ULTRAVIOLET LIGHT EMITTING DIODE USE IN ADVANCED OXIDATION PROCESSES

THESIS

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Abstract

Cleanup from a hazardous chemical release can result in large volumes of water containing hazardous materials, such as organophosphates. Unfortunately, this water cannot be treated in a municipal wastewater treatment plant without adversely affecting the performance of the plant. A known method for pretreating this water to prepare it for processing in a traditional treatment plant includes the addition of hydrogen peroxide, followed by ultraviolet (UV) light exposure to form reactive hydroxyl radicals which oxidize the chemical.

Light emitting diodes (LEDs) are explored as a UV source as they are durable; compact; can be powered by low voltage, direct current from solar cells or batteries; and do not contain other hazardous materials, making them useful in a tactical environment. This research evaluated the operating mode (continuous or pulsed current) of 240 nanometer UV LEDs for application in such an advanced oxidation process. The experimental results demonstrated the production of hydroxyl radicals from hydrogen peroxide from both continuously driven and pulsed UV LEDs. However, continuously driven UV LEDs were shown to be more effective than pulsed in this application.

Acknowledgments

First I would like to thank the United States Environmental Protection Agency's National Homeland Security Research Center for sponsoring this project. Next I would like to thank Lt Col LeeAnn Racz for her continual guidance and encouragement over the course of the project. I would like to thank Dr. Michael Miller and Dr. Michael Grimaila for their willingness to help on all things electrical. I would like to thank Dr. Daniel Felker for carving out space in the lab for me to occupy as well as setting me up with the correct lab equipment. Capt Chris Bates and Capt Mike Spencer were instrumental in getting the LEDs working; without them no experiments would have been conducted. I would like to thank Ms. Kandace Bailey for teaching me the very basics of lab procedure. Finally I would like to thank Maj Tho Tran for the collaboration through this thesis process.

Table of Contents

Page

List of Figures

Page

ULTRAVIOLET LIGHT EMITTING DIODE USE IN ADVANCED OXIDATION PROCESSES

I. Literature Review

Personnel, facilities, or equipment may become contaminated for various reasons ranging from a terrorist attack to an unintentional hazardous chemical release, and water is likely to be used in the decontamination process. Wastewater from decontamination might need to be treated before entering the wastewater treatment plant to avoid damaging the plant as well as to ensure the wastewater is treated properly. The use of an advanced oxidation process, such as one that employs ultraviolet (UV) light to decompose hydrogen peroxide into hydroxyl radicals, is one way to potentially treat the contaminated water.

Traditionally UV light sources for water disinfection have been low or medium pressure mercury lamps, but UV light emitting diodes (LEDs) have the capacity to be used for water disinfection also. Traditional mercury-based florescent lamps are problematic, because as the name suggests, they contain the heavy metal mercury which must be disposed of as hazardous waste. The mercury lamps also require a warm up period before use and must be handled gently as they are fragile. LEDs provide benefits over the mercury lamps. LEDs are compact in size and can be arrayed according to their purpose. LEDs also have an instant on/off capability, are durable, and have no hazardous material issues upon end of life. Further, LEDs can be powered by low voltage, direct current from solar cells or batteries making them useful in tactical situations. When testing mercury lamps for disinfection capacity, there is a standardized procedure established, so results can easily be compared. There is no standardized procedure to use

when testing UV LEDs. Additionally, while UV LEDs are not currently efficient and have relatively short lifetimes, each of these issues have been readily addressed for visible light LEDs, and it is not unreasonable to assume both the power requirements and lifetimes of UV LEDs will improve rapidly in the coming decades.

LEDs turn electrical energy into light energy. LEDs contain a semiconductor chip which is comprised of two areas separated by a junction. One area contains p-type material which has extra holes, and the other area contains n-type material which has extra electrons. Current only flows in one direction: from the p-type side to the n-type side. When voltage is applied and current begins to flow, electrons are able to cross the junction and combine with holes. The recombination produces a high energy state and as relaxation occurs, the materials in LEDs provide a photon of light. The wavelength of the light emitted depends on the semiconductor material used in the LED (Harris and Fenlon, 2002). Manufacture of LEDs began in the 1960s, but only recently have LEDs been manufactured to produce UV light. UV LEDs remain fairly expensive to purchase, and only a few companies currently produce them.

The wavelength produced by a UV source varies between different sources. A low pressure mercury lamp emits at 254 nanometers (nm) (and also at 185 nm if certain lamp materials are used). A medium pressure mercury lamp is polychromatic producing outputs at a range of wavelengths between approximately 200 nm and 600 nm, based upon the phosphors that are selected and used to coat the inside of the glass tube from which these lamps are produced. A UV LED is manufactured to produce an output at a specific wavelength of light through the selection of dopants, which permit the release of energy at specific wavelengths.

Because of their instant-on capability, UV LEDs can be operated in pulsed or continuous mode. Lenk and Lenk (2011:10, 65) asserted the lifetime of an LED is greatly influenced by its operating temperature and drive current, and pulsing may have an important positive effect on the LED's lifetime. Lenk and Lenk (2011:93) also note a pulsed LED will have a lower average current than a continuously operated one when both are turned on with the same peak current. Therefore, driving an LED in a pulsed manner as opposed to a continuous drive level can influence the power consumption. Other researchers have found mixed results when attempting to understand the lifetime of an LED in pulsed and continuous operating modes. Meneghini et al. (2012:1621) determined current plays a large part in the degradation of LEDs. They tested LEDs with both continuous and pulsed current and found the LEDs driven by a pulsed current degraded faster than those driven by a continuous current for equal luminous flux. Buso et al. (2008:312) tested over fifty high-brightness LEDs from three different manufacturers comparing various issues such as expected lifetime based on driving strategy and quality of emitted light. They were unable to draw any conclusions regarding lifetime due to great variability between LEDs from different manufacturers. More investigation to compare the characteristics of LEDs subjected to pulsed and continuous currents needs to be conducted to provide a better understanding of the implications from pulsing the UV source.

Experiments have been completed to test the ability of UV LEDs to disinfect. Würtele et al. (2011:1481) found LEDs at 269 and 282 nm could inactivate *Bacillus subtilis* spores. Bowker et al. (2011:2011) concluded LEDs at 255 and 275 nm could inactivate *Escherichia coli*, MS-2, and T7. Mori et al. (2007:1237) and Hamamoto et al.

(2007:2291) both achieved inactivation of *Escherichia coli* DH5α, Enteropathogenic *E. coli*, *Vibrio parahaemolyticus*, *Staphylococcus aureus*, and *Salmonella* Enteritidis with LEDs at 365 nm. Chatterly and Linden (2010:483) inactivated *E. coli* with LEDs at 265 nm. Li et al. (2010:2183) used LEDs at 365 nm to disinfect *Candida albicans* and *Escherichia coli* biofilms. These experiments showed LEDs maintain the same disinfection capability as mercury lamps.

Researchers have investigated the effectiveness of pulsed UV for disinfection. Bohrerova et al. (2008:2975) found pulsed UV polychromatic irradiation inactivated *Escherichia coli* and pathogen surrogates phage T4 and T7 more effectively than a low or medium pressure mercury lamp at equivalent fluence levels. Wang et al. (2005:2921, 2925) demonstrated that a xenon flashlamp could efficiently inactivate *Escherichia coli*, and found the germicidal efficiency of the flashlamp is comparable to low pressure mercury lamps of the same wavelength. These studies demonstrated UV employed in a pulsed manner can be as or more effective than UV continuously applied for disinfection.

Several studies have been conducted to evaluate the disinfection capability of pulsed UV LEDs. Mori et al. (2007:1239) showed for the same irradiation dose, LEDs at 365 nm operated in a pulsed mode were just as effective at inactivating bacteria in water as LEDs at 365 nm operated continuously. Li et al. (2010:2185) used an LED at 365 nm to conclude pulsing the LED had a greater inactivation efficiency on biofilms than continuously operating the LED (total dosage was the same for both operating modes). Gadelmoula et al. (2009:150) used LEDs at 365 nm to inactivate *Escherichia coli* DH5α in a moving air stream, and the researchers found inactivation occurred within the same time frame for both constant LED exposure and pulsed LED operation. These reports

establish UV LEDs operated in a pulsed mode can effectively disinfect as well as, and maybe better than, UV LEDs operated in a continuous manner.

An advanced oxidation process combines UV with hydrogen peroxide to produce highly reactive hydroxyl radicals which have the ability to oxidize organic compounds. The effectiveness of the advanced oxidation process can be estimated based on the amount of hydroxyl radicals produced. The effectiveness of advanced oxidation processes has been widely researched for a number of different contaminants. Jung et al. (2012:160) degraded the β-lactam antibiotic amoxicillin with UV and hydrogen peroxide. Wang, D. et al. (2012:4677) used UV and hydrogen peroxide to decay trichloroethylene. He et al. (2012:1501) destroyed the cyanobacterial toxin microcystin by advanced oxidation process using UV and hydrogen peroxide. Zoschke et al. (2012:5365) removed the taste and odor compounds geosmin and 2-methly isoborneol with UV and hydrogen peroxide. Bounty et al. (2012:6273) inactivated adenovirus by UV and hydrogen peroxide. Vogna et al. (2004:414) degraded the anti-inflammatory drug diclofenac with UV and hydrogen peroxide. Lopez et al. (2003:121) degraded two pharmaceutical intermediates, 5-methyl-1,3,4-thiadiazole-2-methylthio and 5-methyl-1,3,4-thiadiazole-2-thiol, by UV and hydrogen peroxide.

Limited research has been conducted using UV LEDs for advanced oxidation processes with hydrogen peroxide. Vilhunen et al. (2011:866) successfully decomposed phenol using LEDs at 257, 269, and 277 nm as the UV source for advanced oxidation processes with hydrogen peroxide. In another study Vilhunen and Sillanpää (2009:1530) employed LEDs at 255, 265, and 280 nm to degrade phenol by an advanced oxidation

process with hydrogen peroxide. These two studies show the potential for UV LEDs to be utilized in advanced oxidation processes.

A study has been completed to investigate the effectiveness of a pulsed UV source for an advanced oxidation process with hydrogen peroxide. McDonald et al. (2000:93) demonstrated a pulsed UV source in conjunction with hydrogen peroxide was more effective at inactivating *Bacillus subtilis niger* than a continuous UV source in conjunction with hydrogen peroxide. However, this advanced oxidation process was once again used to disable living organisms rather than oxidize organic compounds, and it is unclear whether the effectiveness of the pulsed UV source originated from its direct effect upon the *Bacillus subtilis niger* or by providing enhanced production of hydroxyl radicals from the hydrogen peroxide.

Methylene blue is a dye which can be used as an indicator of chemical activity. Methylene blue becomes decolorized after reacting with hydroxyl radicals (Alpert et al., 2010:1801). The concentration of aqueous methylene blue can be determined using a UV-visible spectrophotometer at 664 nm (Keen et al., 2012:5227; Wang, Y. et al., 2012:474). Methylene blue is not affected by direct UV photolysis above 200 nm and is unreactive with hydrogen peroxide alone (Keen et al., 2012:5228; Alpert et al., 2010:1801). In this study, we used methylene blue to indirectly measure the amount of hydroxyl radicals produced from an advanced oxidation process using UV LEDs at 240 nm and hydrogen peroxide.

Various studies have shown pulsing the UV source is as effective, and in some cases more effective, than a continuously operated UV source. Research has demonstrated the ability to use UV LEDs in place of mercury lamps to achieve the same

disinfection capacity, and limited research has shown UV LEDs can be used for advanced oxidation processes to successfully degrade chemicals. LEDs have many advantages over the traditionally used mercury lamps. No reports have yet been written using a pulsed UV LED as the UV source for an advanced oxidation process with hydrogen peroxide. This research aims to evaluate the efficiency of pulsed UV LEDs to produce hydroxyl radicals in an advanced oxidation process.

Two main questions were investigated during the course of research: 1) does the operating mode (continuous current or pulsed) of UV LEDs change their effectiveness at generating hydroxyl radicals from hydrogen peroxide when used for an advanced oxidation process and 2) if pulsed mode is more effective, is there an optimum duty cycle to maximize hydroxyl radical generation.

II. Scholarly Article

Abstract

Ultraviolet (UV) light emitting diodes (LEDs) are a viable option as a UV source for advanced oxidation processes. UV LEDs also possess qualities which are more favorable than the traditionally used mercury lamps. This study investigated an advanced oxidation process with hydrogen peroxide and UV LEDs at 240 nm. The LEDs were operated in two modes: continuously on or pulsed. Three pulsed duty cycles were utilized: 10%, 50% and 70%. Methylene blue, a dye, was used as an indicator to indirectly assess the effectiveness of the advanced oxidation process. The advanced oxidation process took place in a flow through reactor where the solution came in direction contact with the LEDs. All LED modes of operation degraded the methylene blue, but none of the pulsed duty cycles achieved as much degradation as having the LEDs on continuously. The degradation rates for the pulsed experiments increased exponentially with increasing duty cycle.

1. Introduction

Personnel, facilities, or equipment may become contaminated for various reasons ranging from a terrorist attack to an unintentional hazardous chemical release, and water is likely to be used in the decontamination process. Wastewater from decontamination might need to be treated before entering the wastewater treatment plant to avoid damaging the plant, as well as, to ensure the wastewater is treated properly. The use of an advanced oxidation process, such as ultraviolet (UV) light combined with hydrogen peroxide, is one way to potentially treat the contaminated water.

Traditionally low or medium pressure mercury lamps have been applied as UV light sources for water disinfection. However, these lamps are not ideal, because they contain mercury which must be disposed of as hazardous waste. Also, the lamps are fragile, creating the potential for accidental release of the mercury into the environment. Further, these lamps require a warm up period before use and generally require a high voltage source for operation (Würtele et al., 2011:1482).

UV light emitting diodes (LEDs) have recently become available and have the capacity to be used as an alternate source for water disinfection (Peters, 2012). These sources have advantages over traditional light sources as they are compact, can be arrayed according to their purpose, have an instant on/off capability, are durable, and have no hazardous material issues upon end of life. LEDs can be powered by direct current at low voltage from solar cells or batteries making them useful in tactical situations. Therefore, LEDs provide maintenance and operating benefits over mercury lamps for disinfection. While visible light LEDs have advanced rapidly in recent years, now having efficiency and lifetimes that exceed traditional lighting sources, the development of UV LEDs is in its infancy (Kneissl, 2010:4). Currently these lamps are less efficient, have shorter lifetimes, and produce significantly less power than traditional UV lamps.

Another significant difference between LEDs and mercury based lamps is the wavelength of light produced. A low pressure mercury lamp emits at 254 nanometers (nm) (and also at 185 nm if certain lamp materials are used). A medium pressure mercury lamp is polychromatic producing outputs at a range of wavelengths between approximately 200 nm and 600 nm. Alternatively, UV LEDs are manufactured to

produce an output at a specific wavelength through the selection of the semiconductor material used in the LED (Harris and Fenlon, 2002).

Because of their instant-on capability, UV LEDs can be operated in pulsed or continuous mode. Lenk and Lenk (2011:10, 65) asserted the lifetime of an LED is greatly influenced by its drive current, and pulsing may have an important positive effect on the LED's lifetime. Lenk and Lenk (2011:93) also note a pulsed LED will have a lower average current than a continuously operated one when both are turned on with the same peak current, requiring lower average currents. Therefore, driving an LED in a pulsed manner as opposed to a continuous drive level can influence the power consumption. Other researchers have found mixed results when attempting to understand the lifetime of an LED in pulsed and continuous operating modes. For example, Meneghini et al. (2012:1621) tested visible light LEDs with both continuous and pulsed current and found the LEDs driven by a pulsed current degraded faster than those driven by a continuous current. Buso et al. (2008:312) tested over fifty high-brightness LEDs from three different manufacturers comparing various issues such as expected lifetime based on driving strategy. They were unable to draw any conclusions regarding lifetime due to great variability between LEDs from different manufacturers. However, given the published literature, it is possible the use of pulsed LEDs may extend their lifetime and reduce their power consumption if pulsing the LEDs provided more effective water disinfection than continuously driving these same LEDs.

Experiments have been completed to test the ability of UV LEDs to disinfect water, primarily through destroying organisms in water. Multiple researchers have continuously operated UV LEDs and maintained the same disinfection capability as

mercury lamps (Würtele et al, 2011:1481; Bowker et al., 2011:2011; Mori et al., 2007:1237; Hamamoto et al., 2007:2291; Chatterley and Linden, 2010:483; Li et al., 2010:2183). Several studies have been conducted to evaluate the disinfection capability of pulsed UV LEDs, and these studies established UV LEDs operated in a pulsed mode can effectively disinfect as well, and maybe better, than UV LEDs operated in a continuous manner (Mori et al., 2007:1239; Li et al., 2010:2185; Gadelmoula et al., 2009:150).

Researchers have investigated the effectiveness of pulsed UV for disinfection. Bohrerova et al. (2008:2975) found pulsed UV polychromatic irradiation inactivated *Escherichia coli* and pathogen surrogates phage T4 and T7 more effectively than a low or medium pressure mercury lamp at equivalent fluence levels. Wang et al. (2005:2921, 2925) demonstrated that a xenon flashlamp could efficiently inactivate *Escherichia coli*, and found the germicidal efficiency of the flashlamp is comparable to low pressure mercury lamps of the same wavelength. Based upon this research, UV employed in a pulsed manner can be as or more effective than UV continuously applied for destroying organisms in water.

An advanced oxidation process combines UV with hydrogen peroxide to produce highly reactive hydroxyl radicals which have the ability to oxidize organic compounds in water, rendering these organic compounds inert. The effectiveness of the advanced oxidation process can be estimated based on the amount of hydroxyl radicals produced. The degradation capability of advanced oxidation processes has been widely researched for a number of different contaminants ranging from taste and odor compounds to

trichloroethylene to antibiotics and pharmaceutical intermediates (Zoschke et al., 2012:5365; Wang et al., 2012:4677; Jung et al., 2012:160; Lopez et al., 2003:121).

Limited research has been conducted using UV LEDs for advanced oxidation processes with hydrogen peroxide. Past research successfully decomposed phenol by an advanced oxidation process using UV LEDs of various wavelengths and hydrogen peroxide (Vilhunen et al., 2011:866; Vilhunen and Sillanpää, 2009:1530). These two studies show the potential for UV LEDs to be utilized in advanced oxidation processes.

A study has been completed to investigate the effectiveness of a pulsed UV source for an advanced oxidation process with hydrogen peroxide. McDonald et al. (2000:93) demonstrated a pulsed UV source in conjunction with hydrogen peroxide was more effective at inactivating *Bacillus subtilis niger* than a continuous UV source in conjunction with hydrogen peroxide. However, this advanced oxidation process was once again used to disable living organisms rather than oxidize organic compounds, and it is unclear whether the effectiveness of the pulsed UV source originated from its direct effect upon the *Bacillus subtilis niger* or by providing enhanced production of hydroxyl radicals from the hydrogen peroxide.

Various studies have shown pulsing the UV source is as effective, and in some cases more effective, than a continuously operated UV source. Research has demonstrated the ability to use UV LEDs in place of mercury lamps to achieve the same disinfection capacity, and limited research has shown UV LEDs can be used for advanced oxidation processes to successfully degrade chemicals. No studies have been conducted using a pulsed UV LED as the UV source for an advanced oxidation process with

hydrogen peroxide. This research aims to evaluate the efficiency of pulsed UV LEDs to produce hydroxyl radicals in an advanced oxidation process.

2. Materials and methods

2.1 Chemicals

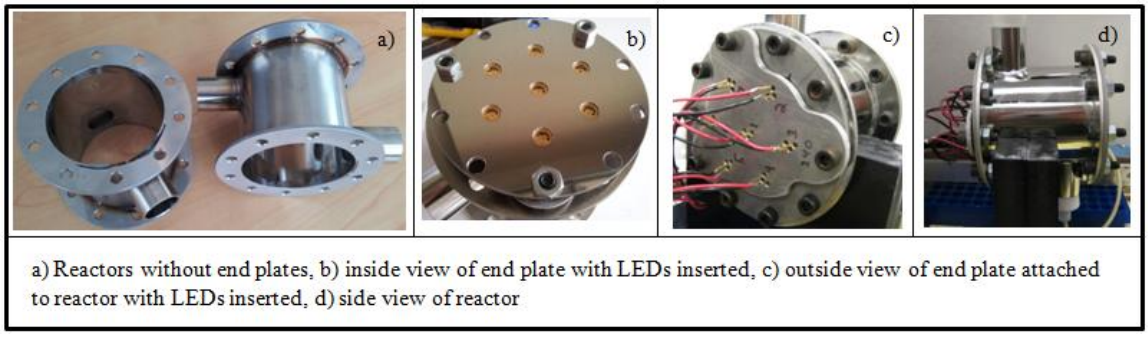
For each experiment, hydrogen peroxide (30% in water from Fisher Scientific, Pittsburgh, PA), deionized water, and methylene blue (powdered from Fisher Chemical, Pittsburgh, PA) were combined to produce one liter of solution containing approximately 5 millimolar (mM) hydrogen peroxide and 0.01 mM methylene blue. Each experiment used the same initial solution concentration.

Methylene blue is a dye which serves as an indicator of chemical activity. Methylene blue becomes decolorized after reacting with hydroxyl radicals, is not affected by direct UV photolysis above 200 nm, and is unreactive with hydrogen peroxide alone (Keen et al., 2012:5228; Alpert et al., 2010:1801). The concentration of aqueous methylene blue can be determined using a UV-visible spectrophotometer at 664 nm, providing an indirect measure of hydroxyl radicals produced from the advanced oxidation process using UV LEDs at 240 nm and hydrogen peroxide (Keen et al., 2012:5227; Wang et al., 2012:474).

2.2 Advanced Oxidation Process

The advanced oxidation process was carried out in a flow through reactor. The reactor was cylindrical (height and diameter of 3 inches) and made of electro polished 314 stainless steel. Seven 240 nm LEDs (from Sensor Electronic Technology, Incorporated, Columbia, SC) were placed in an end plate of the reactor. The reactor was

oriented so the end plates were perpendicular to the ground. The solution entered the reactor from the bottom near one end plate and exited from the top near the other end plate. The energy emitting front of the LEDs came in direct contact with the solution in the reactor. Photographs of the reactor are shown in Figure 1. A MasterFlex Console Drive (model number 77521-50, Gelsenkirchen, Germany) was employed to move the solution through the reactor at 1.4 milliliters per minute. PharMed® BPT tubing (inner diameter of 0.8 millimeters, Valley Forge, PA) was used to convey the solution between the various parts of the experiment. A driver board was constructed to run the LEDs. The board was controlled by Data Acquisition System Laboratory (DASYLab, version 12, Stamford, CT) installed on a laptop. The laptop was connected to the board through a driver box (Measurement Computing device: USB-2408-2AO, Norton, MA). Figure 2 depicts the layout of the experiment.



a) Reactors without end plates, b) inside view of end plate with LEDs inserted, c) outside view of end plate attached to reactor with LEDs inserted, d) side view of reactor

Figure 1. Reactor Photographs

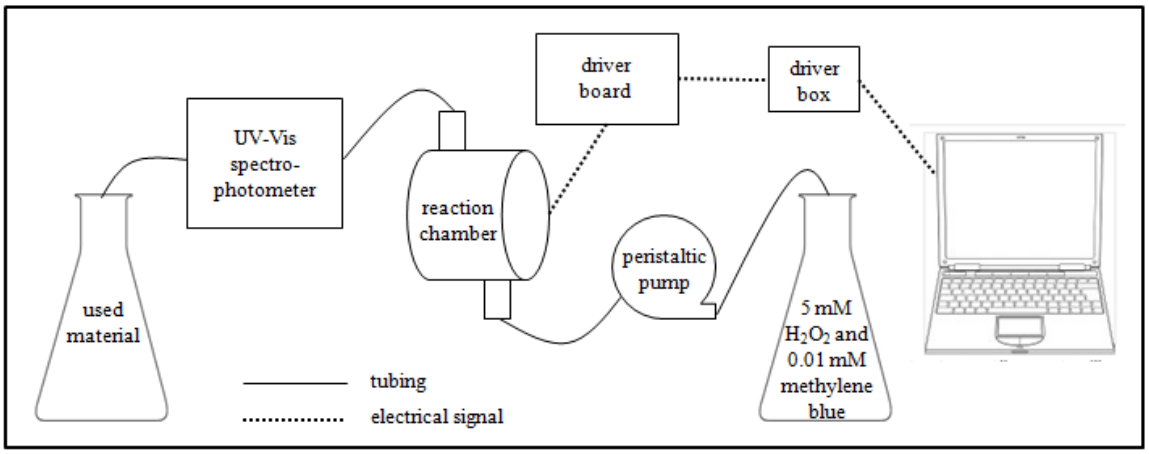


Figure 2. Experimental Set Up

Hydroxyl radicals were produced from continuously running the LEDs or pulsing the LEDs. Three pulsed duty cycles were tested, and all duty cycles had the same frequency of 9.09 hertz. A ten percent duty cycle (11 milliseconds (ms) on, 99 ms off), a fifty percent duty cycle (55 ms on, 55 ms off), and a seventy percent duty cycle (77 ms on, 33 ms off) were evaluated.

2.3 Experimental Procedure

DASYLab was programmed to produce a single voltage which was applied to all seven LEDs. Due to variation between individual LEDs, the same voltage applied to different LEDs produced different currents across the LEDs. To maintain the same current of 20 milliamperes (mA) across each LED, a potentiometer, which is an adjustable resistor, was used to correct the current to each LED. The potentiometer method of maintaining 20 mA to each LED was used for all the continuously on experiments. For the pulsed experiments a LUXdrive DynaOhm (4006-020 1338, Randolph, VT) was used to maintain a 20 mA current to each LED. The DynaOhm is a semiconductor based resistor that supplies constant current of 20 mA when active but has

a fast response time to permit the current to be pulsed between 0 and 20 mA according to the input signal. An oscilloscope (OWON PDS5022T, Zhangzhou, China) was used to verify the timing of the pulse frequency and to measure the voltage drop across a known 50 ohm resister to permit the 20 mA current to the LEDs to be verified.

The reactor was initially filled by pouring the solution into the reactor. From then on, fresh solution was pumped into the reactor by the peristaltic pump. The solution leaving the reactor passed through an Agilent Technologies Cary 60 UV-Vis Spectrophotometer (Santa Clara, CA) before entering a used material flask. The spectrophotometer measured the amount of light absorbed by the solution at ten minute intervals. A 5-point calibration curve of absorbance and methylene blue concentration ranging from 0.005-0.05 mM was used to convert the absorbance values for each experiment into methylene blue concentrations.

Multiple experiments were conducted for each duty cycle. Five experiments were completed for the continuously on LEDs, three experiments for the 10% and 70% duty cycles, and four experiments for the 50% duty cycle.

3. Results and discussion

The continuously on LEDs and all the pulsed duty cycles degraded the methylene blue, but the rate and amount of degradation varied as shown in Figure 3. The reduced duty cycle conditions did not match or exceed the degradation ability of the continuously on LEDs. New 240 nm LEDs have an optical power of approximately 0.55 milliwatt in air. The continuously run LEDs and all the duty cycles initially displayed first order degradation before approaching a final, steady state concentration. The mean

degradation rate for the continuously on LEDs was 0.011 minute^{-1}, for 70% duty cycle the mean degradation rate was 0.0059 minute^{-1}, for 50% duty cycle the mean degradation rate was 0.0035 minute^{-1}, and for 10% duty cycle the mean degradation rate was 0.0012 minute^{-1}. An analysis of variance showed the degradation rate for the continuously on and the 70% duty cycle are statistically different from each other with ninety-five percent confidence (p-value of 0.0004 from a t-test). When analyzing the degradation rates between the 70% and 50% duty cycle (p-value of 0.0576 from a t-test) and then between the 50% and 10% duty cycle (p-value of 0.0623 from a t-test), we are ninety percent confident these values are statistically different.

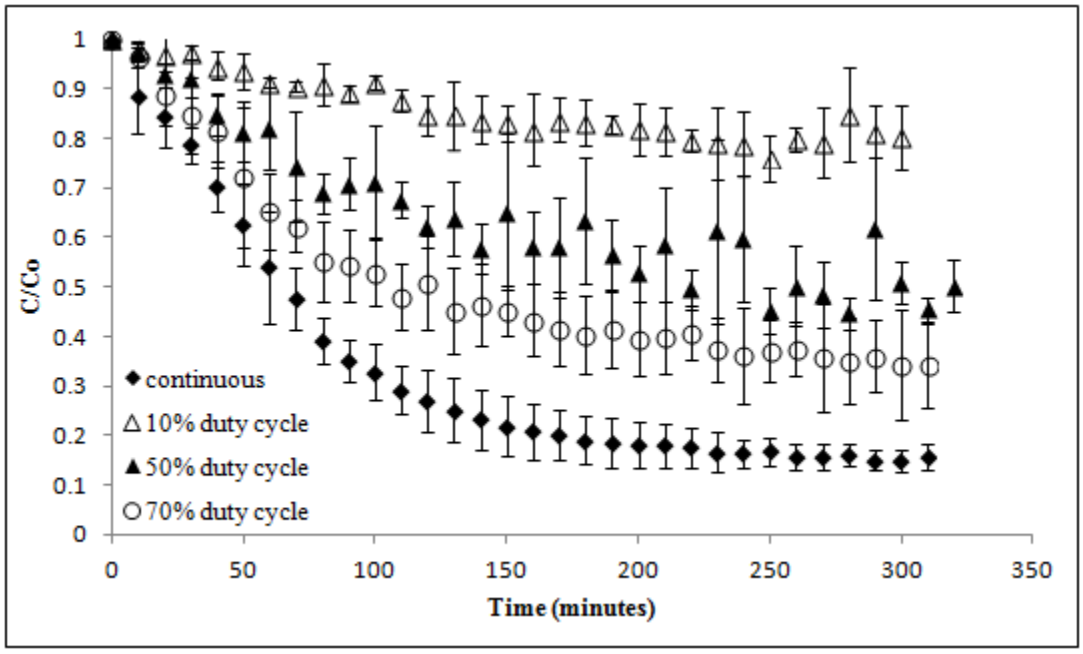


Figure 3. Mean normalized concentrations for continuously on and all duty cycles, includes one standard deviation error bars

Both a linear and an exponential relationship between the duty cycle and degradation rate were examined. A linear trend line applied to the data produced an R^2

value of 0.845, and a linear trend line with an intercept set to zero produced an R^2 value of 0.829 (shown in Figure 4). A log transformation of the degradation rate plotted against the duty cycle (shown in Figure 5) produced a linear trend line with an R^2 value of 0.950 showing an exponential relationship may also fit. These three possible relationships between the duty cycle and degradation rate were examined to see which relationships met the four assumptions for linear regression (the relationship is linear, the errors have the same variance, the errors are independent of each other, and the errors are normally distributed). The log transformation of the degradation rate met all four assumptions, and both the linear relationships did not meet the assumptions of the errors have the same variance and the errors are independent of each other. The log transformation of the degradation rate (meaning an exponential relationship with equation $y=0.001e^{2.4514x}$) was the best description of the relationship between duty cycle and degradation rate. A possible reason for an exponential increase in degradation rate may be due to a solvent cage effect. This effect is caused when the solvent molecules act as a cage around the hydroxyl radicals allowing them to recombine before they can interact with a methylene blue molecule; only fifty percent of the hydroxyl radicals are estimated to escape the cage (Fitzgerald, 2012:5).

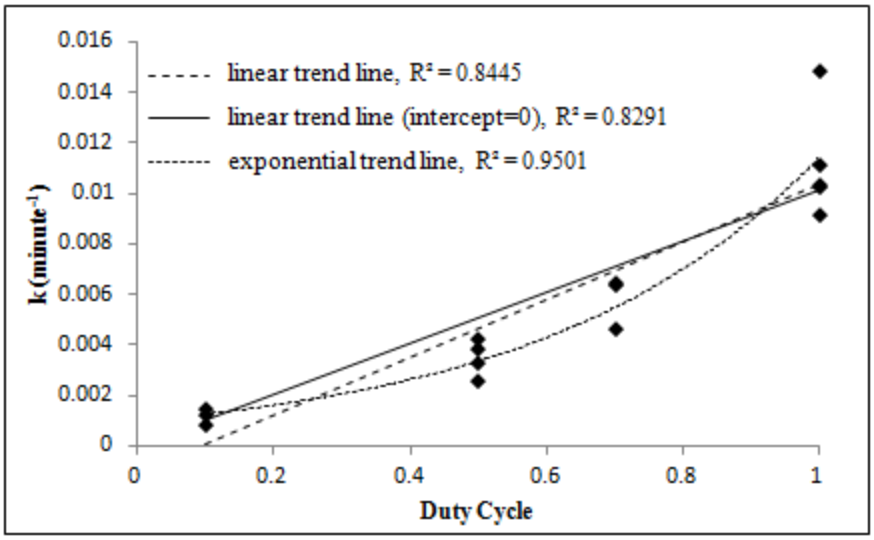


Figure 4. Methylene blue degradation rate plotted against duty cycle

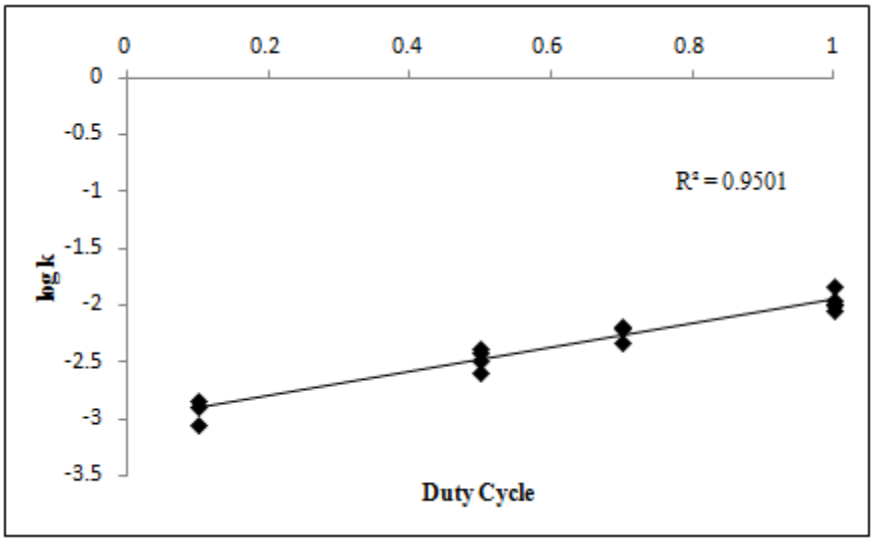


Figure 5. Log transformation of the degradation rate plotted against duty cycle

The degradation rate increasing exponentially with duty cycle impacts the practical application of the LEDs. Consider applications where pulsed operation might be desired for reasons such as reducing energy consumption or limiting the time the LED is powered, but do not require the highest possible rate of contamination destruction.

This might occur in situations where a low level of contaminant periodically enters the water, such that the goal is to maintain water quality and not perform initial purification of a high level of contaminant. Compared to a 10% duty cycle, increasing the duty cycle to 50% does not equate to a fivefold increase in destruction, even if a fivefold longer reaction time is allowed. In fact, the increase is only threefold, meaning some energy and LED on-time savings is lost. Clearly this impacts the design of systems that may wish to utilize pulsed LEDs. For instance, in the LED reactor system shown in the paper, the optimal conditions might be operating at around a 10% duty cycle, assuming the resulting rate of contaminant destruction is acceptable.

When pulsing was employed, only the length of time the LEDs were on was changed in comparison to the continuously on LEDs experiments. The same flow rate and current were used for every experiment. This research established pulsing the UV LEDs for an advanced oxidation process with hydrogen peroxide was not as effective as leaving the LEDs on continuously (when the only difference between the pulsed and continuous experiments was the time the LEDs were powered on).

Previous researchers who had demonstrated UV LEDs operated in a pulsed mode can effectively disinfect as well as, and maybe better than, UV LEDs operated in a continuous manner altered at least one operating parameter of their experiments when changing between continuously running and pulsing the LEDs. These researchers either doubled the pulsed current in comparison to the continuous current or maintained the exposure time between all experiments: pulsed and continuous (Mori et al., 2007:1239; Li et al., 2010:2185; Gadelmoula et al., 2009:155). These researchers were investigating disinfection with UV LEDs. The current research found when maintaining all operating

parameters between continuously on and pulsed LEDs, the results from the pulsed LEDs did not match the continuous LEDs. Therefore, the successful parameter changes for disinfection with pulsed UV LEDs should be applied to an advanced oxidation process with pulsed UV LEDs. Not only should the parameter changes be evaluated in an advanced oxidation process, but also the effects of those parameter changes on the overall lifetime of an LED.

We observed that the degradation rate as well as the achieved steady state concentration tended to decrease the longer the LEDs had been operated. A regression analysis on the duty cycle, degradation rate, and number of hours previously used showed the number of hours previously used to be statistically significant to the model (p-value of 0.0134 from a t-test). These observations were consistent with past studies. In particular, Kneissl et al. (2010:10) discovered after 100 hours of use (20 mA current maintained) a UV LED had a 40% decrease in emission power. The experiments conducted for this research did not attempt to maintain a certain output power, but only to maintain a constant current to the LEDs. The first four continuous experiments were conducted with the same set of LEDs and covered from about 12 hours of usage to 34 hours of usage. The last continuous experiment was completed with a different set of LEDs which had around 34 hours of usage when the experiment began. All of the pulsed experiments were completed with the same set of LEDs: six LEDs had about 40 hours of usage and the other LED was new when the pulsed experiments began. Over the course of the pulsed experiments the seven LEDs experienced nearly eighty hours of use. The decrease in degradation rates and steady state concentrations over LED usage time appears to correspond with the decrease in emission power Kneissl et al. observed.

Hopefully as the manufacture of UV LEDs becomes more developed the drastic decrease in emission power over a short time period will be resolved which will in turn make UV LEDs a truly practical choice for treating contaminated water.

4. Conclusions

UV LEDs operated in a continuous and pulsed manner are able to degrade methylene blue in an advanced oxidation process with hydrogen peroxide. All methods of powering the LEDs resulted in an initial first order degradation rate for methylene blue. However, when pulsing the LEDs the degradation rate increased exponentially as the duty cycle increased; 10%: 0.0012 $minute^{-1}$, 50%: 0.0035 $minute^{-1}$, 70%: 0.0059 $minute^{-1}$, and continuous: 0.011 $minute^{-1}$. This research maintained all operating parameters except the amount of time the LEDs were on when switching between experiments with the LEDs continually on and pulsing. Further research should investigate changing operating parameters, such as current or total exposure time, when evaluating the effectiveness of pulsed UV LEDs for an advanced oxidation process with hydrogen peroxide.

III. Conclusion

Review of findings

This research found the operating mode (continuous current or pulsed) of UV LEDs changed their effectiveness at generating hydroxyl radicals from hydrogen peroxide when used for an advanced oxidation process. When the LEDs were pulsed, the rate of degradation and thus the amount of degradation for a set period of time were unable to match the results achieved from the LEDs continuously running. The degradation rate increased exponentially as the duty cycle increased.

Significance of research

Only a few studies have used UV LEDs in an advanced oxidation process. This research confirms the ability to use UV LEDs in an advanced oxidation process. This research has shown maintaining all operating parameters except the amount of time the LED is on when pulsing the LEDs impacts the design and application of pulsed LED systems. In the on going process to determine how best to employ UV LEDs in advanced oxidation processes, this study investigated one method and found it was limited as a practical option for UV LED employment, but suggested the choice of appropriate duty cycle could be beneficial to selected applications.

Limitations

The reactor design did not allow for viewing of the LEDs in order to visually confirm the LEDs were indeed turning on when they were supposed to. Current measurements were used to verify the LEDs were turning on for the continuous

experiments. For the pulsed experiments, an oscilloscope was used to verify the current to the LEDs as well as to ensure pulsing was actually taking place.

The optical characteristics of the UV LEDs varied between different bulbs, and the LEDs also degraded at different rates. This made maintaining the same current to all the LEDs difficult with the potentiometers. As the LEDs were operated and they degraded, a point was reached where the potentiometers could no longer be adjusted to set all the currents to 20 mA. Only one experiment was run with the individual LED currents not all at 20 mA. The currents to the different LEDs varied between 11 mA and 20 mA, and the methylene blue degradation achieved by the varying currents was in agreement with the other experiments where 20 mA was supplied to all LEDs. Also the potentiometers were set initially, and then the experiments ran for five and a half hours. The current was not continually checked and the potentiometers not adjusted in order to attempt to maintain the same current to each LED throughout the experiment. So there is the possibility for the continuous runs, the current may have changed from the initial readings. After the DynaOhm was employed, we were able to consistently apply the same current to all LEDs for the entire experiment. For the pulsed experiments, which all used the DynaOhm, there is more certainty that all LEDs were continually supplied with 20 mA.

Methylene blue was used as an indicator to show the formation of hydroxyl radicals in the advanced oxidation process. Many studies have proven the effectiveness of advanced oxidation processes for chemical degradation, but no actual contaminants were destroyed in this current research. It is very likely the same results will be reached with actual contaminants being degraded in pulsed experiments.

The size of the reactor and the flow rate used in these experiments are not appropriate for real world implementation. These experiments were a starting point to test the effectiveness of new technology. A reactor capable of handling a greater volume of water and probably at a greater flow rate would be required for any type of pilot or full-scale application.

The experimental solution used in this project only contained methylene blue, hydrogen peroxide, and deionized water. The potential effects of turbidity and other water quality parameters present in realistic waters were not accounted for in this research. Some water quality parameters, such as hardness, are likely to interfere with the creation of hydroxyl radicals or compete with contaminants for hydroxyl radicals, decreasing the effectiveness of the advanced oxidation process. For an advanced oxidation process where the solution is turbid, mixing may be required to ensure the solution has adequate contact with the LEDs' energy, or the solution may need pretreatment to reduce the turbidity before entering the reactor.

Future research

Future research should test the degradation ability of the current setup on particular target chemicals. Since the present experiments focused only on methylene blue degradation, specific target chemicals should be tested to see if they behave the same as the methylene blue when exposed to the advanced oxidation process. Future research should also investigate modifying operating parameters of the LEDs when changing from experiments with continuously on LEDs to pulsing LEDs. Researchers who examined pulsed UV LEDs for disinfection had success with increasing the pulsed

LEDs' power output compared to the continuous LEDs. This operating parameter change should be tested for UV LEDs used in advanced oxidation processes to determine if there is a non-linear effect in the contaminant degradation when the LED output power is increased. Testing also needs to be completed on the LEDs themselves to determine if increasing the power output will help to increase the life of the LEDs. If this operating parameter change produces similar results between using continuously on and pulsed LEDs and increases the LED's lifetime, then the change should be applied to an experiment where a target chemical is degraded by an advanced oxidation process.

Lessons Learned

There were a few lessons learned while completing this project. First, in terms of using DASYLab, after finishing an experiment using DASYLab and the driver board, the following steps are necessary: in DASYLab put the voltage slider to zero, press play, and then stop the program (even if it was a pulsed experiment); next unplug the LED leads from the driver board; and finally unplug the driver board's power supply from the electrical outlet. Second for pulsed experiments, always use the oscilloscope to verify the pulsing as well as the current; the oscilloscope was very quick and simple to operate. Third, when collecting data from numerous experiments on the UV-visible spectrophotometer, create an easy to understand naming convention and organize the files in a meaningful way.

Finally, a laboratory notebook is very important. Ensure to record all the pertinent details for every experiment. Record as much detail as possible; even if it seems easy to remember at the time, it might be much harder to recall in several months.

Also include the details of problems encountered, trouble shooting steps, and how the issue was resolved.

Summary

This research investigated a UV LED's operating mode (continuous and pulsed) on the effectiveness of generating hydroxyl radicals from an advanced oxidation process with hydrogen peroxide. The dye methylene blue was used to indirectly measure the amount of hydroxyl radicals produced. A UV-visible spectrophotometer was employed to determine the methylene blue degradation. In this study, the LEDs had a 240 nm wavelength, and duty cycles of 10%, 50%, and 70% were investigated. All operating modes achieved degradation of methylene blue, but the degradation rate at the duty cycles was not a simple function of the degradation rate observed when running the LEDs continuously. The degradation rate increased exponentially as the duty cycle increased.

IV. Appendix: Detailed Data

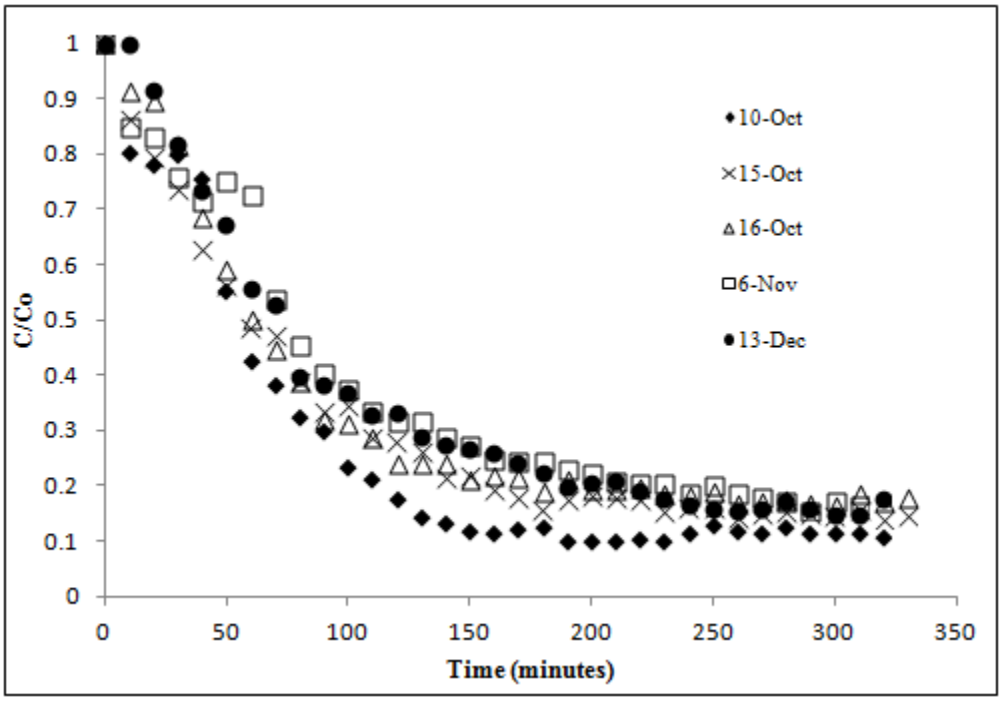


Figure 6. Normalized results for LEDs continuously on

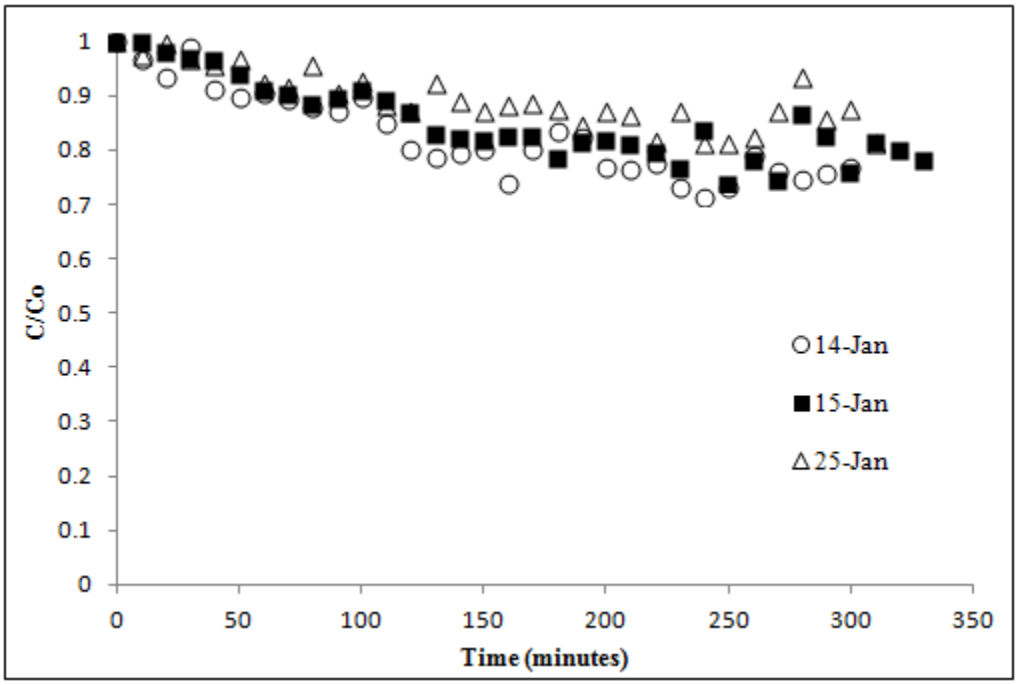


Figure 7. Normalized results for 10% duty cycle

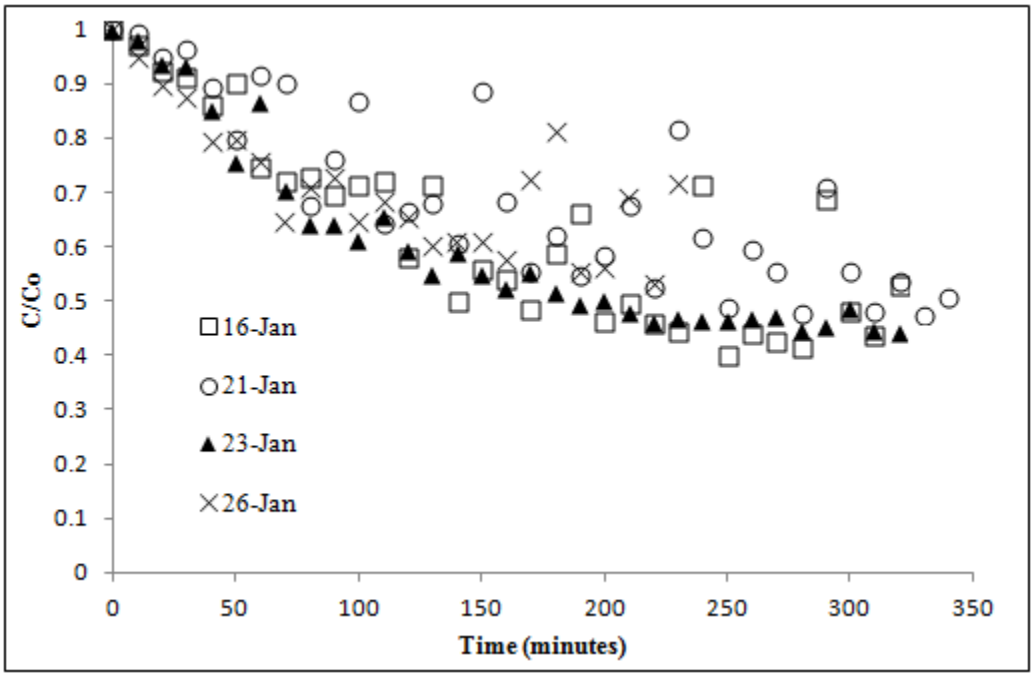


Figure 8. Normalized results for 50% duty cycle

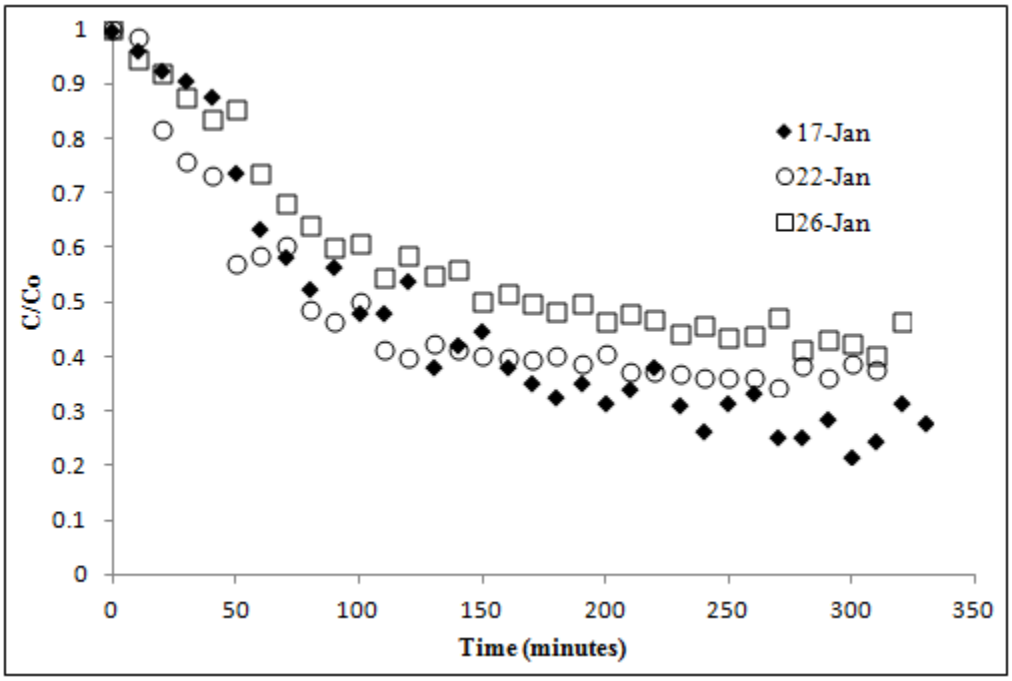


Figure 9. Normalized results for 70% duty cycle

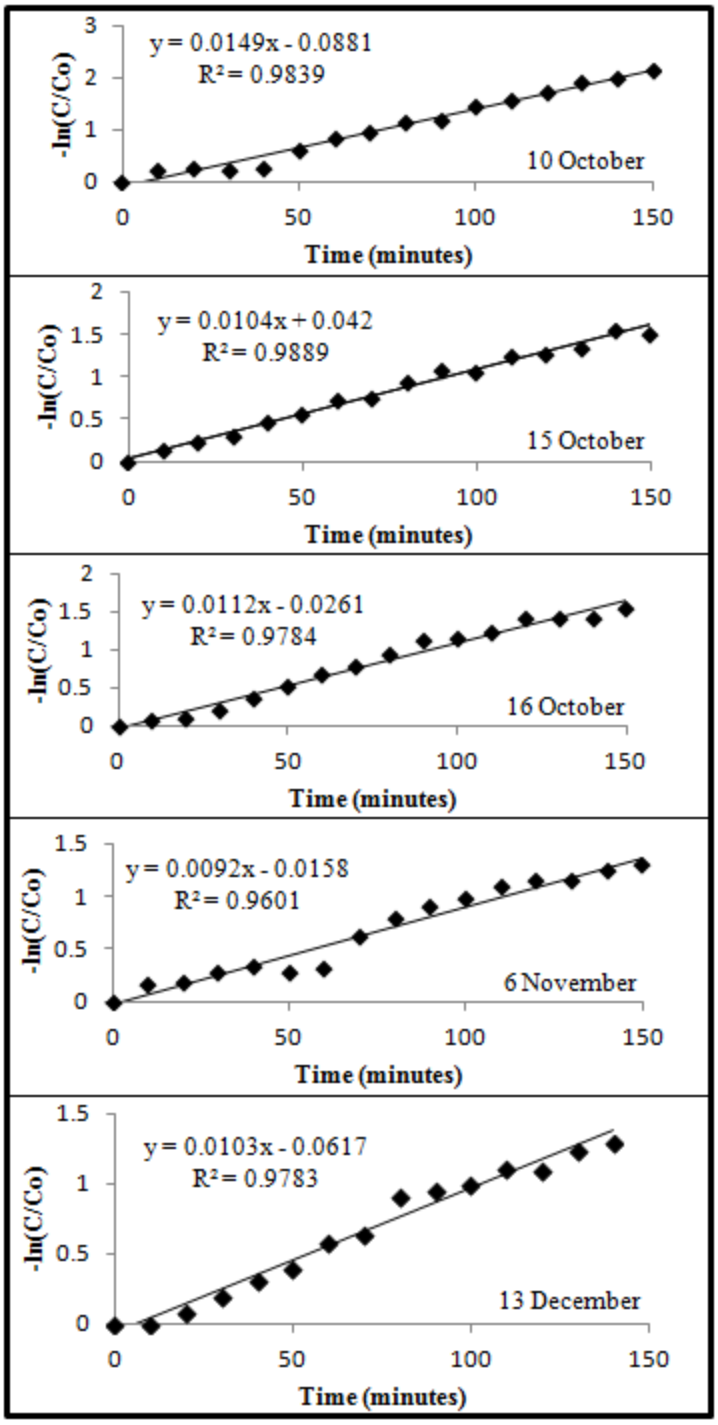


Figure 10. Degradation rates for LEDs continuously on

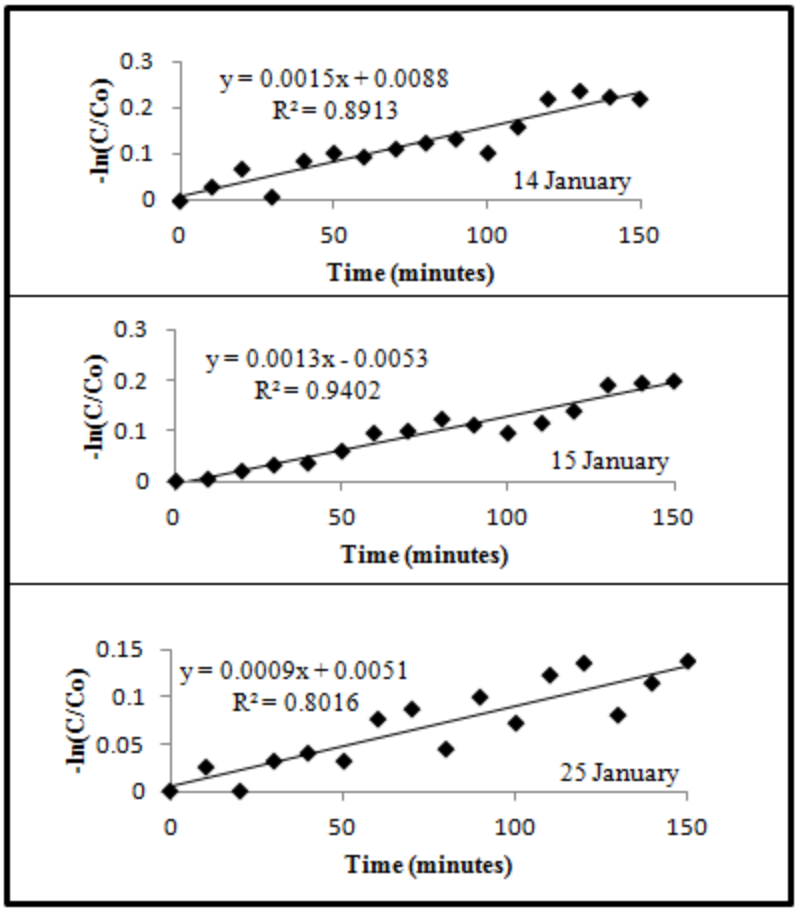


Figure 11. Degradation rates for 10% duty cycle

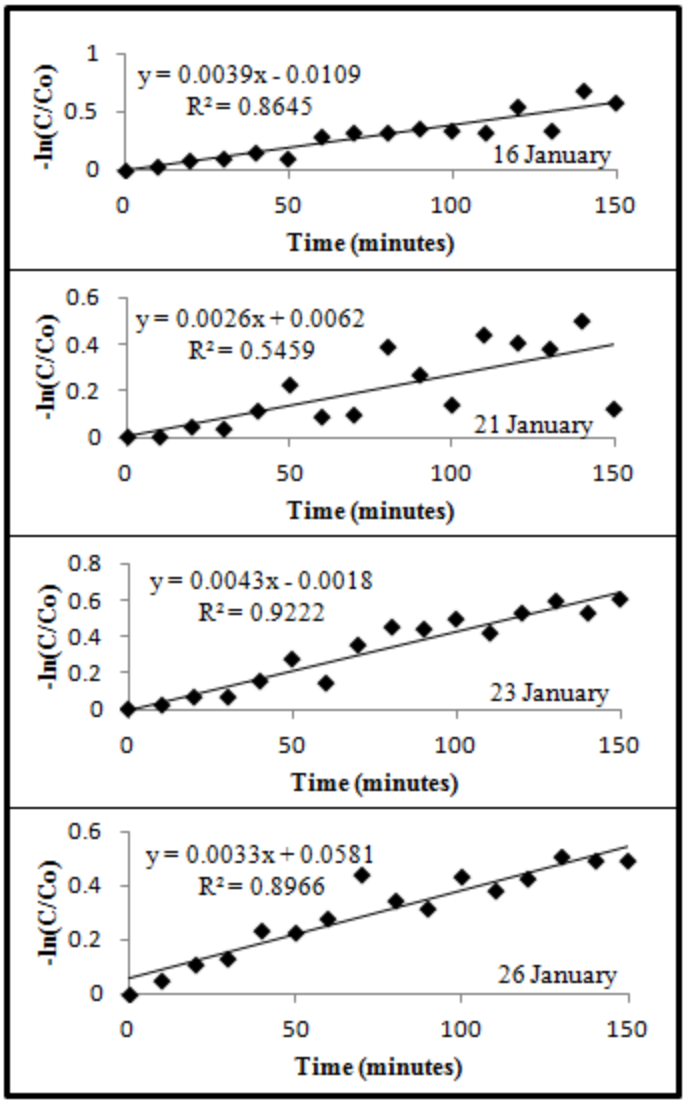


Figure 12. Degradation rates for 50% duty cycle

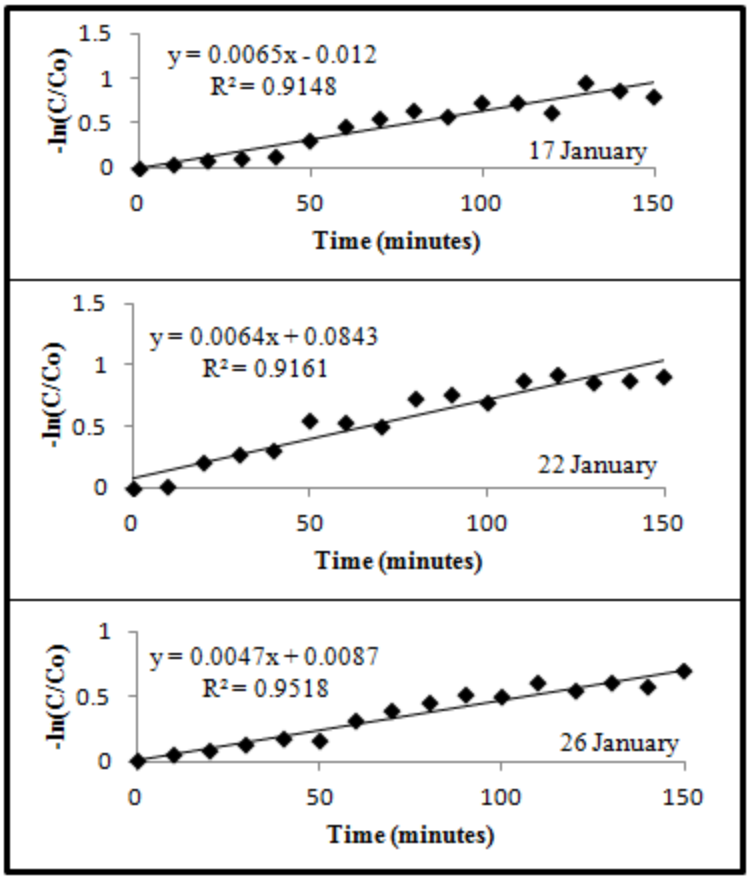


Figure 13. Degradation rates for 70% duty cycle

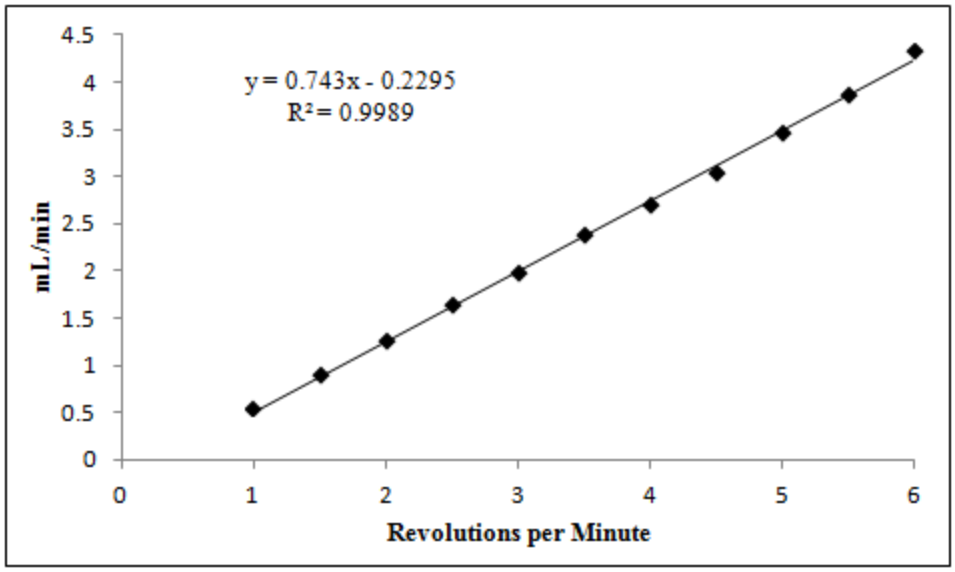


Figure 14. Calibration curve for the peristaltic pump

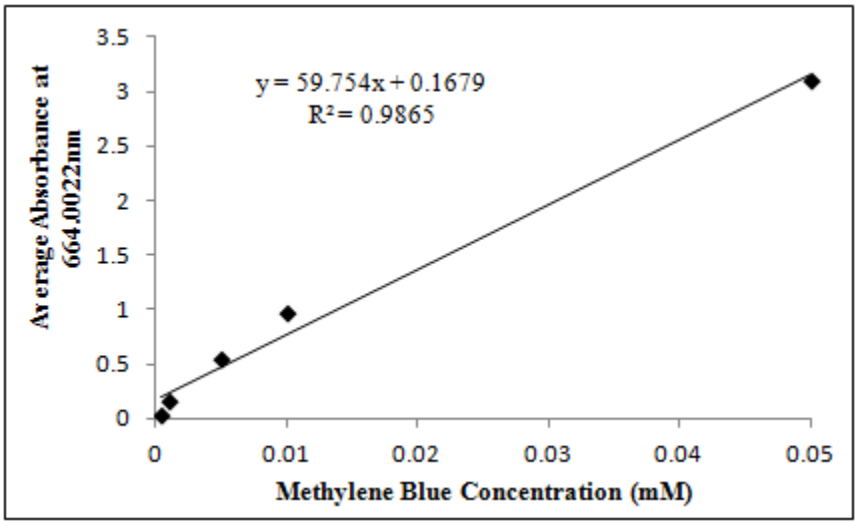


Figure 15. Calibration curve for the UV-Vis spectrophotometer

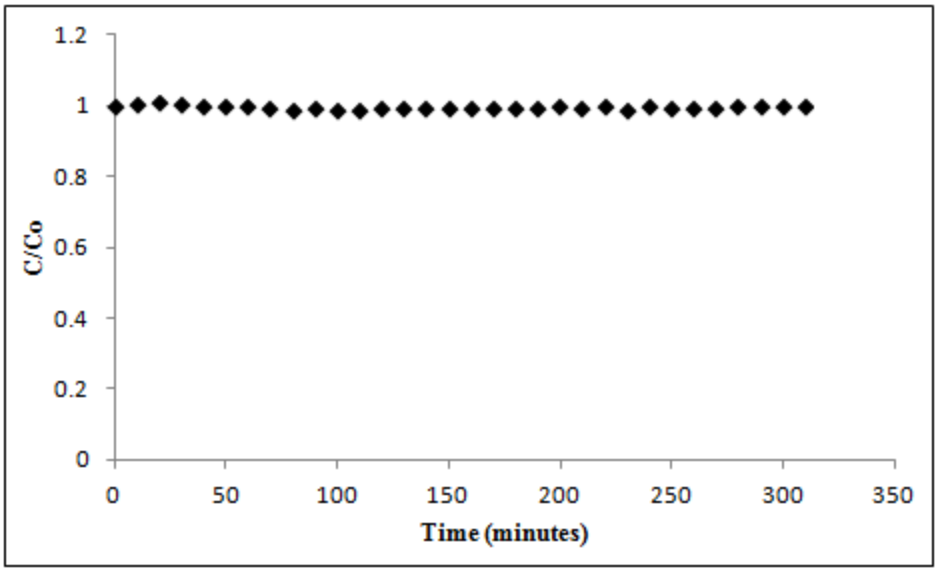


Figure 16. Verifying methylene blue is not affected by direct photolysis above 200 nm. Results of running 0.01 mM methylene blue solution through the reactor with the LEDs continuously on.

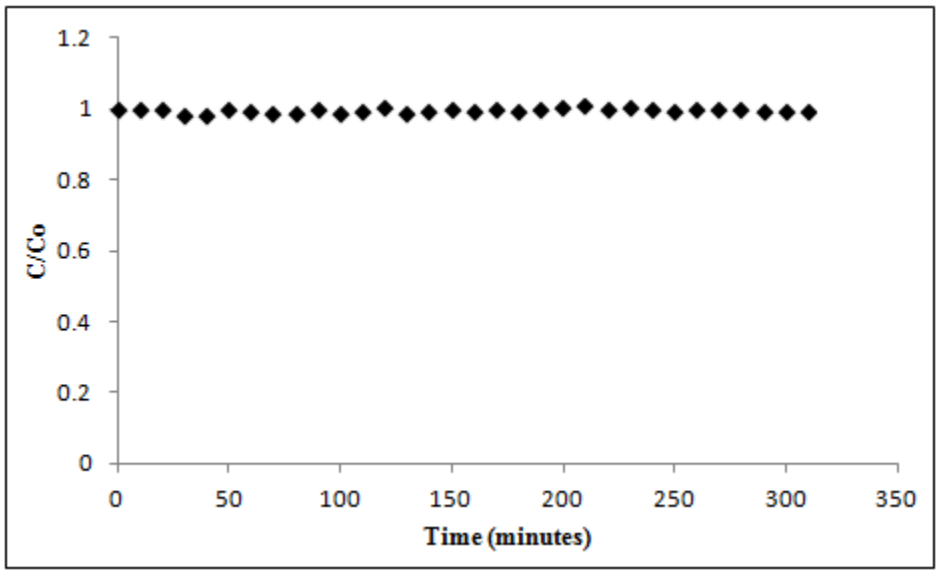
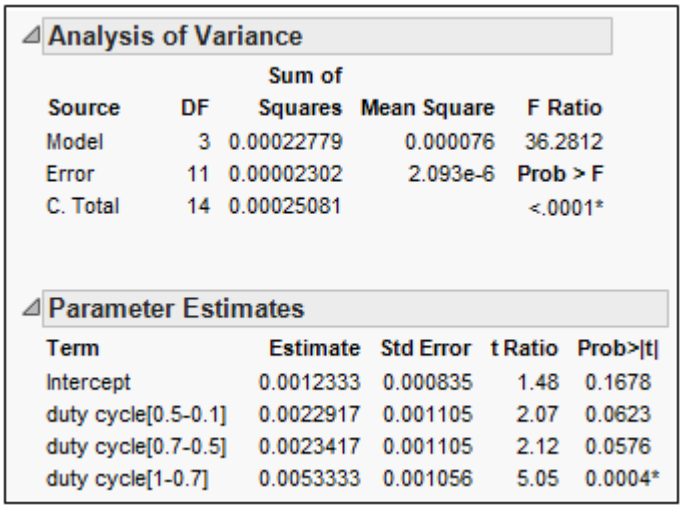


Figure 17. Verifying methylene blue is unreactive with hydrogen peroxide alone. Results from running 5 mM hydrogen peroxide and 0.01 mM methylene blue solution through the reactor with no LEDs on.



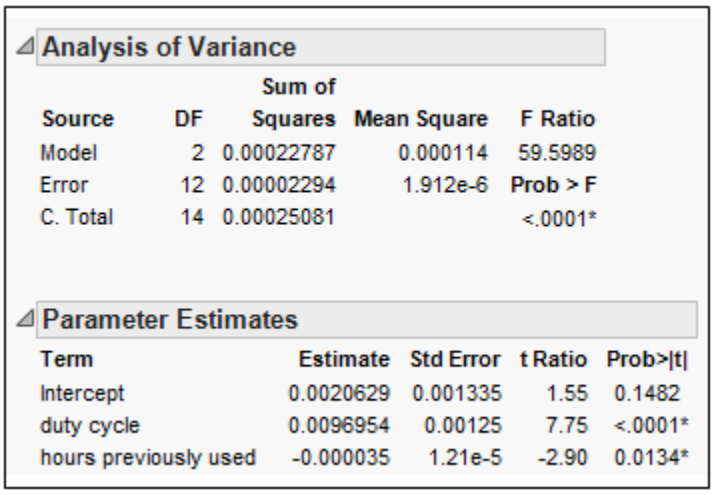
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	0.00022779	0.000076	36.2812
Error	11	0.00002302	2.093e-6	Prob > F
C. Total	14	0.00025081		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.0012333	0.000835	1.48	0.1678
duty cycle[0.5-0.1]	0.0022917	0.001105	2.07	0.0623
duty cycle[0.7-0.5]	0.0023417	0.001105	2.12	0.0576
duty cycle[1-0.7]	0.0053333	0.001056	5.05	0.0004*

Figure 18. JMP output from comparing degradation rates between 100% and 70% duty cycles, 70% and 50% duty cycles, and 50% and 10% duty cycles



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	0.00022787	0.000114	59.5989
Error	12	0.00002294	1.912e-6	Prob > F
C. Total	14	0.00025081		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.0020629	0.001335	1.55	0.1482
duty cycle	0.0096954	0.00125	7.75	<.0001*
hours previously used	-0.000035	1.21e-5	-2.90	0.0134*

Figure 19. JMP output from the regression model of duty cycle, degradation rate, and hours previously used

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14. ABSTRACT
Cleanup from a hazardous chemical release can result in large volumes of water containing hazardous materials, such as organophosphates. Unfortunately, this water cannot be treated in a municipal wastewater treatment plant without adversely affecting the performance of the plant. A known method for pretreating this water to prepare it for processing in a traditional treatment plant includes the addition of hydrogen peroxide, followed by ultraviolet (UV) light exposure to form reactive hydroxyl radicals which oxidize the chemical. Light emitting diodes (LEDs) are explored as a UV source as they are durable; compact; can be powered by low voltage, direct current from solar cells or batteries; and do not contain other hazardous materials, making them useful in a tactical environment. This research evaluated the operating mode (continuous or pulsed current) of 240 nanometer UV LEDs for application in such an advanced oxidation process. The experimental results demonstrated the production of hydroxyl radicals from hydrogen peroxide from both continuously driven and pulsed UV LEDs. However, continuously driven UV LEDs were shown to be more effective than pulsed in this application.

15. SUBJECT TERMS
light emitting diodes, advanced oxidation process, ultraviolet light, hydrogen peroxide

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