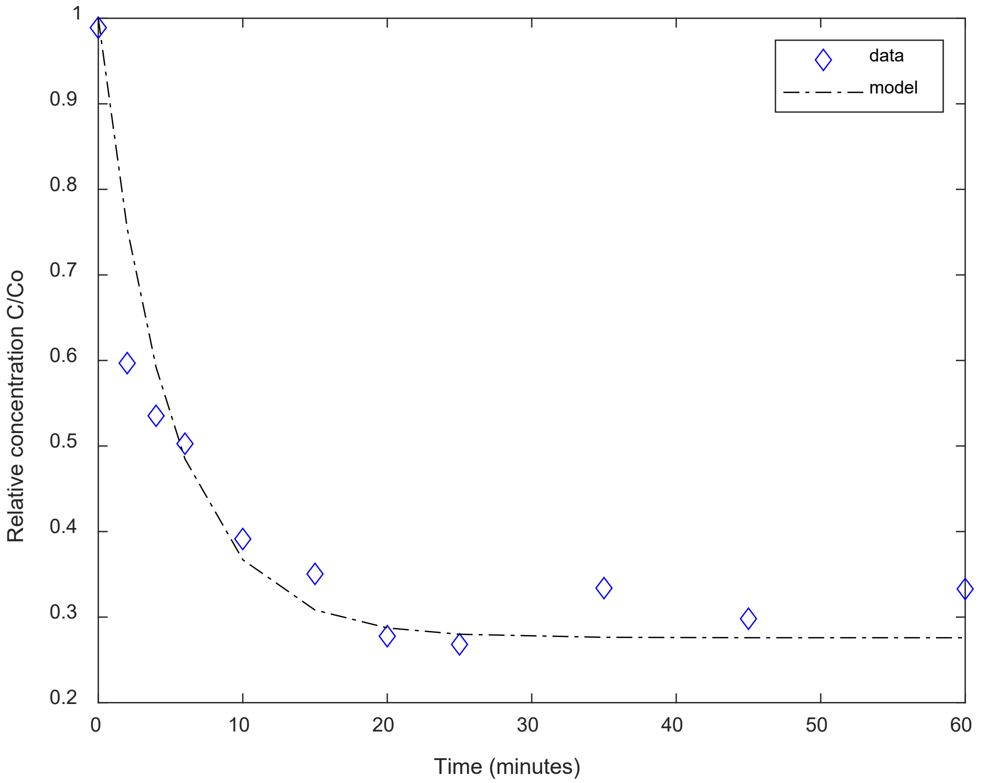
Appendix DD. MATLAB Model – 500:1 ratio, 17 July



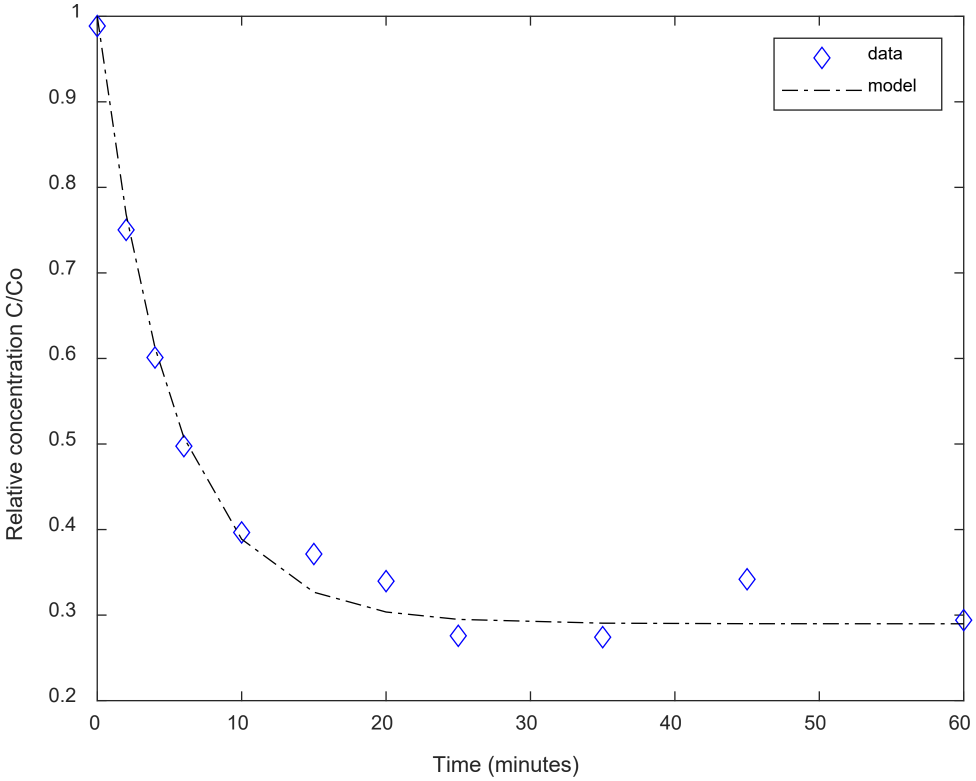
Appendix EE. MATLAB Model – 1000:1 ratio, 24 July



Appendix FF. MATLAB Model – 1000:1 ratio, 31 July



Appendix GG. MATLAB Model – 1000:1 ratio, 7 Aug



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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
03/25/2021

2. REPORT TYPE
Master's Thesis

3. DATES COVERED *(From - To)*
October 2019 - March 2021

4. TITLE AND SUBTITLE
The Effect of Molar Peroxide Ratio on the Oxidation of Bisphenol A in an Ultraviolet Light Emitting Diode/Hydrogen Peroxide Advanced Oxidation Process

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Shade, Megan

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Air Force Institute of Technology
2950 Hobson Way
Wright Patterson Air Force Base, OH 45433

8. PERFORMING ORGANIZATION REPORT NUMBER
AFIT-ENV-MS-21-M-271

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Environment Restoration Account
Air Force Civil Engineer Center
Lackland Air Force Base, TX
DSN: 969-0625
POC: Richard Anderson

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Statement A; Approved for public release; Distribution unlimited

13. SUPPLEMENTARY NOTES
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14. ABSTRACT

Bisphenol A is a compound widely used in industry that is detrimental to human health and ecological systems. Ultraviolet light emitting diodes and hydrogen peroxide can be combined t produces hydroxyl radicals. These highly reactive radicals have the potential to degrade contaminants in water. This research utilized 50, 100, 250, 500, and 1000:1 H2O2:BPA molar ratios for analysis. These results illustrated that the reactions at the 50, 100, and 250:1 ratios were hydrogen peroxide limited. The 1000:1 results exhibited evidence of radical scavenging that limited the degradation of BPA.

15. SUBJECT TERMS
Ultraviolot light; advanced oxidation; water treatment; bisphenol A

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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U	U	U	UU	82	937-255-3636 x4528

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